

József Verhás

THERMODYNAMICS AND RHEOLOGY

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PREFACE

To facilitate the application of physical theories in practice, researchers today must develop new methods not only for the systematization and interpretation of increasing experimental data but also for the simplification, unification and combination of already existing and well-functioning theories. A step toward this goal is served by the present text which attempts to compose a general theory of classical field incorporating continuum mechanics, electrodynamics and thermodynamics. Although looking mainly at the mechanical motion of media, the methods described by this text point far beyond the rheological applications (as indicated in the title) to an exact theory of non-equilibrium thermodynamics, thus making possible a unified description of mechanical, electromagnetic and thermic phenomena together with the interrelations between them. As a result, this theory offers a strong organizational force and an extraordinarily wide range of applications. Knowledge of non-equilibrium thermodynamics is indispensable for the physicists dealing with transport processes, physical chemistry, plasma physics or energetics, for the chemical engineer and even for biophysicist and biologist. To the aforementioned enumeration can be added by electrical, mechanical and civil engineers as well as architects engaged in dielectrics, structural materials, colloid agents or even in liquid crystals. This wide range of application of irreversible thermodynamics arises from the fact that in nature any macroscopic process is irreversible.

This book deals both with the complicated and far-reaching forms of motion of the materials continuously filling up the universe and with establishing principles in joining classical field theoretical methods with irreversible thermodynamics, using macroscopic methods but not forgetting the corpuscular structure of the agents. By elaborating on these methods in detail, the proper means for the quantitative description of irreversible phenomena — means formerly lacking from the viewpoint of generality, mathematical exactness and direct applicability — are now evident.

The results outlined in this book speak for themselves. The general feature of the correlations presented and — at the same time — their simplicity will surprise even the reader familiar with literature of the topics. To those not acquainted with the subject matter of deformation and flow or with the relevant optical and electromagnetic phenomena, it serves as an introduction.

The harmonic coordination of the succinctly expressed vast knowledge assures — beyond the aesthetic experience — its comprehension, understanding and immediate applicability.

Successful striving for mathematical simplicity is an advantage of the book. The author avoided complicated methods too often seen in the literature (for example, he did not apply the Ricci calculus that — considering the Euclidean structure of surrounding classical space — has an advantage only for numerical solutions of

special problems). The importance of the topics presented and the precision and applicability of the new thermodynamic theory (the so called dynamic variables introduced by the author) will usher in a new epoch in the literature of the topics.

István Gyarmati

CONTENTS

INTRODUCTION.	1
I. KINEMATICS.	3
1.1. Motion of continua.	3
1.2. Strain.	5
1.3. Rate of deformation.	9
II. DYNAMICS.	13
2.1. Mass of continua.	13
2.2. The momentum of continuum.	14
2.3. Stress.	15
2.4. Body forces.	16
2.5. Forces of gravity and inertia.	16
2.6. Electromagnetic forces.	18
2.7. Moment of momentum.	20
2.8. Electromagnetic couple density.	22
III. DEFORMATION AND STRESS.	23
3.1. Classical body models.	23
3.1.1. Rigid body.	24
3.1.2. Hooke-body.	24
3.1.3. Pascal-body.	25
3.1.4. Newton-body.	25
3.2. Mechanical models of rheology.	26
3.2.1. Maxwell-body.	26
3.2.2. Kelvin-body (Voigt-body).	28
3.2.3. The rheological model of plastic flow.	29
3.2.4. The spatial loading of the ideally plastic body.	32
3.2.5. Further non-linearities.	33
3.3. On the methods of modern continuum mechanics.	35
3.4. The theory of the simple shear flow.	39
3.5. Viscometric Flows.	41
3.6. Closing remarks.	41
IV. NON-EQUILIBRIUM THERMODYNAMICS.	43
4.1. On the first and second law of thermodynamics.	43
4.1.1. The state variables.	44
4.2. Balance equations.	45
4.2.1. The general form of balance equations.	45
4.2.2. The balance of mass.	47

4.2.3. The balance of momentum and moment of momentum.	47
4.2.4. The balance of kinetic energy.	47
4.2.5. The balance of the internal energy.	48
4.3. Entropy balance.	51
4.4. The linear laws.	53
4.5. Reciprocal relations.	57
4.6. Gyarmati's variational principle of dissipative processes.	59
4.6.1. The local forms of Gyarmati's principle.	60
4.6.2. The governing principle of dissipative processes.	64
4.6.3. The derivation of the von Mises' equations of plasticity.	65
4.6.4. The generalized reciprocal relations and the generalization of Gyarmati's principle for non-linear cases.	66
4.7. The wave approach of thermodynamics.	70
4.8. Transport of dynamic degrees of freedom.	74
4.9. Correlation between rational, entropy-free, extended and Onsager's thermodynamics.	76
V. THERMODYNAMICS OF DEFORMATION.	
SYSTEMS CLOSE TO EQUILIBRIUM.	81
5.1. Media in local equilibrium.	81
5.1.1. Equilibrium of solids.	83
5.1.2. Motion of solids.	85
5.1.3. Motion of fluids.	85
5.2. Material symmetry.	88
5.3. Anisotropy by deformation.	89
5.4. Heat conduction and deformation.	91
5.4.1. Thermoelasticity.	91
5.4.2. Propagation of sound waves in media in local equilibrium.	92
VI. THERMODYNAMICS OF DEFORMATION.	
SYSTEMS FAR FROM EQUILIBRIUM.	95
6.1. Bodies with a single dynamic variable.	96
6.1.1. Motion of incompressible fluids.	97
6.1.2. Shear flow of liquids.	101
6.1.3. Complex-number treatment for shear flow.	103
6.1.4. Transient stress.	104
6.1.5. Plastic behavior. Creep.	106
6.1.6. Extension of complex representation to plane motions.	114
6.1.7. Elementary theory of streaming birefringence.	115
6.1.8. Deviations from linearity.	117
6.1.9. Volume viscosity.	120
6.1.10. Motion of solid bodies.	121
6.1.11. Some remarks on representation.	121
6.2. Motion of a body with several dynamic variables.	125

6.2.1. Small-amplitude oscillations.	125
6.2.2. Shear flow of liquids.	126
6.2.3. Several types of dynamic variables.	130
6.2.4. Analogy with electric two-poles.	131
6.2.5. Streaming birefringence.	133
6.2.6. Matrix representation of constitutive equations.	134
6.2.7. Plastic behavior.	135
6.3. Some limit cases.	141
VII. ELECTRIC POLARIZATION	
IN FLOWING MEDIA.	143
7.1. Thermodynamics of electric polarization.	143
7.2. Flow of dielectrics in electromagnetic field.	146
7.3. Body with several dynamic variables.	151
7.4. Flow and polarization of conductive media.	153
7.5. Thermodynamic theory of streaming birefringence.	154
VIII. APPLICATIONS OF THE THEORY.	157
8.1. Viscosity of globular colloids.	157
8.2. Calculation of the viscosity of globular colloids based on structural considerations.	158
8.3. Effect of interfacial tension: emulsions and foams.	173
8.4. Thermal motion of rigid colloidal particles.	177
8.5. Viscosity of polymers.	182
8.5.1. Equilibrium configurations of chain molecules.	182
8.5.2. Motion of chain molecules.	186
8.5.3. Chemical relaxations in loose networks.	193
8.6. Motion of liquid crystals.	195
8.6.1. Entropy of nematic liquid crystals.	197
8.6.2. Entropy balance.	199
8.6.3. Conditions of equilibrium.	201
8.6.4. Motion of liquid crystals.	204
8.6.5. An example.	210
8.6.6. Shear flow of nematic liquid crystals.	212
APPENDIX. (Mathematical notations and definitions.)	215
A 1. The Basic Operations.	215
A 2. Symmetric and Antisymmetric Tensors.	216
A 3. Tensor products.	216
A 4. Eigenvalues and Invariants.	217
A 5. Orthogonal Tensors.	218
A 6. Isotropic Tensors.	219
A 7. Derivatives.	220
A 8. Integral Theorems.	220
REFERENCES.	221

INTRODUCTION

Thermodynamics as a field theory has the history of a few decades only. Its methods — we dare say — have been elaborated but are not final at all. They are changing and transforming even at present. At the same time the rapid development in technology gives rise the demand for a unified and general theory of classical field incorporating continuum mechanics, electrodynamics, and thermodynamics. The need of practical applications has led to the development of several methods and ideas differing from each other according to the different branches of applications, nevertheless, overlapping and similarity are not rare. The unification is rather hard, partly for the different intentions, partly for the enormous amount of knowledge involved.

I intend to contribute to the unification following Gyarmati [70] who made the first consistent steps in his book in 1970. The starting point of my work is the field theoretical view of thermodynamics — founded by Onsager in 1931 [124, 125] — of irreversible processes. I have fitted the aspects of non-equilibrium thermodynamics to classical and modern concepts and methods of mechanics and electrodynamics.

In this work I made, of course, compromise as well. For example, I avoid the difficulties due to the complexity of mathematical apparatus of general relativity (and not to be hindered in my work by the undeveloped theory of relativistic thermodynamics), I limited my considerations to slowly moving media and accordingly used the correlations of electrodynamics in approximate form.

As my work may be only the first step in the elaborating of this theory, in this book I give only those consequences I deemed as most important. First of all, the linear constitutive equations of Onsager's thermodynamics are applied (although from time to time the linear and non-linear alternatives come in question as well, but only to show the possibilities for continuing this work). The majority of methods and concepts applied in my work belong to non-equilibrium thermodynamics: however, I relied considerably also on the methods of continuum mechanics, rheology and electrodynamics. For example, I borrowed the often applied complex formalism from the linear theory of electric networks.

The composition of this book reflects the synthesizing character of my work. Chapters 1 and 2 include the principles of continuum mechanics to the extent needed to expound a unified theory by giving the definitions taken from continuum mechanics together with their correlations. The apparatus required to consider the effects of gravitational and electromagnetic fields is so defined that it can be applied even in the case of micropolar media.

Chapter 3 outlines the well-known methods relating stress and strain. This Chapter aims partly at summarizing the experimental results and partly at indicating the ideas taken from rheology and continuum mechanics respectively.

Chapter 4 includes the setting forth of irreversible thermodynamics, making the reader acquainted with balance equations and “linear” laws of irreversible thermodynamics as well as with the Onsager-Casimir reciprocal relations, and, further,

with Gyarmati's variational principle. The new theory and applications of dynamic variables is described in this chapter. Chapter sums up some results of irreversible thermodynamics partly reached by me, partly born while writing this book, so their direct application — at least as to rheology — could hardly come on as yet.

Chapter 5 is based on the hypothesis of local equilibrium. It also incorporates theories of classical elasticity, thermoelasticity and Newtonian fluids into the framework of thermodynamics.

Chapter 6 studies media far from equilibrium, rejecting the hypothesis of local equilibrium. New scientific results follow the solution of the linear constitutive equations of Onsager's thermodynamics, thus enabling models of rheology to begin now from a single uniform basic principle. The viscoelastic and plastic response, Ostwald's curve characterizing the generalized Newtonian fluids, the effect of creep, the elastic features preceding plastic flow, the basic interrelations of reopectics, etc. are interpreted with phenomenological methods, quantitatively. The consistent character of the method is shown by the self-evident theoretical proof of the empirical Cox-Mertz rule [28]. It is confirmed that its limit of validity coincides with that of strictly linear rules. This book over-rides the limits of the linear theory, but only in the simplest case to show the direction for the future.

Chapter 7 deals with electromagnetic phenomena including the irreversible thermodynamic theory of streaming birefringence and photoelasticity. Here the *raison d'être* of quasi-linear theory is verified.

Chapter 8 outlines some practical applications of the aforesaid theory. Several colloids, polymers as well as the liquid crystals are described here. In case of colloids — after thermodynamic considerations — the equivalent theory based on microscopic structure is mentioned. The two methods do not exclude each other; in fact, the microscopic considerations complete well those of thermodynamics giving the graphic meaning of phenomenological conductive coefficients. Here I draw the attention of the reader to the thermodynamic method which gives the mathematical form of the functions studied more briefly and elegantly than the mathematical methods based on partial differential equations that are essential for other approximations; moreover it is free from the uncertainties due to not perfect reliability in each case separately of hypothesis regarding the microscopic structure of a particular material.

The Appendix sums up the applied mathematical apparatus, but only to facilitate the interpretation of used notations.

It is a pleasure to thank Prof. I. Gyarmati for his introducing me — at a high international level — to the basis of irreversible thermodynamics at a very high level. During my three-decade research work, he always inspired me to reach considerable results, and placed his wide-range knowledge at my disposal.

CHAPTER I

KINEMATICS

1.1. Motion of continua.

The motion of a body is kinematically known if we know the position of any point at any time. Many methods are known to label the points of the body. One possibility is to use the position occupied at a given time t_0 to denote the moving point. To give the positions, some kind of frame of reference is applied. The usual mathematical means are a system of co-ordinates fixed to a frame of reference. The mode of selecting the reference and coordinate system may be optional in principle: however, the proper selection can simplify the calculus to be done. We can use Cartesian coordinates in Euclidean space; the vectors of the Euclidean space are suitable for indicating positions.

Select a moving body and choose its point P_0 . Denote the rectangular coordinates of the point in time t_0 with x_1, x_2, x_3 in the coordinate system defined by orthonormal base vectors (unit vectors) $\mathbf{j}_1, \mathbf{j}_2, \mathbf{j}_3$. Then call the vector

$$\mathbf{X} = X_1\mathbf{j}_1 + X_2\mathbf{j}_2 + X_3\mathbf{j}_3 \quad (1.1)$$

the position vector of point P_0 in time t_0 . Denote the coordinates of points P_0 in time t with x_1, x_2, x_3 . The vector

$$\mathbf{x} = x_1\mathbf{j}_1 + x_2\mathbf{j}_2 + x_3\mathbf{j}_3 \quad (1.2)$$

is the position vector of point P_0 . It is changing in time. We can regard the motion of point P_0 as kinematically known if we know the function

$$\mathbf{x} = \mathbf{x}(t). \quad (1.3)$$

If we choose another point P instead of point P_0 then the vector \mathbf{X} will be quite different and even the function $\mathbf{x} = \mathbf{x}(t)$ will be replaced. Therefore, we can say that the position vector \mathbf{x} depends not only on time but on the point whose motion it describes. As we apply the \mathbf{X} vector to specify the points of the body, we can mathematically give the motion by the so-called motion function

$$\mathbf{x} = \mathbf{x}(\mathbf{X}, t). \quad (1.4)$$

We can call the numbers x_1, x_2, x_3 as Eulerian or space coordinates and the numbers X_1, X_2, X_3 as material or Lagrange coordinates [27, 42, 75, 154]. The mapping (1.4)

is assumed to be single valued and to have continuous partial derivatives except possibly at some singular points, curves and surfaces. Furthermore, its jacobian

$$j = \frac{\partial(x_1, x_2, x_3)}{\partial(X_1, X_2, X_3)} = \begin{vmatrix} \frac{\partial x_1}{\partial X_1} & \frac{\partial x_1}{\partial X_2} & \frac{\partial x_1}{\partial X_3} \\ \frac{\partial x_2}{\partial X_1} & \frac{\partial x_2}{\partial X_2} & \frac{\partial x_2}{\partial X_3} \\ \frac{\partial x_3}{\partial X_1} & \frac{\partial x_3}{\partial X_2} & \frac{\partial x_3}{\partial X_3} \end{vmatrix} \quad (1.5)$$

is positive i.e.

$$0 < j < \infty. \quad (1.6)$$

This inequality physically means the indestructibility of the material. It shows that during motion the body of finite volume was always of finite volume and will remain under any circumstances. To understand this, consider an infinitesimal parallelepiped with edges dX_1 , dX_2 , dX_3 around the point X_1 , X_2 , X_3 . During the motion, the edges of the parallelepiped $dX_1\mathbf{j}_1$, $dX_2\mathbf{j}_2$, $dX_3\mathbf{j}_3$ deform to edges $\frac{\partial \mathbf{x}}{\partial X_1}dX_1$, $\frac{\partial \mathbf{x}}{\partial X_2}dX_2$, $\frac{\partial \mathbf{x}}{\partial X_3}dX_3$, while the parallelepiped remains parallelepiped, the volume of which can be given by

$$dV = \left(\frac{\partial \mathbf{x}}{\partial X_1}dX_1 \times \frac{\partial \mathbf{x}}{\partial X_2}dX_2 \right) \frac{\partial \mathbf{x}}{\partial X_3}dX_3 \quad (1.7)$$

In coordinates, it makes

$$dV = \begin{vmatrix} \frac{\partial x_1}{\partial X_1} & \frac{\partial x_1}{\partial X_2} & \frac{\partial x_1}{\partial X_3} \\ \frac{\partial x_2}{\partial X_1} & \frac{\partial x_2}{\partial X_2} & \frac{\partial x_2}{\partial X_3} \\ \frac{\partial x_3}{\partial X_1} & \frac{\partial x_3}{\partial X_2} & \frac{\partial x_3}{\partial X_3} \end{vmatrix} dX_1 dX_2 dX_3 = j dV_0 \quad (1.8)$$

where dV_0 is the original volume in time t_0 . It is very important beyond the fundamental physical meaning that the inequality (1.6) assures the invertability of the deformation function, i.e. the inverse function

$$\mathbf{X} = \mathbf{X}(\mathbf{x}, t) \quad (1.9)$$

exists.

In many important cases, making distinction between certain points is only of theoretical importance: therefore the use of spatial or Eulerian description is common, especially when discussing liquids. This means that we regard the motion as known if we know the velocity as a function of time and place:

$$\mathbf{v} = \mathbf{v}(\mathbf{x}, t). \quad (1.10)$$

The connection between these two kinds of description can be summed up as follows: The time derivative of the motion gives the velocity in function of time and starting point:

$$\mathbf{v} = \frac{\partial \mathbf{x}(\mathbf{X}, t)}{\partial t}. \quad (1.11)$$

However, the starting point can be given with the help of (1.9) as a function of the instantaneous position and time. So considering (1.9), we turn (1.11) into (1.10) as

$$\mathbf{v} = \frac{\partial \mathbf{X}(\mathbf{x}, t)}{\partial t} = \mathbf{v}(\mathbf{x}, t). \quad (1.12)$$

Doing the reverse — from (1.12) to (1.04) — is more complicated. Let us regard the function (1.10) as a vectorial differential equation for the position of a selected point P_0

$$\frac{d\mathbf{x}}{dt} = \mathbf{v}(\mathbf{x}, t). \quad (1.13)$$

In the general solution, three arbitrary numbers appear, the value of which are determined by the initial condition

$$\mathbf{x} = \mathbf{X}, \quad \text{if} \quad t = t_0. \quad (1.14)$$

In this way, we can get the motion function

$$\mathbf{x} = \mathbf{x}(\mathbf{X}, t).$$

From the aforesaid it can be seen that from a physical point of view the two descriptions are equivalent: we can change over from one to the other at any time.

1.2. Strain.

The motion of a body, as we mentioned before, is described in general with a function (1.4). As not any motion of the body results in deformation, it is more precise to apply the term “motion” instead of the frequently used term “deformation”.

A characteristic of motions without strain is that during motion the distance between any pair of points remains unchanged. These motions are called rigid body motions.

Let us examine which of the functions (1.4) indicate motion without strain. Consider two different, but otherwise arbitrary points of the medium P_1 and P_2 . The distance between them does not change, so

$$(\mathbf{x}_1 - \mathbf{x}_2)^2 = (\mathbf{X}_1 - \mathbf{X}_2)^2 \quad (1.15)$$

that can be written as

$$\sum_{i=1}^3 (x_{1i} - x_{2i})^2 = \sum_{J=1}^3 (X_{1J} - X_{2J})^2 \quad (1.16)$$

in rectangular coordinates. Making use of the inverse function (1.9), (1.16) becomes:

$$\sum_{i=1}^3 (x_{1i} - x_{2i})^2 = \sum_{J=1}^3 [X_{1J}(\mathbf{x}_1, t) - X_{2J}(\mathbf{x}_2, t)]^2. \quad (1.17)$$

As the point P_1 is arbitrary, this equation holds for any \mathbf{x}_1 ; and also the partial time derivatives with respect to x_{1i} of the right and left sides are equal:

$$x_{1i} - x_{2i} = \sum_{J=1}^3 (X_{1J} - X_{2J}) \frac{\partial X_{1J}}{\partial x_{1i}} \quad (1.18)$$

Introducing the form

$$Q_{iJ} = \frac{\partial X_{1J}}{\partial x_{1i}} \quad (1.19)$$

and rearranging (1.18), we can write

$$x_{2i} = x_{1i} + \sum_{J=1}^3 Q_{iJ} (X_{2J} - X_{1J}) \quad (1.20)$$

whose vector form is

$$\mathbf{x}_2 = \mathbf{x}_1 + \mathbf{Q}(\mathbf{X}_2 - \mathbf{X}_1). \quad (1.21)$$

The Q_{ij} quantities (i.e. the tensor \mathbf{Q}) does not depend on how the point P_2 has been chosen: namely, its components can be calculated by (1.19) only from the coordinates belonging to point P_1 . Exchanging P_1 and P_2 we obtain

$$\mathbf{x}_2 = \mathbf{x}_1 + \mathbf{Q}'(\mathbf{X}_2 - \mathbf{X}_1) \quad (1.22)$$

being fully similar to (1.21) where \mathbf{Q} does not depend on the selection of point P_1 . The equivalence of (1.21) and (1.22) results in $\mathbf{Q} = \mathbf{Q}'$; i.e., \mathbf{Q} is identical for any P_1 and P_2 .

On the basis of (1.15) and (1.21) the tensor \mathbf{Q} leaves the absolute value of any vector unchanged. Based on this and using the equations

$$(\mathbf{Q}\mathbf{A})^2 = \mathbf{A}^2; \quad (\mathbf{Q}\mathbf{B})^2 = \mathbf{B}^2; \quad [\mathbf{Q}(\mathbf{A} + \mathbf{B})]^2 = (\mathbf{A} + \mathbf{B})^2,$$

it is seen that the tensor \mathbf{Q} leaves the scalar product of any two vectors unchanged:

$$(\mathbf{Q}\mathbf{A}, \mathbf{Q}\mathbf{B}) = (\mathbf{A}, \mathbf{B}), \quad (1.23)$$

so \mathbf{Q} is orthogonal; i.e., $\mathbf{Q}^T = \mathbf{Q}^{-1}$ and, therefore, $\mathbf{Q}\mathbf{Q}^T = \boldsymbol{\delta}$. On the other hand, it can be understood that during any motion given by the function

$$\mathbf{x} = \mathbf{a}(t) + \mathbf{Q}(t)\mathbf{X} \quad (1.24)$$

(\mathbf{Q} orthogonal tensor), the distance of any two points is constant. The class of functions which do not result in strain are thus evident. The $\mathbf{a}(t)$ function shows the translation of the body, while the tensor $\mathbf{Q}(t)$, the rotation. The $\mathbf{Q}(t)$ may not mean reflection as the determinant of reflections, is -1 ; and the determinant of $\mathbf{Q}(t)$ is non-negative in accordance with (1.6).

The motions which can be written in a form similar to (1.24)

$$\mathbf{x} = \mathbf{a}(t) + \mathbf{x}\mathbf{X} \quad (1.25)$$

(where \mathbf{x} is not orthogonal) are called homogeneous deformations.

The tensor \mathbf{x} is called the deformation gradient. The deformation gradient describes the strain and rotation of an environment of point P_0 .

To separate the rotation and strain, Cauchy's polar decomposition theorem is used. On the basis of this theorem, any non-singular, and invertible second order tensor \mathbf{x} can be factorized in form

$$\mathbf{x} = \mathbf{R}\mathbf{D} = \mathbf{d}\mathbf{R} \quad (1.26)$$

where \mathbf{D} and \mathbf{d} are symmetric tensors whose proper values are positive, and \mathbf{R} is an orthogonal tensor; i.e. the relations

$$\mathbf{D} = \mathbf{D}^T, \quad \mathbf{d} = \mathbf{d}^T, \quad \mathbf{R}\mathbf{R}^T = \delta \quad (1.27)$$

hold. The decomposition is unique.

By analyzing the deformation gradient tensor on the ground of polar decomposition, it is seen that \mathbf{R} shows the rotation while \mathbf{D} and \mathbf{d} , respectively, the local deformation in the sense that in a rotation-free case \mathbf{R} , in a strain-free case \mathbf{D} and \mathbf{d} equal the unit tensor. Indeed, at a motion without strain, the deformation gradient is orthogonal; i.e., on the basis of polar decomposition

$$\mathbf{x} = \mathbf{Q} = \mathbf{R}\delta = \delta\mathbf{R} = \mathbf{R} \quad (1.28)$$

can be written.

To simplify the notation, we use the following conventions:

- a) the indices denoted by minuscules refer to x coordinates; those denoted by majuscules refer to X coordinates.
- b) in every case when an index occurs twice in an expression we omit the sign of summation \sum and sum up from 1 to 3 for the dummy index (Einstein convention).
- c) the indices following the comma mean the partial derivatives with respect to the relevant variable.

Now study the case where the deformation gradient tensor does not depend on position, and the orthogonal factor received during polar decomposition corresponds to the unit tensor.

Then, according to (1.25), we can write the motion as

$$\mathbf{x} = \mathbf{a}(t) + \mathbf{D}(t)\mathbf{X} \quad (1.29)$$

and after a transformation to principal axis as

$$\begin{aligned} x_1 &= a_1 + D_1 X_1, \\ x_2 &= a_2 + D_2 X_2, \\ x_3 &= a_3 + D_3 X_3. \end{aligned} \quad (1.30)$$

where D_1 , D_2 and D_3 indicate the eigenvalues of the tensor \mathbf{D} . This means that, apart from translations determined by a_1 , a_2 , a_3 , stretchings parallel to the proper vectors have also appeared. We should image the whole process so that, first, we realize the three translations in arbitrary sequence and, afterwards, the stretching.

So, in case of homogeneous deformations when the function (1.4) can be given in form

$$\mathbf{x} = \mathbf{a}(t) + \mathbf{R}(t)\mathbf{D}(t)\mathbf{X}, \quad (1.31)$$

the instantaneous deformation is defined by the tensor \mathbf{D} . The motion to the present configuration can be decomposed to a succession of deformation, rotation and translation. The decomposition in equation (1.31) corresponds to this succession: \mathbf{D} defines the deformation, \mathbf{R} the rotation and \mathbf{a} the translation. Of course, the order of the steps of the motion is important as can be seen

$$\begin{aligned} \mathbf{r} &= \mathbf{a} + \mathbf{R}\mathbf{D}\mathbf{X} = \mathbf{a} + d\mathbf{R}\mathbf{X} = \mathbf{R}\mathbf{D}(\mathbf{A} + \mathbf{X}) = \\ &= d\mathbf{R}(\mathbf{A} + \mathbf{X}) = \mathbf{R}(\mathbf{a}^* + \mathbf{D}\mathbf{X}) = d(\mathbf{A}^* + \mathbf{R}\mathbf{X}). \end{aligned} \quad (1.32)$$

Here we have introduced the notations

$$\mathbf{A} = \mathbf{D}^{-1}\mathbf{R}^T\mathbf{a}, \quad \mathbf{a}^* = \mathbf{R}^T\mathbf{a}, \quad \mathbf{A}^* = \mathbf{R}\mathbf{D}^{-1}\mathbf{R}^T\mathbf{a}$$

as well as having used the identity

$$d = \mathbf{R}\mathbf{D}\mathbf{R}^T$$

due to polar decomposition. We mention that the tensor \mathbf{D} changes during motion, as do the directions of its properectors which means we can regard the foregoing as an instantaneous exposure. The considerations on homogeneous deformation can be applied for arbitrary motion. For that, only a sufficiently small neighborhood of a selected position \mathbf{X}_0 should be regarded.

It is important to mention that the resultant of two sequential deformations without rotation is generally not a strain without rotation as the product of two symmetric tensors is generally not symmetric. The situation is quite different if the deformations are small; i.e., when the tensor \mathbf{D} describing the deformations slightly differs from the unit tensor. In this case it is advisable to introduce the notation

$$\mathbf{D} = \boldsymbol{\delta} + \mathbf{E} \quad (1.33)$$

The tensor \mathbf{E} should be called the deformation tensor, as it is the zero tensor in the case of motions without strain. In case of two sequential deformations without rotation, we get the relation

$$\mathbf{x} = (\boldsymbol{\delta} + \mathbf{E}_1)(\boldsymbol{\delta} + \mathbf{E}_2) \approx \boldsymbol{\delta} + \mathbf{E}_1 + \mathbf{E}_2 \quad (1.34)$$

for the resultant deformation gradient, if we neglect the product $\mathbf{E}_1\mathbf{E}_2$ due to its smallness. The sum of two symmetric tensors is, however, also symmetric, so we can regard the resultant deformation as the sum of two strains. The formula (1.34) can be applied even in cases when the small strains are accompanied by rotations. In this case the resultant deformation gradient is determined from the equation

$$\mathbf{x} = \mathbf{R}_2(\boldsymbol{\delta} + \mathbf{E}_2)\mathbf{R}_1(\boldsymbol{\delta} + \mathbf{E}_1) = \mathbf{R}_2\mathbf{R}_1(\boldsymbol{\delta} + \mathbf{R}_1^T\mathbf{E}_2\mathbf{R}_1 + \mathbf{E}_1) \quad (1.35)$$

which shows that the deformation tensors can be added even now; however, due to the rotations, a common reference-frame should be provided for. The additivity of small deformations tempts one to believe that any deformation can be composed of small deformations. Although this misconception is very common in the old theory of infinitesimal deformations, it is, nevertheless, false as the sum of the terms neglected from (1.34) is not negligible anymore in case of finite resultant.

Finally we can draw attention to (1.35) where only the deformations are small and the rotations and displacements are arbitrary.

As outlined above, the motion of neighborhood of point P was decomposed to translation, rotation and deformation. The deformation is often decomposed to an isochor and a similarity deformation. It is done as follows: Regard the formula (1.8) and use Cauchy's decomposition theorem as well as the multiplication theorem of determinants. Then

$$dV = j dV_0 = \det \mathbf{x} dV_0 = \det \mathbf{R} \det \mathbf{D} dV_0. \quad (1.36)$$

As \mathbf{R} describes rotation, the value of its determinant is 1, so

$$dV = \det \mathbf{D} dV_0 = \det \mathbf{d} dV_0 \quad (1.37)$$

Define now a factor λ_v as well as the tensors \mathbf{D}_0 and \mathbf{d}_0 as follows:

$$\lambda_v = (\det \mathbf{D})^{\frac{1}{3}}; \quad \mathbf{D}_0 = \frac{1}{\lambda_v} \mathbf{D}; \quad \mathbf{d}_0 = \frac{1}{\lambda_v} \mathbf{d}, \quad (1.38)$$

by which the deformation gradient is cast into

$$\mathbf{x} = \lambda_v \mathbf{R} \mathbf{D}_0 = \lambda_v \mathbf{d}_0 \mathbf{R} \quad (1.39)$$

It results from the definitions (1.38) that

$$\det \mathbf{D}_0 = \det \mathbf{d}_0 = 1. \quad (1.40)$$

The factor λ_v describes similarity transformation; i.e., if $\mathbf{d}_0 = \mathbf{D}_0 = \boldsymbol{\delta}$, although the dimensions of the body change (the factor λ defines just the extent of elongation), however, the angle of any two line element is unchanged.

The meaning of the tensors \mathbf{D}_0 and \mathbf{d}_0 becomes clear if the case of $\lambda_v = 1$ is analyzed. In this case the volume of the body remains unchanged, so we regard the formula (1.39) as the product of the required decomposition.

1.3. Rate of deformation.

The separation of deformation and rotation by means of polar decomposition gives an obvious way of defining the rate of deformation. As any of the tensors \mathbf{d} and \mathbf{D} , respectively, show deformation with respect to the reference configuration, it seems, at first sight, that the material time derivative of any of them is suitable to characterize the momentary speed of deformation.

This is not true, as \mathbf{d} changes even if the strain of the body is constant in time but the body is rotating. On the other hand, the \mathbf{D} tensor changes only if the form

of the body changes; i.e., $\dot{\mathbf{D}}$ can be considered as the rate of strain. We have to take into account that the selection of the reference configuration is not free from all arbitrariness (in case of a particular motion, different reference configurations can be applied as well); therefore, the \mathbf{D} tensor and, of course, even $\dot{\mathbf{D}}$ contains subjective elements. But in other relations the reference configurations are not equivalent — think here of elastic bodies — so we cannot refer the role of reference configuration definitely to subjective elements. This question is not answered to complete satisfaction in the literature [42, 144, 153, 154].

We can advance in clearing some ambiguity if we change over from the coordinates X_1, X_2, X_3 to spatial coordinates x_1, x_2, x_3 and we analyze the velocity field in the neighborhood of a point.

To denote the spatial position of a point \mathbf{X} near to point \mathbf{X}_0 , we can apply the linear partial sum of the Taylor-series of the motion function around the point:

$$\mathbf{x} = \mathbf{x}_0(\mathbf{X}_0, t) + \mathbf{x}(\mathbf{X} - \mathbf{X}_0). \quad (1.41)$$

The deformation gradient tensor \mathbf{x} depends, of course even now, on place and time, i.e.

$$\mathbf{x} = \mathbf{x}(\mathbf{x}_0, t). \quad (1.42)$$

By Cauchy's polar decomposition, we can rewrite (1.41) in

$$\mathbf{x} = \mathbf{x}_0 + \mathbf{R}\mathbf{D}(\mathbf{X} - \mathbf{X}_0) = \mathbf{x}_0 + \mathbf{d}\mathbf{R}(\mathbf{X} - \mathbf{X}_0), \quad (1.43)$$

from what, by forming the partial derivatives of (1.11), we get the definition of velocity distribution around the point \mathbf{X}_0 :

$$\mathbf{v} = \mathbf{v}_0 + (\dot{\mathbf{R}}\mathbf{D} + \mathbf{R}\dot{\mathbf{D}})(\mathbf{X} - \mathbf{X}_0) = \mathbf{v}_0 + (\dot{\mathbf{d}}\mathbf{R} + \mathbf{d}\dot{\mathbf{R}})(\mathbf{X} - \mathbf{X}_0). \quad (1.44)$$

Using the invertability of the tensors \mathbf{R} and \mathbf{D} , and applying (1.43), the velocity gets the following alternative forms:

$$\begin{aligned} \mathbf{v} &= \mathbf{v}_0 + (\dot{\mathbf{R}}\mathbf{D} + \mathbf{R}\dot{\mathbf{D}})\mathbf{D}^{-1}\mathbf{R}^T(\mathbf{x} - \mathbf{x}_0) = \\ &= \mathbf{v}_0 + (\dot{\mathbf{d}}\mathbf{R} + \mathbf{d}\dot{\mathbf{R}})\mathbf{R}^T\mathbf{d}^{-1}(\mathbf{x} - \mathbf{x}_0) = \\ &= \mathbf{v}_0 + (\dot{\mathbf{R}}\mathbf{R}^T + \mathbf{R}\dot{\mathbf{D}}\mathbf{D}^{-1}\mathbf{R}^T)(\mathbf{x} - \mathbf{x}_0) = \\ &= \mathbf{v}_0 + (\dot{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}\dot{\mathbf{R}}\mathbf{R}^T\mathbf{d}^{-1})(\mathbf{x} - \mathbf{x}_0). \end{aligned} \quad (1.45)$$

From the latter expressions, the velocity gradient tensor is obtained:

$$\text{Grad } \mathbf{v} = \dot{\mathbf{R}}\mathbf{R}^T + \mathbf{R}\dot{\mathbf{D}}\mathbf{D}^{-1}\mathbf{R}^T = \dot{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}\dot{\mathbf{R}}\mathbf{R}^T\mathbf{d}^{-1}. \quad (1.46)$$

If the form of the body does not change, after a period of time the tensor \mathbf{D} will be constant and its derivative will be zero. The velocity gradient is reduced to $\mathbf{R}\mathbf{R}^T$ which is skew-symmetric as the relationship

$$\mathbf{R}\mathbf{R}^T = \boldsymbol{\delta}$$

leads to the identity

$$\dot{\mathbf{R}}\mathbf{R}^T + \mathbf{R}\dot{\mathbf{R}}^T = 0, \quad \text{i.e.} \quad \dot{\mathbf{R}}\mathbf{R}^T = -(\dot{\mathbf{R}}\mathbf{R}^T)^T$$

We refer to the skew-symmetric $\boldsymbol{\omega} = \dot{\mathbf{R}}\mathbf{R}^T$ tensor as the angular velocity tensor, which we write as

$$\dot{\mathbf{R}}\mathbf{R}^T = \boldsymbol{\omega} = \vec{\omega} \times \boldsymbol{\delta}. \quad (1.47)$$

Here $\vec{\omega}$ is the angular velocity vector, the vector invariant of the skew-symmetric tensor $\mathbf{R}\mathbf{R}^T$. The tensor $\dot{\mathbf{D}}$ may be regarded as the measure for the speed of deformation; however, this tensor is rather connected to the reference configuration than to the moving medium. To avoid this fault, we prefer to regard the

$$\mathbf{R}\dot{\mathbf{D}}\mathbf{R}^T = \dot{\mathbf{d}} \quad (1.48)$$

tensor as the rate of strain rather than $\dot{\mathbf{D}}$.

A relatively simple rule can be introduced to calculate the tensor $\dot{\mathbf{d}}$. As $\mathbf{D} = \mathbf{R}^T \mathbf{d} \mathbf{R}$, we have

$$\dot{\mathbf{d}} = \mathbf{R} \frac{d}{dt} (\mathbf{R}^T \mathbf{d} \mathbf{R}) \mathbf{R}^T = \mathbf{R} (\dot{\mathbf{R}}^T \mathbf{d} \mathbf{R} + \mathbf{R}^T \dot{\mathbf{d}} \mathbf{R} + \mathbf{R}^T \mathbf{d} \dot{\mathbf{R}}) \mathbf{R}^T.$$

From that, on the basis of (1.47), and from the orthogonality of \mathbf{R} , we receive

$$\dot{\mathbf{d}} = \dot{\mathbf{d}} + \mathbf{d}\boldsymbol{\omega} - \boldsymbol{\omega}\mathbf{d}. \quad (1.49)$$

It can be seen that $\dot{\mathbf{d}}$ is in very close connection to tensor \mathbf{d} as it is the time derivative in a particular frame, (co-rotating with the medium). This way of forming the time derivative will be applied for other tensors as this kind of time derivative gives the change rate of a given tensor with respect to the moving medium.

We repeatedly draw attention to the fact that the defined strain rate contains generally subjective elements as well, as the selection of the reference configuration is not free of arbitrariness. The situation is quite different if the deformation is small; i.e., in the case where the \mathbf{d} and \mathbf{D} tensors respectively differ slightly from the unit tensor, or are even, in a moment, just equal to it. The rotation may be, of course, arbitrary. This is the case, e.g., at fluid motions when in each moment the present configuration is applied as a reference configuration. Then (1.46) and (1.49) reduce to

$$\text{Grad } \mathbf{v} = \dot{\mathbf{d}} + \boldsymbol{\omega}, \quad \dot{\mathbf{d}} = \dot{\mathbf{d}} \quad (1.50)$$

From this we can read a really clear result that follows: The tensor describing the rate of strain with respect to the present configuration is identical with the symmetric part of the velocity gradient. In other words, the symmetric part of the velocity gradient can be assumed to be an objective rate of strain. On the basis of the aforesaid concepts, this tensor is given the name 'stretching tensor' in the literature.

Concerning the decomposition (1.39) we can decompose also the strain rate to a part describing dilatation and a part without dilatation. On the basis of differentiating (1.38), we get

$$\dot{\mathbf{d}} = \dot{\lambda}_v \mathbf{d}_0 + \lambda_v \dot{\mathbf{d}}_0. \quad (1.51)$$

This is especially simple if we apply the present configuration as a reference configuration when $\lambda_v = 1$ and $\mathbf{d}_0 = \boldsymbol{\delta}$. Then the first term on the right-hand side of (1.51) is a spherical tensor; and the second one has a zero trace that we can see on the basis of identity

$$\det \mathbf{d}_0 \operatorname{tr}(\dot{\mathbf{d}}_0 \mathbf{d}_0^{-1}) = \frac{d}{dt}(\det \mathbf{d}_0) = 0 \quad (1.52)$$

and (1.40). This means that the zero trace part of the stretching tensor describes a deformation without volume change while the trace characterizes the rate of volume change.

CHAPTER II

DYNAMICS

The dynamics of deformable bodies is based on the axioms of Newton's mechanics. The moving bodies are regarded as continuous media; i.e., in a mechanical sense as continua. At the same time, we must keep in mind that the physical background of the continuum in question is the regulated or chaotic set of atomic particles. This latter circumstance results in the continuum having an intrinsic structure which, (according to its different grades of complexity), manifests itself through its effect on macroscopic motion. (In this work there is no intention of analyzing any motion on microscale). To a quantitative description, the methods of classical space theory are applied, complemented by further hypotheses that are required to describe the macroscopic manifestations of the molecular background and which take into consideration the thermodynamic features of the material as well. The physical quantities are expressed by scalar-, vector- and tensor components that generally depend on time.

2.1. Mass of continua.

In investigating mechanical motion of extended bodies, we credit each body with mass that is connected with kinematic characteristics of motion of continua; likewise, we have to interpret the mass in such a way that the mass assigned to an arbitrary part of the medium is identical with the mass interpreted in a pointmechanical sense. To do this, we use three (in non-relativistic theory) fundamental features of mass:

- a) positive scalar,
- b) additive and
- c) invariant quantity under motion.

It is advisable to examine the additivity from the aforesaid features. Additivity means that by dividing a body into disjunct parts, the amount of mass of the parts equals the mass of the body. This means that in ordering the mass of medium to ranges of space, we receive a totally additive set function of positive value, i.e. in a mathematical sense, the mass is a measure. In the continuum theory we suppose that this measure is totally continuous, and so there exists a function — named density — for which the equality

$$M = \int_V \varrho dV \quad (2.1)$$

holds. Of course, the ϱ density is interpreted as the derivate of the set function M :

$$\varrho = \frac{dM}{dV} \quad (2.2)$$

The law of conservation of mass can be most easily written for a volume element:

$$\varrho dV = \varrho_0 dV_0, \quad (2.3)$$

where ϱ_0 is the density belonging to the reference configuration. Taking equation (1.8) into account i.e. that the volume dV_0 belonging to reference configuration connects to volume dV as $dV = j dV_0$, we receive the equality

$$\varrho j = \varrho_0 \quad (2.4)$$

The better known form of mass conservation is obtained by forming the time derivative of the natural logarithm of both sides. (As space coordinates, we use the X reference coordinates.)

$$0 = \frac{\partial \ln \varrho_0}{\partial t} = \frac{1}{j} \frac{dj}{dt} + \frac{1}{\varrho} \frac{d\varrho}{dt} = \operatorname{div} \mathbf{v} + \frac{1}{\varrho} \frac{d\varrho}{dt}, \quad (2.5)$$

At derivation of (2.5) we applied the identity

$$\frac{d}{d\tau} \det \mathbf{A} = \det \mathbf{A} (\mathbf{A}^{-1})^T : \frac{d\mathbf{A}}{d\tau},$$

the formula (1.46) regarding the derivatives of determinants as well as that j is the determinant of the deformation gradient.

By simple modification of (2.5) we get the well-known form of continuity:

$$\frac{d\varrho}{dt} + \varrho \operatorname{div} \mathbf{v} = 0. \quad (2.6)$$

We note that the partial time derivative of a function depending on the variables (X_1, X_2, X_3, t) is identical with a material time derivative.

2.2. The momentum of continuum.

The respective parts of a moving medium are continuously in interaction with their neighborhood. The interaction determines the further motion and the motion determines the interaction. The changes of mechanical motion are determined by the forces acting upon the medium. Newton's second law gives the connection between the forces and acceleration.

$$\mathbf{F} = \dot{\mathbf{p}} \quad (2.7)$$

where \mathbf{F} is the resultant force acting upon the body, and \mathbf{p} the momentum of the body. If all parts of the body move with the same velocity, the momentum is in simple connection with the velocity:

$$\mathbf{p} = m\mathbf{v}. \quad (2.8)$$

If the velocity field is, however, not homogeneous, then the relation (2.8) can be applied only to infinitesimal (elemental) medium pieces and

$$\mathbf{p} = \int_V \mathbf{v} dm = \int_V \varrho \mathbf{v} dV \quad (2.9)$$

can be written. So the equation (2.7) can be expressed in form

$$\mathbf{F} = \frac{d}{dt} \int_V \varrho \mathbf{v} dV = \frac{d}{dt} \int_{V_0} \varrho_0 \mathbf{v} dV_0 = \int_{V_0} \varrho_0 \frac{d\mathbf{v}}{dt} dV_0 = \int_{V_0} \varrho \frac{d\mathbf{v}}{dt} dV \quad (2.10)$$

Here the law of mass conservation (2.3) was taken into consideration as well.

To examine the forces in full detail, let us regard an arbitrary part of the medium, which is in interaction with other parts of the medium and with the remote surroundings as well. Its close neighborhood exerts force along the surface on the selected part of the medium while the interaction with the remote environment is replaced by a force field acting inside the selected body. Therefore we decompose the forces acting in a continuum into surface and volumetric forces. The volumetric forces (or body forces, long-distance forces) are described by a totally continuous set function. So there exists an $\mathbf{f}(\mathbf{x}, t)$ function named specific force by which the volumetric force is written in

$$\mathbf{F}_v = \int_V \mathbf{f} \varrho dV \quad (2.11)$$

The \mathbf{f} specific force is composed of gravity and electromagnetic forces.

2.3. Stress.

We suppose that the surface forces act along surfaces inside the continuum and describe the interaction between the parts of medium on the two sides of the surface. The force acting on a surface is expressed as

$$\mathbf{F}_A = \int_A \mathbf{t}(\mathbf{x}, t) d\mathbf{A} \quad (2.12)$$

Newton's second law for a continuum reads

$$\int_V \varrho \frac{d\mathbf{v}}{dt} dV = \int_V \varrho \mathbf{f} dV + \oint \mathbf{t} d\mathbf{A}. \quad (2.13)$$

Transforming the surface integral by Gauss' theorem we obtain

$$\int_V \varrho \frac{d\mathbf{v}}{dt} dV = \int_V (\varrho \mathbf{f} + \text{Div } \mathbf{t}) dV \quad (2.14)$$

Because this equality is valid for any region the relation

$$\varrho \frac{d\mathbf{v}}{dt} = \text{Div } \mathbf{t} + \varrho \mathbf{f} \quad (2.15)$$

also holds. This equation is the local form of Newton's second law for continua. The (2.15) equation — referred to as Cauchy's equation of motion — is the balance equation for momentum.

2.4. Body forces.

The present book is devoted to a detailed study of surface forces. The question of what and how the stress tensor depends on leads us far, while the formal description of long-distance forces can be given quite simply. Therefore let us first draw our attention to the long-distance forces.

The reference of force density defined in (2.11) to mass unit is justified by the circumstance that gravity is proportional to the mass. Under conditions on Earth it is very frequent that besides gravity no other notable long-distance force occurs so we can regard the specific force \mathbf{f} as being equal to the gravitational acceleration \mathbf{g} . If Cauchy's equation of motion is extended to rotating reference frames as well, we have to widen the interpretation of gravity forces.

2.5. Forces of gravity and inertia.

The wider interpretation of gravity means that we regard even the forces of inertia in accelerating reference frames as gravity forces in full accordance with the equivalence theorem of general relativity, although we use the classical methods of quantitative study.

Assume two reference frames with position vectors \mathbf{x} and \mathbf{x}^* . The two reference frames should move with respect to one another. Then the transformation

$$\mathbf{x}^* = \mathbf{Q}(t)[\mathbf{x} - \mathbf{a}(t)] \quad (2.16)$$

holds, where $\mathbf{a}(t)$ is the position vector of the origin of the reference system \mathbf{x}^* in system \mathbf{x} , and $\mathbf{Q}(t)$ an orthogonal tensor describing the relative rotation. There exists also the inverse of this transformation:

$$\mathbf{x} = \mathbf{a}(t) + \mathbf{Q}^T(t)\mathbf{x}^*. \quad (2.17)$$

Let \mathbf{x} and \mathbf{x}^* be the position vector of any moving material point and let us suppose the validity of (2.15) in the system \mathbf{x} . By double differentiating of (2.17) :

$$\mathbf{v} = \dot{\mathbf{x}} = \dot{\mathbf{a}} + \mathbf{Q}^T \dot{\mathbf{x}}^* + \dot{\mathbf{Q}}^T \mathbf{x}^*,$$

$$\frac{d\mathbf{v}}{dt} = \ddot{\mathbf{a}} + \mathbf{Q}^T \ddot{\mathbf{x}}^* + 2\dot{\mathbf{Q}}^T \dot{\mathbf{x}}^* + \ddot{\mathbf{Q}}^T \mathbf{x}^*,$$

and by substituting the latter expression into (2.15) we obtain the form of Cauchy's equation of motion valid in \mathbf{x} :

$$\varrho \ddot{\mathbf{a}} + \varrho \mathbf{Q}^T \frac{d\mathbf{v}^*}{dt} + 2\varrho \dot{\mathbf{Q}}^T \mathbf{v}^* + \varrho \ddot{\mathbf{Q}}^T \mathbf{x}^* = \text{Div } \mathbf{t} + \varrho \mathbf{f} \quad (2.18)$$

where the denotation $\dot{\mathbf{x}}^* = \mathbf{v}^*$ is introduced. If both sides are multiplied from left by \mathbf{Q} and reduced, the equation will have the following form:

$$\varrho \frac{d\mathbf{v}^*}{dt} = \mathbf{Q}(\text{Div } \mathbf{t}) + \varrho \mathbf{Q}\mathbf{f} - \varrho \mathbf{Q}\ddot{\mathbf{a}} - 2\varrho \mathbf{Q}\dot{\mathbf{Q}}^T \mathbf{v}^* - \varrho \mathbf{Q}\ddot{\mathbf{Q}}^T \mathbf{x}^*. \quad (2.19)$$

If we introduce the notations

$$\mathbf{t}^* = \mathbf{Q}\mathbf{t}\mathbf{Q}^T$$

and

$$\mathbf{f}^* = \mathbf{Q}\mathbf{f} - \mathbf{Q}\ddot{\mathbf{a}} - 2\mathbf{Q}\dot{\mathbf{Q}}\mathbf{v}^* - \mathbf{Q}\ddot{\mathbf{Q}}^T\mathbf{x}^*$$

we establish the equation

$$\varrho \frac{d\mathbf{v}^*}{dt} = \text{Div } \mathbf{t}^* + \varrho \mathbf{f}^*$$

analogous to (2.15). Here we used the identity

$$\mathbf{Q}(\text{Div } \mathbf{t}) = \text{Div}(\mathbf{Q}\mathbf{t}\mathbf{Q}^T)$$

that has the form

$$Q_{is} \frac{\partial t_{sk}}{\partial x_k} = Q_{is} \frac{\partial t_{sk}}{\partial x_j^*} Q_{jk} = \frac{\partial}{\partial x_j^*} (Q_{is} Q_{jk} t_{sk})$$

in rectangular components.

It can be seen from (2.20) that the tensor \mathbf{t} describing the surface forces transforms into \mathbf{t}^* while the transformed body force is accompanied by additive terms due to relative motion of the reference frames. If the reference frame \mathbf{x} is an inertia frame, then these additive terms are just the forces of inertia. This is easy to see if we rewrite them in the more usual form with the $\vec{\omega}^*$ angular velocity vector defined by

$$\vec{\omega}^* \times \delta = \mathbf{Q}\dot{\mathbf{Q}}^T$$

So the \mathbf{f}^* specific force of inertia defined in (2.20) will have the form

$$\mathbf{f}^* = \mathbf{Q}\mathbf{f} - \mathbf{Q}\ddot{\mathbf{a}} - 2\vec{\omega}^* \times \mathbf{v}^* - \vec{\omega}^* \times (\vec{\omega}^* \times \mathbf{x}^*) - \dot{\vec{\omega}}^* \times \mathbf{x}^*$$

where $\mathbf{Q}\ddot{\mathbf{a}}$ is the specific force of inertia belonging to the translation, $-2\vec{\omega}^* \times \mathbf{v}^*$ the Coriolis force, $-\vec{\omega}^* \times (\vec{\omega}^* \times \mathbf{x}^*)$ the centrifugal force and $-\dot{\vec{\omega}}^* \times \mathbf{x}^*$ Euler's force per unit mass.

Of course, there is no need to suppose that one of the reference frames is an inertia system. In each case, however, we regard (2.20) as transformation formulae. In this case, the (2.15) form of Cauchy's equation of motion is independent of the selection of the frame.

It is easy to see that the peculiarity of the inertia forces, namely, the additional terms, do not depend on real interactions but only on the selection of frame. Decompose the body force into two parts:

$$\mathbf{f} = \mathbf{f}_0 + \mathbf{f}_1,$$

where \mathbf{f}_0 be the resultant of the inertia forces and \mathbf{f}_1 the force describing real interactions. In this decomposition we can write the second half of (2.20) in form

$$\mathbf{f}_0^* + \mathbf{f}_1^* = \mathbf{Q}(\mathbf{f}_0 + \mathbf{f}_1) - \mathbf{Q}\ddot{\mathbf{a}} - 2\mathbf{Q}\dot{\mathbf{Q}}^T\mathbf{v}^* - \mathbf{Q}\ddot{\mathbf{Q}}^T\mathbf{x}^*$$

If no real body force occur, then \mathbf{f}_1 and \mathbf{f}_1^* are zero, i.e. (2.25) formally reduces to (2.20). Accepting this, as transformation between \mathbf{f}_0 and \mathbf{f}_0^* , the transformation

$$\mathbf{f}_1^* = \mathbf{Q}\mathbf{f}_1$$

arises for \mathbf{f}_1 and \mathbf{f}_1^* . This means that the forces describing real interactions transform due to the change of frame, i.e. the real forces are objective.

2.6. Electromagnetic forces.

The Newtonian attraction describes gravitational interactions with exactness far beyond the requirements of practice; in practical applications, it is considered only in the action of the largest masses in the environment. In most cases it is quite a simple task; for that very reason, we do not deal with the forces of gravity any more.

It is worth, however, paying greater attention to the electromagnetic effects partly because of the great practical importance of electromagnetism, and partly because the usual text books deal too little with the general form of ponderomotive force and the results are often ambiguous, [62, 89, 92, 102, 134].

To describe the ponderomotive force we have to start from the first group of Maxwell's equations:

$$\begin{aligned} \operatorname{rot} \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} &= 0, & \operatorname{div} \mathbf{B} &= 0, \\ \operatorname{rot} \mathbf{H} &= \mathbf{j} + \varrho_e \mathbf{v} + \frac{\partial \mathbf{D}}{\partial t}, & \operatorname{div} \mathbf{D} &= \varrho_e. \end{aligned} \quad (2.27)$$

We apply the usual notation: \mathbf{E} is the electric field strength; \mathbf{H} , the magnetic field strength; \mathbf{D} , the electric displacement; \mathbf{B} , the flux density; \mathbf{j} , the conductive electric current density; and ϱ_e , the electric charge density. This form of Maxwell's equations takes into account the characteristics of an electromagnetic field and the effects of the coexisting medium. The division of electromagnetic phenomena to characteristics of field and to effects of medium is not free from all arbitrariness; hereinafter, only one of the possible versions [62] is outlined:

We regard the electric field strength \mathbf{E} and the flux density \mathbf{B} as characteristics of field. The magnetic field strength \mathbf{H} and the electric displacement \mathbf{D} contain already information on polarization of the medium as well; therefore, these latter are eliminated by introducing the magnetization \mathbf{M} and the electric polarization \mathbf{P} . \mathbf{M} and \mathbf{P} are defined by equations

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (2.28)$$

and

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M} - \mathbf{v} \times \mathbf{P}) \quad (2.29)$$

where ε_0 is the permittivity of the vacuum, μ_0 the magnetic permeability of the vacuum and \mathbf{v} means the velocity of the moving medium [62, 102]. On the right-hand side of the equation (2.29) $-\mathbf{v} \times \mathbf{P}$ is the moving electric dipole acting like magnetic dipole; and it is not advisable to range this effect with the magnetic polarization. Here we note that the acceptance of the (2.29) formula in such form means that we must be content with small velocities and the relativistic effects are excluded from the scope of our study.

In order to calculate the ponderomotive force we have to substitute equations

(2.28) and (2.29) into Maxwell's equations:

$$\operatorname{rot} \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \quad (2.30a)$$

$$\operatorname{div} \mathbf{B} = 0 \quad (2.30b)$$

$$\frac{1}{\mu_0} \operatorname{rot} \mathbf{B} = \mathbf{j} + \varrho_e \mathbf{v} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} + \operatorname{rot} \mathbf{M} - \operatorname{rot}(\mathbf{v} \times \mathbf{P}), \quad (2.30c)$$

$$\varepsilon_0 \operatorname{div} \mathbf{E} = \varrho_e - \operatorname{div} \mathbf{P}, \quad (2.30d)$$

and then we have to multiply vectorially the so-established first equation on the right side by $\varepsilon_0 \mathbf{E}$ the third one by \mathbf{B} and to add the two equations:

$$\begin{aligned} \varepsilon_0 \operatorname{rot} \mathbf{E} \times \mathbf{E} + \frac{1}{\mu_0} \operatorname{rot} \mathbf{B} \times \mathbf{B} + \varepsilon_0 \frac{\partial \mathbf{B}}{\partial t} \times \mathbf{E} &= \mathbf{j} \times \mathbf{B} + \varrho_e \mathbf{v} \times \mathbf{B} + \\ + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \times \mathbf{B} + \frac{\partial \mathbf{P}}{\partial t} \times \mathbf{B} + \operatorname{rot} \mathbf{M} \times \mathbf{B} - \operatorname{rot}(\mathbf{v} \times \mathbf{P}) \times \mathbf{B}. \end{aligned} \quad (2.31)$$

Now we apply the identity (\circ notation means dyadic multiplication)

$$\operatorname{rot} \mathbf{u} \times \mathbf{u} = \operatorname{Div} \left(\mathbf{u} \circ \mathbf{u} - \frac{u^2}{2} \boldsymbol{\delta} \right) - \mathbf{u} \operatorname{div} \mathbf{u}$$

at the first two terms of the left-hand side:

$$\begin{aligned} \operatorname{Div} \left[\varepsilon \left(\mathbf{E} \circ \mathbf{E} - \frac{E^2}{2} \boldsymbol{\delta} \right) + \frac{1}{\mu_0} \left(\mathbf{B} \circ \mathbf{B} - \frac{B^2}{2} \boldsymbol{\delta} \right) \right] &= \\ = \frac{\partial}{\partial t} (\varepsilon_0 \mathbf{E} \times \mathbf{B}) + \varepsilon_0 \mathbf{E} \operatorname{div} \mathbf{E} + \mathbf{j} \times \mathbf{B} + \varrho_e \mathbf{v} \times \mathbf{B} + \\ + \frac{\partial \mathbf{P}}{\partial t} \times \mathbf{B} + \operatorname{rot} \mathbf{M} \times \mathbf{B} - \operatorname{rot}(\mathbf{v} \times \mathbf{P}) \times \mathbf{B}. \end{aligned} \quad (2.32)$$

During further transformations we use the identities

$$\operatorname{rot} \mathbf{M} \times \mathbf{B} = \operatorname{Div}[\mathbf{M} \circ \mathbf{B} - (\mathbf{M}\mathbf{B})\boldsymbol{\delta}] + \mathbf{M} \operatorname{Grad} \mathbf{B}, \quad (2.33)$$

$$\mathbf{E} \operatorname{div} \mathbf{P} = \operatorname{Div}(\mathbf{E} \circ \mathbf{P}) - (\mathbf{P} \operatorname{grad})\mathbf{E} \quad (2.34)$$

and

$$\frac{\partial \mathbf{P}}{\partial t} - \operatorname{rot}(\mathbf{v} \times \mathbf{P}) = \varrho \frac{d\mathbf{p}}{dt} - \operatorname{Div}(\mathbf{v} \times \mathbf{P}) \quad (2.35)$$

where the vector \mathbf{p} is defined by relation

$$\mathbf{P} = \varrho \mathbf{p} \quad (2.36)$$

as well as (2.30b) and (2.30d). So we obtain:

$$\begin{aligned} \operatorname{Div} \left[\varepsilon_0 \left(\mathbf{E} \circ \mathbf{E} - \frac{E^2}{2} \boldsymbol{\delta} \right) + \frac{1}{\mu_0} \left(\mathbf{B} \circ \mathbf{B} - \frac{B^2}{2} \boldsymbol{\delta} \right) + (\mathbf{M}\mathbf{B})\boldsymbol{\delta} - \mathbf{M} \circ \mathbf{B} + \mathbf{E} \circ \mathbf{P} \right] &= \\ = \frac{\partial}{\partial t} (\varepsilon_0 \mathbf{E} \times \mathbf{B}) + \varrho_e (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \mathbf{j} \times \mathbf{B} + (\mathbf{P} \operatorname{grad})\mathbf{E} + \\ + \varrho \frac{d\mathbf{p}}{dt} \times \mathbf{B} + \mathbf{M} \operatorname{Grad} \mathbf{B} - \operatorname{Div}(\mathbf{v} \times \mathbf{P}) \times \mathbf{B}. \end{aligned} \quad (2.37)$$

To make clearer aforesaid formula one more transformation is required to which we use the identity

$$\text{Div}(\mathbf{v} \circ \mathbf{P}) \times \mathbf{B} = \text{Div}(\mathbf{v} \times \mathbf{B} \circ \mathbf{P}) - \mathbf{v} \times (\mathbf{P} \text{ grad}) \mathbf{B}. \quad (2.38)$$

So we obtain

$$\begin{aligned} \text{Div} \left[\varepsilon_0 \left(\mathbf{E} \circ \mathbf{E} - \frac{E^2}{2} \boldsymbol{\delta} \right) + \frac{1}{\mu_0} \left(\mathbf{B} \circ \mathbf{B} - \frac{B^2}{2} \boldsymbol{\delta} \right) + \right. \\ \left. + (\mathbf{M}\mathbf{B})\boldsymbol{\delta} - \mathbf{M} \circ \mathbf{B} + (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \circ \mathbf{P} \right] = \\ = \frac{\partial}{\partial t} (\varepsilon_0 \mathbf{E} \times \mathbf{B}) + \varrho \mathbf{f}_{EM} \end{aligned} \quad (2.39)$$

where

$$\varrho \mathbf{f}_{EM} = \varrho_e \mathbf{E} + (\varrho_e \mathbf{v} + \mathbf{j} + \varrho \frac{d\mathbf{P}}{dt}) \times \mathbf{B} + (\mathbf{P} \text{ grad}) \mathbf{E} + \mathbf{v} \times (\mathbf{P} \text{ grad}) \mathbf{B} + \mathbf{M} \text{ Grad } \mathbf{B}. \quad (2.40)$$

We regard the equation (2.39) as a balance of momentum for the electromagnetic field. On the left hand side, the tensor after Div is the electromagnetic stress tensor; the $\varepsilon_0 \mathbf{E} \times \mathbf{B}$ quantity is called momentum density of the electromagnetic field while $\varrho \mathbf{f}_{EM}$ is the ponderomotive force density.

This expression of the ponderomotive force is in full accordance with molecular aspects and complies with the nonrelativistic dipole approach [62, 102].

The analysis of electromagnetic stress tensor is not mentioned; we only draw attention to the fact that it is generally non-symmetric, which means that the electromagnetic field plays a part in the transport of moment of momentum.

Finally we mention that the above-outlined separation of medium and electromagnetic field involves difficulties in case of diamagnetic materials, showing by this the arbitrariness of the method [118].

Nevertheless, the reported method can be considered as useful as it describes the effect of the electromagnetic field on mechanical motion rather simply.

2.7. Moment of momentum.

The continuum-mechanical definition of momentum defined by (2.8) and (2.9) respectively is unambiguous only in the case where the velocity field is exactly determined. For velocity the definition (1.11) seems to be exact; however, attention should be drawn to a circumstance not negligible in modern continuum-theory; i.e., that the real media are of molecular configuration and the aforesaid mode of description leaves this fact out of consideration. If we intend to consider the molecular background of a continuum, the starting point may not be the motion function (1.4). We insist on the continuum model, henceforward, because of its simplicity and effectiveness. However, we give a new meaning to the fundamental concept by interpreting it on the basis of molecular configuration. We do not intend to enter the labyrinth of such a model that reflects the details of the molecular motions; it would lead us to an extremely complicated problem and would not bring

any considerable advantage in a fundamentally macroscopic theory. In interpreting the continuum-mechanical conceptions, we adopt statistical considerations and interpret the macroscopic quantities by expected values defined on the basis of the theory of probability. The density ϱ of a continuum is substituted by the expected value of corpuscular mass density; and the macroscopic momentum density $\varrho\mathbf{v}$ by that of microscopic momentum-density. The proper selection of event-space as a basis of calculating expected value (taking into account the thermal motion of the molecules) results in functions which do not show deviations within the molecular length scale.

On the basis of density and momentum density thus obtained, we can interpret the baricentric velocity (mentioned as velocity so far and even in the future). Based on formulas (1.10), (1.12) and (1.13), we obtain the function (1.4). The conception shows that the (1.4) motion function describes the motion of a continuum with molecular structure only approximately and not in full detail.

So it does not seem surprising that the moment density of momentum is not identical with the moment of momentum density. The moment of momentum can be interpreted by formula

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} + \mathbf{L}^i \quad (2.41)$$

or expressed with values referred to as local by formula

$$\mathbf{l} = \mathbf{r} \times \mathbf{v} + \mathbf{l}^i \quad (2.42)$$

where \mathbf{l} is the specific moment of momentum, \mathbf{v} =baricentric velocity, and \mathbf{l}^i the specific internal moment of momentum which can be interpreted as the macroscopic manifestation of molecular rotations. The reality of concept of internal moment of momentum is confirmed experimentally by the Einstein-de Haas effect. [38].

The balance of moment of momentum can be obtained with the aid of the theorem of mechanical moment of momentum. The theorem of moment of momentum says that the time derivative of moment of momentum is equal to the torque acting on the body. In integral form, it is

$$\frac{d}{dt} \int_V (\mathbf{r} \times \varrho\mathbf{v} + \varrho\mathbf{l}^i) dV = \int_A (\mathbf{r} \times \mathbf{t} + \mathbf{\Pi}) d\mathbf{A} + \int_V (\mathbf{r} \times \varrho\mathbf{f} + \varrho\mathbf{m}) dV, \quad (2.43)$$

where $\mathbf{\Pi}$ is the so-called couple stress tensor and \mathbf{m} is the couple density per unit mass. In differential form,

$$\mathbf{r} \times \varrho \frac{d\mathbf{v}}{dt} + \varrho \frac{d\mathbf{l}^i}{dt} = \text{Div}(\mathbf{r} \times \mathbf{t} + \mathbf{\Pi}) + \mathbf{r} \times \varrho\mathbf{f} + \varrho\mathbf{m}. \quad (2.44)$$

This equation can be reduced if we use Cauchy's equation of motion.

Substitute the term $\varrho \frac{d\mathbf{v}}{dt}$ into (2.44) from (2.15):

$$\mathbf{r} \times \text{Div}\mathbf{t} + \mathbf{r} \times \varrho\mathbf{f} + \frac{d\mathbf{l}^i}{dt} = \text{Div}(\mathbf{r} \times \mathbf{t} + \mathbf{\Pi}) + \mathbf{r} \times \varrho\mathbf{f} + \varrho\mathbf{m},$$

whereof we obtain after reductions the equation

$$\varrho \frac{d\mathbf{l}^i}{dt} = 2\mathbf{w}(\mathbf{t}) + \text{Div}\mathbf{\Pi} + \varrho\mathbf{m} \quad (2.45)$$

where $\mathbf{w}(\mathbf{t})$ is the vector invariant of Cauchy's stress tensor which is defined in rectangular components by equations

$$w_1 = \frac{1}{2}(t_{32} - t_{23}), \quad w_2 = \frac{1}{2}(t_{13} - t_{31}), \quad w_3 = \frac{1}{2}(t_{21} - t_{12}) \quad (2.46)$$

If neither couple stress nor torque density occur and the internal moment of momentum is zero, we conclude the symmetry of Cauchy's stress tensor. In practically all important cases it is true, but exceptions exist: e.g., the liquid crystals prove experimentally the reality of couple stress tensor while the interaction with electromagnetic field serves as an example for torque density.

2.8. Electromagnetic couple density.

The torque exerted by the electromagnetic field is defined by the balance equation (2.39) complemented by the hypothesis that no internal moment of momentum exists in the electromagnetic field. The balance equation of moment of momentum in the electromagnetic field is

$$\frac{\partial}{\partial t} [\mathbf{r} \times \varepsilon_0 (\mathbf{E} \times \mathbf{B})] + \mathbf{r} \times \varrho \mathbf{f}_{EM} + \varrho \mathbf{m} = \text{Div}(\mathbf{r} \times \mathbf{T}) \quad (2.47)$$

where \mathbf{m} is the torque density exerted by the electromagnetic field to the medium, and \mathbf{T} is the electromagnetic stress tensor

$$\mathbf{T} = \varepsilon_0 \left(\mathbf{E} \circ \mathbf{E} - \frac{E^2}{2} \boldsymbol{\delta} \right) + \frac{1}{\mu_0} \left(\mathbf{B} \circ \mathbf{B} - \frac{B^2}{2} \boldsymbol{\delta} \right) + (\mathbf{M}\mathbf{B})\boldsymbol{\delta} - \mathbf{M} \circ \mathbf{B} + (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \circ \mathbf{P}. \quad (2.48)$$

The meaning of \mathbf{f}_{EM} has already been given in (2.40). To calculate the specific torque density we have to multiply vectorially both sides of (2.39) by the position vector from the left and to subtract it from (2.47). Thus we obtain the equation

$$\varrho \mathbf{m} = \text{Div}(\mathbf{r} \times \mathbf{T}) - \mathbf{r} \times \text{Div} \mathbf{T} = 2\mathbf{w}(\mathbf{T}) \quad (2.49)$$

from what, by using the expression (2.48),

$$\varrho \mathbf{m} = \mathbf{M} \times \mathbf{B} + \mathbf{P} \times (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (2.50)$$

is given. This form of torque corresponds to the popular notion on electric and magnetic dipole and confirms, at the same time, our presumptions [102].

In addition we mention that considerable torque does not generally belong to the gravitational and inertial forces; therefore, the specific torque is mostly of electromagnetic origin. This justifies the notation \mathbf{m} used in equations (2.47) to (2.50) without any distinction.

CHAPTER III

DEFORMATION AND STRESS

Without knowledge of a specific force, Cauchy's equation of motion (2.15) in itself is as unproductive in continuum mechanics as Newton's second law is in point mechanics. To describe the motion, i.e. to solve the equations, the quantities that describe the interactions must be known. In a continuum, these are the stress tensor \mathbf{t} and the body force \mathbf{f} . To manage such a problem, one has to know on what and how the stress tensor \mathbf{t} and the body force \mathbf{f} depend.

The body force \mathbf{f} can easily be given (in the preceding chapter rather general relationships were presented to determine it). The situation is rather different with the stress tensor \mathbf{t} . This comes from the fact that Cauchy's stress tensor describes the interactions of the neighboring parts of the medium; it has many aspects according to the complexity of the molecular interactions.

The conditions determining the stress tensor \mathbf{t} and the way of dependence is not generally given; one has to rely on modeling. There are several ways for making models. Since our main purpose is to survey modeling based on the methods of irreversible thermodynamics, other widely used methods will only briefly be discussed in this chapter. As a complete survey of methods is beyond the scope of this book, only the methods of rheology are outlined and the most significant results of modern non-linear continuum mechanics are presented.

3.1. Classical body models.

The simplest models from both the theoretical and simplest practical point of view are known from classical mechanics. Considering the classical branches of continuum mechanics as a pattern, a model in an exact theory is constructed in a quantitative form. The variables that the stress depends on are given and also the manner of dependence. In some cases the stress can also be regarded as an independent variable and the dependence of deformation on stress (and perhaps on other parameters: temperature, electric or magnetic polarization etc.) is given, as well.

Any idealized medium is called a body. Such a body is realized in the classical idea of rigid body, the perfectly elastic body obeying Hook's law, the ideal fluid in which the interaction is described by Pascal's law and the laminar flow of viscous fluid formulated by the Navier-Stokes equations. In the literature of rheology, these bodies are called: Euclid-body, Hooke-body, Pascal-body, Newton-fluid or Navier-Stokes-fluid and sometimes (in the special case of incompressibility) Stokes-fluid [96, 137].

Let us discuss now the classical models by giving the forms of the material equations that are called constitutive equations in modern literature.

3.1.1. Rigid body. The rigid body (Euclid-body) represents the idealized limit behavior of the solid material. During the motion of a rigid body, deformation does not arise so tensor \mathbf{d} defined in (1.26) is the unite tensor:

$$\mathbf{d} = \boldsymbol{\delta} \quad (3.1)$$

Since, deformation does not occur in a rigid body, this model will not be discussed.

3.1.2. Hooke-body. The Hooke-body is the material of classical elasticity. A substantial property of this material is that the forces are proportional to the deformation. It is not, of course, a definition of mathematical precision; however, it reflects the essence of the matter. To establish an exact definition several problems should be examined.

The first is that the tensor \mathbf{d} or \mathbf{D} , describing the deformation of the body, depends also on the reference configuration. Nevertheless, the interactions between the different parts of the body may not depend on the choice of reference configuration. The classical theory of elasticity offers the observation that elastic bodies change their shape as a result of load; after unloading they regain their original shape. This means that there exists a favored configuration that the body takes on if no stresses are applied. In finite pieces of a medium, it does not always hold; but if one considers a sufficiently small vicinity of a point, the complications are avoided [42, 57, 75, 96, 121, 144, 154]. If the stress-free configuration is chosen as a reference configuration, Cauchy's stress is non-zero in any deformed state. Choosing the reference configuration in such a way, the defining constitutive equation of Hooke's body is given as

$$\mathbf{t} = \mathcal{L}(\mathbf{d} - \boldsymbol{\delta}). \quad (3.2)$$

For a Hooke-body, Cauchy's stress tensor is a homogeneous and linear function of tensor $\mathbf{d} - \boldsymbol{\delta}$, which is regarded as the measure of deformation. Choosing another tensor as an independent variable as a measure of deformation would, of course, reach a different body-model which could also be called "Hooke-body". Difficulties arising from this are not very important in practice, since Hooke's law — constitutive equation (3.2) — gives a good approximation for real media only if small deformations are concerned, in this case, the usual measures of deformation are essentially the same.

As the homogeneous linear tensor-tensor function (3.2) reflects also the symmetry of the medium, strictly speaking, the family of Hooke-bodies should be mentioned according to the possible symmetry classes. Since we are not going to deal with the mechanical behavior of crystals, we confine ourselves to isotropic media and (3.2) is written in the much simpler form:

$$\mathbf{t} = 2\mu(\mathbf{d} - \boldsymbol{\delta}) + \lambda \operatorname{tr}(\mathbf{d} - \boldsymbol{\delta})\boldsymbol{\delta} \quad (3.3)$$

which is the best known form of Hooke's law [45]. Here μ and λ are the so-called Lamé-coefficients, which are generally regarded as constant. However, in real cases, they depend on the temperature of the medium.

3.1.3. Pascal-body. The model in the theory of ideal fluids rests upon the hypothesis that shear stresses do not arise even during motion. Cauchy's stress is reduced to a spherical tensor and is given by a scalar pressure p :

$$\mathbf{t} = -p \boldsymbol{\delta} \quad (3.4)$$

An often used simplifying assumption is that fluid is incompressible and formulates on the basis of (2.6):

$$\operatorname{div} \mathbf{v} = 0 \quad (3.5)$$

The behavior of the incompressible Pascal-body is determined by equations (3.4) and (3.5). For compressible Pascal-bodies the (2.6) form of the continuity equation has to be used instead of (3.5); furthermore, to accomplish the model, one has to ascertain on what and how the pressure p depends. A relatively simple case is the model of the so-called barotrop-fluid where the pressure and the density are in a unique relation.

The Pascal-body is an extreme model that undergoes without resistance the deformations not associated with changes of volume. One can say that the Pascal-body is the other extreme compared to the Euclid-body. Deformations are not connected with surface forces.

3.1.4. Newton-body. The flow of numerous ordinary fluids is described by excellent approximation with the help of an ideal fluid model (Pascal-body; see hydrodynamics, ideal fluids [75, 137]); while in other cases, observations show significant deviations. The observed deviations are described in a first approximation by Newton's law of viscosity, according to which in real fluids shear stresses also arise during flow; these excess stresses, compared to the Pascal-body, are linear functions of the speed of deformation. Mathematically, the constitutive equation of the Newton-body is formulated as

$$\mathbf{t} = 2\eta(\operatorname{Grad} \mathbf{v})^s + (\eta_v \operatorname{div} \mathbf{v} - p)\boldsymbol{\delta} \quad (3.6)$$

where η and η_v are the shear and volume viscosity respectively, and p the pressure. The determination of the latter is done as in the case of the compressible Pascal-body. Confining the examinations to incompressible fluids, (3.6) takes the simpler

$$\mathbf{t} = 2\eta(\operatorname{Grad} \mathbf{v})^s - p\boldsymbol{\delta} \quad (3.7)$$

form. Substituting the constitutive equation (3.6) into Cauchy's equation of motion (2.15), the Navier-Stokes equations are obtained which, together with continuity and the relation for the pressure, give the basis of the classical theory of viscous fluids.

The body models surveyed so far are called classical bodies after M. Reiner since classical chapters of mechanics are based upon them. The solution of the differential equations has been well-known in many cases. The unsolved problems, however, belong to the field of applied mathematics, not physics. The theory of classical bodies plays an important role in the practice of engineering. Classical bodies are also applied in many cases when the practice markedly deviates from

them. The main reason for this is the fact that, in the case of the discussed models, the mathematical methods are thoroughly worked out and accessible.

A great many materials are applied in practice, the motion of which can not be described by the preceding simple models. Such materials are, for instance, pastry, polymer melts, steel preheated for forging or bitumen. To meet the needs of practice, rheology makes new models generalizing the classical constitutive equations.

3.2. Mechanical models of rheology.

The behavior of the rheological bodies are illustrated by mechanical models. The properties of the Hooke-body are usually illustrated by a spring, the elongation of which is proportional to the force (Figure 3.1). To illustrate a Newton-body, a device similar to the shock absorber of vehicles called a ‘dashpot’ is used. In it, the speed of elongation varies with the force (Figure 3.2). Modeling the materials that show viscous and elastic behavior at the same time, rheology applies different combinations of the Hooke- and Newton-body obtaining a variety of the so-called viscoelastic bodies.

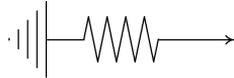


Figure 3.1
Hooke-body

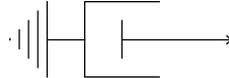


Figure 3.2
Newton-body

3.2.1. Maxwell-body. The mechanical model of the Maxwell-body is obtained by connecting a Hooke-body and a Newton-body in series (Figure 3.3).



Figure 3.3
Maxwell-body

The deformation is split into two parts:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \quad (3.8)$$

for which

$$\tau = \eta \dot{\varepsilon}_1 \quad (3.9)$$

and

$$\tau = \mu \varepsilon_2 \quad (3.10)$$

The equation of the Maxwell-body is attained to by combining them:

$$\dot{\varepsilon} = \frac{1}{\eta} \tau + \frac{1}{\mu} \dot{\tau}. \quad (3.11)$$

A characteristic feature of a Maxwell-body is that by keeping the deformation at a constant value the stress gradually decreases and the Maxwell-body relaxes. This

is demonstrated from (3.11). Assuming constant deformation, the left hand side of (3.11) is zero and the solution of the homogeneous, first order, linear differential equation reads:

$$\tau = \tau_0 \exp\left(-\frac{\mu}{\eta}t\right), \quad (3.12)$$

where τ_0 is the initial stress. The $\frac{\eta}{\mu}$ quotient is generally called relaxation time.

In the case of rapidly changing stresses the derivative on the right hand side of (3.11) is very large and the first term is neglected. Integrating the equation and dissolving the integration constant into the measure of deformation, the relation

$$\varepsilon = \frac{1}{\mu}\tau \quad (3.13)$$

is obtained, which is the equation of a Hooke-body. This means that, against a rapidly increasing load, the Maxwell-body acts elastically.

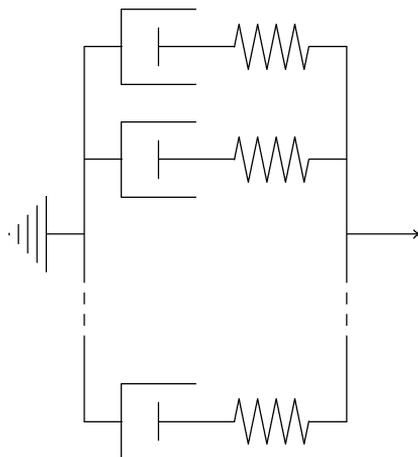


Figure 3.4
Generalized Maxwell-body

Quite different properties appear when long and slow loads are present. Now the second term is neglected on the right side in (3.11), returning so to the equation of a Newton-body. Under slow loads the Maxwell-body behaves like a viscous fluid. A lot of real material shows properties like the outlined ones (e.g. plastics); however, the quantitative coincidence with the Maxwell-body is not complete in general. To improve the quantitativity, new models are constructed connecting two or more Maxwell-bodies in parallel. They are usually called generalized Maxwell-body (Figure 3.4). The constitutive equations are obtained by splitting the stress into parts:

$$\tau = \sum_i \tau_i \quad (3.14)$$

and (3.11) is used to each element:

$$\dot{\varepsilon} = \frac{1}{\eta_i}\tau_i + \frac{1}{\mu_i}\dot{\tau}_i \quad (i = 1, 2, \dots, n) \quad (3.15)$$

The constitutive equation is attained by combining them.

The calculation is quite easily carried out with operators or supposing the time dependence to be of $\exp(pt)$, where p is some complex number. Then the equations (3.15) simplify to algebraic ones, from which unknowns are expressed and substituted into (3.14):

$$\tau = \sum_i \frac{p}{\frac{1}{\eta_i} + \frac{p}{\mu_i}} \varepsilon. \quad (3.16)$$

The equation with operators is similar, then p is the differential operator.

3.2.2. Kelvin-body (Voigt-body). The model of the Kelvin-body is obtained by connecting a Hooke-body and a Newton-body in parallel (Figure 3.5). The resulting stress is split up to two parts:

$$\tau = \tau_1 + \tau_2 \quad (3.17)$$

for which

$$\tau_1 = \eta \dot{\varepsilon} \quad (3.18)$$

and

$$\tau_2 = \mu \varepsilon. \quad (3.19)$$

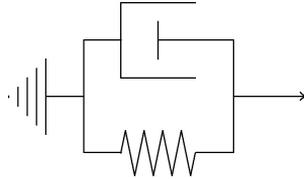


Figure 3.5
Kelvin-body

Therefore the constitutive equation of the Kelvin-body is:

$$\tau = \mu \varepsilon + \eta \dot{\varepsilon} \quad (3.20)$$

The Kelvin-body is a solid which deforms when loaded but after unloading it regains its original form. The deformation of a Kelvin-body follows the load with delay. This is shown when the stress suddenly arises, and remains constant. The solution of the differential equation (3.20) reads:

$$\varepsilon = \frac{\tau}{\mu} [1 - \exp(-\frac{\mu}{\eta} t)] \quad (3.21)$$

The deformation gradually follows the changes of the load. This phenomenon is called relaxation, where the quotient $\frac{\eta}{\mu}$ is the relaxation time. Similarly as in the case of the Maxwell-body, one can show that the Kelvin-body behaves viscously against rapid loads while in the case of slow deformations has elastic properties. For the sake of better quantitative agreement with materials of technology, new

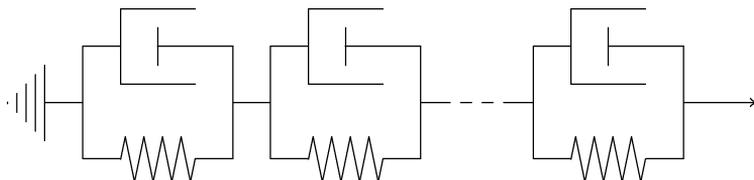


Figure 3.6
Generalized Kelvin-body

models are constructed by connecting several Kelvin-bodies in series, which are called generalized Kelvin-body (Figure 3.6).

The constitutive equation is obtained by splitting up the deformation;

$$\varepsilon = \sum \varepsilon_i, \quad (3.22)$$

and applying (3.20) to each element connected in series:

$$\tau = \mu_i \varepsilon_i + \eta_i \dot{\varepsilon}_i \quad (3.23)$$

and combining them. It can also be given in a complex number form:

$$\varepsilon = \left(\sum \frac{1}{\mu_i + \eta_i p} \right) \tau. \quad (3.24)$$

Besides the above-discussed generalized Maxwell- and Kelvin-bodies, further mechanical models can be constructed by other combinations of the Hooke- and Newton-bodies. The models attained in this way are not new. Literature [137, 144] is recommended to readers who are interested in the details.

3.2.3. The rheological model of plastic flow. A comprehensive survey of the methods of linear viscoelasticity would require too much space and the alternative methods already have an extensive literature [27, 84, 89, 132, 155]. It is appropriate here to give a short account of the rheological methods describing the bodies deviating from linearity.

An important model of rheology is the ideally plastic body, describing the permanent deformations due to load exceeding the elastic limit.

In the terminology of rheology, the ideally plastic body is called St. Venant-body. On balance, it is not a well-defined body but rather a number of models behaving similarly and differing from each other just in the correlation of the material coefficients appearing during different ways of loading. The St. Venant-body is characterized by the constitutive relationships

$$\begin{aligned} \tau &= \tau_0 & \text{if } \dot{\varepsilon} > 0 \\ \tau &= -\tau_0 & \text{if } \dot{\varepsilon} < 0 \\ -\tau_0 < \tau < \tau_0 & & \text{if } \dot{\varepsilon} = 0 \end{aligned} \quad (3.25)$$

(e.g. in the case of simple shear) (Figure 3.7). The mechanical model of the St. Venant-body is the frictional joint that does not yield up to a critical force but elongates freely if affected by an excess force (Figure 3.8).

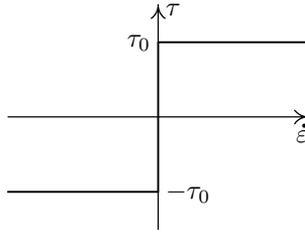
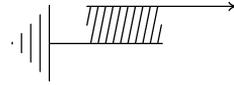
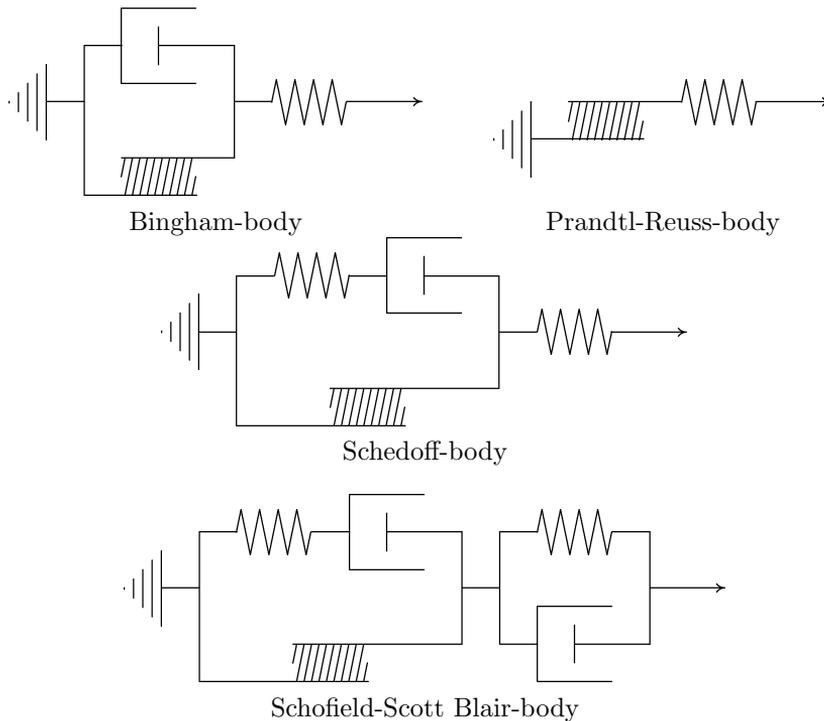


Figure 3.7

Figure 3.8
St. Venant-body

Combination of the St. Venant-body with either the Newton-body or the Hooke-body makes possible the introduction of further body models [138]. The viscoplastic, elastoplastic and viscoelastic bodies can be obtained this way, or by more complicated combinations. Because of the non-linear behavior of the St. Venant-body, the hierarchy of these cannot be classified simply like the system of the viscoelastic bodies. The mechanical models of some bodies are illustrated in Figure 3.9. Their behavior is not examined in detail; the mechanical models are self-explanatory.

Figure 3.9
Some visco-elasto-plastic bodies

There are some elastoplastic bodies together with their elongation diagram in Figure 3.10. To calculate using the models, one must take into account that the

stress is not a single valued function of the deformation, according to the appearance of the plastic flow. So on the diagrams belonging to the figures, the history of the deformation is also denoted.

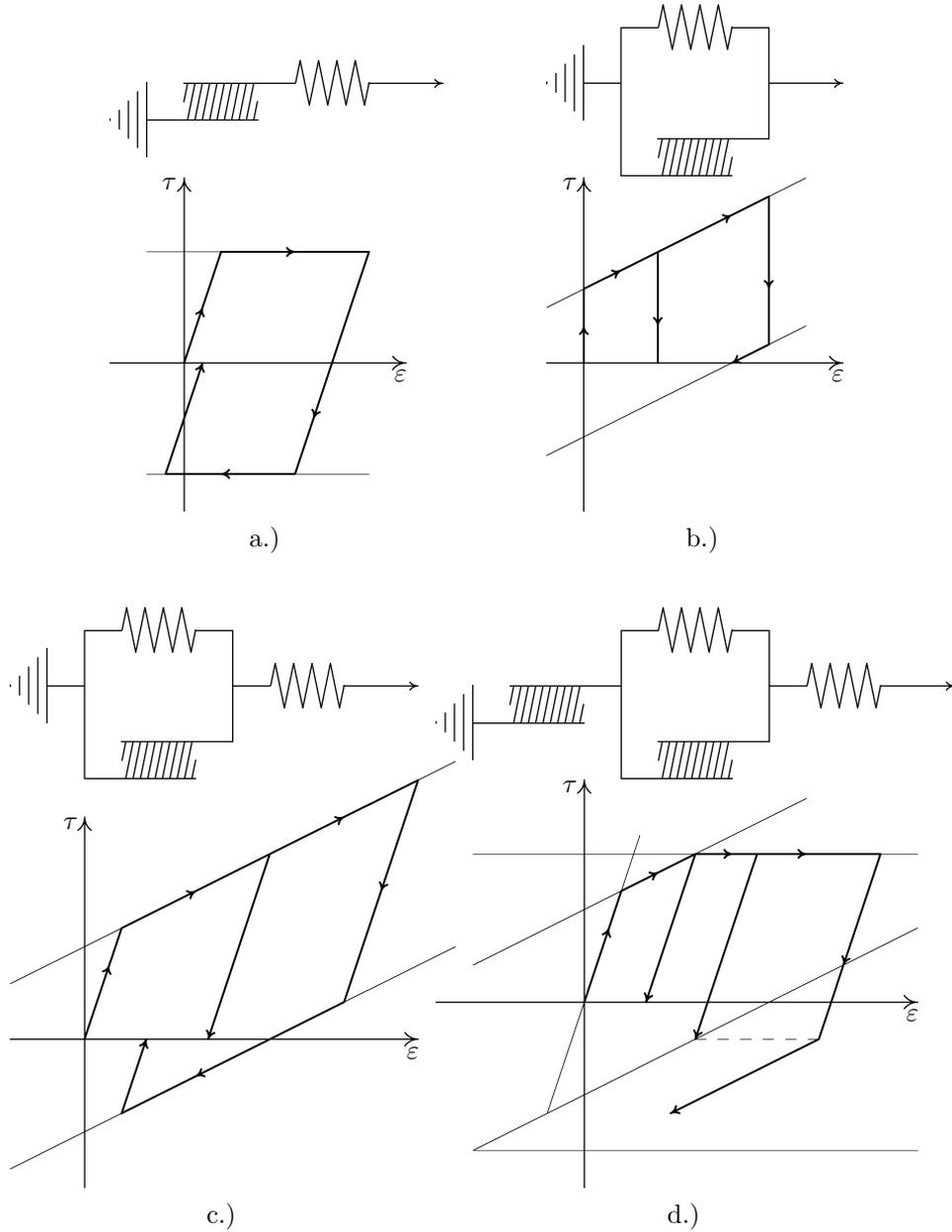


Figure 3.10
Some elasto-plastic bodies and their behavior

3.2.4. Three dimensional loading of the ideally plastic body. Plastic behavior is typically non-linear and so the discussion of its possible constitutive equations can only be solved more or less by the methods of modern non-linear mechanics, which is to be discussed later. At this point, it is satisfactory to survey the methods of plasticity that can be assumed classical today. All the models start from the hypothesis that the deformation of the plastic materials can be divided up into two parts: an elastic- and a permanent deformation. A further hypothesis is that the tensor describing the speed of permanent deformation can be obtained from the traceless part of the stress tensor (stress deviator) with the help of a scalar multiplier. For ideally plastic bodies, i.e. when there is no elastic deformation, the stress deviator is gained by multiplying the deformation rate with some number:

$$\mathbf{t}_0 = \lambda \dot{\mathbf{d}}. \quad (3.26)$$

According to the classical theories, the multiplier λ has to be chosen so that the load corresponding to tensor \mathbf{t}_0 would satisfy the yield condition. In calculation, equation (3.26) is to be substituted into the yield condition

$$f(\mathbf{t}_0) = 0 \quad (3.27)$$

and hence the equation

$$f(\lambda \dot{\mathbf{d}}) = 0 \quad (3.28)$$

is obtained. From this equation, λ can be determined. This also means that

$$f(\mathbf{t}_0) = 0 \quad (3.29)$$

is regarded as the condition of the plastic flow. The form of function in (3.27) may not depend on the choice of the coordinate system, but it can contain the trace of the tensor \mathbf{t} as a parameter, i.e., the scalar pressure.

To describe ideally plastic bodies in a traditional way, two kinds of flow condition are used: the Mises- and the Mohr-condition. Because of its simple analytical form, the Mises-condition is easier for calculating complicated flow patterns:

$$\text{tr}(\mathbf{t}_0^2) = 2k^2. \quad (3.30)$$

According to this, the constitutive equation reads:

$$\mathbf{t}_0 = \frac{k\sqrt{2}}{\sqrt{\text{tr}(\dot{\mathbf{d}}_0^2)}} \dot{\mathbf{d}}_0 \quad (3.31)$$

This yield condition was proposed by Mises, who emphasized just the simplicity. He also showed that his method gave the same result as the accepted flow conditions, apart from a difference of a few percentage points. Later, Hencky arrived at the same condition starting from a hypothesis that the medium can store elastic energy only up to a limited value [137].

According to the Tresca-condition, a special case of Mohr's, plastic flow arises if the shear stress reaches a critical value on any surface in the medium. This

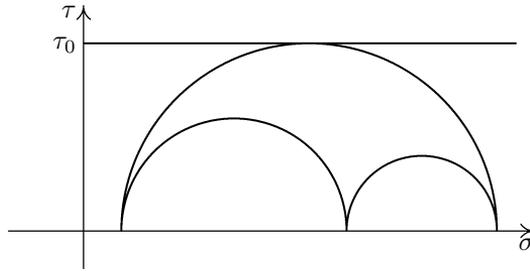


Figure 3.11
Tresca's yield condition in Mohr's diagram

condition is clearly illustrated on the Mohr-diagram. On the Mohr-diagram, the shear stress is on the vertical axis, so the meaning of the Tresca-condition is that the horizontal line is the tangent of the circle with the largest radius (Figure 3.11).

It is seen from the figure that the Tresca-condition means that the difference between the largest and smallest eigenvalues of the stress tensor is twice as much as the value of the critical stress. To formulate this condition for analytical calculations is rather difficult.

The Tresca condition was generalized by Mohr. According to the Mohr-condition the critical shear stress can depend on the normal stress arising on the given surface. This means that the Mohr circle touches some other curve and not a horizontal line. This curve in practice is mostly a slightly sloping line or an elongated ellipse (Figure 3.12), the shape of which is induced solely by practical applicability.

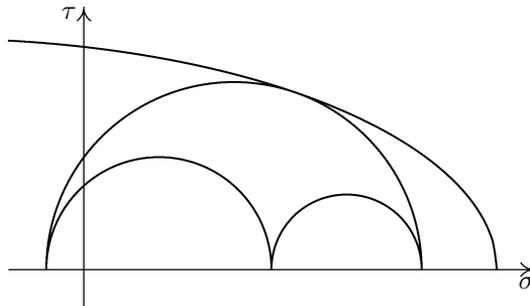


Figure 3.12
Mohr's yield condition

3.2.5. Further non-linearities. The above-discussed bodies apply very well in most of the practical cases, especially if the deformations are small. There are, however, large deformations where neither the linear constitutive equations nor the models of plasticity work well. A typical example of this is the deformation of the vulcanized rubber.

Vulcanized rubber regains its original shape after having unloaded. For slow deformations, we have a good approximation (in equilibrium, an exact one) if stating that the stress depends only on the deformation:

$$\mathbf{t} = \mathbf{t}(\mathbf{d}) \quad (3.32)$$

In isotropic medium, this function has the form

$$\mathbf{t}(\mathbf{d}) = f_0 \boldsymbol{\delta} + f_1 \mathbf{d} + f_2 \mathbf{d}^2 \quad (3.33)$$

where f_1, f_2, f_3 are functions depending on the invariants of tensor \mathbf{d} . In the particular case of the rubber elasticity, equation (3.33) becomes

$$\mathbf{t}_0 = G \left[\mathbf{d}^2 - \frac{1}{3} (\text{tr } \mathbf{d}^2) \boldsymbol{\delta} \right] \quad (3.34)$$

where G is the shear modulus. The forms of the functions in (3.33) are

$$f_0 = -\frac{1}{3}(I_1^2 - 2I_2), \quad f_1 = 0, \quad f_2 = G \quad (3.35)$$

where I_1 , and I_2 are the usual invariants of the tensor \mathbf{d} which are given with the eigenvalues in the form

$$I_1 = d_1 + d_2 + d_3, \quad I_2 = d_1 d_2 + d_2 d_3 + d_3 d_1$$

Supposing the existence of an elastic energy, the elastic potential is introduced as

$$\psi = \psi(I_1, I_2, I_3) \quad (3.36)$$

from which the (3.33) form of the stress is derived by differentiating with respect to the components of the tensor \mathbf{d} :

$$d\psi = (\mathbf{d}^{-1} \mathbf{t}) : d\mathbf{d} \quad (3.37)$$

The materials which have elastic potential are usually called hyperelastic bodies [42, 96].

Non-linear behavior is observed quite often in fluids as well. The qualitative form of the relation between force and motion was found by Oswald in 1926. The relation between shear rate and shear stress is shown in Figure 3.13. It is called Oswald-curve [129, 130].

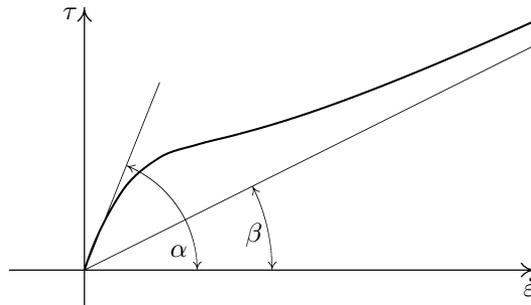


Figure 3.13
Oswald's curve

The survey of basic methods of rheology is closed by mentioning the phenomenon of tixotropy. The non-linearity, described by the Oswald curve, can also be assumed as a decrease in the viscosity of the fluid caused by shear. Considering the molecular structure, the phenomenon is interpreted by supposing that the equilibrium structure of the fluid disintegrates during flow.

This consideration does not explain the fact that most of the measurements result in a decrease of viscosity and an increase is rare. According to the explanation based on the change of the structure, this kind of phenomenon is usually called structural viscosity.

There are several media in practice in which the structural changes follow the motion but slowly. The viscosity decreases with some delay. This latter phenomenon is called tixotropy. Since, in most of the experiments, the viscosity decreases, the term tixotropy is reserved for materials decreasing viscosity. The behavior of the materials increasing viscosity during motion is often called reopexy. Sometimes it is called dilatancy, too. There is no common terminology for the above field [137]. This deficiency is explained by the fact that an increase of viscosity caused by motion is rare, it is observed in some colloids of complicated structure, e.g. in some clay-water suspension and in some paints.

3.3. On the methods of modern continuum mechanics.

In the last decades significant results were achieved in the non-linear mechanical theory of continua. It was motivated, above all, by the claims of practice and technology. On the one hand, engineers created the framework of the new methods; on the other hand, mathematicians also took part in it. They could manage to formulate and solve the non-linear mathematical problems put forward by non-linear processes, and did not shrink back even from applying the most abstract chapters of modern mathematics.

The modern non-linear continuum mechanics describes the motions of continua in quite a different way than rheology does. It rejects creating models as a general method and approaches the solution of the problem from physics and even from philosophy in an abstract way. The deductive procedure applies extended mathematics and uses, almost exclusively, the methods of classical physics. This theory successively goes forward from general towards particular and therefore the fidelity of the theorems and conclusions can easily be confined. Having listed the basic principles, the main features will be shown in section 3.4., on the example of “incompressible, simple fluid”.

Nevertheless, the circumstances determining the stress play a central role, and the basic principles are formulated in general terms. The reason for the great generality is that the basic principles — on which the whole method is based — hold not only for mechanical interactions, but also for the largest range of phenomena.

In the spirit of this, the definition of the constitutive equation is the following: The constitutive equation is the mathematical formulation of the essential relationship between the basic quantities determining the physical process and depending on the properties of the medium. The constitutive equations — which are often called material equations — give the models with mathematical accuracy for the examined media. This is the reason for the name. Obviously, the equations defining rheological models are particular constitutive equations.

Using the general method, one does not start with the detailed definition of a model but tries to postpone as much specification as possible. Some of them are needed, of course, right at the beginning since the aim is the mechanical description — and remaining on the level of philosophical generality is rather fruitless. Therefore the definition of a constitutive equation is reformulated.

The constitutive equation in continuum mechanics is the mathematical form of how Cauchy's stress tensor depends on the motion. In its simplest form all non-mechanical effects are ignored. This means that the constitutive equation of the medium brings the motion into relation with the stress tensor, i.e. the constitutive equation is the relation between the motion, (1.4), and the stress:

$$\mathbf{x}(\mathbf{X}, t) \mapsto \mathbf{t}(\mathbf{x}, t). \quad (3.38)$$

We mention that the relation (3.38) refers to the mechanism of the interactions in the medium. Its role in the description of motion is just to get a relationship, by substituting it into Cauchy's equation of motion, which is satisfied by the function of motion, and from which the particular form of the function of motion (i.e. the details of the motion) can be determined. At this point the question arises: how can the mapping (3.38) be formulated mathematically? The possible mathematical forms are restricted by the following principles:

a. *The principle of determinism* states that the structure of the stress field at a given moment of time is determined by the section of the function of motion that belong to $t \leq t_0$. This means that the medium can have memory but it is not gifted with prophecy; i.e., the stress can depend on the history of the motion, even in a complicated way, but it does not depend on the motion in the future.

b. *The principle of the local action* states that to determine the stress at a given point \mathbf{X}_0 it is sufficient to know the function of motion in any small neighborhood of the point.

The principles of determinism and local action are guides in determining the stress tensor in a given point and in a given moment. It is sufficient to know the history of the function of motion in an arbitrary small vicinity of this point. The question immediately arises: how accurately must the history of deformation be known? The arbitrarily small vicinity suggests that a partial sum of the Taylor-series belonging to a given point of the function of motion provides a satisfactory level of accuracy. This, of course, can not be stated in general since the errors of the partial sums of the Taylor-series can be made arbitrarily small only by decreasing the vicinity; and by decreasing the vicinity, the satisfactory accuracy increases. So one single partial sum can not be suitable for every media but one of the partial sums provides satisfactory accuracy for any medium. This fact makes possible the classification of the media from which only the first category is defined according to the present state of practical claims:

A medium is called simple, when the linear partial sum of the Taylor-series determines the stress. This means that in the case of a simple medium it is sufficient to know the history of the deformation gradient tensor:

$$\mathbf{t}(\mathbf{X}, t) = \mathbb{T}_{s=0}^{\infty} \{\mathbf{x}(\mathbf{X}, t - s)\}, \quad (3.39)$$

where \mathbb{T} is a functional which relates a second order tensor to a tensor valued s -dependent function.

Further restrictions are imposed upon the form of the functional by

c. *The principle of homogeneity of time.* It states that the form of the functional does not change by shifting time:

$$\mathbf{t}(\mathbf{X}, t + \tau) = \mathbb{T}_{s=0}^{\infty} \{\mathbf{x}(\mathbf{X}, t + \tau - s)\}. \quad (3.40)$$

d. *The principle of objectivity* states that the form of constitutive equations is independent of the frame of reference; i.e., the behavior of the medium is objective and does not depend on the subjective elements of the description. The consequent application of the principle of objectivity contributed significantly to the success of the modern continuum mechanics, so it is worth formulating it in detail.

Let us regard a medium, the mechanical behavior of which is described by a formula like (3.39), and beside the chosen reference frame, let us respect another reference frame, as it has been done in (2.6). The new frame is attained by the transformation:

$$\mathbf{x}^* = \mathbf{Q}(t)[\mathbf{x} - \mathbf{a}(t)]$$

The principle of objectivity states that to determine the stress, any of the frames is suitable; so it is also a possible procedure converting the deformation gradient to the frame nominated by the asterisk and then calculating the form of the stress tensor in this system according to (3.39) and at last turning back to the original frame. The result obtained in this way has to equal the one obtained without changing the frame. Since

$$d\mathbf{x}^* = \mathbf{Q}(t)d\mathbf{x}$$

and

$$d\mathbf{x} = \mathbf{x}d\mathbf{X}, \quad d\mathbf{x}^* = \mathbf{x}^*d\mathbf{X}$$

so

$$\mathbf{x}^* = \mathbf{Q}(t)\mathbf{x}$$

Applying this to a simple material, the statement can be formulated:

$$\mathbf{t}(\mathbf{X}, t) = \mathbb{T}_{s=0}^{\infty} \{\mathbf{x}(\mathbf{X}, t - s)\} = \mathbf{Q}^T(t) \mathbb{T}_{s=0}^{\infty} \{\mathbf{Q}(t - s)\mathbf{x}(\mathbf{X}, t - s)\}\mathbf{Q}(t), \quad (3.41)$$

where $\mathbf{Q}(t)$ can arbitrarily depend on time.

Nevertheless, the principle of objectivity can be generally applied; naturally the mathematics is more complicated for cases other than simple media.

e. According to *the principle of material invariance* the elements of the isotropy group describing the material symmetry leave the constitutive equation invariant.

This means that transforming the medium, at first, from an X reference configuration to an X^* reference configuration, which is equivalent to the previous one i.e. the transformation

$$\mathbf{X}^* = \mathbf{X}^*(\mathbf{X}) \quad (3.42)$$

corresponds to the symmetry of the medium. Then the same stress state belongs to the motion

$$\mathbf{x} = \mathbf{x}(\mathbf{X}, t) \quad (3.43)$$

and to the motion

$$\mathbf{x} = \mathbf{x}[\mathbf{X}^*(\mathbf{X}), t] \quad (3.44)$$

in any moment and in any point. In a simple material, the relation

$$d\mathbf{x} = \mathbf{x}^* d\mathbf{X}^* = \mathbf{x}^* \mathbf{A} d\mathbf{X} \quad (3.45)$$

involves the equality

$$\mathbb{T}_{s=0}^{\infty} \{\mathbf{x}^*(\mathbf{X}, t-s)\} = \mathbb{T}_{s=0}^{\infty} \{\mathbf{x}(\mathbf{X}, t-s) \mathbf{A}(\mathbf{X})\} \quad (3.46)$$

where the meaning of the tensor \mathbf{A} is given by

$$d\mathbf{X}^* = \mathbf{A} d\mathbf{X}.$$

The determinant of the tensor \mathbf{A} describing symmetry is one or minus one. Otherwise the volume of the material would change with symmetry operation according to (1.8), which is impossible since the inverse of the symmetry operation and every power of it is also a symmetry operation. Consequently, if the volume of the medium decreased during the operation \mathbf{A} or \mathbf{A}^{-1} , after repeating the operation several times, the volume could decrease endlessly, which contradicts the indestructibility of the matter. This means that the group of symmetry operations is a subgroup of the unimodular group.

According to this, media can be classified. The media whose symmetry is described by the complete unimodular group are called isotropic fluids. If the symmetry group of the medium in some configuration is identical with the orthogonal group, it is called isotropic solid; and if it is identical with some subgroup of the orthogonal group, it is called crystalline material. The mentioned categories do not utilize all the mathematical possibilities; namely, it is imaginable that the unimodular group also has a real subgroup which is not similar to any part of the orthogonal group. The materials of such symmetry are usually called subfluids, e.g., the liquid crystals. In this chapter only fluids are to be discussed [27, 54, 56, 100, 120, 152, 153, 162].

In the handbooks of modern continuum mechanics, further principles are formulated, as well. They are listed bellow, although they are not used in this book:

- f. *The principle of coordinate invariance* states that the results of calculations can not depend on the coordinate system.
- g. *The principle of dimensional invariance* states that the form of the constitutive equations can not depend on the choice of the units of measure.
- h. According to *the principle of compatibility*, the constitutive equation can not contradict any fundamental physical law.
- i. According to *the principle of mathematical completeness*, a constitutive equation together with the fundamental physical laws have to display a uniquely soluble mathematical problem.
- j. *The principle of equipresence* states that if an independent variable appears in one of the constitutive equations it can appear in every constitutive equation.
- k. According to *the principle of unification*, different constitutive variables that characterize particular materials should be present in a constitutive equation for all the above materials. This principle states the possibility of generalization.

3.4. The theory of the simple shear flow.

Let us examine a simple fluid which is in mechanical interaction with its environment. Let the examined motion be simple shear flow:

$$\frac{dx_1}{dt} = \kappa x_2, \quad \frac{dx_2}{dt} = \frac{dx_3}{dt} = 0. \quad (3.47)$$

Since it is a fluid and its volume does not change, the configuration at any moment can be chosen as a reference configuration. Let us choose a t_0 moment, when the stress is to be determined and the configuration for reference. In doing so one has to determine the time dependent coordinates of the individual particles. The equations (3.47) can easily be solved:

$$x_1 = \kappa C_2 t + C_1, \quad x_2 = C_2, \quad x_3 = C_3. \quad (3.48)$$

Since in the moment t_0 $x_i = X_i$ ($i=1, 2, 3$), the constants C_i can be determined and so (3.48) takes the clearer form:

$$x_1 = \kappa X_2(t - t_0) + X_1, \quad x_2 = X_2, \quad x_3 = X_3. \quad (3.49)$$

According to this, the matrix form of the deformation gradient is:

$$\mathbf{x} = \begin{bmatrix} 1 & \kappa(t - t_0) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (3.50)$$

A useful notation will be:

$$\mathbf{x} = \boldsymbol{\delta} + \kappa(t - t_0)\mathbf{M} \quad (3.51)$$

where

$$\mathbf{M} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (3.52)$$

To determine Cauchy's stress, equation (3.51) is substituted into (3.41), so

$$\mathbf{t}_0(\mathbf{X}, t_0) = \int_{s=0}^{\infty} \{\mathbf{x}(\mathbf{X}, t_0 - s)\} = \int_{s=0}^{\infty} \{\boldsymbol{\delta} - s\kappa\mathbf{M}\} \quad (3.53)$$

is obtained. Since there is no volume change, the motion determines the stress leaving a scalar pressure free, which can be determined when integrating the equations. Therefore the traceless part of the stress tensor appears on the left hand side of (3.53).

Since the form of the function, which is the independent variable of the functional, depends solely on tensor $\kappa\mathbf{M}$, the functional reduces to a symmetrical, tensor valued function depending on a tensor variable:

$$\mathbf{t}_0(\mathbf{X}, t_0) = \mathbf{T}(\kappa\mathbf{M}) \quad (3.54)$$

According to the principle of objectivity

$$\mathbf{T}(\kappa\mathbf{M}) = \mathbf{Q}^T \mathbf{T}(\kappa\mathbf{Q}\mathbf{M}\mathbf{Q}^T) \mathbf{Q} \quad (3.55)$$

has to hold for any \mathbf{Q} orthogonal tensor. It should be mentioned that $\mathbf{Q}\mathbf{M}\mathbf{Q}^T$ appears as the variable of \mathbf{T} instead of $\mathbf{Q}\mathbf{M}$, since the reference configuration is also changed simultaneously when applying the \mathbf{Q} transformation. According to the principles of objectivity and material invariance, equation (3.53) transforms to:

$$\mathbb{T}_{s=0}^{\infty} \{\delta - s\kappa\mathbf{M}\} = \mathbf{Q}^T(t_0) \mathbb{T}_{s=0}^{\infty} \{\mathbf{Q}(t_0 - s)(\delta - s\kappa\mathbf{M})\mathbf{A}\} \mathbf{Q}(t_0) \quad (3.56)$$

where, choosing $\mathbf{A} = \mathbf{Q}^T$, $\delta - s\kappa\mathbf{Q}\mathbf{M}\mathbf{Q}^T$ becomes the argument of the functional \mathbb{T} . The relation (3.55) means that any \mathbf{Q} tensor for which the equality

$$\mathbf{Q}\mathbf{M}\mathbf{Q}^T = \mathbf{M} \quad (3.57)$$

holds, leaves also the stress tensor invariant. Since the only non-trivial solution of (3.57) is the tensor

$$\mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad (3.58)$$

the equations

$$T_{13} = T_{23} = 0 \quad (3.59)$$

are obtained from the invariance of \mathbf{T} . This means that the function $\mathbf{T}(\kappa\mathbf{M})$ has to take the form

$$\mathbf{T}(\kappa\mathbf{M}) = \begin{bmatrix} T_{11}(\kappa) & T_{12}(\kappa) & 0 \\ T_{12}(\kappa) & T_{22}(\kappa) & 0 \\ 0 & 0 & -T_{11}(\kappa) - T_{22}(\kappa) \end{bmatrix} \quad (3.60)$$

Using the orthogonal tensors

$$\mathbf{Q}_1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{and} \quad \mathbf{Q}_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

in equation (3.55), the relations

$$T_{11}(\kappa) = T_{11}(-\kappa), \quad T_{22}(\kappa) = T_{22}(-\kappa), \quad -T_{12}(\kappa) = T_{12}(-\kappa) \quad (3.61)$$

are obtained.

To get the expressions used in the literature, we introduce the notations:

$$\begin{aligned} \sigma_1(\kappa) &= 2T_{11}(\kappa) + T_{22}(\kappa), \\ \sigma_2(\kappa) &= 2T_{22}(\kappa) + T_{11}(\kappa), \\ \tau(\kappa) &= T_{12}(\kappa). \end{aligned} \quad (3.62)$$

Their meaning can easily be expressed by the components of the stress tensor, since according to equations (3.62) and (3.54)

$$\mathbf{t} = \mathbf{t}_0 - p\boldsymbol{\delta} = \begin{bmatrix} -p + \frac{2\sigma_1 - \sigma_2}{3} & \tau & 0 \\ \tau & -p + \frac{2\sigma_2 - \sigma_1}{3} & 0 \\ 0 & 0 & -p - \frac{\sigma_1 + \sigma_2}{3} \end{bmatrix} \quad (3.63)$$

from which

$$\sigma_1 = t_{11} - t_{33}, \quad \sigma_2 = t_{22} - t_{33}, \quad \tau = t_{12} \quad (3.64)$$

are gained, where t_{ij} are the components of the stress. The above relation makes it reasonable to call σ_1 and σ_2 normal-stress differences. The $\sigma_1(\kappa)$, $\sigma_2(\kappa)$ and $\tau(\kappa)$ functions are the so-called viscometric functions. It can be shown from (3.61) that the shear stress is an odd function, while the normal stresses are even functions of the shear rate κ .

A demonstrative result of the general theory presented is that the viscometric functions correlate with the Ostwald-curves, given in subsection 3.2.5. (the shear stress depends on the shear rate) and gives also a qualitative account on the so-called normal-stress effects. Unfortunately, the actual form of the viscometric functions can not be derived from the general theory.

3.5. Viscometric flows.

The viscometric functions presented above can be applied not only to simple shear flow, but also to every case when the relative deformation gradient takes the form :

$$\mathbf{x} = \mathbf{Q}(t)[\boldsymbol{\delta} - \kappa(t - t_0)\mathbf{M}] \quad (3.65)$$

where \mathbf{Q} is an arbitrary orthogonal tensor, and \mathbf{M} is the dyadic product of two mutually perpendicular unit vectors. This is a direct consequence of (3.56). The flows of this kind are called viscometric since they occur in the most familiar viscometers. A detailed discussion of viscometric flows is given in [26].

3.6. Closing remarks.

In this chapter modern information on the relationship between deformation and stress, based upon macroscopic considerations, has been briefly summarized. The methods listed can be classified into two groups. The first group contains the methods of rheology which today are assumed to be classical; the other one includes methods of modern non-linear mechanics, built upon general considerations and applications of functionals.

Both methods have deficiencies as far as the practical application is concerned. The bodies of rheology are complete from the viewpoint of the description of mechanical motion, i.e. accepting the validity of a given body any problem can be solved by mathematical methods. The system of bodies is, however, not complete; moreover, there is no exact criterion according to which a proper model to describe

a given material can be chosen; i.e., the choice of the model depends on the intuition of the researcher. Nor have we any method at our disposal to denote a way of further generalizations leading to better models.

Modern methods based upon functionals have made viscometric flows completely known for simple fluids, and the practical utilization requires only the tabulation of the viscometric functions for particular materials one by one, similar to the tables of viscosity for Newtonian fluids. It should be mentioned, however, that the flow in tubes is not strictly viscometric, since the required conditions are not realized at the entrance and the end sections. The condition of a stationary state is also problematic. Until the stabilization of stationary flow, the flow is not viscometric.

At this point a serious problem arises. The latter theory can hardly state anything about non-viscometric flows, even about whether a stationary state exists or not some time after the start of a flow. This problem is eased by the principle of fading memory which states that the effect of an action on a fluid is the weaker the earlier it happens. According to this the occurrence of the stationary state is forecasted, but nothing general is stated on the time when it happens. So in a tube with a circular cross-section, for example, even a rough estimation can hardly be given for the length of its entrance and end section. Further on, all the considerations have been restricted to the simple fluid, the behavior of which does not depend on gravitational fields nor on inertial forces. This means that the theory of the simple fluid is an elegant way of neglecting these latter effects.

All these deficiencies urge us to look for further methods. One is based upon Onsager's theory of irreversible thermodynamics. The above-mentioned deficiencies are eliminated, and the complete hierarchy of the bodies is given by the sequence of constitutive equations derived by the methods of irreversible thermodynamics. Placing blame on the thermodynamic theory for being linear is rather misleading, since the linearity in the sense of Onsager's theory much exceeds the linearity in the sense of rheology. Therefore the characteristic features of the experimentally observed non-linearities can properly be accounted for by Onsager's linear thermodynamics. It is rather a new theory, so the question of quantitative agreement can be discussed, above all, by comparing it to the former theories.

Before dealing with deformations by thermodynamic methods, the basic principles of Onsager's non-equilibrium thermodynamics are summarized in the following chapter.

NON-EQUILIBRIUM THERMODYNAMICS

4.1. On the first and second law of thermodynamics.

The first law of thermodynamics postulates the conservation of the energy of macroscopic systems. Energy can neither be produced, nor can be destroyed; consequently, the energy increase of a physical object during any real process is exactly equal to the energy influx into the object. For a system that is closed with respect to chemical component transport this law reads

$$\Delta U = Q + W. \quad (4.1)$$

Here ΔU is the energy increase in the system, Q is the amount of heat being flown into the system and W is the work done on the system. The sign of W is taken negative if the system performs the work, Q is negative when the heat flows out of the system, so ΔU is negative if the energy of the system has decreased. The meaning of the first law of thermodynamics is clear in its traditional form, and misunderstandings seldom arise from alternative interpretations.

In thermodynamics, the concept of entropy is usually introduced through the theorem on the impossibility of the (so-called) perpetuum mobile of the second kind. The introduction of entropy is necessary to get a general formulation for the amount of work a system is able to perform which is determined by the properties of both the system and its environment, collectively.

Let us consider the formula, well known from thermostatics [93].

$$W = U - U_0 + T_0(S_0 - S) - W^e \quad (4.2)$$

where U is the internal energy and S is the entropy of the system, while T_0 is the absolute temperature of the environment. The symbols U_0 and S_0 denote the internal energy and entropy of the system, respectively, after the equilibrium with the environment is reached, while W^e stands for the minimum work done on the environment. If, during the process, the only work done on the surrounding is the work of expansion, then

$$W^e = p_0(V_0 - V). \quad (4.3)$$

Naturally, W^e may contain further terms, too.

The formula (4.2) has been known for a long time; it provided the basis to the introduction of the exergy, which quantity served for the easier description of the available work [10].

Defining the non-equilibrium entropy, we make use of the fact that each quantity in (4.2) is well defined, even for non-equilibrium systems. Thus entropy is defined, by a plausible extension of equation (4.2), as

$$S = S_0 + \frac{1}{T}(U - U_0 - W - W^e). \quad (4.4)$$

This definition is based on the following hypotheses:

- i. The environment is a sufficiently large, but finite, thermostatic system; its changes of state do not alter considerably the state of systems in equilibrium with it.
- ii. From the system in a given environment only a finite amount of work is available, the least upper bound is W .
- iii. The final state of the system in the given environment is uniquely determined.
- iiii. Any process occurring without external motivation involves the ability of performing work.

These hypotheses are supported by the empirical background of thermodynamics.

The entropy defined by (4.4) suffices the requirements of non-equilibrium thermodynamics, viz. entropy is a totally additive set function of state which, in an adiabatically closed system, can only increase.

The entropy, defined so, does not depend on the nature of the environment; that is, the entropy is a state function, even out of equilibrium.

4.1.1. The state variables. Let us consider the motion of a medium with a macroscopically uniform chemical composition that is homogeneous in space and constant in time. According to experience, the equilibrium properties of such a medium are functions only of temperature deformation and the electromagnetic field intensities (if the presence of these fields is also assumed). So the local equilibrium state of the medium is uniquely determined by the tensor \mathbf{d} , describing the deformation, the temperature T , the electric field \mathbf{E} , and magnetic induction \mathbf{B} . Using the terms of classical thermodynamics, the listed quantities are the state variables. Any other property of the medium can be given as a function of these variables. Of course, the form of these functions depends on what the particular medium is. Equilibrium thermodynamics deals with the possible form of these functions. In the following, we shall regard these functions as known and put our attention on processes.

In equilibrium, the state variables do not depend on time and their spatial distribution is determined by the environment. There are cases, however, even out of equilibrium when the specific entropy and other properties of the system can still be given in the space of the equilibrium state variables. For such media — more exactly — for such processes the potential functions of equilibrium thermodynamics are also applicable (with proper restrictions, of course). In this situation the processes are caused by the interaction of spatially different parts of the system. So, if the interaction of a sufficiently small part of the medium and its environment is prevented somehow, then, after the interaction has ceased, the properties of this separated part will be constant. Systems that can be described in the space of the equilibrium state variables in non-equilibrium states, as well, are referred to

as systems in local equilibrium. It means that the systems in local equilibrium can be characterized locally by the same variables in non-equilibrium as in equilibrium; that is to say, equilibrium and non-equilibrium states differ only in the spatial distribution of the variables.

In most of the practically important cases, the media are out of local equilibrium; i.e., not even the local properties can be given with the help of the equilibrium state variables only. Thus the space of the non-equilibrium states has more dimensions than the space of the equilibrium states has. The description of the non-equilibrium state requires further variables, which are referred to as dynamic degrees of freedom or dynamic variables. The dynamic degrees of freedom serve the phenomenological description of dissipative structures developing in the course of the motion.

4.2. Balance equations.

Balance equations play an important role in all field theories; they are fundamental, especially in the non-equilibrium thermodynamics of continua. Laws of conservation (of mass, charge etc.) are formulated in balance equations. However, balance equations of non-conservative quantities are defined as well. Since the balance equations of different extensive quantities show considerable similarity, we give their general form first.

4.2.1. The general form of balance equations. Let us consider an extensive quantity A of arbitrary tensorial order. For the sake of convenience, we use a cartesian frame and in the case of a quantity A of non-zero tensorial order, its components to be examined one by one. In field theories, it is essential that the extensive quantities be totally continuous, differentiable set functions; viz., for any extensive quantity A there exists a density ϱ_A so that for any volume V

$$A = \int_V \varrho_A dV. \quad (4.5)$$

For the sake of further considerations, it is useful to introduce the specific quantities:

$$a = \frac{\varrho_A}{\varrho} \quad (4.6)$$

the quantity of A per unit mass. Making use of this, equation (4.5) reads

$$A = \int_V a \varrho dV \quad (4.7)$$

The change rate of the quantity A in a volume V is

$$\dot{A} = \frac{d}{dt} \int_V a \varrho dV \quad (4.8)$$

even for a moving volume V . Specifically, if the volume is moving together with the medium, then — due to the conservation of mass — equation (4.8) reads

$$\dot{A} = \int_V \varrho \frac{da}{dt} dV. \quad (4.9)$$

The substantial time derivative $\frac{da}{dt}$ is the total time derivative of the specific quantity a taken in a point moving together with the medium.

The cause of the changing of the quantity A can be twofold: one is the transport through the boundary; the other is the production within the volume V . To describe these, two further quantities are introduced. The first is the current density \mathbf{J}_A , describing the transport of A . By its help the quantity $d_n A$ — that is the amount of A flown, during the time dt , through the surface element dA , which moves together with the medium — can be given as

$$d_n A = \mathbf{J}_A d\mathbf{A} dt. \quad (4.10)$$

The tensorial order of the current density \mathbf{J}_A is naturally higher by one than the order of the quantity A , as seen from the expression (4.10).

The other quantity to be introduced is the source density σ_A . By its help the production $d_i A$ of A in the volume dV during the time dt can be written as

$$d_i A = \sigma_A dV dt \quad (4.11)$$

In terms of the quantities introduced above, the rate of change of the quantity A can be expressed as

$$\dot{A} = \int_V \varrho \frac{da}{dt} dV = - \oint \mathbf{J}_A d\mathbf{A} + \int \sigma_A dV. \quad (4.12)$$

In this formula volume V is moving together with the medium. Since this expression is valid to any co-moving volume, after applying Gauss' theorem, the differential equation

$$\varrho \frac{da}{dt} + \operatorname{div} \mathbf{J}_A = \sigma_A \quad (4.13)$$

is obtained, which is called the substantial balance equation for the quantity A .

Using the identity

$$\varrho \frac{da}{dt} = \varrho \frac{\partial a}{\partial t} + \varrho(\mathbf{v} \operatorname{grad})a = \varrho \frac{\partial a}{\partial t} + a \frac{\partial \varrho}{\partial t} + a \operatorname{div}(\varrho \mathbf{v}) + \varrho(\mathbf{v} \operatorname{grad})a = \frac{\partial \varrho a}{\partial t} + \operatorname{div}(\varrho a \mathbf{v}),$$

the corresponding local balance equation is derived:

$$\frac{\partial \varrho a}{\partial t} + \operatorname{div}(\mathbf{J}_A + \varrho a \mathbf{v}) = \sigma_A. \quad (4.14)$$

Balance equations have occurred already in the previous chapters, but more conventional notations were followed. The comparison requires a few transformations.

4.2.2. The balance of mass. If the extensive quantity A is the mass, then the mass balances are obtained from the general forms by substituting

$$A = m, \quad \varrho_A = \varrho, \quad a = 1.$$

Comparing the local mass balance

$$\frac{\partial \varrho}{\partial t} + \operatorname{div}(\mathbf{J}_m + \varrho \mathbf{v}) = \sigma_m \quad (4.15)$$

— obtained so — to equation (2.6), it is seen that

$$\sigma_m = 0 \quad \text{and} \quad \mathbf{J}_m = \mathbf{0}. \quad (4.16)$$

The vanishing of the source density expresses the conservation of the mass, while the vanishing of the substantial mass current density expresses that the mass is not shifted relative to itself.

4.2.3. The balance of momentum and moment of momentum.

Cauchy's equation of motion for continua is the substantial balance equation of momentum. The current density of momentum is Cauchy's stress tensor multiplied by (-1) and the source density of momentum is the force per unit volume, $\varrho \mathbf{f}$.

We mention that though the momentum is conserved in an inertial system, its source density is not necessarily zero. The cause of this is that body forces (i.e. fields) also transport momentum; thus, the source density has its "credits" in the field. The situation is essentially different in an accelerating frame. Then the force density contains the inertial forces, too, which describe production of momentum without external "credit".

The balance equation for the moment of momentum is equation (2.44). Thence, its current and source density are

$$\mathbf{J}_l = -\mathbf{r} \times \mathbf{t} - \mathbf{\Pi} \quad (4.17)$$

and

$$\vec{\sigma}_l = \mathbf{r} \times \varrho \mathbf{f} + \varrho \mathbf{m}. \quad (4.18)$$

respectively. The balance of the internal moment of momentum is equation (2.49), whence

$$\mathbf{J}_{li} = -\mathbf{\Pi}, \quad \vec{\sigma}_{li} = \varrho \mathbf{m} + 2\mathbf{W}(\mathbf{t}). \quad (4.19)$$

4.2.4. The balance of kinetic energy. The balance of the kinetic energy derives from Cauchy's equation of motion by multiplying its sides (scalar product) with the velocity. After a rearrangement it reads

$$\varrho \frac{d}{dt} \left(\frac{v^2}{2} \right) + \operatorname{div}(-\mathbf{v} \mathbf{t}) = \varrho \mathbf{f} \mathbf{v} - \mathbf{t} : \operatorname{Grad} \mathbf{v}, \quad (4.20)$$

where $\mathbf{t} : \operatorname{Grad} \mathbf{v} = \operatorname{tr}(\mathbf{t}^T \operatorname{Grad} \mathbf{v})$.

4.2.5. The balance of the internal energy. The balance of the internal energy is approached through the law of energy conservation. Let ε denote the specific total energy of the continuum. In ε all kinds of energy — being present at a locus — are included, except the energy of the fields of the body forces. The latter one covers all energy types that are usually referred to as potential energy.

The energy increase in a volume moving together with the medium is due to two causes: First, the energy flows in through the boundary from the surrounding medium; second, the fields supply energy. The influent energy is usually divided into two parts: the first of which is the mechanical work, while the second is the heat flow. The energy supply of the field is usually also split into the work and the heating effect of the field. The latter one does not occur in gravitational, but in electromagnetic fields. Finally, the work by a field can also be regarded of two types: viz. the translational work of the body force and the work of the torque.

Thus the conservation of energy is formulated as

$$\begin{aligned} \frac{d}{dt} \int \varrho \varepsilon dV = & - \oint \mathbf{J}_q d\mathbf{A} + \oint \mathbf{v} \mathbf{t} d\mathbf{A} + \oint \vec{\omega}_0 \mathbf{\Pi} d\mathbf{A} + \\ & + \int \varrho \mathbf{f} \mathbf{v} dV + \int \varrho \mathbf{m} \vec{\omega}_0 dV + \int \sigma_{uEM} dV. \end{aligned} \quad (4.21)$$

The left hand side is the rate of energy increase of the examined part of the medium. The integrals on the right hand side have the following meaning: The first is the heat flux from the surrounding; the second is the power of the forces acting on the surface; the third is the power of the couple stress on the boundary; the fourth and the fifth are the powers of the body force and torque; and the last term is the heat supply from the (electromagnetic) field.

In the formula (4.21) the symbol $\vec{\omega}_0$ stands for the angular velocity. Its interpretation, however, can be ambiguous in particular models. The definition of the angular velocity, given by equation (1.47), depends on the choice of the reference configuration, while $\vec{\omega}_0$ is, due to the nature of the energy balance, independent of that. In many cases it is expedient to regard the angular velocity with respect to the present configuration as $\vec{\omega}_0$, i.e. $\vec{\omega}_0 = \frac{1}{2} \text{rot } \mathbf{v}$, which is also consistent to equation (1.50). In other cases the interpretation may be different.

Further details are omitted here, as we wish to call attention only to the fact that — in spite of its considerable generality — the expression (4.21) cannot be regarded as universal. On the one hand, the interpretation of the quantities figuring therein may raise problems; on the other hand, the splitting of the energy present at a locus into parts corresponding to material and field may also cause confusion, as it is not entirely free of arbitrariness. Despite all these, equation (4.21) can be regarded valid — without reservation — to the models occurring in the practice of continuum mechanics and thermodynamics.

Applying Gauss' theorem to (4.21) and changing over to the differential form, the balance of the total energy is obtained:

$$\varrho \frac{d\varepsilon}{dt} + \text{div}(\mathbf{J}_q - \mathbf{v} \mathbf{t} - \vec{\omega}_0 \mathbf{\Pi}) = \varrho \mathbf{f} \mathbf{v} + \varrho \mathbf{m} \vec{\omega}_0 + \sigma_{uEM}. \quad (4.22)$$

Since the total energy of the medium — with no potential energy involved — depends not only on the properties of the substance but also on the frame of reference,

the use of this quantity can be inconvenient in thermodynamic considerations. To avoid this inconvenience, the idea, — or rather the concept — of internal energy is introduced, viz. the value of the energy in a frame moving (i.e. both translating and rotating) together with the substance. The total energy is the sum of the internal and kinetic energy. Thus, the specific internal energy can be given as

$$u = \varepsilon - \frac{1}{2}v^2 - \varepsilon_{\text{rot}}^i, \quad (4.23)$$

where $\varepsilon_{\text{rot}}^i$ is the rotational energy accompanying to the internal moment of momentum.

The internal energy — as we have seen — is frame independent, that is a so-called objective quantity. Now, using equations (4.23), (4.22) and (4.20) the balance of the internal energy is obtained:

$$\varrho \frac{du}{dt} + \frac{d\varepsilon_{\text{rot}}^i}{dt} + \text{div}(\mathbf{J}_q - \vec{\omega}_0 \mathbf{\Pi}) = \varrho \mathbf{m} \vec{\omega}_0 + \sigma_{uEM} + \mathbf{t} : \text{Grad } \mathbf{v}. \quad (4.24)$$

Henceforth, we shall omit internal rotation, viz. only those substances will be considered in which the internal moment of momentum, the rotational energy and the torque of inertial forces are each zero. By this assumption, the balance of the internal moment of momentum reduces to

$$2\mathbf{w}(\mathbf{t}) + \text{Div } \mathbf{\Pi} + \varrho \mathbf{m} = 0. \quad (4.25)$$

(Here equation (4.19) was also applied.) Now the internal energy balance can be put into the form

$$\varrho \frac{du}{dt} + \text{div} \mathbf{J}_q = \sigma_{uEM} + \mathbf{t}^s : (\text{Grad } \mathbf{v})^s + \text{div}(\vec{\omega}^b \mathbf{\Pi}) + \varrho \mathbf{m} \vec{\omega}^b + \mathbf{\Pi} : \text{Grad } \vec{\omega} \quad (4.26)$$

In the transformation, beside the use of the identities

$$\mathbf{w}(\boldsymbol{\omega}) = \vec{\omega}, \quad \mathbf{t}^a : \boldsymbol{\omega} = 2\mathbf{w}(\mathbf{t})\vec{\omega}, \quad \text{and} \quad \text{Grad } \mathbf{v} = (\text{Grad } \mathbf{v})^s + \boldsymbol{\omega}$$

the notation $\vec{\omega}^b = \vec{\omega}_0 - \vec{\omega}$ was introduced. Here \mathbf{t}^a denotes the antisymmetric part of Cauchy's stress, while \mathbf{t}^s stands for the symmetric part.

The calculation of the thermic effect of the electromagnetic field demands the energy balance of the electromagnetic field. It will be formulated here in the local form. We start from the form (2.30) of the Maxwell equations. Taking the scalar product of the first equation with $\mu_0 \mathbf{B}$ and the third equation with \mathbf{E} , then adding the left hand side to the left hand side and the right hand side to the right hand side, we get

$$\frac{1}{\mu_0} \mathbf{B} \text{rot } \mathbf{E} + \frac{1}{\mu_0} \mathbf{B} \dot{\mathbf{B}} - \frac{1}{\mu_0} \mathbf{E} \text{rot } \mathbf{B} = -\mathbf{E}(\mathbf{j} + \varrho_e \mathbf{v}) - \varepsilon_0 \mathbf{E} \dot{\mathbf{E}} - \mathbf{E} \dot{\mathbf{P}} - \mathbf{E} \text{rot } \mathbf{M} + \mathbf{E} \text{rot}(\mathbf{v} \times \mathbf{P}).$$

The application of some vectoranalytical identities and the repeated use of (2.30) leads to

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\frac{1}{2} \varepsilon_0 E^2 + \frac{1}{2\mu_0} B^2 - \mathbf{B} \mathbf{M} \right) + \text{div} \left(\mathbf{E} \times \frac{1}{\mu_0} \mathbf{B} - \mathbf{E} \times \mathbf{M} - \mathbf{P}(\mathbf{E} \mathbf{v}) - \mathbf{v}(\mathbf{M} \mathbf{B}) \right) + \\ & + \left(\mathbf{j} + \varrho \frac{d\mathbf{P}}{dt} \right) (\mathbf{E} + \mathbf{v} \times \mathbf{P}) + \varrho \frac{d\mathbf{P}_m}{dt} \mathbf{B} + \varrho \mathbf{f}_{EM} \mathbf{v} = 0. \end{aligned} \quad (4.27)$$

Here the ponderomotive force density, defined in (2.40), and the $\mathbf{p}_m = \frac{1}{\varrho} \mathbf{M}$ specific magnetic momentum were introduced. Equation (4.27) is regarded as the energy balance of the electromagnetic field. Thence we read the energy density of the electromagnetic field as

$$w_{EM} = \frac{1}{2} \varepsilon_0 E^2 + \frac{1}{2\mu_0} B^2 - \mathbf{B}\mathbf{M}. \quad (4.28)$$

This, beyond quantities characterizing the field, contains the magnetization of the medium. This fact at first seems strange — namely that the energy of the magnetic dipole can change even if the dipole is unchanged and only the field is altered — it claims the introduction of the potential energy of the magnetic dipole. This energy, according to the above concepts, is a part of the field energy. These considerations need not be transferred to the electric dipole.

The current density of the electromagnetic field energy, read from (4.27), is

$$\mathbf{S} = \frac{1}{\mu_0} \mathbf{E} \times \mathbf{B} - \mathbf{E} \times \mathbf{M} + \mathbf{P}(\mathbf{E}\mathbf{v}) - \mathbf{v}(\mathbf{M}\mathbf{B}). \quad (4.29)$$

The power supply from the electromagnetic field to the medium, again from (4.27), is

$$\sigma_{uEM} + \vec{\omega} \varrho \mathbf{m} + \varrho \mathbf{v} \mathbf{f}_{EM} = \left(\mathbf{j} + \varrho \frac{d\mathbf{P}}{dt} \right) (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \varrho \frac{d\mathbf{p}_m}{dt} \mathbf{B} + \varrho \mathbf{v} \mathbf{f}_{EM}. \quad (4.30)$$

From this expression the heat supply from the electromagnetic field is calculated using (2.40):

$$\sigma_{uEM} = [\mathbf{j} + \varrho(\dot{\mathbf{p}} - \vec{\omega}^b \times \mathbf{p})] (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \varrho(\dot{\mathbf{p}}_m - \vec{\omega}^b \times \mathbf{p}_m) \mathbf{B}. \quad (4.31)$$

The quantities

$$\dot{\mathbf{p}} = \frac{d\mathbf{P}}{dt} - \vec{\omega} \times \mathbf{p} \quad \text{and} \quad \dot{\mathbf{p}}_m = \frac{d\mathbf{p}_m}{dt} - \vec{\omega} \times \mathbf{p}_m$$

are the time derivatives of the specific electric and magnetic momenta, taken in a frame moving (translating and rotating) together with the examined element of the medium.

The internal energy production density, according to (4.25) and (4.31) is given as

$$\sigma_u = (\mathbf{j} + \varrho \dot{\mathbf{p}})(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \varrho \dot{\mathbf{p}}_m \mathbf{B} + \mathbf{t}^s : (\text{Grad } \mathbf{v})^s + \text{div}(\vec{\omega}^b \mathbf{\Pi}). \quad (4.32)$$

In the derivation of this formula, a further hypothesis was involved, viz. the specific torque is entirely of electromagnetic origin.

4.3. Entropy balance.

The balance equation of the entropy plays a fundamental role in non-equilibrium thermodynamics, providing the means to the direct application of the second law. The construction of the balance starts from the actual form of the entropy function. Let the local equilibrium state variables be chosen so that their values change only in a system interacting with its environment. This requirement can easily be satisfied, since such is the situation in classical thermodynamics. Thus, for example a rather wide field of application is assured by choosing the set of equilibrium state variables as

$$\{u, \mathbf{d}, \mathbf{p}, \mathbf{p}_m\}. \quad (4.33)$$

Here u is the specific internal energy, \mathbf{d} the tensor measuring deformation, \mathbf{p} the specific electric and \mathbf{p}_m the specific magnetic polarization.

The description of non-equilibrium states requires further variables. Let us denote these by ξ_i , and, for some time, let us not be concerned with their explicit physical meaning. The specific entropy is given as a function of the state variables. Of course, the form of the function alters from medium to medium, from model to model. The choice of the state variables in the mentioned way assures that if a sufficiently small part of the medium is isolated with respect to energy transfer — that is to say it is surrounded by rigid, adiabatic, apermable walls and the electromagnetic fields (if present) are controlled so that the field changes no energy with the medium element — then the equilibrium state variables remain unchanged despite any process taking place therein. (The inverse of this statement is not always true.)

In other words, the equilibrium state variables alone — regardless of the values of the dynamic variables ξ_i — determine the equilibrium state that a small part of the medium would reach after it was isolated from its surrounding. It means, at the same time, that even the equilibrium values of the dynamic variables are uniquely determined by the equilibrium state variables. Thus it is possible to choose dynamic variables having zero value in local equilibrium and, of course, in global equilibrium, too. By the suitable choice of the dynamic variables, it can always be assured that the form of the non-equilibrium entropy function would be

$$s = s_0(u, \mathbf{d}, \mathbf{p}, \mathbf{p}_m) - \sum_i \frac{1}{2} \xi_i^2. \quad (4.34)$$

Here $s_0(s, \mathbf{d}, \mathbf{p}, \mathbf{p}_m)$ is the equilibrium entropy function [22, 111].

Next we determine the actual form of the entropy balance. The required balance equation should conform to the general pattern:

$$\varrho \frac{ds}{dt} + \operatorname{div} \mathbf{J}_s = \sigma_s. \quad (4.35)$$

First the value of $\varrho \frac{ds}{dt}$ is calculated from equation (4.34):

$$\sigma_s - \operatorname{div} \mathbf{J}_s = \varrho \frac{ds}{dt} = \varrho \frac{\partial s_0}{\partial u} \frac{du}{dt} + \varrho \frac{\partial s_0}{\partial \mathbf{d}} : \dot{\mathbf{d}} + \varrho \frac{\partial s_0}{\partial \mathbf{p}} \dot{\mathbf{p}} + \varrho \frac{\partial s_0}{\partial \mathbf{p}_m} \dot{\mathbf{p}}_m - \varrho \sum_i \xi_i \dot{\xi}_i. \quad (4.36)$$

This formula calls for a few comments:

First, the time derivatives need some explanation. These can be taken in any rotating frame, but since there are vectors and even tensors among the state variables their time derivatives shall describe objective material processes only if they are taken in a moving frame — viz. translating and rotating — together with the material point.

The second comment concerns the partial derivatives of the entropy functions with respect to tensor and vector variables. These are defined by the formulae

$$\begin{aligned} \left. \frac{d}{dx} s_0(u, \mathbf{d} + x\mathbf{Z}, \mathbf{p}, \mathbf{p}_m) \right|_{x=0} &= \frac{\partial s_0}{\partial \mathbf{d}} : \mathbf{Z} \\ \left. \frac{d}{dx} s_0(u, \mathbf{d}, \mathbf{p} + x\mathbf{z}, \mathbf{p}_m) \right|_{x=0} &= \frac{\partial s_0}{\partial \mathbf{p}} \mathbf{z} \\ \left. \frac{d}{dx} s_0(u, \mathbf{d}, \mathbf{p}, \mathbf{p}_m + x\mathbf{z}) \right|_{x=0} &= \frac{\partial s_0}{\partial \mathbf{p}_m} \mathbf{z} \end{aligned} \quad (4.37)$$

in which \mathbf{Z} is an arbitrary symmetric tensor, and \mathbf{z} is an arbitrary vector.

Thirdly, the derivative $\frac{du}{dt}$ is connected to the quantities characterizing the rate of the processes through the corresponding balances. Making use of these, instead of formula (4.36), the formula

$$\begin{aligned} \sigma_s - \operatorname{div} \mathbf{J}_s &= \frac{\partial s_0}{\partial u} (\sigma_u - \operatorname{div} \mathbf{J}_q) + \varrho \frac{\partial s_0}{\partial \mathbf{d}} : \dot{\mathbf{d}} + \varrho \frac{\partial s_0}{\partial \mathbf{p}} \dot{\mathbf{p}} + \varrho \frac{\partial s_0}{\partial \mathbf{p}_m} \dot{\mathbf{p}}_m - \varrho \sum_i \xi_i \dot{\xi}_i = \\ &= -\operatorname{div} \left(\frac{\partial s_0}{\partial u} \mathbf{J}_q \right) + \mathbf{J}_q \operatorname{grad} \frac{\partial s_0}{\partial u} + \left[\frac{\partial s_0}{\partial u} \frac{1}{2} (\mathbf{d}^{-1} \mathbf{t}^s + \mathbf{t}^s \mathbf{d}^{-1}) + \varrho \frac{\partial s_0}{\partial \mathbf{d}} \right] : \dot{\mathbf{d}} + \\ &+ \frac{\partial s_0}{\partial u} [\operatorname{div} (\vec{\omega}^b \mathbf{\Pi}) + \mathbf{\Pi} : \operatorname{Grad} \vec{\omega}] + \frac{\partial s_0}{\partial u} \mathbf{j} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \\ &+ \varrho \left[\frac{\partial s_0}{\partial u} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \frac{\partial s_0}{\partial \mathbf{p}} \right] \dot{\mathbf{p}} + \varrho \left[\frac{\partial s_0}{\partial u} \mathbf{B} + \frac{\partial s_0}{\partial \mathbf{p}_m} \right] \dot{\mathbf{p}}_m - \varrho \sum_i \xi_i \dot{\xi}_i \end{aligned} \quad (4.38)$$

is obtained.

The last step is the separation of the entropy production from the divergence of the entropy current. This proves an easy task if we remember that the entropy is a continuous function of the state variables, which are also assumed to depend continuously on the space coordinates. On the one hand, it is evident that the transport of extensive quantities corresponding to the state variables is accompanied by an entropy transport; while, on the other hand, this current of the extensive variable, flowing through an imaginary surface, cannot directly cause entropy production. Hence it is concluded that the entropy current density can be constructed as a linear combination of the current densities of the state variables. The coefficients of the linear combination are the partial derivatives of the entropy with respect to the corresponding state variables. So, if we assume that only the internal energy has transport while the other state variables, like electric and magnetic polarization, and the dynamic variables have not, then the entropy current density is given by the formula

$$\mathbf{J}_s = \frac{\partial s_0}{\partial u} \mathbf{J}_q. \quad (4.39)$$

Since only the equilibrium entropy function is present here, the partial derivative is identified with the help of Gibbs' relation:

$$\frac{\partial s_0}{\partial u} = \frac{1}{T} \quad (4.40)$$

so

$$\mathbf{J}_s = \frac{1}{T} \mathbf{J}_q \quad (4.41)$$

Finally, from equation (4.38) the entropy production density is obtained:

$$\begin{aligned} \sigma_s = & \mathbf{J}_q \text{grad} \frac{1}{T} + \left[\frac{1}{T} \frac{1}{2} (\mathbf{d}^{-1} \mathbf{t}^s + \mathbf{t}^s \mathbf{d}^{-1}) + \varrho \frac{\partial s_0}{\partial \mathbf{d}} \right] : \dot{\mathbf{d}} + \\ & + \frac{1}{T} [\text{div}(\bar{\omega}^b \mathbf{\Pi}) + \mathbf{\Pi} : \text{Grad} \bar{\omega}] + \frac{1}{T} \mathbf{j} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \\ & + \varrho \left[\frac{1}{T} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \frac{\partial s_0}{\partial \mathbf{p}} \right] \dot{\mathbf{p}} + \varrho \left[\frac{1}{T} \mathbf{B} + \frac{\partial s_0}{\partial \mathbf{p}_m} \right] \dot{\mathbf{p}}_m - \varrho \sum_i \xi_i \dot{\xi}_i. \end{aligned} \quad (4.42)$$

It can be seen that the entropy production density is a linear combination of the objective material processes. Arranging the “scalar” components of the material process rates in a sequence, and denoting them by J_i , the entropy production can be put into the general form

$$\sigma_s = \sum_i X_i J_i \quad (4.43)$$

where X_i denotes the coefficient of the process rate component in equation (4.42). The J_i quantities are called currents (in analogy to the transport processes), while the X_i quantities are called thermodynamic forces.

It follows from the second law that the entropy production density σ_s can be zero if and only if no material process takes place. In any other case the entropy production density is positive. This fact has far-reaching consequences concerning the laws describing the rate of the material processes.

4.4. The linear laws.

As can be seen from equation (4.43), the entropy production density is zero in equilibrium. (When no process takes place, then all J_i vanish.) Let us examine the situation in the neighborhood of the equilibrium. First, consider a process in which only one current, e.g. J_k , differs from zero. Then

$$\sigma_s = X_k J_k > 0. \quad (4.44)$$

It means that when J_k is positive then the conjugate force X_k is also positive, and when J_k is negative then X_k must be negative as well. From the continuity of the forces in the state space, we conclude that since the X_k force changes sign at equilibrium, its value has to be zero in equilibrium. Thus, it is declared: The general condition of the equilibrium is that each and every force must vanish there. This circumstance is the reason for the terminology “thermodynamic force”.

The thermodynamic forces depend partly on the state variables and partly on interactions with the environment. So the existence or the non existence of equilibrium depends partly on the medium and partly on the environment it interacts with.

On the basis of the condition of vanishing forces (with the help of (4.42)), the physical meaning of the entropy derivatives is found. In the present approach

$$\begin{aligned} \frac{1}{T} \frac{1}{2} (\mathbf{d}^{-1} \mathbf{t}^s + \mathbf{t}^s \mathbf{d}^{-1}) + \varrho \frac{\partial s_0}{\partial \mathbf{d}} &= 0, \\ \frac{1}{T} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \frac{\partial s_0}{\partial \mathbf{p}} &= 0, \\ \frac{1}{T} \mathbf{B} + \frac{\partial s_0}{\partial p_m} &= 0 \end{aligned} \quad (4.45)$$

must hold in equilibrium. It means that the derivatives are related to the stress tensor and the electric and magnetic fields, namely, in the equilibrium state defined by the given equilibrium state variables. Thus it is convenient to introduce the notations

$$\begin{aligned} \frac{\partial s_0}{\partial \mathbf{d}} &= -\frac{1}{T} \frac{1}{2} (\mathbf{d}^{-1} \mathbf{t}^{es} + \mathbf{t}^{es} \mathbf{d}^{-1}), \\ \frac{\partial s_0}{\partial \mathbf{p}} &= -\frac{1}{T} (\mathbf{E}^e + \mathbf{v} \times \mathbf{B}^e), \\ \frac{\partial s_0}{\partial p_m} &= -\frac{1}{T} \mathbf{B}^e, \end{aligned} \quad (4.46)$$

where the upper index “e” refers to the equilibrium situation. The quantities \mathbf{t}^e , \mathbf{E}^e and \mathbf{B}^e are, naturally, functions of the equilibrium state variables, which can be determined from the thermostatic properties of the medium. (The form of the functions may change from model to model.)

We mention that for a conducting medium in equilibrium

$$\mathbf{E} + \mathbf{v} \times \mathbf{B} = 0 \quad (4.47)$$

must hold, which can be read from the fourth term on the right hand side of (4.42). For an insulator, however, $\mathbf{j} = 0$ identically, so then (4.47) need not hold in equilibrium.

Now, turning to the laws describing dynamic behavior, it can be said that the speed of material processes is determined on the one hand by the local and regional properties of the material, and on the other hand, by the intensity of interactions with the environment, in such a way that the entropy production is positive for all processes. Consequently, the process rates and thermodynamic forces vanish simultaneously in equilibrium. This latter fact and, at the same time, the most general linear dependence of independent currents on forces is expressed by Onsager’s laws [124, 125].

$$J_i = \sum_k L_{ik} X_k. \quad (4.48)$$

These linear laws can be regarded as a convenient description of currents depending on state variables; from another view, they can be interpreted as the first non-vanishing terms of a series expansion. Consequently, Onsager's L_{ik} conductivity coefficients may depend on the local state variables, especially so on the temperature and deformation but even on the dynamic variables. These dependencies, however, cannot be too strong, at least not enough to have a decisive influence on the currents. Still these dependencies cannot be entirely neglected as these account for the different dynamic behavior of systems different in state and quality.

In the most simple cases the L_{ik} coefficients can be taken as constants not changing during the examined process. This is called the strictly linear case. In other cases the changes of the coefficients must be taken into account. We can distinguish two further possibilities and two different types of corresponding theories. Their clear separation has fundamental importance in the exact classification of the non-linear thermodynamic theories. When the conductivity coefficients depend on the local equilibrium state variables and further changes — e.g. dependence on thermodynamic forces — need not be taken into account, we can speak of quasi-linear constitutive equations and of a quasi-linear thermodynamic theory. The terminology “strictly non-linear” is used for constitutive equations and theory, when the laws (4.38) explicitly do fail, i.e. the currents are strictly non-linear functions of the forces. It is another question that even in the strictly non-linear case, the constitutive equations can be put in the form of (4.38) if the dependence of the L_{ik} coefficients on the X_k forces is allowed.

It should be mentioned here that this classification of constitutive equations and theories of thermodynamics into strictly linear (L_{ik} -s are constant), quasi-linear (L_{ik} -s are functions of the state variables) and strictly non-linear ones (L_{ik} -s are functions of the forces) is due to Gyarmati. (See also references [43, 44, 46, 141, 145, 146, 149, 157, 160] where several thermodynamic problems are examined on the basis of the classes given here.)

If the number of the independent scalar components of the currents is denoted by f , then the system of the L_{ik} coefficients in the linear laws (4.38) has f^2 components which, however, are not all independent of each other. The well-known relations among them are the so-called reciprocal relations of Onsager and Casimir, which govern the symmetry properties of the conductivity matrix. These relations in the symmetric — Onsagerian — case read

$$L_{ik} = L_{ki} \quad (4.49)$$

while, for the antisymmetric, Casimir-type case

$$L_{ik} = -L_{ki} \quad (4.50)$$

holds. The question whether the first or the second relation holds in a particular case shall be discussed in the next section.

Another requirement beyond the reciprocal relations imposed on the phenomenological coefficients is that they must be consistent with the material symmetries (see 3.3.1). The linear laws comply with the principle of material objectivity; thus this requirement gives no further restrictions on the coefficients.

The dynamic laws can be formulated in forms different from (4.38) by the help of so-called representations and pictures which give mathematically equivalent formulae with a shape similar to that of (4.38). The general theory of the “pictures” was worked out and applied by Gyarmati [70] and Farkas [43] (see also [7, 46, 141, 145, 146]). Different pictures are obtained by multiplying both sides of (4.43) by an always positive state function, G , i.e.

$$G\sigma_s = \sum_j J_j X_j G. \quad (4.51)$$

The quantity $G\sigma_s$ is evidently non-negative, taking a zero value in equilibrium only. The coefficients of the current, J_j , namely,

$$X_j^G = X_j G \quad (4.52)$$

regarded as forces, and substituted in (4.48) give the linear laws in the “ G -picture”:

$$J_i = \sum_k \frac{1}{G} L_{ik} X_k^G = \sum_k L_{ik}^G X_k^G. \quad (4.53)$$

The coefficients obey the Onsager-Casimir reciprocal relations. By choosing various functions for G , various pictures for the description of dissipative processes are obtained [43, 70].

Naturally, even within a given picture, the currents and forces can be chosen in several ways — from a given set of currents or by an invertible linear transformation — and another set of currents, having the same properties, can be obtained. Consideration of reciprocal relations and of material symmetries — moreover, the suitable choice of representation, picture and the use of the possible linear transformations — often lead to the cessation of dependence on the state for the L_{ik} coefficients, under given circumstances. [43, 46, 70]

By the above formalism any dissipative process can be described; yet, sometimes it is more convenient to give the dependence of currents on the state in a different form, although this provides simpler description for that particular phenomenon only. This is the case in Mises’ theory of plastic flow.

We shall show later that media usually regarded categorically of non-linear behavior, namely, the generalized newtonian systems, can be described well by linear Onsager equations.

Substituting the linear laws (4.48) into (4.43), we get a positive definite quadratic form for entropy production:

$$\sigma_s = \sum_{i,k} L_{ik} X_i X_k, \quad (4.54)$$

hence, by the help of the theory of quadratic forms several inequalities are derived for the coefficients. The most important of them are:

$$L_{ii} > 0, \quad L_{ii}L_{kk} - L_{ik}L_{ki} > 0. \quad (4.55)$$

Note that these inequalities are the direct consequence of the second law.

4.5. Reciprocal relations.

Before giving the precise definition of the reciprocal relations, we have to define time reversal. Though the concept of time reversal is usually introduced in the statistical foundation of irreversible thermodynamics, here an entirely macroscopic construction is presented and only for the sake of a clearer view shall the existence of a microscopic background be referred to. The macroscopic construction of time reversal starts off from the observation that the basic laws of classical mechanics and electrodynamics are reversible, i.e. if they describe a process then they describe the reversed process as well. Precisely, if the variable t , standing for time, is changed to the variable

$$t' = -t, \quad (4.56)$$

while the coordinates remain unchanged, then the fundamental equations expressed by the variable t' will have the same form as the original equations.

For time reversal, of course, some of the physical quantities must be transformed as well. Thus, for example, the velocity — defined in mechanics as the time derivative of the position vector — changes sign since

$$\mathbf{v} = \frac{d\mathbf{r}}{dt}, \quad \mathbf{v}' = \frac{d\mathbf{r}}{dt'} \quad \text{and so} \quad \mathbf{v}' = -\mathbf{v}. \quad (4.57)$$

Thus two groups of physical quantities are distinguished. The first group contains those which are not altered by time reversal (e.g. the coordinates, the acceleration, etc.): these are called α -type variables. The second group consists of the variables changing their sign under time reversal (e.g. velocity): these are called β -type variables.

Regarding the invariance of the fundamental equations with respect to time reversal as a requirement, the transformation properties of physical quantities can be worked out; i.e., we can distinguish α and β -type quantities. No contradiction is found as long as the dynamic laws of dissipative processes — i.e. the linear laws — are not considered. This means that the laws of mechanics, electrodynamics, and the laws of quantum mechanics are reversible: one could say they do not tell to which direction the time passes.

Now, let us consider the most important physical quantities, one after the other. Due to the definition of time reversal, the space coordinates are α -type and the velocity and the time itself are β -type variables. Acceleration is an α -type, thus due to Newton's second law, force and mass are also α -type variables. Following from the invariance of the coordinates, α -type variables are the volume, the density and the deformation tensor. Examining the form (2.30) of the Maxwell equations, it is seen that the electric field, the charge and electric polarization are α -type, while the magnetic field \mathbf{B} , magnetization \mathbf{M} , and electric current \mathbf{j} , are β -type variables.

From the invariance of the balance equations and the definition (4.4) of the entropy it is seen that α -type variables are the energy, the body forces, the torque, as well as Cauchy's stress, the couple stress and, finally, the entropy. Mass current, the heat current, the moment of momentum and angular velocity are all β -type variables. Finally, we stress that on the basis of the entropy balance, entropy production should be a β -type variable. In the expression (4.42) of the entropy

production one can see in detail while in its (4.43) general form, one can see generally that from the conjugate current and force pairs one is always an α -type while the other is a β -type quantity. By this we have reached the limits of the concept of time reversal. For if we substitute the linear laws (4.48), into the general form (4.43) of entropy production, then we arrive at a contradiction in any case.

Before examining this in detail, we present the precise form of the Onsager-Casimir reciprocal relations. These can be put into the unified form

$$L_{ik} = (-1)^{n_i+n_k} L_{ki}, \quad (4.58)$$

in which $n_i = 0$ if X_i is an α -type, and $n_i = 1$ if X_i is a β -type force. This means that the (4.49) Onsager reciprocal relation holds when X_i and X_k are of the same type (both are α or both are β -type forces), while Casimir's reciprocal relation is valid if the forces are of a different character (one is of α -type and the other is of β -type). If this form of the reciprocal relations is also taken into account, then we find that the entropy production density (4.54) (expressed by the help of the dynamic laws) is an α -type expression, as the phenomenological coefficients are constant in strictly linear theory and are equilibrium state functions in quasi-linear theory since in this latter case they depend only on the equilibrium state variables. Equilibrium is, invariant under time reversal. There are two generalizations of the Onsager relations, well known in the literature, that are equivalent to the Onsager relations in the linear case, while their formulation does not refer to linearity. Thus they seem suitable for making the Onsager relation adaptable to non-linear dynamic laws, yet an adequate way of generalization has not yet been found.

The first generalizations for the theory to strictly non-linear cases — that were given in the years 1958-1962 [66, 67, 101] — are based on the Gyarmati-Li reciprocal relations

$$\frac{\partial J_i}{\partial X_k} = \frac{\partial J_k}{\partial X_i}, \quad (4.59)$$

that, in the linear case, are equivalent to (4.49). These relations in non-linear cases lead to interdependence between higher order coefficients, besides the Onsager-Casimir relations. As we shall see later, the basic importance of the (4.59) generalized reciprocal relations is that they guarantee the existence of the dissipation potentials (to be introduced later) both for the linear and non-linear case, which potentials seem to be essential from the point of a general and unified theory of thermodynamics.

The wording of the generalization by Meixner, called the principle of macroscopic reversibility, is somewhat more complicated [150]. On the basis of linear laws (4.48) we can say that the quantities in the expression (4.43) of the entropy production are not all independent: For given X_i forces the J_i currents can be determined. The set of independent variables, however, can be chosen in other ways as well. Let us regard one of a conjugate current-force pairs as an independent variable and the other of the pair as a dependent variable. Then, if the linear laws hold, by the help of (4.48) the value of the dependent variables can always be determined, as can any particular positive definite form be determined by the L_{ik} coefficients. The explicit expression of the dependent variable is always linear and follows always the Onsager-Casimir relations but with the slight modification that it is not the types

of the X_i forces but the types of the independent variables which decide the sign of reciprocity. The principle of macroscopic reversibility states that the expression (4.43) of the entropy production, after the substitution of the dynamic laws, shall be invariant with respect to time inversion. So the entropy production must be an α -type quantity, for any set of independent variables that are chosen from the conjugate pairs.

4.6. Gyarmati's variational principle of dissipative processes.

Like mechanics and electrodynamics, the fundamental laws of the thermodynamics of dissipative processes can be condensed into a variational principle. This variational principle both in its differential (local) and in integral (global) forms was formulated by Gyarmati in 1965. This principle was applied to several fields of irreversible processes: first of all, his colleagues (Verhás [157], Böröcz [13], Farkas [43, 44], Sándor [141], Vincze [160], Stark [149]); but also many others (Singh [145, 147], Bhattacharya [7], Dickel [32] etc.).

Consistent application of both the local and the global forms of Gyarmati's principle provides all the advantages throughout the explication of the theory of irreversible thermodynamics that are provided in the study of mechanics and electrodynamics by the corresponding classical variational principles, e.g., Gauss' differential principle of least constraint, or Hamilton's integral principle.

Gyarmati's principle is based on the fact that the generalization of the dissipation functions — that were introduced by Rayleigh and Onsager for special cases — always exist locally in continua [104, 125, 126]. In linear theory these functions are defined as:

$$\Psi(X) = \frac{1}{2} \sum_{i,k} L_{ik} X_i X_k \quad (4.60)$$

and

$$\Phi(J) = \frac{1}{2} \sum_{i,k} R_{ik} J_i J_k. \quad (4.61)$$

The R_{ik} coefficients (general resistivities) are the components of the inverse of the conductivity matrix (L_{ik}).

The most important property of the dissipation function is that it is a homogeneous quadratic function of the X_i forces in the strictly linear theory, while in the quasi-linear theory it depends also on the state variables. The other fundamental property of Ψ is that its partial derivative with respect to X_k is equal to the current J_k conjugate to the force X_k in the entropy production density:

$$J_k = \frac{\partial \Psi}{\partial X_k} \quad (4.62)$$

Finally, the equality of the mixed second derivatives of Ψ with respect to the forces are equivalent to Onsager's reciprocal relations:

$$\frac{\partial^2 \Psi}{\partial X_i \partial X_k} = \frac{\partial J_i}{\partial X_k} = L_{ik} = L_{ki} \frac{\partial J_k}{\partial X_i} = \frac{\partial^2 \Psi}{\partial X_k \partial X_i}. \quad (4.63)$$

Because of the above properties, the function Ψ is called a dissipation potential, more precisely: it is the flux-potential (see (4.62)).

The function Φ has similar properties. In the strictly linear theory the function Φ is a homogeneous quadratic function of the currents J , while in the quasi-linear case it depends also on the local state variables (through the coefficients). The partial derivative of the function Φ with respect to J_k is equal to X_k :

$$X_k = \frac{\partial \Phi}{\partial J_k} \quad (4.64)$$

Due to this relation the function Φ is also a dissipation potential, more exactly: it is the force potential.

The equality of the mixed second derivatives of Φ with respect to the J -s are equivalent to the Onsager relations, now expressed in terms of the R_{ik} resistances

$$\frac{\partial^2 \Phi}{\partial J_i \partial J_k} = \frac{\partial X_i}{\partial J_k} = R_{ik} = R_{ki} = \frac{\partial X_k}{\partial J_i} = \frac{\partial^2 \Phi}{\partial J_k \partial J_i} \quad (4.65)$$

Hence, it can be seen that the necessary and sufficient condition of the existence of the dissipation potentials Ψ and Φ is the existence of the Onsager reciprocal relations.

It is possible to define the weighted potentials Ψ^G and Φ^G . Those show all the essential properties of Ψ and Φ , but correspond to the weighted entropy production $G\sigma_s$ (defined in (4.51)). Making use of equations (4.52) and (4.53), we obtain the forms of the dissipation potentials in the general G -picture [43, 70]:

$$\Psi^G = G\Psi, \quad \Phi^G = G\Phi. \quad (4.66)$$

Finally we note another essential property of the functions Ψ and Φ ; namely, that they are invariant scalar quantities with respect to the linear transformations of the currents and forces.

4.6.1. The local forms of Gyarmati's principle. Gyarmati's variational principle of non-equilibrium thermodynamics can be derived from the properties (4.62) and (4.64) of the functions Ψ and Φ . We mention that this derivation does not make use of the homogeneous quadratic forms of the functions Ψ and Φ given in (4.60) and (4.61); thus the variational principle is applicable to strictly non-linear phenomena that cannot be described by the linear laws (4.48), yet the currents are uniquely determined by the forces and the local variables of state. This is the situation with all the phenomena the Gyarmati-Li generalization

$$\frac{\partial J_i}{\partial X_k} = \frac{\partial J_k}{\partial X_i} \quad (4.67)$$

of the Onsager relations corresponds to. These relations are necessary and sufficient conditions of the existence of dissipation potentials, obeying equations (4.62) and (4.64).

Notice, that equation (4.64) can be written in the form

$$\frac{\partial}{\partial J_k}(\sigma - \Phi) = 0, \quad (4.68)$$

where, in executing the partial differentiation, the currents must be regarded variables independent of the forces and local state variables. It means that the constitutive relations given by equation (4.64) are equivalent to the following statement: those currents correspond to a given set of forces and state variables, at which the function

$$\mathcal{L}_J = \sigma - \Phi \quad (4.69)$$

has a stationary point in the space of the currents. This form of the principle, which stands nearest to Onsager's principle for small fluctuations around an equilibrium in an adiabatically closed discontinuous system, is called the flux representation of Gyarmati's principle [69].

The force representation of Gyarmati's principle is obtained by putting the relation (4.62) in the form

$$\frac{\partial}{\partial X_k}(\sigma - \Psi) = 0. \quad (4.70)$$

During partial differentiation the forces and the fluxes must be regarded again as independent variables. Thus, those forces correspond to a given set of currents and state variables at which the function

$$\mathcal{L}_X = \sigma - \Psi \quad (4.71)$$

has a stationary point in the space of the forces.

It is easily seen that the functions \mathcal{L}_J and \mathcal{L}_X in (4.69) and (4.71) can be put in the same form, as the subtraction of function independent of the J -s from \mathcal{L}_J has no influence on equation (4.68). The function Ψ just fits the purpose. On the other hand, Φ can be subtracted from \mathcal{L}_X (due to the same reasons). Now a universal Lagrange density of Gyarmati's principle has been obtained:

$$\mathcal{L} = \mathcal{L}_J - \Psi = \mathcal{L}_X - \Phi = \sigma - \Psi - \Phi, \quad (4.72)$$

by which the extremum properties (4.68) and (4.70) can be expressed universally.

It can be said, quite generally, that if a sufficient number of the currents and forces is known — that is either every force or every current, or even one part of the currents and the other part of the forces — then the remaining variables must be chosen so that the universal Lagrangian (4.72) is stationary. This is a necessary and sufficient condition for the set of the currents and forces describe a real process. In other words, the variation of the universal Lagrangian in Gyarmati's principle is zero around the real forces and fluxes, with respect to the simultaneous variation of the currents and forces.

In the quasi-linear theory the functions Ψ and Φ depend on the state variables through the conductivities L_{ik} and resistivities R_{ik} due to (4.60) and (4.61). The matrices of the conductivities L_{ik} and resistivities R_{ik} are reciprocal matrices:

$$\sum_r L_{ir} R_{rk} = \delta_{ik}. \quad (4.73)$$

Let us calculate the partial derivative of the \mathcal{L} Lagrange density with respect to a local state variable denoted by Γ :

$$\frac{\partial \mathcal{L}}{\partial \Gamma} = -\frac{1}{2} \sum_{i,k} \frac{\partial L_{ik}}{\partial \Gamma} X_i X_k - \frac{1}{2} \sum_{i,k} \frac{\partial R_{ik}}{\partial \Gamma} J_i J_k. \quad (4.74)$$

The partial derivatives $\partial R_{ik}/\partial\Gamma$, making use of (4.73), are expressed by the coefficients R_{ik} and the derivatives $\partial L_{ik}/\partial\Gamma$ as

$$\frac{\partial R_{ik}}{\partial\Gamma} = - \sum_{r,s} R_{ir} \frac{\partial L_{rs}}{\partial\Gamma} R_{sk}. \quad (4.75)$$

Substituting this in (4.74) and applying the reciprocal relations, the form

$$\frac{\partial\mathcal{L}}{\partial\Gamma} = -\frac{1}{2} \sum_{i,k} \frac{\partial L_{ik}}{\partial\Gamma} (X_i - \sum_s R_{is} J_s) (X_k + \sum_s R_{ks} J_s). \quad (4.76)$$

is obtained. Hence it is seen that the partial derivatives of the universal Lagrangian with respect to the local state variables, at real processes, are zero. So the parameters Γ can also be varied independently.

This theorem is Gyarmati's supplementary theorem [72], which guarantees the validity of the universal local form of the variational principle to the quasi-linear case, too.

The universal form of the local Gyarmati principle states, consistently with the supplementary theorem, that the Lagrangian $\mathcal{L} = \sigma - \Psi - \Phi$ has an extremum in all points that describe a real process in the unified space of forces, currents and state variables.

In examining the type of the extremum, instead of considering second variations, we had better use another form of the Lagrangian which is advantageous in other respects, as well. This form is

$$\mathcal{L} = -\frac{1}{2} \sum_{i,k} R_{ik} (J_i - \sum_s L_{is} X_s) (J_k - \sum_s L_{ks} X_s). \quad (4.77)$$

Executing the multiplications the form (4.72) of the universal Lagrange density is obtained again. This very form, however, clearly shows that the extremum for real processes is always a maximum and the value of this maximum is zero; in other cases the Lagrangian is always negative, since the R_{ik} -s are the coefficients of a positive definite quadratic form and the variables of this quadratic form are $(J_i - \sum_s L_{is} X_s)$. This form of the local principle is considerably similar to Gauss' principle of least constraint, so this form is often called the Gaussian form of Gyarmati's principle. As the value of (4.77) is zero only in the absence of local constraints, while in other cases the value of this maximum depends on the constraints, the Gauss type local principle is an excellent tool for introducing the notion of thermodynamic constraint forces; consequently it is of great help in discussing problems with local constraints (Verhás [157], Gyarmati [70], Dickel [32]).

The local Gyarmati principle of irreversible thermodynamics is of universal validity, yet its most important consequence to the fact it is regarded as the basis for integral principles. Before the discussion of integral principles, however, the place of the local principle in the frame-work of the theory should be examined. To this end, the local principle is resumed more explicitly.

The essence of the local principle is that it replaces the set of linear laws by a single scalar function. If either the function Ψ or the function Φ is known, the

constitutive equations can be obtained by the variational principle. Actually, it is sufficient to know only one of the dissipation potentials Ψ or Φ , since the matrix of the coefficients can be read from one of them, and the other potential is determined by the elements of the reciprocal matrix.. This calculation can be executed via a more elegant method. Let us regard, for example, the function Ψ as the given one. Then the Legendre-transformation of the function Ψ leads to the function $\Phi\left(\frac{\partial\Psi}{\partial X}\right)$. Putting J in the place of $\frac{\partial\Psi}{\partial X}$ the function Φ is obtained. The function Ψ is got from Φ in the same way, ([69, 72]).

The advantage of the method of Legendre transformation lies in the fact that its formulation and application is independent of the linear or quasi-linear character of the theory; thus it is applicable to dissipation potentials of entirely different character. From the fact that the dissipation potentials Ψ and Φ are the Legendre transforms of each other, it is also seen that the validity of Gyarmati's supplementary theorem is not restricted to the quasi-linear case, but holds to any strictly non-linear theory, subject to the Gyarmati-Li generalized reciprocal relations (and where the higher order coefficients also depend on the variables of state). This, at the same time, means that the Lagrangian $\mathcal{L} = \sigma - \Psi - \Phi$ must be stationary at every point of space in every instant of time in the case of any non-linear theory, provided that dissipation potentials exist at all.

The next question is how a dissipation potential can be constructed from the constitutive equations. The potential character of the functions Ψ and Φ is defined by equations (4.62) and (4.64). The condition to the existence of such functions with potential character to a given (say: empirically proven) set of constitutive equations is that they be subjected to the Gyarmati-Li generalized reciprocal relations. It is rather inconvenient that no general physical law, or exact proof based on such laws, is known which would guarantee the fulfillment of the Gyarmati-Li generalized reciprocal relations, or of other equivalent conditions, for all possible constitutive equations. If, however, the reciprocal relations (4.67) hold in a particular case or approximation, then the dissipation potentials can be given and the Gyarmati principle can be applied. Dissipation potentials for non-linear cases were given first (and independently) by Verhás [157], Edelen [35] and Presnov.

The function Ψ can be obtained as follows. Combining equations (4.43) and (4.62) we get

$$\sigma_s = \sum_i X_i \frac{\partial\Psi}{\partial X_i} = \sum_i X_i J_i(X) = \sigma_s(X) \quad (4.78)$$

for the entropy production. This expression can be regarded as a quasi-linear inhomogeneous partial differential equation. Its only solution subject to the condition $\Psi(0) = 0$ is the function

$$\Psi(X) = \int_0^1 \frac{1}{t} \sigma_s(tX) dt \quad (4.79)$$

A similar formula is obtained for $\Phi(J)$:

$$\Phi(J) = \int_0^1 \frac{1}{t} \sigma_s(tJ) dt \quad (4.80)$$

The knowledge of the function Ψ or Φ defined so, is equivalent to the knowledge of the original constitutive equations [157].

4.6.2. The governing principle of dissipative processes. Though the local form of Gyarmati's principle is indispensable for the description of local constraints, an integral form of the principle is of much greater importance in practical calculations. The integral forms are obtained by the integration of the universal Lagrange density with respect to space or space and time coordinates. The universal (global) principle, obtained so, is called the governing principle of dissipative processes [72].

Since the universal Lagrange density is everywhere and always stationary, it is also true that

$$\delta \int_V (\sigma - \Psi - \Phi) dV = 0, \quad (4.81)$$

and

$$\delta \int_{t_1}^{t_2} \int_V (\sigma - \Psi - \Phi) dV dt = 0. \quad (4.82)$$

The governing principle of dissipative processes given by Gyarmati can be regarded the most widely valid and the most widely applied integral principle of irreversible thermodynamics. From this principle the parabolic transport equations of irreversible transport processes can be derived both in the linear and quasi-linear case, as well as in all those non-linear cases where dissipation potentials can be determined by (4.79) and (4.80) due to the validity of the generalized reciprocal relations (4.67), [35, 43, 70, 73, 141, 146, 149, 157, 160].

The application of the governing principle can be understood through the properties of the local principle. The variational principle alone does not contain sufficient information about the system, the functional takes its absolute maximum in several points of the (Γ, X, J) space; but if the Γ and X values are given, then J can be determined. Obviously, not only the knowledge of Γ and X is suitable but any other restrictive circumstance denoting an equivalent hypersurface in the (Γ, X, J) space. Such a restrictive condition is the ensemble of the balance equations and the definition of the forces (read from the entropy production (4.36)) together with the equation of state.

Hence it follows that the variational principles (4.81) and (4.82) are to be understood with the above subsidiary conditions, and thus the processes occurring in the system are uniquely described.

The extraordinary importance of the formula (4.81) arises from the fact that the Euler-Lagrange equations are identical to the parabolic transport equations. Its use has the greatest advantage in the entropy picture, since the substitution of Γ with the entropy balance gives a particular form. The corresponding Euler-Lagrange equations have a separable subsystem of differential equations (viz. independently solvable) for the Γ parameters, and neither the consideration of the balance equations as subsidiary conditions nor the determination of the J currents is necessary [70].

The governing principle of dissipative processes — like any other integral principle of physics — contains information on the boundary conditions, too. They have to be given so as the absolute maximum be provided, viz. any further weakening of the proper boundary conditions may not increase the value of the maximum.

We mention that for strictly linear problems there are two partial forms also valid:

$$\delta \int_V (\sigma - \Psi) dV = 0, \quad \delta J = 0,$$

and

$$\delta \int_V (\sigma - \Phi) dV = 0, \quad \delta X = 0.$$

The first of these is called force, and the second is called flux representation. Both representations were widely applied to the solution of several practical problems. [145, 146, 149]. It is also well known that the force representation of Gyarmati's governing principle is equivalent to the local potential method of Prigogine and Glandsdorff [55], while the flux representation is the equivalent of the variational methods of Biot [8]. (For details see references [72, 145, 147].)

4.6.3. The derivation of the von Mises' equations of plasticity. Here we present an application of the local principle to a typical non-linear case: we derive Mises' theory of plastic flow (Verhás [157]). The existence of the function Φ is assumed.

Let us consider a homogeneous, isotropic, incompressible fluid continuum in local equilibrium and ignore heat conduction. The energy dissipation for this case is obtained from equation (4.38) in the form

$$T\sigma_s = \mathbf{t}_0 : \dot{\mathbf{d}}. \quad (4.83)$$

It is well known that the direct application of the linear laws to this expression leads to Newton's viscosity law [61, 70]. Instead, choose a different procedure, assuming the constitutive relation between the single thermodynamic force and flux non-linear but still deducible from a Φ dissipation potential. This dissipation potential is a scalar and isotropic function of $\dot{\mathbf{d}}$, thus

$$\Phi = \Phi(\text{tr } \dot{\mathbf{d}}, \text{tr } \dot{\mathbf{d}}^2, \text{tr } \dot{\mathbf{d}}^3). \quad (4.84)$$

In course of isochoric motions the trace of $\dot{\mathbf{d}}$ is zero, so

$$\Phi = \Phi(\text{tr } \dot{\mathbf{d}}^2, \text{tr } \dot{\mathbf{d}}^3). \quad (4.85)$$

If Φ is assumed to be a continuous function of its variables (remember that $\Phi = 0$ at $\dot{\mathbf{d}} = 0$), then, for sufficiently slow flows, we can ignore the $\text{tr } \dot{\mathbf{d}}^3$ variable, too, as its value is small relative to $\text{tr } \dot{\mathbf{d}}^2$. The trace of $\dot{\mathbf{d}}^3$ is strictly zero for viscometric flows. Thus the form of the potential Φ , for viscometric flows exactly and for nearly viscometric flows approximately is

$$\Phi = \Phi(\text{tr } \dot{\mathbf{d}}^2). \quad (4.86)$$

Since Φ is regarded a function of $\dot{\mathbf{d}}$, let us introduce (to simplify calculations) the notation

$$\dot{\mathbf{d}} = \lambda \mathbf{a}, \quad (4.87)$$

where λ is a scalar variable. The tensor \mathbf{a} can be arbitrarily normed, which norm now is

$$\text{tr } \mathbf{a}^2 = 1. \quad (4.88)$$

Thus instead of (4.86) we can use the function

$$\Phi = \Phi(\lambda^2) = g(\lambda). \quad (4.89)$$

It is obvious that the function $g(\lambda)$ has a physical meaning, but for the positive values of its variable; consequently, for negative λ the function $g(\lambda)$ can be defined at will. It is plausible to assume $g(\lambda)$ differentiable at $\lambda = 0$. Then for a sufficiently small value of λ , $g(\lambda)$ can be approximated by its tangent, so the function

$$g = a\lambda \quad (4.90)$$

can be taken. Hence, with respect to equations (4.87) and (4.88), the form

$$\Phi = a(\text{tr } \dot{\mathbf{d}}^2)^{\frac{1}{2}} \quad (4.91)$$

is obtained, from which the constitutive relation

$$\mathbf{t} = \frac{2a}{(\text{tr } \dot{\mathbf{d}}^2)^{\frac{1}{2}}} \dot{\mathbf{d}} \quad (4.92)$$

does follow. Introducing the notation

$$a\sqrt{2} = k, \quad (4.93)$$

the expression

$$\mathbf{t}_0 = \frac{k\sqrt{2}}{(\text{tr } \dot{\mathbf{d}}^2)^{\frac{1}{2}}} \dot{\mathbf{d}} \quad (4.94)$$

is obtained for the stress, which is identical to the equation (3.31) of the ideal plastic body.

From the above results it is clear that Gyarmati's local principle furnished with various approximations for the potential ϕ leads to the various theories of viscous flow or plasticity.

4.6.4. The generalized reciprocal relations and the generalization of Gyarmati's principle for non-linear cases. The possibility of generalizing the reciprocal relations for non-linear constitutive equations has already been mentioned in section 4.5. dealing with the reciprocal relations and in section 4.6. describing Gyarmati's variation principle. However, the practical value of the suggestions made there is doubtful. The reason for this is that neither the macroscopic

reversibility principle proposed by Meixner [109] nor the generalized reciprocal relations by Gyarmati and Li [66, 101] could be proved satisfactorily up to now, either theoretically or experimentally. Moreover, it is well known that the dynamic equations equivalent to the Guldberg-Waage equations for chemical reactions, which are regarded as prototypes of non-linear constitutive equations, definitely violate the general reciprocal relations of Gyarmati and Li, as well as Meixner's macroscopic reversibility principle — at least in the case where we consider affinities the real driving force of chemical reactions in the non-linear region far from equilibrium. We cannot deal here with this very important problem which is at present in the limelight of non-linear thermodynamics, but the interested reader is referred to the literature on the subject [99].

Nevertheless, in what follows a generalization will be presented which is proved by strict mathematics and whose validity is not restricted if we have doubly continuously differentiable constitutive equations.

Start from the bilinear form of entropy production

$$\sigma_s = \sum_i J_i X_i, \quad (4.95)$$

but let us drop our usual notation, viz. that J_i stands for “current” and X_i for “force” of the process rate. Let X_i be the independent variable from among the canonically conjugate force and current and J_i the other variable characteristic for the i -th process. The independent variables should be chosen so that close to equilibrium — i.e. in the range of validity of the linear laws — only Onsager's reciprocal relations should hold. We do not suppose the linearity of the constitutive equations, but require that they be doubly continuously differentiable with respect to X_i -s. The role of equilibrium state parameters is not restricted in the constitutive equations. For them, it may be written in a general way that

$$J_i = J_i(X_1, X_2, \dots, \Gamma_1, \Gamma_2, \dots), \quad (4.96)$$

where X_1, X_2, \dots are the independent variables selected from the expression of entropy production. For brevity, let us now call them forces — $\Gamma_1, \Gamma_2, \dots$ are other local state parameters whose determination is not necessary at present. Let us then take function

$$J_i = J_i(\lambda X_1, \lambda X_2, \dots) \quad (4.97)$$

depending on λ and expand it into a Taylor series with respect to the powers of λ and stop after the linear term. On writing also the remainder, expression

$$J_i = \sum_k \frac{\partial J_i}{\partial X_k} \Big|_0 X_k \lambda + \frac{1}{2} \sum_{k,j} \frac{\partial^2 J_i}{\partial X_k \partial X_j} \Big|_{\xi X_1, \xi X_2, \dots} X_k X_j \lambda^2 \quad (4.98)$$

results, which at $\lambda = 1$, gives again constitutive equation (4.96). If the remainder is negligible, equation (4.98) is identical with Onsager's linear laws and the derivatives included in it may be identified with the Onsager coefficients:

$$\frac{\partial J_i}{\partial X_k} \Big|_0 = L_{ik}^0 = L_{ki}^0 = \frac{\partial J_k}{\partial X_i} \Big|_0. \quad (4.99)$$

We note that reciprocal relations do not follow from the expression; their validity has been taken from the linear theory. Now, for brevity, we introduce coefficients

$$l_{ijk} = \frac{1}{2} \frac{\partial^2 J_i}{\partial X_k \partial X_j} \Big|_{\xi X_1, \xi X_2, \dots} \quad (4.100)$$

Following from the nature of the Taylor series, derivatives should be taken at $\xi X_1, \xi X_2, \dots$ where ξ lies between 0 and 1 and whose actual value is determined by the structure of constitutive equation (4.96) and the actual values of the independent variables. (If more than one ξ is possible, the smallest should be chosen.) Now the constitutive equations may be written in form

$$J_i = \sum_k L_{ik}^0 X_k + \sum_{j,k} l_{ijk}(X_r) X_j X_k \quad (4.101)$$

where coefficients l_{ijk} may also depend on X ; but on the basis of equation (4.100), correlations

$$l_{ijk} = l_{ikj} \quad (4.102)$$

hold between them. Let us now introduce coefficients

$$L_{ik} = L_{ik}^0 + \sum_j (l_{ijk} + l_{kji} - l_{jik}) X_j \quad (4.103)$$

for which, on the one hand, Onsager's reciprocal relations of the linear theory are valid and, on the other hand, as a consequence of equation (4.102) generalized reciprocal relations

$$L_{ik} = L_{ki} \quad (4.104)$$

hold. By using them, the constitutive equations may be written as

$$J_i = \sum_k L_{ik} X_k = \sum_k L_{ik}^0 X_k + \sum_{j,k} l_{ijk} X_j X_k + \sum_{j,k} (l_{kji} - l_{jik}) X_j X_k \quad (4.105)$$

Since the last term on the right hand side is zero, equations (4.101) are obtained again.

Our results can be summarized as follows. The constitutive equations, also for non-linear cases, may be written in the form

$$J_i = \sum_k L_{ik} X_k \quad (4.106)$$

where coefficients L_{ik} may depend also on X , and between conductivity coefficients reciprocal relations

$$L_{ik} = L_{ki}$$

hold if they are valid in the linear limiting case, i.e. close to equilibrium.

The selection of independent variables can be varied by a linear transformation of forces and currents which is formally analogous to that applied in the linear theory. This means that in the equation with the changed independent variables,

Casimir-type reciprocal relations also appear, similar to the linear theory. Of course, from the viewpoint of the validity of the generalized Onsager-Casimir reciprocal relations between coefficients L_{ik} , it is of no importance what the independent variables of the coefficients are. Since the determinant of the matrix constructed from coefficients L_{ik} is positive at equilibrium, the constitutive equations are doubly continuously differentiable and thus the above determinant is a continuous function of the independent variables. From this it follows that the matrix constructed from coefficients L_{ik} can be inverted in a wider range around equilibrium than the realm of linear laws. A similar consideration is applied for the principal minors of matrix L_{ik} ; hence the homogeneous quadratic form using coefficients L_{ik} remains positive definite.

The above generalization of Onsager's reciprocal relations permits the writing of the Lagrange function belonging to Gyarmati's principle provided by equation (4.77) in its usual form as

$$\mathcal{L} = -\frac{1}{2} \sum_{i,k} R_{ik} \left(J_i - \sum_s L_{is} X_s \right) \left(J_k - \sum_s L_{ks} X_s \right) \quad (4.107)$$

where numbers R_{ik} again mean the elements of the reciprocal matrix. Since the homogeneous quadratic form constructed with coefficients L_{ik} is positive definite — and, consequently, also that formed by coefficients R_{ik} — the Lagrange function \mathcal{L} is always negative if constitutive equations (4.106) are not satisfied. If they are satisfied, \mathcal{L} is zero. This means, at the same time, that in the case of X and J values corresponding to the real process, \mathcal{L} is maximum — even an absolute maximum.

The Lagrange function can be reduced to its well-known simpler form by removing the parentheses:

$$\mathcal{L} = \sum_i J_i X_i - \frac{1}{2} \sum_{i,k} L_{ik} X_i X_k - \frac{1}{2} \sum_{i,k} R_{ik} J_i J_k = \sigma - \Psi - \Phi. \quad (4.108)$$

From this expression dissipation potentials may be determined as

$$\Psi = \frac{1}{2} \sum_{i,k} L_{ik}(X) X_i X_k, \quad \Phi = \frac{1}{2} \sum_{i,k} R_{ik}(X) J_i J_k. \quad (4.109)$$

It is very important and striking that relative to the linear theory the only change is that dissipation potential Ψ is not a quadratic function of X -s any more and potential Φ also depends on X -s. However, a significant difference is that although equality

$$\frac{\partial \Phi}{\partial J_i} = \sum_k R_{ik}(X) J_k = X_i \quad (4.110)$$

holds also here, partial derivative

$$\frac{\partial \Psi}{\partial X_i} = \sum_k L_{ik} X_k + \frac{1}{2} \sum_{i,k} \frac{\partial L_{jk}}{\partial X_i} X_j X_k \neq J_i \quad (4.111)$$

does not give the currents, since in this non-linear theory Ψ cannot be regarded as a potential. It should also be noted that the problem of these derivatives becomes

even more complicated if X -s are not chosen as independent variables in the conduction coefficients, but this does not interfere with the validity of the variational principle.

The unchanged validity of the local form of Gyarmati's principle in non-linear cases and the existence of an absolute maximum allows the integration of the local form with respect to time and space. Therefore we can say that the validity of the governing principle of dissipative processes whose basis is the integrated form of equation (4.108) with respect to space and time is not restricted to linear thermodynamics, but it is almost general since the requirement of its being doubly continuously differentiable is not a strong restriction from a physical point of view.

Recently a new variational principle was proposed [52, 53, 105] that gives the transport equations as Euler-Lagrange equations for the potential functions introduced. Nyíri showed out [122] that a particular form of Gyarmati's variational principle is valid even if the constitutive equations are non-linear and no reciprocal relation holds in the linear approximation.

4.7. The wave approach of thermodynamics.

One of the newest generalizations of so-called classical irreversible thermodynamics based on the hypothesis of local equilibrium is the wave approach, which (apart from some ad hoc and special cases (Cattaneo, Vernotte)) has been elaborated in its most complete form strictly on the basis of Onsager's theory by Gyarmati in 1977 [74]. The comprehensive practical applicability of this theory for temperature waves originating in solid bodies has been pointed out by Fekete [46], whereas its application and further development for diffusion, thermodiffusion and other phenomena has been credited to Bhattacharya [7].

The starting point of the wave approach is the recognition that the current densities of transport processes have inertia; thus part of the internal energy of the medium is a "kinetic" energy ascribable to these processes. In such cases the entropy of the medium is not a function exclusively of local equilibrium state parameters, but also includes an additive term depending in a homogeneous quadratic manner on current densities describing the rate of the processes. The main features of the method will be demonstrated on the example of heat conduction in solid bodies, but it must be emphasized that the procedure can be applied for any transport process. Even the simultaneous presence of several transport processes does not exclude its applicability, since Gyarmati's wave theory of thermodynamics is, in fact, the direct and consequent generalization of the theory elaborated by Onsager and Machlup in 1951 for adiabatically closed systems with a "kinetic" energy for non-equilibrium continua [104, 126].

Consider a solid body whose mechanical motion is, for simplicity, negligible and in which heat conduction is the only transport process. The specific entropy of the medium, according to the above, is then

$$s = s_0(u) - \frac{1}{2}m\mathbf{J}_q^2 \quad (4.112)$$

where $s_0(u)$ is the equilibrium entropy function and m a material constant characteristic for the inertia of heat current density. The actual form of entropy balance is now

$$\sigma_s = \varrho \dot{s} + \operatorname{div} \left(\frac{1}{T} \mathbf{J}_q \right) = \varrho \frac{1}{T} \left(\dot{u} - m \mathbf{J}_q \dot{\mathbf{J}}_q \right) + \frac{1}{T} \operatorname{div} \mathbf{J}_q + \mathbf{J}_q \operatorname{grad} \frac{1}{T} \quad (4.113)$$

By utilizing the balance equation of internal energy

$$\varrho \dot{u} + \operatorname{div} \mathbf{J}_q = 0, \quad (4.114)$$

we have for entropy production

$$\sigma_s = \mathbf{J}_q \left(-m \dot{\mathbf{J}}_q + \operatorname{grad} \frac{1}{T} \right) = \mathbf{J}_q \mathbf{X}_q \quad (4.115)$$

whence it is apparent that the force \mathbf{X}_q adjoint to thermodynamic current \mathbf{J}_q is

$$\mathbf{X}_q = \operatorname{grad} \frac{1}{T} - m \dot{\mathbf{J}}_q = \mathbf{X}_q^0 + \mathbf{Y}_q \quad (4.116)$$

which now consists of two parts: the classical force belonging to heat conduction \mathbf{X}_q^0 and force $\mathbf{Y}_q = -m \mathbf{J}_q$ belonging to the non-equilibrium state. This leads to the extension of the classical theory into the wave theory.

Until now, we have used the entropy picture, expedient for the discussion of the general theory, for providing the basic equation of temperature waves in solid bodies; it is, however, more appropriate to use the so-called Fourier picture, which was first elaborated for the wave theory by Fekete [46]. In this picture, instead of equation (4.115), we may write

$$T^2 \sigma_s = -\mathbf{J}_q (m^{**} \dot{\mathbf{J}}_q + \operatorname{grad} T) = \mathbf{J}_q \mathbf{X}_q^{**} \quad (4.117)$$

where we introduced the general force \mathbf{X}_q^{**} and the material coefficient $m^{**} = T^2 m$ from the Fourier picture. The constitutive equation of the process in linear approximation and according to the Fourier picture is

$$\mathbf{J}_q = \lambda \mathbf{X}_q^{**} = -\lambda (m^{**} \dot{\mathbf{J}}_q + \operatorname{grad} T). \quad (4.118)$$

We obtain a clearer formula if we introduce the characteristic relaxation time $\tau = \lambda m^{**}$, by use of which equation (4.118) transforms into the alternative form

$$\tau \dot{\mathbf{J}}_q + \mathbf{J}_q = -\lambda \operatorname{grad} T \quad (4.119)$$

The transport equation may be obtained by comparing equations (4.119) and (4.114):

$$\varrho c (\tau \ddot{T} + \dot{T}) = \operatorname{div} (\lambda \operatorname{grad} T) \quad (4.120)$$

This differential equation of hyperbolic type is analogous to Kelvin's telegraph equation which, at low frequencies, ($\tau \ddot{T}$ is negligible as compared to \dot{T}), leads to the parabolic Fourier equation; whereas at high frequencies (\dot{T} is negligible as compared to $\tau \ddot{T}$), it transforms into the classical undamped wave equation.

An interesting feature of equation (4.120) is that it provides a maximum for the propagation velocity of temperature perturbation.

$$v \leq \sqrt{\frac{\lambda}{\rho c \tau}} \quad (4.121)$$

It is easy to see that the thermodynamic consideration outlined eliminates the contradiction existing between the classical Fourier equation and the finite propagation velocity required by the special theory of relativity.

This simple variant of the wave approach is easily identifiable with heat radiation in semitransparent media if the other ways of heat transport are negligible and the heat capacity of the medium is small. This is the case, for example, with nocturnal heat radiation through a wet atmosphere.

Let us consider here only a one-dimensional problem in which heat radiation passes through an absorbing medium upwards and downwards (Figure 4.1.). Assume further that the medium immediately radiates back the absorbed energy due to the isotropy of the medium, half of it upwards and the other half downwards. Let us write the balance equations for both components of the radiation in the case of a very thin layer with a thickness of Δx , where x is the coordinate pointing upwards:

$$\begin{aligned} J_u \left(x + \Delta x, t + \frac{\Delta x}{v} \right) &= J_u(x, t) - a\Delta x J_u + \frac{e}{2}\Delta x \\ J_d \left(x, t + \frac{\delta x}{v} \right) &= J_d(x + \Delta x, t) - a\Delta x J_d + \frac{e}{2}\Delta x, \end{aligned} \quad (4.122)$$

where J_u is the heat current density upward,

J_d the same in the downward,

a the absorption coefficient, and

e the emission density.

The first equation expresses that upward radiation J_u decreases by $a\Delta x J_u$ while passing through the distance Δx in a time of $\frac{\Delta x}{v}$ due to the absorption in the medium, whereas it increases by $\frac{e}{2}\Delta x$ owing to back-radiation. The second equation may be interpreted in the same sense. The condition that the medium radiates back the absorbed radiation immediately is reflected by equation

$$e = a(J_u + J_d). \quad (4.123)$$

On rearranging both equations, dividing them by Δx and letting $\Delta x \rightarrow 0$, we obtain

$$\begin{aligned} \frac{\partial J_u}{\partial x} + \frac{1}{v} \dot{J}_u &= -aJ_u + \frac{e}{2}, \\ -\frac{\partial J_d}{\partial x} + \frac{1}{v} \dot{J}_d &= -aJ_d + \frac{e}{2}. \end{aligned} \quad (4.124)$$

Let us introduce notations now

$$u = \frac{1}{v}(J_u + J_d), \quad J = J_u - J_d \quad (4.125)$$

with which, considering also equation (4.123) from equation (4.124), we arrive at

$$\dot{u} + \frac{\partial J}{\partial x} = 0, \quad \frac{1}{av} \dot{J} + J = -\frac{v}{a} \frac{\partial u}{\partial x}. \quad (4.126)$$

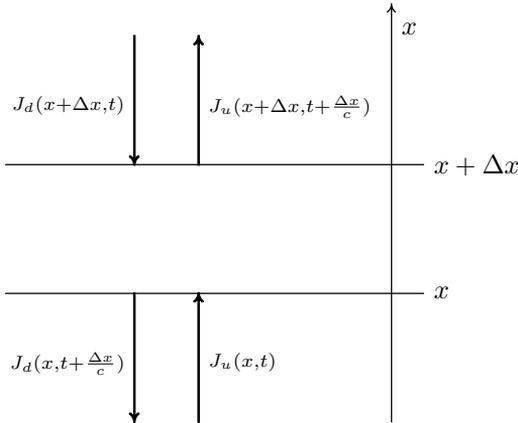


Figure 4.1

The first equation is identical with the balance equation of energy, since J is the resultant heat current density and u is the energy density according to the electromagnetic theory of radiation. If we now take into account that on the basis of the Stefan-Boltzmann law, the energy density of heat radiation is proportional to the fourth power of temperature, the second equation may be transformed into

$$\tau \dot{J} + J = -\lambda \frac{\partial T}{\partial x} \quad (4.127)$$

where quantities

$$\tau = \frac{1}{av}, \quad \lambda = \frac{v}{a} \frac{\partial u}{\partial T} \quad (4.128)$$

have been introduced. Equation (4.127) is obviously the one-dimensional variant of constitutive equation (4.119).

We shall now show that Gyarmati's wave approach of thermodynamics may also be interpreted as a special case of the theory based on dynamic degrees of freedom elaborated in Chapter 4 of this book and applied for numerous rheological phenomena in later sections. For this, consider a medium whose only equilibrium state parameter is the specific internal energy and suppose that the non-equilibrium state of this medium can be characterized by a single β -type vectorial dynamic variable. The actual form of entropy is now

$$s = s_0(u) - \frac{1}{2} \vec{\beta}^2 \quad (4.129)$$

whereas entropy production is

$$\sigma_s = \mathbf{J}_q \text{grad} \frac{1}{T} - \vec{\beta} \dot{\vec{\beta}}. \quad (4.130)$$

When thinking in terms of the Fourier picture, we obtain

$$T^2 \sigma_s = -\mathbf{J}_q \text{grad} T - T \vec{\beta} T \dot{\vec{\beta}}. \quad (4.131)$$

On writing Onsager's laws with currents \mathbf{J}_q and $T\dot{\vec{\beta}}$, we arrive at linear equation

$$\begin{aligned} -\text{grad } T &= R_{11}\mathbf{J}_q + R_{12}T\dot{\vec{\beta}}, \\ -T\dot{\vec{\beta}} &= R_{21}\mathbf{J}_q + R_{22}T\dot{\vec{\beta}} \end{aligned} \quad (4.132)$$

for whose coefficients now Casimir's reciprocal relations hold: $R_{12} = -R_{21}$. Obviously, in our case relations

$$R_{11} > 0, R_{22} > 0, \quad R_{11}R_{22} + R_{12}^2 > 0 \quad (4.133)$$

should be satisfied, which express the law of entropy increase. The latter relations do not exclude the limiting case $R_{22} = 0$. In this case, from equations (4.132) the dynamic variable may easily be eliminated:

$$-\text{grad } T = R_{11}\mathbf{J}_q + R_{12}^2\dot{\mathbf{J}}_q. \quad (4.134)$$

On introducing quantities

$$\tau = \frac{R_{12}^2}{R_{11}} \quad \text{and} \quad \lambda = \frac{1}{R_{11}} \quad (4.135)$$

we may establish that the linear constitutive equation (4.134) of our theory based on the introduction of the new degrees of freedom transforms into the constitutive equation (4.119) of Gyarmati's wave approach.

Thus we can summarize our result that the wave approach of Gyarmati may be regarded as a special case of our theory based on the use of the dynamic degrees of freedom. The reason is that in this case, the dynamic variables are identical with the current densities of transport processes — except for a linear transformation — as is readily seen from the comparison of equations (4.112), (4.115) and (4.129), and (4.130).

4.8. Transport of dynamic degrees of freedom.

Throughout this book, we assume that the expression for the current density of the entropy \mathbf{J}_s , is identical with the expression valid for local equilibrium, which (in the simultaneous presence of heat conduction and diffusion) is

$$\mathbf{J}_s = \frac{1}{T}\mathbf{J}_q - \sum_i \frac{\mu_i}{T}\mathbf{J}_i. \quad (4.136)$$

Outside local equilibrium, the unanimity of the coefficients of current densities is ensured by the canonical choice of dynamic variables; then

$$\frac{1}{T} = \frac{\partial s}{\partial u} = \frac{\partial s_0}{\partial u}, \quad \frac{\mu_i}{T} = \frac{\partial s}{\partial c_i} = \frac{\partial s_0}{\partial c_i} \quad (4.137)$$

This assumption — i.e. to postulate the validity of equation (4.136) — is, however, quite arbitrary, and its correctness is proved merely by the practical applicability of the relationships derived from it.

In what follows, we shall examine the consequences resulting from the rejection of this hypothesis. For simplicity the model of heat conduction in solid bodies will be used again for this purpose; however, it should be emphasized that this is only in order to simplify the calculations and considerations and that there is no difficulty in the simultaneous consideration of various transport processes in a completely general manner.

Let us take a solid body with specific internal energy as the only equilibrium state parameter, but in which the processes are to be characterized by dynamic variables. Then entropy may be given by

$$s = s_0(u) - \frac{1}{2} \sum_i \xi_i^2. \quad (4.138)$$

In the general form of the entropy balance given by

$$\rho \dot{s} + \operatorname{div} \mathbf{J}_s = \sigma_s, \quad (4.139)$$

\mathbf{J}_s may now differ from the usual form $\mathbf{J}_s = \frac{1}{T} \mathbf{J}_q$ and be

$$\mathbf{J}_s = \frac{1}{T} \mathbf{J}_q + \mathbf{K}, \quad (4.140)$$

where vector \mathbf{K} expresses the deviation from the formula valid in local equilibrium. Equation (4.140) may even be regarded as the definition for \mathbf{K} .

\mathbf{K} is obviously zero in all cases when the medium is in local equilibrium; hence, we can say that \mathbf{K} is a function of its variables whose value is zero if all the dynamic variables disappear. Based on this, \mathbf{K} may be defined in the form

$$\mathbf{K} = - \sum_i \mathbf{J}_i \xi_i \quad (4.141)$$

where quantities \mathbf{J}_i depend on the same variables as vector \mathbf{K} and they are continuous if \mathbf{K} is continuously differentiable. Dynamic coordinates ξ_i are treated here as if they were scalar quantities, but they can also be components of tensors of different orders. Entropy production can be obtained in the usual way by comparing equations (4.138), (4.139), (4.140) and (4.140):

$$\sigma_s = \rho \left(\frac{1}{T} \dot{u} - \sum_i \xi_i \dot{\xi}_i \right) + \frac{1}{T} \operatorname{div} \mathbf{J}_q + \mathbf{J}_q \operatorname{grad} \frac{1}{T} - \mathbf{J}_i \operatorname{grad} \xi_i - \xi_i \operatorname{div} \mathbf{J}_i. \quad (4.142)$$

Let us now utilize the balance equation of internal energy given by equation (4.114) and rearrange the equation into the form

$$\sigma_s = \mathbf{J}_q \operatorname{grad} \frac{1}{T} - \sum_i \mathbf{J}_i \operatorname{grad} \xi_i - \sum_i \xi_i (\rho \dot{\xi}_i + \operatorname{div} \mathbf{J}_i). \quad (4.143)$$

We will not write the linear laws although they are very important for applications. For the interpretation of the result derived, let us introduce correlation

$$\rho \dot{\xi}_i + \operatorname{div} \mathbf{J}_i = \sigma_{\xi_i} \quad (4.144)$$

which is actually the balance equation of a certain extensive quantity. If this extensive quantity Ξ_i is defined in the usual way as

$$\Xi_i = \int_V \varrho \xi_i dV \quad (4.145)$$

then it is obvious that vector \mathbf{J}_i can be interpreted as the current density of the transport of extensive quantity Ξ_i . The form of entropy current density (4.140) is written as

$$\mathbf{J}_s = \frac{\partial s}{\partial u} \mathbf{J}_q + \sum_i \frac{\partial s}{\partial \xi_i} \mathbf{J}_i \quad (4.146)$$

which may be considered the natural generalization of classical equation (4.136). Constitutive equations describing transport and source densities can be determined on the basis of the actual expression of entropy production (in linear theories, based on the forms of Onsager's linear laws; in non-linear theories, according to those corresponding to the former).

All this proves unambiguously that the formalism of irreversible thermodynamics elaborated by Onsager does not fail for systems outside local equilibrium either. On the other hand, it is also important that Onsager's works do not contain any explicit restrictions for the selection of the system of state parameters; thus it can be correctly stated that the possibility for introducing dynamic variables is a priori given in them.

4.9. Correlation between rational, entropy-less, extended and Onsager's thermodynamics.

The rapid development of non-equilibrium thermodynamics which started in recent decades is still in progress and has produced a multitude of methods and theories. Though the theories in question use different methods, their common feature is that they are based on the main principles of thermodynamics and concern the irreversible processes taking place in nature.

In what follows, we attempt to outline the differences and correlations between these various approaches. Six more or less fundamental features are selected as the basis of comparison:

1. Which method is used for the determination of the momentary properties of a thermodynamic system?
2. What is its attitude towards non-equilibrium entropy?
3. How does it interpret entropy current?
4. How does it interpret entropy supply?
5. Does it consider the Onsager-Casimir reciprocal relations valid?
6. Does it use linear or non-linear constitutive equations?

For comparison, a continuum will always be considered and a sufficiently small (infinitesimal) part of it will be called a thermodynamic system.

All modern thermodynamic theories are motivated by thermostatics; however, the departure from equilibrium is a source of significant differences.

When classifying thermodynamic theories, special emphasis should be placed on traditional, often called classical irreversible thermodynamics. Its basic principles

and linear constitutive equations, together with the Onsager-Casimir reciprocal relations, have been experimentally proved in a wide range. The application range of the full theory is comparable with that of various fundamental disciplines of physics and chemistry, and even surpasses many of them, but it is still closely related to thermostatics. However, this theory deals only with systems not too far from equilibrium; thus, it can circumvent the difficulties of defining the non-equilibrium thermodynamic quantities by accepting the hypothesis of local equilibrium. This means, at the same time, that the local values of equilibrium state parameters determine the local properties of the thermodynamic system; entropy exists, which depends on the same variables in the same way as it does in equilibrium. Entropy current — except for diffusion — equals the ratio of heat current and temperature; constitutive equations are linear. More precisely, only Onsager's theory operating with linear approximation may be considered a unified and experimentally proved theory. The most significant results in the field — theoretical elaboration and the practical application of traditional irreversible thermodynamics — have been achieved by Eckart [34], Meixner [109, 110], Prigogine, de Groot [59, 61] and Gyarmati [65-74].

The original works of Onsager [124-126] are deliberately omitted since they go significantly beyond the limits of local equilibrium. Onsager used the hypothesis of local equilibrium as one, but not the only method for circumventing the difficulties. For accuracy it should be noted that Onsager elaborated the general theory only for adiabatically closed, non-continuous systems; i.e., he did not deal explicitly with the thermodynamics of continua based on the general and exact basic principles of classical field theories. Therefore, in his basic works, he did not even postulate the validity of local equilibrium, at least not in a definite way. On the other hand, it is also true that the authors cited above while elaborating the irreversible thermodynamics of continua, also transgressed the frames of local equilibrium; moreover, Gyarmati's wave approach is definitely based on the existence of the locally non-equilibrium entropy function [74].

In the course of the growing widespread application of irreversible thermodynamics, the framework set by local equilibrium proved to be too tight. A demand arose for the description of thermodynamic systems which are no longer characterized by the fields of traditional local state parameters, because even they are locally non-equilibrium in nature. There are two possibilities for the description of non-equilibrium states. One of them, which is used in this book, is based on the introduction of further variables (dynamic degrees of freedom). The modern theories using this approach are collectively called classical or extended irreversible thermodynamics [83, 112, 113].

Choosing another way to describe theories differing a priori from the basic principles and methods of the axiom-system which Onsager's thermodynamics accepted (used and in every respect proved) are usually called "rational thermodynamics" [80, 152]. The basis of the method of rational thermodynamics is that the momentary properties of the thermodynamic system (a small enough cell of the medium) are determined by its interaction with its environment. Thus only the values of a few parameters describing this interaction have to be taken into account; however, not only in the given moment but also at any time prior to the actual moment. The role of state parameters is played by the functions providing these parameters,

and thus the constitutive equations (the determination of which for certain general classes of materials exclusively theoretically and “rationally” is the main goal of “rational thermodynamics”) become functionals. The efficiency of this method is illustrated to a certain extent by sections 3.3., 3.4. and 3.5.

The methods used in “extended irreversible thermodynamics” and “rational thermodynamics” are at first sight completely different. However, a deeper analysis shows that the differences are rather methodological than essential in nature. Namely, the two approaches become equivalent if we allow for infinite series of dynamic degrees of freedom for the characterization of non-equilibrium states in the extended theory. This equivalence can be best proved if Euclidean metrics is introduced in the field of functions representing the independent variables in the constitutive functionals of rational thermodynamics. In this case, the field of the above functions becomes a separable Hilbert space whose isomorphism with the l^2 space proves the equivalence of “extended irreversible thermodynamics” and “rational thermodynamics”. Not even the obviously superfluous combination of the two types of theory is missing from the literature [25].

With respect to the views on non-equilibrium entropy, the theories may be classified in four groups. We mention first the “entropy-less” thermodynamics (Meixner) according to which non-equilibrium entropy cannot be defined, at least unambiguously. In this case, entropy production cannot be interpreted either, and its positive character is replaced by Meixner’s fundamental inequality. The relationship between “entropy-less” thermodynamics and the method used in this book may be illustrated as follows. On substituting $\text{div } \mathbf{J}_q$ into the equation of entropy production

$$\sigma_s = \text{div } \frac{\mathbf{J}_q}{T} + \varrho \dot{s} = \mathbf{J}_q \text{grad } \frac{1}{T} + \frac{1}{T} \text{div } \mathbf{J}_q + \varrho \dot{s}_0 - \sum_i \varrho \xi_i \dot{\xi}_i \quad (4.147)$$

from the balance equation of internal energy

$$\varrho \dot{u} + \text{div } \mathbf{J}_q = \sigma_u \quad (4.148)$$

we obtain for entropy production

$$\sigma_s = \mathbf{J}_q \text{grad } \frac{1}{T} + \frac{1}{T} (\sigma_u - \varrho \dot{u}) + \varrho \dot{s}_0 - \sum_i \varrho \xi_i \dot{\xi}_i \quad (4.149)$$

If we divide this expression by the density and integrate it with respect to time, we arrive at

$$\int_{-\infty}^t \frac{1}{\rho} \sigma_s dt = \int_{-\infty}^t \left[\frac{1}{\rho} \mathbf{J}_q \text{grad } \frac{1}{T} + \frac{1}{T} \left(\frac{\sigma_u}{\rho} - \dot{u} \right) + \dot{s}_0 \right] dt - \frac{1}{2} \sum_i \xi_i^2 \geq 0. \quad (4.150)$$

Here we assumed that the medium at its starting state was in equilibrium ($t = -\infty$), i.e. that the dynamic variables were zero at $t = -\infty$. Since the sum $\frac{1}{2} \sum \xi_i^2$ is always positive, inequality

$$\int_{-\infty}^t \left[\frac{1}{\rho} \mathbf{J}_q \text{grad } \frac{1}{T} + \frac{1}{T} \left(\frac{\sigma_u}{\rho} - \dot{u} \right) + \dot{s}_0 \right] dt \geq 0 \quad (4.151)$$

should hold. In this inequality, no non-equilibrium entropy is included; thus its validity can also be required if we postulate that unambiguous entropy can only be defined in equilibrium. From this fundamental inequality, surprisingly, far-reaching conclusions can be drawn [109].

The remaining three groups of theories do not deny the existence of non-equilibrium entropy. (All these theories derive their results from the inequality reflecting the positive nature of entropy production. The rational thermodynamic theories normally do not explicitly refer to entropy production and call the inequality written for its actual form Clausius-Duhem inequality.) Theories of the first group postulate the existence of non-equilibrium entropy as well as its additivity similar to equilibrium entropy. This method is characteristic for the majority of “rational thermodynamic” theories [23, 121, 152].

Theories in the second group only slightly differ from those in the first one. Non-equilibrium entropy exists also here and is additive; however, its existence is not given a priori. In these theories entropy is a derived quantity similar to thermostatics. The shortcomings of these theories originate from the insufficiently convincing arguments in the course of the various derivations of entropy that often lead also to different results [31, 132, 155].

In the theories of the third group entropy is not an additive quantity, entropy production density cannot be interpreted, and the inequality representing the second law of thermodynamics may only be written for the whole of the medium. Their fault is that they are in contradiction with the results obtained by statistical methods; and by the assumption of interactions not being local, they reject the principle of local action successfully applied since the activity of Faraday.

Our third aspect for comparing the various theories is the form of entropy current. In this respect, three cases can be distinguished.

In theories of the first type, correlation

$$\mathbf{J}_s = \frac{1}{T} \mathbf{J}_q \quad \frac{1}{T} = \frac{\partial s}{\partial u} \quad (4.152)$$

holds similar to traditional irreversible thermodynamics based on the hypothesis of local equilibrium.

In the second type, the current of entropy remains parallel to the heat current; however, the coefficient is not the temperature as it is in thermostatics, i.e.

$$\mathbf{J}_s = \frac{1}{T} \mathbf{J}_q \quad \frac{1}{T} \neq \frac{\partial s}{\partial u} \quad (4.153)$$

where T is the so-called non-equilibrium temperature.

Finally, in the third type, the entropy current is not necessarily parallel to the heat current:

$$\mathbf{J}_s = \frac{1}{T} \mathbf{J}_q + \mathbf{K} \quad \frac{1}{T} = \frac{\partial s}{\partial u} \quad (4.154)$$

It should be noted that at present very great confusion exists with both the different theories and their nomenclature. There are authors who call only theories characterizable by equation (4.154) “extended irreversible thermodynamics”.

It is noteworthy that the “entropy-less” thermodynamics of Meixner — though it does not interpret explicitly any entropy current — belongs to the second type.

The aspects discussed so far characterize the essential differences between the various types of modern thermodynamic theories; however, it is worthwhile to mention the problem of entropy supply as well.

In several theories it is usual to introduce the concepts of heat and entropy supply. In these theories the internal energy balance has the form

$$\rho \dot{u} + \operatorname{div} \mathbf{J}_q = \sigma_u + r, \quad (4.155)$$

where r is the so-called heat supply, which may be, e.g., the heat taken up by radiation in unit volume and time. By analogy, the entropy balance is also extended:

$$\rho \dot{s} + \operatorname{div} \mathbf{J}_s = \sigma_s + r_s, \quad (4.156)$$

where r_s is e.g. the entropy transfer by radiation. On the basis of the correlation between entropy supply and heat supply, the theories can be classified in three groups:

$$r_s = \frac{1}{T} r, \quad \frac{1}{T} = \frac{\partial s}{\partial u}, \quad (4.157)$$

$$r_s = \frac{1}{T} r, \quad \frac{1}{T} \neq \frac{\partial s}{\partial u}, \quad (4.158)$$

$$r_s = \frac{1}{T} r + k, \quad \frac{1}{T} = \frac{\partial s}{\partial u}, \quad (4.159)$$

respectively, where k is analogous to \mathbf{K} in equation (4.154).

These alternative correlations are analogous to the formulae concerning entropy current. This question will not be discussed in detail, since the introduction or non-introduction of heat and entropy supply is not a fundamental question; in many cases, however, it is very convenient for describing the phenomena, as the heat arriving at a certain point (e.g. radiation) may be included in heat current \mathbf{J}_q .

The acceptance or rejection of Onsager-Casimir reciprocal relations is also a difference of minor importance (part of the experts of rational thermodynamics reject them owing to the lack of an exact phenomenological proof) since their existence is a fact which can be checked experimentally. On the other hand, the history of the theory of liquid crystals demonstrates that the Onsager-Casimir reciprocal relations can be added to a theory later on as Parodi has done with Leslie's theory [131]. The question of linearity vs. non-linearity is mentioned last. This also belongs to the problems of minor importance, since the experts using linear theories are aware that the linear constitutive laws are only approximations; however, in quasi-linear theories using non-constant material coefficients, these approximations are very good, indeed, and with few exceptions satisfy the demand of practical applications. The strictly non-linear theories are also often capable of producing results experimentally provable and practically applicable only up to a linear approximation. They are similarly valid for certain modern theories of mixtures, which consider the simultaneous existence in space and time of superimposed continua. Their classification according to the above aspects is double: other regularities are true for the individual component continua than for their ensemble [4].

**THERMODYNAMICS OF DEFORMATION.
SYSTEMS CLOSE TO EQUILIBRIUM**

Although we have expounded the foundation of thermodynamics using a fairly involved (even though far from general) model of continuous media, we present here the thermodynamics of deformations for less complicated media, as this simplification does not prevent demonstration of the general characteristics of the method. The entropy production expressed in equation (4.42) pertains to anisotropic systems in which heat conduction, conduction of electricity and transport of internal moment of momentum take place, and electric and magnetic polarization phenomena and also deformation occur. Such a general examination of various interactions is rather laborious. Therefore, we are going to study bodies of constant composition in which macroscopic electric and magnetic phenomena are absent and the couple-stress is a zero tensor. In most cases we shall presume isotropic media and assume that they continue being isothermal during motion. We shall return to some of the neglected interactions later on.

5.1. Media in local equilibrium.

First, we shall treat media which during their motion, remain in the state of local equilibrium. According to this condition, specific internal energy u and deformation tensor \mathbf{d} will be sufficient for the complete description of the state of the medium. Specific entropy s and entropy production density σ_s have the forms

$$s = s(u, \mathbf{d}) \tag{5.1}$$

and

$$T\sigma_s = \left[\mathbf{t}^s + \varrho T \mathbf{d} \frac{\partial s}{\partial \mathbf{d}} \right] : \frac{1}{2} \left(\dot{\mathbf{d}} \mathbf{d}^{-1} + \mathbf{d}^{-1} \dot{\mathbf{d}} \right), \tag{5.2}$$

respectively. Equation (5.2) was obtained by reducing equation (4.42). Because of the lack of internal moment of momentum, zero torque and zero couple-stress (the former due to the absence of electromagnetic phenomena; see equation (2.50)), Cauchy's stress tensor becomes symmetric:

$$\mathbf{t} = \mathbf{t}^s$$

(see equation (2.45); superscript s will be neglected for this reason). Generalized fluxes and forces in equation (5.2) are

$$\mathbf{J} = \frac{1}{2} (\dot{\mathbf{d}} \mathbf{d}^{-1} + \mathbf{d}^{-1} \dot{\mathbf{d}}) \quad \text{and} \quad \mathbf{X} = \mathbf{t} + \varrho T \mathbf{d} \frac{\partial s}{\partial \mathbf{d}} \tag{5.3}$$

respectively. Since in our case both the thermodynamic force and the thermodynamic current density are symmetric tensors of second order, we have six independent scalar components for each.

First, we examine the case of equilibrium ensured by the conditions

$$\mathbf{J} = \frac{1}{2}(\mathring{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\mathring{\mathbf{d}}) = 0 \quad \text{and} \quad \mathbf{X} = \mathbf{t} + \varrho T \mathbf{d} \frac{\partial s}{\partial \mathbf{d}} = 0. \quad (5.4)$$

The second of these equations gives us the sense of $\frac{\partial s}{\partial \mathbf{d}}$, namely

$$\frac{\partial s}{\partial \mathbf{d}} = -\frac{1}{\varrho T} \mathbf{d}^{-1} \mathbf{t}. \quad (5.5)$$

This equation, however, holds in equilibrium only. In order to arrive at a graphic description we introduce the notation

$$\mathbf{t}^e = -\varrho T \mathbf{d} \frac{\partial s}{\partial \mathbf{d}} \quad (5.6)$$

and, using it, rewrite equation (5.5) as

$$\mathbf{t}^e = \mathbf{t}. \quad (5.7)$$

Since the entropy depends on the variables u and \mathbf{d} only, the same holds for its derivatives; e.g., for \mathbf{t}^e ,

$$\mathbf{t}^e = \mathbf{t}^e(u, \mathbf{d}). \quad (5.8)$$

Comparing equations (5.7) and (5.8) we see that \mathbf{t}^e is the stress in an equilibrium state characterized by energy u and deformation \mathbf{d} . In the literature it is usually referred to as “equilibrium (or elastic) stress”. For the description of systems outside equilibrium, it is practical to introduce the tensor

$$\mathbf{t}^v = \mathbf{t} - \mathbf{t}^e \quad (5.9)$$

which is called viscous stress. Since in equilibrium

$$\mathbf{t}^v = 0,$$

zero viscous stress can be considered as a condition for equilibrium. Substituting \mathbf{t}^v into equation (5.2), we obtain the entropy production density as

$$\sigma_s = \frac{1}{2T} (\mathbf{d}^{-1} \mathbf{t}^v + \mathbf{t}^v \mathbf{d}^{-1}) : \mathring{\mathbf{d}} = \frac{1}{2T} \mathbf{t}^v : (\mathring{\mathbf{d}} \mathbf{d}^{-1} + \mathbf{d}^{-1} \mathring{\mathbf{d}}) \quad (5.10)$$

and, in the energy picture, the energy dissipation as

$$T \sigma_s = \mathbf{t}^v : \frac{1}{2} (\mathring{\mathbf{d}} \mathbf{d}^{-1} + \mathbf{d}^{-1} \mathring{\mathbf{d}}) = \mathbf{t}^v : (\text{Grad } \mathbf{v})^s. \quad (5.11)$$

In linear theory the components of the viscous stress tensor \mathbf{t}^v are homogeneous linear functions of the components of tensor $(\text{Grad } \mathbf{v} =)^s$, as expressed in isotropic media, by the well-known [61, 70] linear constitutive equations

$$\mathbf{t}^v = \eta[\text{Grad } \mathbf{v} + (\text{Grad } \mathbf{v})^T] + \eta_v \text{div } \mathbf{v} \boldsymbol{\delta} \quad (5.12)$$

where η and η_v are coefficients of shear and volume viscosity, respectively. The relations

$$\eta > 0 \quad 2\eta + 3\eta_v > 0 \quad (5.13)$$

hold, since entropy production is always positive. Owing to isotropy, Onsager's reciprocal relations are trivially satisfied.

Finally, in the case of an isotropic medium in local equilibrium, Cauchy's stress tensor is given by the relation

$$\mathbf{t} = \mathbf{t}^e(u, \mathbf{d}) + \eta[\text{Grad } \mathbf{v} + (\text{Grad } \mathbf{v})^T] + \eta_v \text{div } \mathbf{v} \boldsymbol{\delta} \quad (5.14)$$

where η and η_v may depend on u and \mathbf{d} , in the general case. It is important to mention that inequalities (5.13) must always be satisfied and dependence on u can be reformulated as dependence on the temperature. At first sight, equation (5.14) seems to be unambiguous; however, we must keep in mind that the choice of the reference configuration had not been made so far. The equation describing the behavior of the medium under fixed experimental conditions must be expected to give the same stress independent of the choice of the reference configuration. However, owing to the change of the forms of the functions $\mathbf{t}^e(\mathbf{d})$, $\eta(\mathbf{d})$, and $\eta_v(\mathbf{d})$, the actual form of equation (5.14) will depend on the choice of reference configuration. An unsuitable choice can result in an unreasonably complicated form of equation (5.14).

Concerning the choice of the reference configuration, let us assume that for every medium at least one configuration exists where the stress tensor will become zero if the configuration is maintained for a sufficiently long period. In order to realize the existence of such a state free from stress let us cut out a fairly small portion of the medium and, put it into an environment of the same temperature. It is supposed that this environment is in equilibrium and no forces act upon the sample. Sooner or later, the sample will reach a certain state of equilibrium. Its configurations in this equilibrium state are usually denominated "undeformed configurations". The use of the plural is justified by the fact that there are no preferred directions in the environment; consequently, during rotation, equilibrium is conserved. Properties of the sample of an anisotropic medium, however, are relevantly changed by rotation.

5.1.1. Equilibrium of solids. In media at rest $\mathbf{d} = 0$. If a state free of stress has been chosen for reference configuration, equation (5.14) reduces to

$$\mathbf{t} = \mathbf{t}^e(\mathbf{d}) \quad (5.15)$$

which, due to isotropy of the medium takes the analogous form

$$\mathbf{t}^* = \mathbf{t}^e(\mathbf{d}^*) \quad (5.16)$$

in another reference frame. In equation (5.16),

$$\mathbf{t}^* = \mathbf{Q}\mathbf{t}\mathbf{Q}^T \quad \text{and} \quad \mathbf{d}^* = \mathbf{Q}\mathbf{d}\mathbf{Q}^T \quad (5.17)$$

and \mathbf{Q} is the orthogonal tensor of the change of frame (see chapter 3.4). In other words, function $\mathbf{t}^e(\mathbf{d})$ satisfies the identity

$$\mathbf{Q}\mathbf{t}^e(\mathbf{d})\mathbf{Q}^T = \mathbf{t}^e(\mathbf{Q}\mathbf{d}\mathbf{Q}^T) \quad (5.18)$$

for any orthogonal tensor \mathbf{Q} , i.e., $\mathbf{t}^e(\mathbf{d})$ is a so-called isotropic function that can, in any case, be written as

$$\mathbf{t}^e(\mathbf{d}) = f_1\boldsymbol{\delta} + f_2\mathbf{d} + f_3\mathbf{d}^2 \quad (5.19)$$

where f_1 , f_2 and f_3 are scalar-valued functions dependent on the scalar invariants of tensor \mathbf{d} . The functions f_1 , f_2 and f_3 cannot be arbitrary because, according to equation (5.6), function $\mathbf{t}^e(\mathbf{d})$ is derived from the scalar-valued function $\varrho T s(\mathbf{d})$, and, therefore, the identity

$$-\varrho T \frac{ds(\mathbf{d})}{dt} = (\mathbf{d}^{-1}\mathbf{t}^e) : \dot{\mathbf{d}} = f_1\mathbf{d}^{-1} : \dot{\mathbf{d}} + f_2 \text{tr} \dot{\mathbf{d}} + f_3\mathbf{d} : \dot{\mathbf{d}} \quad (5.20)$$

must be satisfied whatever be the value of $\mathbf{t}^e(\mathbf{d})$. The conditions for this can be obtained by elementary, though laborious, calculations, as follows. Substituting the scalar invariants of tensor \mathbf{d} , i.e.,

$$\begin{aligned} J_1(\mathbf{d}) &= \text{tr} \mathbf{d} = d_1 + d_2 + d_3 \\ J_2(\mathbf{d}) &= \frac{1}{2}(\text{tr} \mathbf{d})^2 - \frac{1}{2}\mathbf{d} : \mathbf{d} = d_1d_2 + d_2d_3 + d_1d_3 \\ J_3(\mathbf{d}) &= \det \mathbf{d} = d_1d_2d_3 \end{aligned} \quad (5.21)$$

we can rewrite equation (5.20) as

$$\begin{aligned} -\varrho T \left[\frac{\partial s}{\partial J_1} \text{tr} \dot{\mathbf{d}} + \frac{\partial s}{\partial J_2} \text{tr} \mathbf{d} \text{tr} \dot{\mathbf{d}} - \mathbf{d} : \dot{\mathbf{d}} \right] + \frac{\partial s}{\partial J_3} J_3\mathbf{d}^{-1} : \dot{\mathbf{d}} &= \\ = f_1\mathbf{d}^{-1} : \dot{\mathbf{d}} + f_2 \text{tr} \dot{\mathbf{d}} + f_3\mathbf{d} : \dot{\mathbf{d}} & \end{aligned}$$

and since \mathbf{d} and $\dot{\mathbf{d}}$ can be chosen arbitrarily, we obtain the equations

$$\begin{aligned} f_1 &= -\varrho T J_3 \frac{\partial s}{\partial J_3} \\ f_2 &= -\varrho T \left(\frac{\partial s}{\partial J_1} + J_1 \frac{\partial s}{\partial J_2} \right) \\ f_3 &= \varrho T \frac{\partial s}{\partial J_2}. \end{aligned} \quad (5.22)$$

Using the equality of the mixed second partial derivatives, we finally obtain interrelations between f_1 , f_2 and f_3 . It must be remembered that ϱ and T change in

the course of deformation. Derivation of the relations can be made easier by introducing the free energy in the case of isothermal systems. Media for which equation (5.19) — non-linear in \mathbf{d} — holds are termed hyperelastic materials. A well-known example is the rubber elasticity where equation (5.19) takes the form

$$\mathbf{t}^e = f_1 \boldsymbol{\delta} + \mu \mathbf{d}^2 \quad (5.23)$$

In the case of such a model rubber $f_2 = 0$ and $f_3 = \mu = \text{constant}$. (Further details of hyperelasticity will not be treated here.)

According to the chosen stress-free reference state, function (5.19) is zero if $\mathbf{d} = \boldsymbol{\delta}$, i.e. in the absence of deformation. In the case of small deformations, function (5.19) is well approximated by a function linear in the components of \mathbf{d} :

$$\mathbf{t}^e = \lambda \text{tr}(\mathbf{d} - \boldsymbol{\delta}) \boldsymbol{\delta} + 2\mu(\mathbf{d} - \boldsymbol{\delta}) \quad (5.24)$$

and in equation (5.24) we have Hooke's law of elasticity. Its familiar form

$$\mathbf{t}^e = 2\mu \boldsymbol{\varepsilon} + \lambda \Theta \boldsymbol{\delta} \quad (5.25)$$

is obtained by the substitutions

$$\mathbf{d} - \boldsymbol{\delta} = \boldsymbol{\varepsilon} \quad \text{and} \quad \text{tr} \boldsymbol{\varepsilon} = \Theta.$$

5.1.2. Motion of solids. If the solid moves, a stress proportional to the rate of deformation will be added to the equilibrium stress \mathbf{t}^e as it is seen from equation (5.14). Restricting the treatment to small deformations, we certainly may neglect the dependence of η and η_v on deformation. Therefore, according to equation (5.24), equation (5.14) becomes

$$\mathbf{t} = 2\mu(\mathbf{d} - \boldsymbol{\delta}) + \lambda \text{tr}(\mathbf{d} - \boldsymbol{\delta}) \boldsymbol{\delta} + 2\eta(\text{Grad } \mathbf{v})^s + \eta_v \text{div } \mathbf{v} \boldsymbol{\delta} \quad (5.26)$$

For this reason, the stress can be split into two parts. One is linear in $\mathbf{d} - \boldsymbol{\delta}$ describing deformation, the other one is homogeneous linear function of deformation rate $(\text{Grad } \mathbf{v})^s = \dot{\mathbf{d}}$. We have here a full analogy to equation (3.20). Therefore, identity of a solid in local equilibrium with Kelvin body is affirmed.

5.1.3. Motion of fluids. Reference configurations free of stress will be used in the treatment of motion of liquids and gaseous media, too. Relations for fluids can be obtained by adaptation of those valid for solids taking Pascal's law into account, i.e., the isotropic nature of the equilibrium stress tensor:

$$\mathbf{t}^e = -p \boldsymbol{\delta} \quad (5.27)$$

This is equivalent to $f_2 = f_3 = 0$ in the general formula (5.19). Thus, according to equation (5.22), the entropy merely depends on $J_3(\mathbf{d})$ (but not on the two other invariants). In other words, the entropy is a function of volume change only (and, of course, of the internal energy) as seen from equation (1.37). Consequently, in the case of fluids instead of equation (5.1) we have the simpler equation

$$s = s(u, v) \quad (5.28)$$

where v denotes specific volume that is related to tensor \mathbf{d} by

$$v = v_0 \det \mathbf{d}, \quad (5.29)$$

(see equation (1.37)). Thus, from (5.28) we obtain

$$\frac{\partial s}{\partial \mathbf{d}} = v \frac{\partial s}{\partial v} \mathbf{d}^{-1} \quad (5.30)$$

and, using (5.6)

$$\mathbf{t}^e = -\varrho T \mathbf{d} v \frac{\partial s}{\partial v} \mathbf{d}^{-1} = -T \frac{\partial s}{\partial v} \boldsymbol{\delta}. \quad (5.31)$$

Comparing equations (5.27) and (5.31) we arrive at the well-known relation

$$p = T \left(\frac{\partial s}{\partial v} \right)_u. \quad (5.32)$$

For moving isotropic fluids in local equilibrium, Cauchy's stress tensor takes the form

$$\mathbf{t} = -p^e(u, v) \boldsymbol{\delta} + \eta [\text{Grad } \mathbf{v} + (\text{Grad } \mathbf{v})^T] + \eta_v \text{div } \mathbf{v} \boldsymbol{\delta} \quad (5.33)$$

that is the material equation for a Navier-Stokes fluid. Substituting equation (5.33) into Cauchy's equation of motion (2.15), we obtain the fundamental equation of the hydrodynamic theory of viscous fluids, i.e., Navier-Stokes' equation. Together with the equation of conservation of mass, this is a complete set of differential equations:

$$\begin{aligned} \varrho \frac{d\mathbf{v}}{dt} &= -\text{grad } p^e(u, v) + \eta \Delta \mathbf{v} + (\eta + \eta_v) \text{grad } \text{div } \mathbf{v} + \varrho \mathbf{f} \\ \frac{d\varrho}{dt} + \varrho \text{div } \mathbf{v} &= 0. \end{aligned} \quad (5.34)$$

Out of fluid motions those without volume change are of distinguished importance. For such cases the term "incompressible fluids" is used. The point of the matter is that very small change in the specific volume (or density) involves significant change of equilibrium stress or, conversely, stresses occurring during motion generate negligible changes in density. That is the reason for the use of the term "incompressible". In the case of motion without volume change, the Navier-Stokes equations take the simple form

$$\begin{aligned} \varrho \frac{d\mathbf{v}}{dt} &= -\text{grad } p + \eta \Delta \mathbf{v} + \varrho \mathbf{f} \\ \text{div } \mathbf{v} &= 0. \end{aligned} \quad (5.35)$$

The fact that the pressure p in equation (5.35) is not identical to the equilibrium pressure function $p^e(u, v)$ does not involve any problem; together with the solution of equations (5.35), the value of p is also obtained as a function of position and time.

Due to the structure of equations describing motion of incompressible fluids and also due to the properties of isotropic functions, it is reasonable to express Cauchy's stress as the sum of two tensors:

$$\begin{aligned}\mathbf{t} &= -p\boldsymbol{\delta} + \mathbf{t}_D \\ \text{tr } \mathbf{t}_D &= 0.\end{aligned}\tag{5.36}$$

Equations (5.36) imply the relation

$$p = -\frac{1}{3} \text{tr } \mathbf{t}\tag{5.37}$$

where p is the scalar pressure and \mathbf{t}_D the deviatoric stress. Using these, we may rewrite equation (5.14) as

$$\begin{aligned}-p &= -p^e(u, \mathbf{d}) + \left(\frac{2}{3}\eta + \eta_v\right) \text{div } \mathbf{v} \\ \mathbf{t}_D &= \mathbf{t}_D^e(u, \mathbf{d}) + 2\eta(\text{Grad } \mathbf{v})^{s0}\end{aligned}\tag{5.38}$$

where

$$(\text{Grad } \mathbf{v})^{s0} = \frac{1}{2} \text{Grad } \mathbf{v} + \frac{1}{2} (\text{Grad } \mathbf{v})^T - \frac{1}{3} (\text{div } \mathbf{v}) \boldsymbol{\delta}\tag{5.39}$$

denotes the symmetric and trace free part of the velocity-gradient which is related to tensor \mathbf{d}_0 introduced towards the end of section 1.2. Combination of equations (1.46), (1.47) and (1.48) leads to

$$\text{Grad } \mathbf{v} = \dot{\mathbf{d}}\mathbf{d}^{-1} + \boldsymbol{\omega}\tag{5.40}$$

and hence

$$\text{Grad } \mathbf{v} + (\text{Grad } \mathbf{v})^T = \dot{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\dot{\mathbf{d}}.\tag{5.41}$$

Further, by the use of equation (1.51) and of λ_v and \mathbf{d}_0 as introduced in equation (1.38)

$$\text{Grad } \mathbf{v} + (\text{Grad } \mathbf{v})^T = 2\dot{\lambda}_v\lambda_v^{-1} + \dot{\mathbf{d}}_0\mathbf{d}_0^{-1} + \mathbf{d}_0^{-1}\dot{\mathbf{d}}_0\tag{5.42}$$

is obtained, which combined with equation (1.52) leads to

$$\begin{aligned}\text{div } \mathbf{v} = \text{tr}(\text{Grad } \mathbf{v}) &= 3\dot{\lambda}_v\lambda_v^{-1} = \frac{1}{v} \frac{dv}{dt} \\ (\text{Grad } \mathbf{v})^{s0} &= \frac{1}{2}(\dot{\mathbf{d}}_0\mathbf{d}_0^{-1} + \mathbf{d}_0^{-1}\dot{\mathbf{d}}_0).\end{aligned}\tag{5.43}$$

The second of equations (5.43) becomes very simple if the present configuration is selected as reference configuration, for then we have $\mathbf{d}_0 = \boldsymbol{\delta}$ and hence $(\text{Grad } \mathbf{v})^{s0} = \dot{\mathbf{d}}_0$. The last equation is an approximation in the case of small deformations while, however, high degrees of volume change and rotation are allowed. In these cases the second of equations (5.38) is rewritten and, for the stress deviator,

$$\mathbf{t}_D = \mathbf{t}_D^e + \eta(\dot{\mathbf{d}}_0\mathbf{d}_0^{-1} + \mathbf{d}_0^{-1}\dot{\mathbf{d}}_0)\tag{5.44}$$

is obtained and, for the special case of fluids,

$$\mathbf{t}_D = 2\eta\dot{\mathbf{d}}_0.\tag{5.45}$$

Equation (5.45) can very advantageously be used in the study of incompressible liquids where the equation pertaining to the scalar pressure is of no use.

As it appears from equation (5.45), the deviatoric part of stress for a fluid in local equilibrium is proportional to the rate of deformation. In other words, a fluid in local equilibrium is identical to the rheological Newton body.

5.2. Material symmetry.

Let us now turn to some details and questions pertaining to equivalent reference configurations. In the case of most media for any reference configuration, we may find another one that is equivalent to the first. In other words, properties of and processes in the medium will be unchanged if the motion is preceded by another one leading to a configuration equivalent to the original. In order to present a more exact formulation, we shall consider two equivalent reference configurations whose position vectors should be denoted by \mathbf{X} and \mathbf{X}^* . The corresponding two deformation-gradient tensors will be represented by \mathbf{x} and \mathbf{x}^* . Equivalence of the two reference configurations means that the quantities characterizing the medium are not affected by the exchange of \mathbf{x} and \mathbf{x}^* . The motion connecting the two reference configurations is described by the tensors $\mathbf{x}^{-1}\mathbf{x}^*$ and $\mathbf{x}^*\mathbf{x}^{-1}$, respectively. We call these tensors symmetry operations of the medium pertaining to its given configuration.

Let us now study some properties of symmetry operations.

Theorem 1: Symmetry operations belonging to a given configuration constitute a group.

For the proof of this, it is enough to show that (a) the inverse of any symmetry operation is a symmetry operation, too, and (b) the product of any two symmetry operations is also a symmetry operation. The associative law is guaranteed by the fact that symmetry operations are non-degenerate tensors of order two and the unit element is a symmetry operation which can be associated with any configuration ($\mathbf{x}^* = \mathbf{x}$).

Interchanging configuration \mathbf{x} with an equivalent one, say \mathbf{x}^* , we can see that the inverse of the symmetry operation exists, for

$$\mathbf{s} = \mathbf{x}^{-1}\mathbf{x}^*, \quad \mathbf{x}^{*-1}\mathbf{x} = (\mathbf{x}^{-1}\mathbf{x}^*)^{-1} = \mathbf{s}^{-1}. \quad (5.46)$$

We show now that symmetry operations belonging to equivalent configurations are identical. Equations

$$\mathbf{x}^* = \mathbf{x}\mathbf{s}_1 \quad \text{and} \quad \mathbf{x}^{**} = \mathbf{x}\mathbf{s}_2 \quad (5.47)$$

can be given as forms of the deformation gradients belonging to any actual configuration. In equations (5.47) \mathbf{s}_1 and \mathbf{s}_2 are two given symmetry operations; \mathbf{x} is the deformation gradient pertaining to the chosen reference configuration while \mathbf{x}^* and \mathbf{x}^{**} pertain to the configurations resulting from the chosen one by the use of \mathbf{s}_1 and \mathbf{s}_2 , respectively. Since \mathbf{s}_1^{-1} is a symmetry operation as well, a configuration equivalent to the chosen one exists, and the deformation gradient belonging to this equivalent configuration is

$$\mathbf{x}' = \mathbf{x}\mathbf{s}_1^{-1} \quad (5.48)$$

Therefore, we have

$$\mathbf{s}_1\mathbf{s}_2 = (\mathbf{x}'^{-1}\mathbf{x})(\mathbf{x}^{-1}\mathbf{x}^{**}) = \mathbf{x}'^{-1}\mathbf{x}^{**} = \mathbf{s}, \quad (5.49)$$

i.e., the relation we wanted to prove.

Theorem 2: Symmetry operations are unimodular tensors.

Using the rules for the multiplication of determinants and considering equation (1.36), we have

$$\det \mathbf{s} = \frac{\det \mathbf{x}^*}{\det \mathbf{x}} = \frac{v_0^*}{v_0} \quad (5.50)$$

where v_0 and v_0^* are the volumes belonging to the respective configurations paired by \mathbf{s} . The absolute values of v_0 and v_0^* must be equal; otherwise, the volume of the body could be unlimitedly reduced by repeated application of \mathbf{s} or \mathbf{s}^{-1} , without any change of the properties of the medium. This, however, contradicts the law of conservation of matter.

Replying upon the theorems just proved, we may declare that the symmetry group pertaining to any configuration is a subgroup of the unimodular group. Symmetry groups belonging to two different non-equivalent configurations, though different, are, of course, similar. Let the motion coupling the two different configurations K and K' be \mathbf{A} and the symmetry operation belonging to configuration K be \mathbf{s} . Configuration K will be transformed into K' by \mathbf{A} and into K_1 by \mathbf{s} . However, K_1 is equivalent to K ; thus \mathbf{A} will transform configuration K_1 into K'_1 equivalent to K' . Therefore, $\mathbf{A}\mathbf{s}\mathbf{A}^{-1}$ is a symmetry operation belonging to configuration K' , for it transforms K' into K and the latter into K_1 and finally into K'_1 which is equivalent to K' .

Media can be classified according to the properties of their symmetry groups.

If the symmetry group of the medium is similar to some subgroup of the orthogonal group we will call the medium a solid. If the symmetry group includes the orthogonal group, the medium will be called isotropic. If the symmetry group of the medium and the complete unimodular group coincide, the medium will be named isotropic liquid. It should be mentioned that the unimodular group includes proper subgroups not similar to any part of the orthogonal group. Such symmetry groups characterize liquid crystals. A detailed descriptive account of the possible symmetry groups is a rather difficult task and, in spite of important results (Wang [162]), unsolved so far.

5.3. Anisotropy by deformation.

In solids, deformation may lead to anisotropy even if the reference configuration is isotropic. Deformation anisotropy occurs in viscous phenomena, too. Then, viscous stress must be expressed by homogeneous linear relations more intricate than equation (5.12). Their general form is rather complicated and follows the symmetry of tensor \mathbf{d} . If the deformation is small enough, the linear terms of the power series of the coefficients with respect to the components of \mathbf{d} will be sufficient. The form of the linear relations expressing the viscous stress can easily be derived from Gyarmati's principle by the use of the dissipation potential $\Phi(\mathbf{J})$ defined by equation (4.61). The reader is reminded here that thermodynamic current is equal to the symmetric part of the velocity gradient, while the thermodynamic force is identical to the viscous stress as defined by the second of equations (5.3). Dissipation potential $\Phi(\mathbf{J})$ is a homogeneous quadratic function of the components of tensor \mathbf{J} and, by means of coefficients R_{ik} in equation (4.61), depends also on \mathbf{d} . Owing to isotropy of the chosen reference configuration, Φ is an isotropic function

of its variables. If we think that an expression linear in \mathbf{d} is satisfactory, we shall write

$$\Phi(\mathbf{J}, \mathbf{d}) = \Phi_0(\mathbf{J}) + \Phi_1(\mathbf{J}) : \mathbf{d}. \quad (5.51)$$

Since both the scalar-valued function Φ and the symmetric tensor-valued function Φ_1 are homogeneous, quadratic and isotropic functions of the tensor \mathbf{J} , the following forms can be given for Φ_0 and Φ_1

$$\begin{aligned} \Phi_0 &= \frac{1}{2}c_1(\text{tr } \mathbf{J})^2 + \frac{1}{2}c_2\mathbf{J} : \mathbf{J} \\ \Phi_1 &= \left[\frac{1}{2}c_3(\text{tr } \mathbf{J})^2 + \frac{1}{2}c_4\mathbf{J} : \mathbf{J} \right] \delta + c_5(\text{tr } \mathbf{J})\mathbf{J} + c_6\mathbf{J}^2 \end{aligned} \quad (5.52)$$

where $c_1, c_2, c_3, c_4, c_5,$ and c_6 are material constants depending exclusively on temperature. Combining equations (5.51) and (5.52), we obtain

$$\Phi = \frac{1}{2}c_1(\text{tr } \mathbf{J})^2 + \frac{1}{2}c_2\mathbf{J} : \mathbf{J} + \frac{1}{2} [c_3(\text{tr } \mathbf{J})^2 + c_4\mathbf{J} : \mathbf{J}] \text{tr } \mathbf{d} + c_5(\text{tr } \mathbf{J})\mathbf{J} : \mathbf{d} + c_6\mathbf{J}^2 : \mathbf{d} \quad (5.53)$$

Hence, owing to the general relation (4.64) for the viscous stress as thermodynamic force, we arrive at

$$\mathbf{t}^v = (c_1 \text{tr } \mathbf{J} + c_3 \text{tr } \mathbf{d} \text{tr } \mathbf{J} + c_5 \mathbf{d} : \mathbf{J})\delta + c_5 \mathbf{J} \mathbf{d} + (c_2 + c_4 \text{tr } \mathbf{d})\mathbf{J} + c_6(\mathbf{d}\mathbf{J} + \mathbf{J}\mathbf{d}). \quad (5.54)$$

In an undeformed state ($\mathbf{d} = \delta$), this expression must reduce to equation (5.14). Thus we have the relations

$$\begin{aligned} c_1 + 3c_3 + 2c_5 &= \eta_v \\ c_2 + 3c_4 + 2c_6 &= 2\eta. \end{aligned} \quad (5.55)$$

Concerning equation (5.54), we have to remember that it is not more than the sum of the first terms in a power series. Therefore, it will be reliable only if tensor \mathbf{d} does not differ much from the unit tensor. It must also be taken into account that relations approximated by power series, like equation (5.54), may have different physical senses depending on the choice of currents and forces, since this choice, as the choice of any quantity to the description of material processes, is more or less arbitrary. Entropy production, for example, is always a product of current and force. However, concerning the process of deformation for the resolution of entropy production into currents and forces, equation (5.2) is not the only possibility. Since $\mathring{\mathbf{d}}$ also can be taken as the rate of the material process and,

$$T\sigma_s = \mathbf{t}^v : \frac{1}{2}(\mathring{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\mathring{\mathbf{d}}) = \frac{1}{2}(\mathbf{t}^v \mathbf{d}^{-1} + \mathbf{d}^{-1}\mathbf{t}^v) : \mathring{\mathbf{d}} \quad (5.56)$$

the choice

$$\mathbf{X}^* = \frac{1}{2}(\mathbf{t}^v \mathbf{d}^{-1} + \mathbf{d}^{-1}\mathbf{t}^v); \quad \mathbf{J}^* = \mathring{\mathbf{d}} \quad (5.57)$$

is as permitted as (5.3). The two choices are related by the equations

$$\begin{aligned} \mathbf{X}^* &= \frac{1}{2}(\mathbf{X}\mathbf{d}^{-1} + \mathbf{d}^{-1}\mathbf{X}) \\ \mathbf{J} &= \frac{1}{2}(\mathbf{J}^*\mathbf{d}^{-1} + \mathbf{d}^{-1}\mathbf{J}^*), \end{aligned} \quad (5.58)$$

i.e., by a linear transformation whose coefficients depend merely on the local state variables, namely, on the components of \mathbf{d} . According to Onsager's theory there is a homogeneous linear interdependence between currents and forces, specialized by reciprocal relations. However, nothing is said in this theory as to how the coefficients depend on the local state variables. Therefore, in the forms of the linear laws belonging to different representations, the dependence of the coefficients on the local state variables is different. Thus, we are advised by these circumstances to be very careful while comparing power series approximations belonging to different representations.

5.4. Heat conduction and deformation.

5.4.1. Thermoelasticity. We proceed now to the study of deformation in the simultaneous processes of mechanical motion and heat conduction. While for the specific entropy, we have equation (5.1) as before, equation (5.2) of the entropy production must be extended according to non-zero temperature gradient. Specialization of the general equation (4.42) leads to

$$T\sigma_s = -\mathbf{J}_q \frac{1}{T} \text{grad } T + (\mathbf{t} - \mathbf{t}^e) : \frac{1}{2}(\dot{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\dot{\mathbf{d}}) \quad (5.59)$$

where for small deformations we take

$$\frac{1}{2}(\dot{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\dot{\mathbf{d}}) \approx \dot{\mathbf{d}}. \quad (5.60)$$

By the choice

$$\begin{aligned} \mathbf{X}_q &= -\frac{1}{T} \text{grad } T; & \mathbf{J}_q; \\ \mathbf{X}_d &= \mathbf{t} - \mathbf{t}^e = \mathbf{t}^v; & \mathbf{J}_d = \dot{\mathbf{d}} \end{aligned} \quad (5.61)$$

for thermodynamic forces and currents, we have the linear "laws" as

$$\mathbf{J}_q = -\frac{1}{T} L_{qq} \text{grad } T = -\lambda_q \text{grad } T \quad (5.62)$$

and

$$\mathbf{X}_d = \mathbf{t}^v = 2\eta \mathbf{J}_d + \eta_v (\text{tr } \mathbf{J}_d) \boldsymbol{\delta} = 2\eta \dot{\mathbf{d}} + \eta_v \text{div } \mathbf{v} \boldsymbol{\delta}, \quad (5.63)$$

since in an isotropic body the third order tensors of the material coefficients relating vectorial currents to second-order tensorial forces vanish for symmetry reasons. As equation (5.63) shows, the temperature does not occur explicitly in the expression of viscous stress. Heat conduction influences viscous phenomena to the extent that the material constants η and η_v in equation (5.63) depend on temperature and, accordingly, on position and time. An impact of viscous motion on heat conduction exists as well, since the dissipation of power occurs as a source term in the balance equation of internal energy.

The case will be of practical importance if the deformation is so slow that viscous stress can be neglected. Then, deformation may be considered as exclusively owing

to temperature change. And for the stress, we have (in terms of temperature instead of internal energy)

$$\mathbf{t} = \mathbf{t}^e(T, \mathbf{d}). \quad (5.64)$$

A stressless reference configuration corresponding to uniform temperature independent of position is a suitable choice. For small deformations, equation (5.64) can be well approximated by the linear relation

$$\mathbf{t}^e = 2\mu(\mathbf{d} - \boldsymbol{\delta}) + \lambda \operatorname{tr}(\mathbf{d} - \boldsymbol{\delta})\boldsymbol{\delta} - (2\mu + 3\lambda)\alpha_T(T - T_0)\boldsymbol{\delta} \quad (5.65)$$

where T_0 is the reference temperature and α_T the linear dilatation coefficient of the medium. Equation (5.65) is the fundamental equation of thermoelasticity and the immediate generalization of Hooke's law (see equation (5.24)). In some cases also viscous stress must be taken into account and heat conduction as well. As an example, calculation of the attenuation of acoustic waves should be mentioned.

5.4.2. Propagation of sound waves in media in local equilibrium. In order to simplify calculations pertaining to sound waves, we assume small deviations of the particles from their equilibrium position. The state of the medium in the absence of propagating acoustic waves will be chosen as reference configuration. This state will be assumed isothermal and stresses leading to anisotropy excluded. Owing to small motions with respect to the reference configuration, the motion function (1.4) can be rewritten in the form

$$\mathbf{x} = \mathbf{X} + \vec{\xi}(\mathbf{X}, t) \quad (5.66)$$

where $\vec{\xi}(\mathbf{X}, t)$ is the displacement. The deformation gradient is approximated, in this case, as

$$\mathbf{x} = \boldsymbol{\delta} + \frac{\partial \vec{\xi}}{\partial \mathbf{X}} \approx \boldsymbol{\delta} + \operatorname{Grad} \vec{\xi}. \quad (5.67)$$

Hence, using the relations

$$[\boldsymbol{\delta} + (\operatorname{Grad} \vec{\xi})^s][\boldsymbol{\delta} + (\operatorname{Grad} \vec{\xi})^a] \approx \boldsymbol{\delta} + \operatorname{Grad} \vec{\xi} \quad (5.68)$$

and

$$[\boldsymbol{\delta} + (\operatorname{Grad} \vec{\xi})^a][\boldsymbol{\delta} - (\operatorname{Grad} \vec{\xi})^a] \approx \boldsymbol{\delta}$$

we arrive at

$$\mathbf{d} = \boldsymbol{\delta} + (\operatorname{Grad} \vec{\xi})^s; \quad \mathbf{R} = \boldsymbol{\delta} + (\operatorname{Grad} \vec{\xi})^a. \quad (5.69)$$

The last three relations hold in linear order. $(\operatorname{Grad} \vec{\xi})^s$ is the symmetric; $(\operatorname{Grad} \vec{\xi})^a$ the antisymmetric part of the displacement gradient. The system of equations describing wave propagation is derived from: the internal energy balance equation (4.26), the Fourier law of heat conduction (5.62), the equation of viscous stress (5.63), Cauchy's equation of motion (2.15), the actual expression for equilibrium stress by neglect of some terms and linearization with respect to the components of $\vec{\xi}$. Since we need not distinguish the time derivatives of different kinds, they will be denoted by a point. For simplification we shall use the notations

$$\mathbf{d} - \boldsymbol{\delta} = \boldsymbol{\varepsilon}, \quad T - T_0 = \Theta \quad (5.70)$$

where T_0 is the temperature in the reference state.

Comparing the balance equation of internal energy with Fourier's law, we obtain the equations describing acoustic phenomena in the form

$$\varrho \dot{u} = \lambda_q \Delta T + \mathbf{t}^e : \dot{\boldsymbol{\varepsilon}} \quad (5.71)$$

where the term $\mathbf{t}^v : \dot{\mathbf{d}}$, since it is quadratic, was omitted. Expressing the time derivative of internal energy by the time derivatives of temperature and of deformation tensor $\boldsymbol{\varepsilon}$, i.e.,

$$\dot{u} = c_v \dot{T} + \left(\frac{\partial u}{\partial \boldsymbol{\varepsilon}} \right)_T : \dot{\boldsymbol{\varepsilon}} \quad (5.72)$$

and for $\frac{\partial u}{\partial \boldsymbol{\varepsilon}}$ substituting the well-known thermostatic relation

$$\left(\frac{\partial u}{\partial \boldsymbol{\varepsilon}} \right)_T = v \left(\mathbf{t}^e - T \frac{\partial \mathbf{t}^e}{\partial T} \right) \quad (5.73)$$

and substituting equation (5.72) into (5.71) we arrive at

$$\varrho c_v \dot{\Theta} - T_0 \frac{\partial \mathbf{t}^e}{\partial T} : \dot{\boldsymbol{\varepsilon}} = \lambda_0 \Delta \Theta \quad (5.74)$$

which is at least partly an equation of transport character. In order to obtain the complete form of the transport equation, we have to find the explicit form of the second term on the left hand side, using an explicit expression for \mathbf{t}^e . To this end, we use an analogous method as in the case of equation (5.65), considering, however, that our reference state is not free of stress. Thus, we may write

$$\mathbf{t}^e = \mathbf{t}^0 + 2\mu \boldsymbol{\varepsilon} + \lambda (\operatorname{div} \vec{\xi}) \boldsymbol{\delta} - (2\mu + 3\lambda) \alpha_T \Theta \boldsymbol{\delta} \quad (5.75)$$

where \mathbf{t}^0 is the stress in the reference state. Partially differentiating with respect to T ($\boldsymbol{\varepsilon} = \text{constant}$) and introducing the result into equation (5.74) we have

$$\varrho c_v \dot{\Theta} + (2\mu + 3\lambda) \alpha_T T_0 \operatorname{div} \vec{\xi} = \lambda_q \Delta T. \quad (5.76)$$

Cauchy's stress is obtained by the addition of equations (5.75) and (5.12):

$$\mathbf{t} = \mathbf{t}^0 + 2\mu \boldsymbol{\varepsilon} + \lambda \operatorname{div} \vec{\xi} \boldsymbol{\delta} - (2\mu + 3\lambda) \alpha_T \Theta \boldsymbol{\delta} + 2\eta \dot{\boldsymbol{\varepsilon}} + \eta_v \operatorname{div} \dot{\vec{\xi}} \boldsymbol{\delta} \quad (5.77)$$

Substituting this into equation (2.15) we arrive at the differential equation describing the propagation of sound waves in non-isothermal systems

$$\varrho \ddot{\vec{\xi}} = \mu \Delta \vec{\xi} + (\mu + \lambda) \operatorname{grad} \operatorname{div} \vec{\xi} - (2\mu + 3\lambda) \alpha_T \operatorname{grad} \Theta + \eta \Delta \dot{\vec{\xi}} + (\eta + \eta_v) \operatorname{grad} \operatorname{div} \dot{\vec{\xi}}. \quad (5.78)$$

It is important to remark that the body is at rest in the reference state and, consequently,

$$0 = \operatorname{Div} \mathbf{t}^0 + \varrho \mathbf{f}. \quad (5.79)$$

Equation (5.79) was used in the derivation of equation (5.78). Equations (5.76) and (5.78) form a system of differential equations for acoustic phenomena in non-isothermal systems.

The dispersion relations can be obtained from these equations by the use of plane-wave solutions. Substituting the “ansatz”

$$\begin{aligned}\Theta &= \Theta_0 e^{i(\mathbf{k}\mathbf{r}-\omega t)} \\ \vec{\xi} &= \vec{\xi}_0 e^{i(\mathbf{k}\mathbf{r}-\omega t)}\end{aligned}\quad (5.80)$$

into equations (5.76) and (5.78), we obtain

$$\begin{aligned}-i\omega\rho c_v\Theta + (2\mu + 3\lambda)\alpha_T T_0\omega\mathbf{k}\vec{\xi} &= -\lambda_q k^2\Theta - \rho\omega^2\vec{\xi} = \\ &= -(\mu - i\omega\eta)k^2\vec{\xi} - [(\lambda + \mu) - i\omega(\eta + \eta_v)]\mathbf{k}(\mathbf{k}\vec{\xi}) - (2\mu + 3\lambda)\alpha_T i\mathbf{k}\Theta.\end{aligned}\quad (5.81)$$

From these equations we have

$$\omega^2 = \frac{\mu - i\omega\eta}{\rho} k_{\perp}^2 \quad (5.82)$$

for the transversal wave ($\mathbf{k}\vec{\xi} = 0$) and

$$\rho\omega^2 = k_{\parallel}^2 \left[(2\mu + \lambda) - i\omega(2\eta + \eta_v) + \frac{(2\mu + 3\lambda)^2\alpha_T^2 T_0\omega}{\rho c_v\omega + i\lambda_q k_{\parallel}^2} \right] \quad (5.83)$$

for the longitudinal wave, the latter one being rather involved. We see that the propagation velocity of the transversal waves is not affected by heat conduction whose influence, however, upon the propagation velocity of longitudinal waves can be very relevant, particularly in the range of high frequencies.

**THERMODYNAMICS OF DEFORMATION.
SYSTEMS FAR FROM EQUILIBRIUM**

In the preceding chapter the motion of media in local equilibrium was studied. The possible form of the stress tensor derived from the linear theory of non-equilibrium thermodynamics shows that media in local equilibrium always behave as a Kelvin body or, in the case of fluids, as a newtonian fluid. The constitutive equation (5.14) will describe the behavior of a rheological Kelvin body in principle, if the stiffness of the spring and the viscosity of the dashpot in the mechanical model depends on deformation (see Figure 6.1).

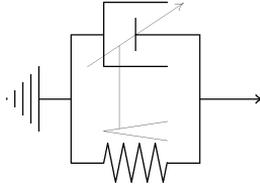


Figure 6.1
Non-linear Kelvin body

The derived equations, however, do not reflect the multifariousness of the actual behavior of media occurring in practice. To cite an instance, in the case of media containing macromolecules, equation (5.14) does not explain the decrease of viscosity with the increasing deformation rate or, similarly, it does not account for thixotropy and plastic behavior. Such phenomena indicate that during their motion certain media often cease to remain in the state of local equilibrium and microscopic (dissipative) structures develop in them which extend their influence to the macroscopic behavior of the medium. Clearly, determining the developing stress we have to take into account the presence of dissipative structures. This prerequisite condition is met by formal introduction of dynamic variables even if deeper knowledge on the physical nature of the non-equilibrium structure of the medium is lacking. However, we do not drop forever the endeavor to understand the physical meaning of the dynamic variables introduced and we do not consider them as “hidden variables”, hidden for ever. Soon, we shall be able to draw conclusions concerning macroscopic manifestations of the dynamic variables if some of their main mathematical properties are known. We do not abandon this advantage in spite of the fact that the physical nature of the applied dynamic variables is temporarily unidentified.

In order to simplify the calculations we restrict the treatment to isotropic and isothermal media without diffusion, chemical reactions, transport of moment of momentum, macroscopic electric and magnetic phenomena. Dynamic variables, however, are indispensable for the description of non-equilibrium states. The dynamic variables will be assumed not to have transport and to be symmetric second order tensors. The latter assumption corresponds to the fact that, owing to isotropy, other tensorial quantities have no impact on the relation between stress and deformation, at least not in linear order.

6.1. Bodies with a single dynamic variable.

A medium should be considered whose equilibrium states are determined by internal energy u and deformation tensor \mathbf{d} . To the characterization of the non-equilibrium states, a symmetric zero trace second order tensor — as dynamic variable — is required as well.

In light of section 4.3., by suitable choice of the dynamic variable, we can always arrive at the form

$$s = s_0(u, \mathbf{d}) - \frac{1}{2} \boldsymbol{\xi} : \boldsymbol{\xi} \quad (6.1)$$

for the specific entropy as function of the independent variables. In equation (6.1) $s_0(u, \mathbf{d})$ is the equilibrium specific entropy and $\boldsymbol{\xi}$ the dynamic variable. The entropy production can be obtained as a particular form of equation (4.36), i.e.

$$T\sigma_s = \left(\mathbf{t} + \varrho T \mathbf{d} \frac{\partial s}{\partial \mathbf{d}} \right) : \frac{1}{2} \left(\dot{\mathbf{d}} \mathbf{d}^{-1} + \mathbf{d}^{-1} \dot{\mathbf{d}} \right) - \varrho T \boldsymbol{\xi} : \dot{\boldsymbol{\xi}}. \quad (6.2)$$

The choice

$$\mathbf{J}_1 = \frac{1}{2} \left(\dot{\mathbf{d}} \mathbf{d}^{-1} + \mathbf{d}^{-1} \dot{\mathbf{d}} \right), \quad \mathbf{J}_2 = \sqrt{\varrho T} \dot{\boldsymbol{\xi}} \quad (6.3)$$

for the thermodynamic fluxes will turn out to be very useful. The conjugate thermodynamic forces are read off from equation (6.2) as

$$\mathbf{X}_1 = \mathbf{t} + \varrho T \mathbf{d} \frac{\partial s_0}{\partial \mathbf{d}}; \quad \mathbf{X}_2 = -\sqrt{\varrho T} \boldsymbol{\xi} \quad (6.4)$$

The odd choice of current \mathbf{J}_2 is explained by the relation

$$\mathbf{J}_2 = -\dot{\mathbf{X}}_2 \quad (6.5)$$

for isothermal constant-volume motions that are of high practical importance. The usefulness of equation (6.5) will turn out in calculations later on. It should be emphasized, however, that this choice has no principal reasons. It is merely aimed to simplify relations to be derived.

In equilibrium, both the currents and the forces are zero; consequently, owing to vanishing of \mathbf{X}_1 we may conclude that equation (5.5) holds. Introducing the equilibrium stress tensor $\mathbf{t}^e(u, \mathbf{d})$ and, according to equation (5.9), for the viscous stress \mathbf{t}^v we obtain $\mathbf{X}_1 = \mathbf{t}^v$. In this case we may rewrite Onsager's linear laws in the general form

$$\begin{aligned} \mathbf{J}_1 &= \mathcal{L}_{11} : \mathbf{X}_1 + \mathcal{L}_{12} : \mathbf{X}_2 \\ \mathbf{J}_2 &= \mathcal{L}_{21} : \mathbf{X}_1 + \mathcal{L}_{22} : \mathbf{X}_2 \end{aligned} \quad (6.6)$$

where \mathcal{L}_{11} , \mathcal{L}_{12} , \mathcal{L}_{21} and \mathcal{L}_{22} are fourth order tensors reflecting the symmetry of the medium, satisfying the Onsager-Casimir reciprocal relations and depending on the local state variables u , \mathbf{d} and $\boldsymbol{\xi}$.

This form of the Onsager relations may involve rather complicated relationships. Attention should be drawn here to the misleading nature of the term “linear laws”. Naming equations in (6.6) “linear laws” we mean that thermodynamic currents are linear functions of the thermodynamic forces where the coefficients still may depend on the local state variables. It must be remembered, however, that in our special case, thermodynamic force \mathbf{X}_2 is proportional to the dynamic local variable $\boldsymbol{\xi}$ (see equation (6.4)). In general, any dependence of the coefficient of the “linear laws” on the dynamic variable enables us to describe essential non-linearities even in systems far from equilibrium. Attention should be paid to the fact that the sharp boundary between quasi-linearity and strict non-linearity prevailing in media in local equilibrium becomes resolved in systems far from equilibrium by the existence of dynamic variables.

Not far from equilibrium, media present a simpler situation to us since dependence of the conductivity coefficients on the dynamic variable may be neglected. In this case, the “linear laws” represented by equation (6.6) are inherently linear in the thermodynamic sense of the word, namely, linear in the thermodynamic forces. The differential equations derived from them, however, are non-linear ones in the mathematical sense. The calculations to be carried out later on will illustrate this comment. In any case, the expression “linear laws” obviously originates from tradition rather than from the mathematical structure of these relationships. Returning from philosophy to the subject, we shall show that relations (6.6) can be utilized in description of rather complicated motion forms. Let us begin with the simplest model of the motion of incompressible fluids.

6.1.1. Motion of incompressible fluids. In a description of the motion of fluids, specific internal energy and specific volume can suitably be selected as equilibrium state variables (see subsection 5.1.3.). If the volume change of the fluid is negligible, the present configuration can be taken as reference configuration. As integration of the equation of motion shows, the negative equilibrium pressure can be identified with the spherical part of Cauchy’s stress tensor (see equation (5.27)), and the trace of viscous stress is zero. Thermodynamic current \mathbf{J}_1 (see equation (6.3)) is a zero-trace tensor as well and, owing to the above mentioned choice of reference configuration, takes the form

$$\mathbf{J}_1 = \dot{\mathbf{d}}. \quad (6.7)$$

Let us presume that the medium is not so far from equilibrium that the dependence of the conductivity coefficients on the dynamic variable has to be taken into account. Then, linear laws (6.6) reduce to the simpler form

$$\begin{aligned} \dot{\mathbf{d}} &= L_{11} \mathbf{t}^v - L_{12} \sqrt{\varrho T} \boldsymbol{\xi} \\ \sqrt{\varrho T} \dot{\boldsymbol{\xi}} &= L_{21} \mathbf{t}^v - L_{22} \sqrt{\varrho T} \boldsymbol{\xi} \end{aligned} \quad (6.8)$$

where, in this case, coefficients L_{11} , L_{12} , L_{21} and L_{22} depend purely on the temperature. With respect to reciprocal relation, two cases can be distinguished. In the

first case variable ξ is an even function of time and Onsager's reciprocal relation hold. In the other one, ξ is an odd function of time and Casimir's reciprocal relation is valid. Since, at present, isothermal constant-volume motions are our subject, we shall profitably use variables α and β , respectively, where

$$\sqrt{\varrho T} \xi = \begin{cases} \alpha & \text{if } \xi \text{ is an even} \\ \beta & \text{odd} \end{cases} \quad (6.9)$$

type variable. Instead of equation (6.8) we have in the first case

$$\begin{aligned} \dot{\mathbf{d}} &= L_{11} \mathbf{t}^v - L_{12} \alpha \\ \dot{\alpha} &= L_{12} \mathbf{t}^v - L_{22} \alpha \end{aligned} \quad (6.10)$$

and, in the second case

$$\begin{aligned} \dot{\mathbf{d}} &= L_{11} \mathbf{t}^v - L_{12} \beta \\ \dot{\beta} &= -L_{12} \mathbf{t}^v - L_{22} \beta \end{aligned} \quad (6.11)$$

The motion-stress relationship

$$\tau_t \dot{\mathbf{t}}^v + \mathbf{t}^v = 2\eta(\tau_d \ddot{\mathbf{d}} + \dot{\mathbf{d}}) \quad (6.12)$$

is obtained from equations (6.10) and (6.11) by eliminating the respective dynamic variable and by the use of the notations

$$\tau_t = \frac{L_{11}}{L_{11}L_{22} \pm L_{12}^2}; \quad \tau_d = \frac{1}{L_{22}}; \quad 2\eta = \frac{L_{22}}{L_{11}L_{22} \pm L_{12}^2}. \quad (6.13)$$

In the formulae of τ_t and 2η the negative sign should be taken in the case of α and the positive one in that of β . Substituting equation (6.12) into Cauchy's equation of motion, we obtain the differential equation which, together with the initial condition

$$\dot{\mathbf{d}} = \frac{\tau_t}{2\eta\tau_d} \mathbf{t}^v, \quad (6.14)$$

describes the motion of the medium. Equation (6.14) will hold if the motion starts from local equilibrium or from complete rest, as can be derived from equations (6.10) and (6.11), respectively, and equations (6.13). The other initial and boundary conditions will not be discussed here, since they are well known from classical hydrodynamics.

It is important to mention that equation (6.12) can experimentally be checked for real media whose material coefficients τ_t , τ_d and η can be measured. Starting from the defining equations (6.13), we can easily show that the important relation

$$\frac{1}{\tau_t} = \frac{1}{\tau_d} \pm \frac{L_{12}^2}{L_{11}} \quad (6.15)$$

holds. From equation (6.15) we see that $\tau_t > \tau_d$ for a dynamic variable of type α and $\tau_t < \tau_d$ for a β -type dynamic variable. Thus, to the question as to which type (α or β) of dynamic variable should be used, an answer can be given based

on experimental determination of the material coefficients (6.13) of the studied medium.

Let us turn now to small-amplitude oscillations in media where, owing to the absence of convection, material and partial time derivatives are equal. Using the complex formulation of subsection 3.3.3. we get

$$\tau_t p \mathbf{t}^v + \mathbf{t}^v = 2\eta(\tau_d p^2 \mathbf{d} + p \mathbf{d}) \quad (6.16)$$

or resolved for the stress

$$\mathbf{t}^v = 2\eta p \frac{\tau_d p + 1}{\tau_t p + 1} \mathbf{d} = 2Y(p) \mathbf{d}. \quad (6.17)$$

The complex modulus,

$$Y(p) = \eta \frac{\tau_d}{\tau_t} p + \frac{p}{\frac{\tau_t}{\eta(\tau_t - \tau_d)} + p \frac{\tau_t^2}{\eta(\tau_t - \tau_d)}} \quad (6.18)$$

is identical with the complex viscosity of the generalized Maxwell body (see equation (3.72) if $\tau_t > \tau_d$, i.e., if the dynamic variable is of α type. The corresponding mechanical model is given in Figure 6.2. where from the parameters we may see that the model cannot be used for β type ($\tau_t < \tau_d$) dynamic variables. Beyond that, it can be shown that in this case, none of the mechanical models usual in of rheology can be used.

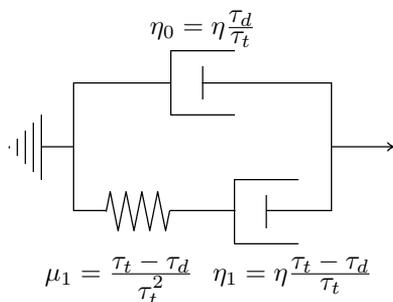


Figure 6.2
The Jeffrey body

The derivative of the complex modulus of any model of rheology with respect to p is a positive real number, if p is real. Let us confirm this. From equation (6.17) we see that

$$\frac{dY(p)}{dp} = \frac{\tau_d \tau_t p^2 + 2\tau_d p + 1}{(\tau_t p + 1)^2} \quad (6.19)$$

which, for real p values, will be positive if the numerator on the right does not vanish, i.e. if the discriminant

$$4\tau_d^2 - 4\tau_d \tau_t = 4\tau_d(\tau_d - \tau_t) < 0 \quad (6.20)$$

corresponding to α -type dynamic variable ($\tau_t > \tau_d$) since $\tau_d > 0$.

The case $\tau_t = \tau_d$ should be mentioned here, too. Then, according to equation (6.15), $L_{12}^2 = 0$, i.e., the dynamic variable cannot be excited as can be seen from the second of equations (6.10) and (6.11), respectively, by substitution of $L_{12} = 0$. Then, the fluid behaves as newtonian provided that it has already been in equilibrium or is aged enough to reach zero dynamic degree of freedom. Its model is a simple dashpot.

However, we need not drop the advantage of the mechanical model even in the case of β type dynamic variables if we introduce a new element in addition to those current in rheology. Its behavior is described by the relation

$$\sigma = \Theta \ddot{\epsilon} \quad (6.21)$$

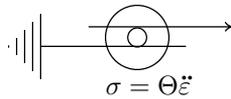


Figure 6.3
The inertia element

(see Figure 6.3) and it can be realized by a high-inertia though zero-mass fly wheel with the axis between two parallel planes. Acceleration does not require considerable force while the force required for stretching is described by equation (6.21). Rewriting the complex modulus in the form

$$Y(p) = \eta p + \frac{1}{\frac{\tau_t}{\eta(\tau_d - \tau_t)p} + \frac{1}{\eta(\tau_d - \tau_t)p^2}} \quad (6.22)$$

we see that the behavior of the medium can be described by the model shown in Figure 6.4.

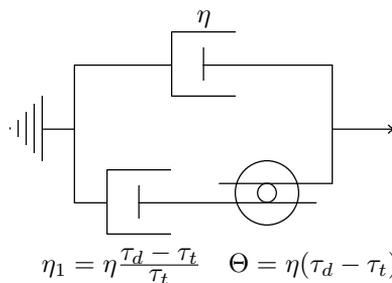


Figure 6.4

6.1.2. Shear flow of liquids. Let us investigate now the shear-flow of liquids whose motion is described by equation (6.12). First we treat steady flow. Using the rectangular coordinates x_1, x_2, x_3 and assuming rectilinear shear flow, i.e. taking

$$v_1 = \kappa x_2; \quad v_2 = v_3 = 0 \quad (6.23)$$

for the velocity field, we obtain

$$\dot{\mathbf{d}} = \frac{\kappa}{2} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \boldsymbol{\omega} = \frac{\kappa}{2} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (6.24)$$

and hence

$$\ddot{\mathbf{d}} = \frac{\kappa^2}{2} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (6.25)$$

$$\dot{\mathbf{t}}^v = \frac{\kappa}{2} \begin{bmatrix} -2t_{12}^v & t_{11}^v - t_{22}^v & -t_{23}^v \\ t_{11}^v - t_{22}^v & 2t_{12}^v & t_{13}^v \\ -t_{23}^v & t_{13}^v & 0 \end{bmatrix}$$

Inserting these into equation (6.12) we arrive at a matrix equation with the component equations

$$\begin{aligned} -\tau_t \kappa t_{12}^v + t_{11}^v &= -\eta \tau_d \kappa^2 \\ \tau_t \frac{\kappa}{2} (t_{11}^v - t_{22}^v) + t_{12}^v &= \eta \kappa \\ -\tau_t \frac{\kappa}{2} t_{23}^v + t_{13}^v &= 0 \\ \tau_t \frac{\kappa}{2} t_{13}^v + t_{23}^v &= 0 \\ \tau_t \kappa t_{12}^v + t_{22}^v &= \eta \tau_d \kappa^2 \\ t_{33}^v &= 0. \end{aligned} \quad (6.26)$$

Equation (6.26) can easily be solved for the elements of the extra stress tensor. By combination we obtain: from the third and fourth equations $t_{13}^v = t_{23}^v = 0$, and from the first and fifth equations $-t_{22}^v = t_{11}^v$. Inserting this last relation into the second equation and combining it with the first one we finally obtain

$$t_{12}^v = \eta \kappa \frac{1 + \tau_t \tau_d \kappa^2}{1 + \tau_t^2 \kappa^2} \quad t_{11}^v = \frac{\eta (\tau_t - \tau_d) \kappa^2}{1 + \tau_t^2 \kappa^2} = -t_{22}^v \quad (6.27)$$

in complete correspondence with the description given in section 3.5. Thus, we may summarize that from the linear thermodynamic theory we have derived the viscometric functions (shear and normal stresses)

$$\tau = \eta \kappa \frac{1 + \tau_d \tau_t \kappa^2}{1 + \tau_t^2 \kappa^2} \quad \sigma_1 = -\sigma_2 = \frac{\eta (\tau_t - \tau_d) \kappa^2}{1 + \tau_t^2 \kappa^2} \quad (6.28)$$

which are plotted in Figures 6.5 and 6.6. We see that in the instance $\tau_t > \tau_d$ (i.e. dynamic variable of type α) the Ostwald diagrams treated in subsection 3.3.7 are

well represented by the shear stress calculated above. After having determined the shear stress function and thus the values of η , τ_t , and τ_d by viscometric measurements we can calculate the normal stress functions by the use of equation (6.28). Since we can determine the quantities in equation (6.12) if we know the functions \mathbf{t}^v , \mathbf{d} and $\boldsymbol{\omega}$ and their first time derivatives, it is obvious that a medium with a single dynamic variable is a simple liquid (see section 3.4) and the functions in (6.28) are really viscometric functions applicable to any viscometric flow.

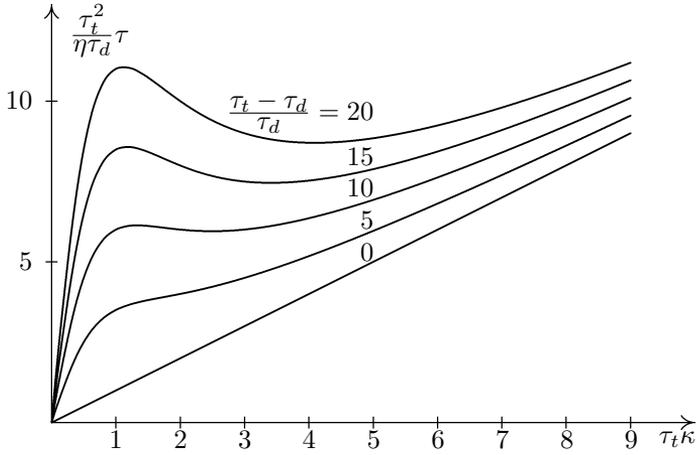


Figure 6.5

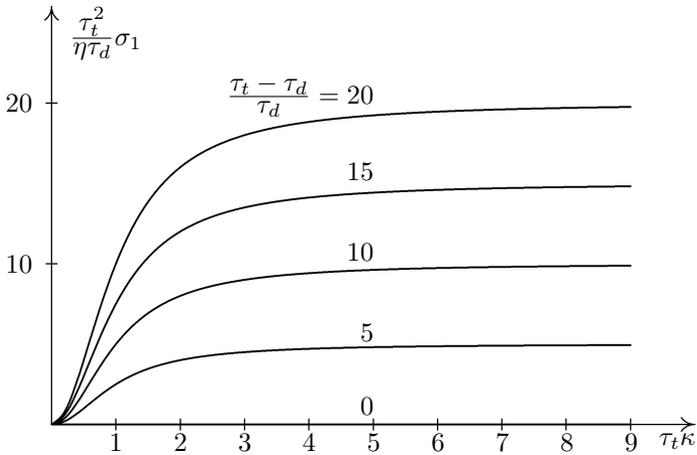


Figure 6.6

6.1.3. Complex-number treatment for shear flow. For the velocity field given in equation (6.23), in row 3 and column 3 of the matrices of the tensors in equation (6.12), all elements are zero. This fact can be used to simplify the calculations carried out in section 3.2 even if shear rate changes in time. The order of the matrices can, namely, be reduced from 3×3 to 2×2 by omitting the third rows and third columns. Moreover, it is sufficient to use one row or one column instead of the matrices, since they are zero-trace and, with the exception of $\boldsymbol{\omega}$, symmetric matrices. The objective derivatives

$$\begin{bmatrix} a & b \\ b & -a \end{bmatrix}^\circ = \begin{bmatrix} \dot{a} - \kappa b & \dot{b} + \kappa a \\ \dot{b} + \kappa a & -\dot{a} + \kappa b \end{bmatrix} \quad (6.29)$$

can be calculated by the use of the substitutions

$$\begin{bmatrix} a & b \\ b & -a \end{bmatrix} \iff [b \ a] \quad (6.30)$$

where for the ordered array (b, a) the operation of addition and multiplication with a number is defined as in matrix algebra. The material time derivative can be calculated as follows (see equation (6.29))

$$(b, a)^\circ = (\dot{b}, \dot{a}) + \kappa(a, -b) \quad (6.31)$$

or, projected onto complex numbers

$$\begin{aligned} (b, a) &\iff b - ia \\ (b, a)^\circ &\iff (\dot{b} - i\dot{a}) + i\kappa(b - ia). \end{aligned} \quad (6.32)$$

By the last correspondence the calculations will become very simple if complex numbers are used instead of the second columns of the 2 by 2 matrices [76, 157]. Thus, in steady state, equation (6.12) takes the form

$$\tau_t i \kappa \mathbf{t}^v + \mathbf{t}^v = 2\eta[\tau_d (i\kappa)^2 \mathbf{d} + i\kappa \mathbf{d}] \quad (6.33)$$

where the tensorial notation refers to complex numbers. The complex number corresponding to the stress tensor is easily obtained from equation (6.33). Before turning to the calculation of \mathbf{t}^v let us substitute p for $i\kappa$

$$\mathbf{t}^v = 2\eta \frac{\tau_d p + 1}{\tau_t p + 1} \dot{\mathbf{d}}, \quad (6.34)$$

Formula (6.34) is completely analogous to relation (6.14) valid for small-amplitude oscillations; hence: the viscometric functions of shear flow as functions of the shear rate on the one side and the real and imaginary parts of the shear stress as functions of the angular frequency in the case of small-amplitude oscillations, on the other side, have the same forms [28].

The complex treatment introduced here makes the calculations very easy. This is very useful in complicated cases as, e.g., in the cases of shear flow with changing

shear rate or of media needing several dynamic variables for description. Steady shear flow should be taken as a first example and it should be shown how simple the calculation of the dynamic variable from equation (6.10) becomes. The complex form of equation (6.10) is

$$\begin{aligned} \dot{\mathbf{d}} &= L_{11}\mathbf{t}^v - L_{12}\boldsymbol{\alpha} \\ i\kappa\boldsymbol{\alpha} &= L_{12}\mathbf{t}^v - L_{22}\boldsymbol{\alpha} \end{aligned} \quad (6.35)$$

hence

$$\boldsymbol{\alpha} = \frac{L_{12}}{L_{11}L_{22} - L_{12}^2 + iL_{11}\kappa} \dot{\mathbf{d}}. \quad (6.36)$$

Substituting the notations of equation (6.13) we obtain

$$\boldsymbol{\alpha} = \frac{\sqrt{2\eta(\tau_t - \tau_d)}}{1 + i\tau_t\kappa} \dot{\mathbf{d}}.$$

Since, according to equation (6.24), $\dot{\mathbf{d}}$ has the real value $\kappa/2$, the canonical form of $\boldsymbol{\alpha}$ is

$$\boldsymbol{\alpha} = \sqrt{2\eta(\tau_t - \tau_d)} \frac{1 - i\kappa\tau_t}{1 + (\tau_t\kappa)^2} \frac{\kappa}{2} \quad (6.37)$$

and the matrix of the tensor is

$$\boldsymbol{\alpha} = \frac{\sqrt{2\eta(\tau_t - \tau_d)}}{1 + (\tau_t\kappa)^2} \begin{bmatrix} \frac{\kappa^2}{2}\tau_t & \frac{\kappa}{2} & 0 \\ \frac{\kappa}{2} & -\frac{\kappa^2}{2}\tau_t & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (6.38)$$

6.1.4. Transient stress. The complex-variable treatment can be well exploited in tracing transient processes. For illustration, development of shear stress is determined in the process of sudden emergence of shear flow. Let the velocity field be given by equation (6.23), however, with κ as a function of time

$$\kappa(t) = \begin{cases} 0 & \text{for } t < 0 \\ \kappa & \text{for } t \geq 0 \end{cases} \quad (6.39)$$

We have to solve equation (6.12) in the time range $t > 0$ under initial conditions (6.14). The differential equation in complex variables takes the form

$$\tau_t \dot{\mathbf{t}}^v + (1 + i\kappa\tau_t)\mathbf{t}^v = 2\eta(\tau_d i\kappa + 1) \frac{\kappa}{2}. \quad (6.40)$$

The steady viscometric functions stand as one of the particular solutions, since equation (6.40) is an inhomogeneous first order linear differential equation. The general solution

$$\mathbf{t}^v(t) = \eta\kappa \frac{1 + i\kappa\tau_d}{1 + i\kappa\tau_t} + C \exp\left(-\frac{1 + i\kappa\tau_t}{\tau_t} t\right) \quad (6.41)$$

is the sum of the particular solution of the inhomogeneous and the general solution of the homogeneous equation. The initial condition (6.14) gives the constant C as

$$C = \frac{\eta\kappa(\tau_d - \tau_t)}{\tau_t(1 + i\kappa\tau_t)}, \tag{6.42}$$

whose substitution into equation (6.41) leads to the real part

$$t_{12}^v = \eta\kappa \frac{1 + \tau_d\tau_t\kappa^2}{1 + \tau_t^2\kappa^2} - \eta\kappa \frac{\tau_t - \tau_d}{\tau_t\sqrt{1 + \tau_t^2\kappa^2}} \exp\left(-\frac{t}{\tau_t}\right) \cos(\kappa t - \varphi) \tag{6.43}$$

with

$$\tan \varphi = \tau_t\kappa.$$

From the imaginary part, we obtain the time evolution of the normal stresses as

$$t_{11}^v = \frac{\eta(\tau_t - \tau_d)\kappa^2}{1 + \tau_t^2\kappa^2} + \eta\kappa \frac{\tau_t - \tau_d}{\tau_t\sqrt{1 + \tau_t^2\kappa^2}} \exp\left(-\frac{t}{\tau_t}\right) \sin(\kappa t - \varphi). \tag{6.44}$$

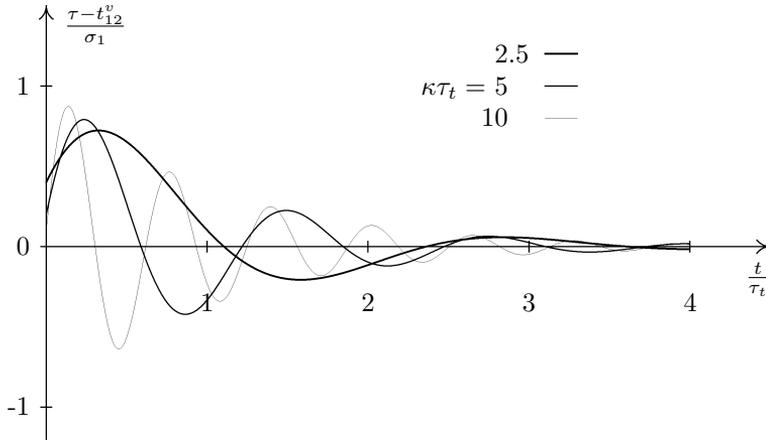


Figure 6.7

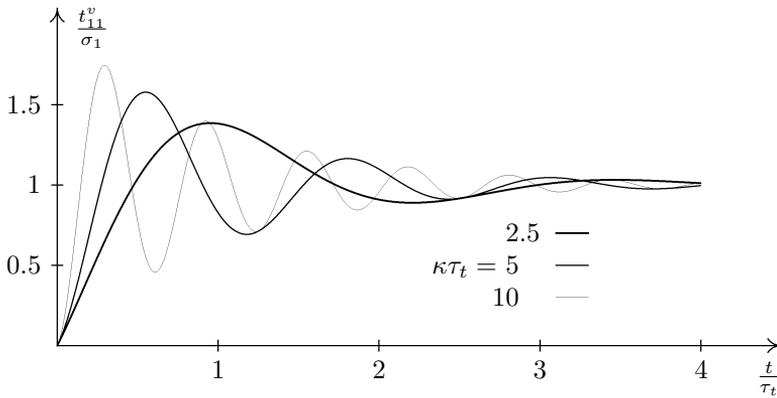


Figure 6.8

Figure 6.7 and 6.8 show the evolution of the shear and normal stresses. It will be much more difficult to calculate these if at the outset we have a shear flow with constant shear stress and we have to calculate the evolution of the shear rate and of the normal stress. In this complicated case the system of differential equations is non-linear; hence, the solution must be left to the computer.

6.1.5. Plastic behavior. Creep. Let us return now to the form of the shear stress function given in equation (6.28). If the shear stress is gradually increased in the way that time is always left for reaching stationary state (the smaller the τ_t the shorter the waiting time is), increase of the stress in media with high τ_t/τ_d values will cause small shear rate. Above a critical value of the shear stress, however, the stress rate will suddenly and abruptly increase. If we now decrease the shear stress, the relatively high shear rate will survive provided that $\tau_t/\tau_d > 9$. Arriving at a second critical value of the shear stress (below the first one) we shall meet with a sudden decrease of the shear rate. The relation can be seen in Figure 6.9. where the thin line shows the unstable range of the shear stress function.

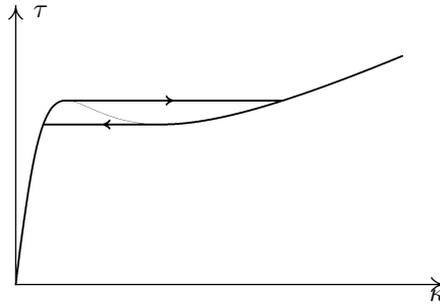


Figure 6.9

(The curve of Figure 6.9 corresponds to a value of $\tau_t/\tau_d = 15$.) The described behavior is typically plastic displaying the phenomenon of creep as well, i.e., the medium does flow but very slowly under stress below the critical one.

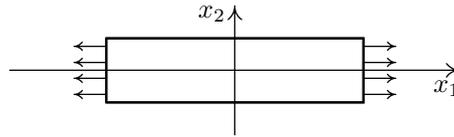


Figure 6.10

Let us examine now the behavior of the medium in elongational flow. The material will be assumed practically solid under slight load, since η has a very high value. Thus a sample bar can be prepared. The bar will be stretched with the stress σ along the x_1 axis, its lateral faces will be left free. Then, the only non-zero component of the stress tensor will be $t_{11} = \sigma$. We must remember that the medium is a fluid and, accordingly, the deviatoric stress (i.e. the traceless part of the stress tensor) totally belongs to the viscous stress and will be identical with the latter if we neglect volume change. Therefore, the matrix of the viscous stress

becomes

$$\mathbf{t}^v = \frac{\sigma}{3} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (6.45)$$

In order to calculate the velocity gradient tensor, we assume that lines parallel to the x_1 axes do not rotate; and thus the matrix of the velocity gradient will take the form

$$\text{Grad } \mathbf{v} = \dot{\mathbf{d}} + \boldsymbol{\omega} = \begin{bmatrix} \dot{d}_{11} & \dot{d}_{12} - \omega_3 & \dot{d}_{13} + \omega_2 \\ 0 & \dot{d}_{22} & \dot{d}_{23} - \omega_1 \\ 0 & \dot{d}_{23} + \omega_1 & \dot{d}_{33} \end{bmatrix} \quad (6.46)$$

Supposing stationary motion we may take $\omega_2 = 0$ by suitable choice of axes x_2 and x_3 . Then, the stretching tensor $\dot{\mathbf{d}}$ and the spin tensor $\boldsymbol{\omega}$ are represented by the matrices

$$\boldsymbol{\omega} = \begin{bmatrix} 0 & -\omega_3 & 0 \\ \omega_3 & 0 & -\omega_1 \\ 0 & \omega_1 & 0 \end{bmatrix}, \quad \dot{\mathbf{d}} = \begin{bmatrix} \dot{d}_{11} & -\omega_3 & 0 \\ -\omega_3 & \dot{d}_{22} & \dot{d}_{23} \\ 0 & \dot{d}_{23} & \dot{d}_{33} \end{bmatrix} \quad (6.47)$$

In order to determine the tensor components we substitute equations (6.47) into the differential equations (6.12) and omit the total time derivatives. To this end we have to calculate the actual expressions of \mathbf{t}^v and $\ddot{\mathbf{d}}$:

$$\mathbf{t}^v = \mathbf{t}\boldsymbol{\omega} - \boldsymbol{\omega}\mathbf{t} = \sigma \begin{bmatrix} 0 & -\omega_3 & 0 \\ -\omega_3 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (6.48)$$

$$\ddot{\mathbf{d}} = \dot{\mathbf{d}}\boldsymbol{\omega} - \boldsymbol{\omega}\dot{\mathbf{d}} = \begin{bmatrix} -2\omega_3^2 & \omega_3(\dot{d}_{22} - \dot{d}_{11}) & \omega_3(\omega_1 + \dot{d}_{23}) \\ \omega_3(\dot{d}_{22} - \dot{d}_{11}) & 2\omega_3^2 + 2\omega_1\dot{d}_{23} & -\omega_1(\dot{d}_{11} + 2\dot{d}_{22}) \\ \omega_3(\omega_1 + \dot{d}_{23}) & -\omega_1(\dot{d}_{11} + 2\dot{d}_{22}) & -2\omega_1\dot{d}_{23} \end{bmatrix}$$

Rewriting equation (6.12) in the form

$$\frac{1}{2\eta\tau_d}(\tau_t\dot{\mathbf{t}}^v + \mathbf{t}^v) = \ddot{\mathbf{d}} + \frac{1}{\tau_d}\dot{\mathbf{d}} \quad (6.49)$$

and taking into account equations (6.45), (6.47) and (6.48) we obtain

$$\frac{\sigma}{6\eta\tau_d} \begin{bmatrix} 2 & -3\tau_t\omega_3 & 0 \\ -3\tau_t\omega_3 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \frac{1}{\tau_d}\dot{d}_{11} - 2\omega_3^2 & \left(-\frac{1}{\tau_d} + \dot{d}_{22} - \dot{d}_{11}\right)\omega_3 & \omega_3(\omega_1 + \dot{d}_{23}) \\ \left(-\frac{1}{\tau_d} + \dot{d}_{22} - \dot{d}_{11}\right)\omega_3 & \frac{1}{\tau_d}\dot{d}_{22} + 2\omega_3^2 + 2\omega_1\dot{d}_{23} & \frac{1}{\tau_d}\dot{d}_{23} - \omega_1(\dot{d}_{11} + 2\dot{d}_{22}) \\ \omega_3(\omega_1 + \dot{d}_{23}) & \frac{1}{\tau_d}\dot{d}_{23} - \omega_1(\dot{d}_{11} + 2\dot{d}_{22}) & \frac{1}{\tau_d}\dot{d}_{33} - 2\omega_1\dot{d}_{23} \end{bmatrix} \cdot \quad (6.50)$$

The elements of the matrices of equations (6.47) are calculated from the equations between the respective elements of the two matrices in equations (6.50). From the equation belonging to position (1,1) we obtain

$$\dot{d}_{11} = \frac{\sigma}{3\eta} + 2\tau_d\omega_3^2. \quad (6.51)$$

Comparison of the elements in position (2,2) gives an equation containing \dot{d}_{23} . Similar comparison pertaining to position (2,3) leads to an equation containing, in addition to \dot{d}_{22} and \dot{d}_{23} , also \dot{d}_{11} which, however, can be eliminated by equation (6.51). The system of these two equations has the solution

$$\dot{d}_{22} = -\frac{\sigma}{6\eta} - \tau_d\omega_3^2 - \frac{\frac{1}{\tau_d}\omega_3^2}{\tau_d^{-2} + 4\omega_1^2} \quad (6.52)$$

$$\dot{d}_{23} = -\frac{2\omega_1\omega_3^2}{\tau_d^{-2} + 4\omega_1^2} \quad (6.53)$$

The equation between the elements in position (3,3), after substitution of equation (6.53), gives

$$\dot{d}_{33} = -\frac{\sigma}{6\eta} - \tau_d\frac{4\omega_1^2\omega_3^2}{\tau_d^{-2} + 4\omega_1^2} \quad (6.54)$$

From the equation for position (1,3) after substitution of equation (6.51) we obtain

$$\omega_3\omega_1 \left[1 - \frac{2\omega_3^2}{\tau_d^{-2} + 4\omega_1^2} \right] = 0 \quad (6.55)$$

There are three solutions of this equation: $\omega_3 = 0$ (case 1), $\omega_1 = 0$ (case 2) and

$$\frac{2\omega_3^2}{\tau_d^{-2} + 4\omega_1^2} = 1 \quad (6.56)$$

(case 3). Substitution of equation (6.51) into (6.52) shows that in case 3

$$2\dot{d}_{22} + \dot{d}_{11} = -\frac{1}{\tau_d}.$$

In case 1, equations (6.51)-(6.54) reduce to

$$\begin{aligned} \dot{d}_{11} &= \frac{\sigma}{3\eta} \\ \dot{d}_{22} &= -\frac{\sigma}{6\eta} \\ \dot{d}_{23} &= 0 \\ \dot{d}_{33} &= -\frac{\sigma}{6\eta} \end{aligned} \quad (6.57)$$

and the matrix of the stretching tensor takes the form

$$\dot{\mathbf{d}} = \frac{\sigma}{6\eta} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (6.58)$$

In this case $\dot{\mathbf{t}}^v$ and $\ddot{\mathbf{d}}$ become zero tensors and, therefore, equation (6.12) reduces to

$$\mathbf{t}^v = 2\eta\dot{\mathbf{d}}. \quad (6.59)$$

Under the conditions given in case 1, ω_1 cannot be evaluated. This, however, is irrelevant, since it is the extension rate of the bar, i.e. \dot{d}_{11} , we are primarily interested in.

In case 2 where $\omega_1 = 0$, from the equation for position (1,2), after substitution of equations (6.51) and (6.52) we obtain

$$\omega_3^2 = \frac{1}{4\tau_d^2} \left[\frac{\sigma}{2\eta} (\tau_t - \tau_d) - 1 \right] \quad (6.60)$$

and

$$\dot{d}_{11} = \frac{\sigma(3\tau_t + \tau_d)}{12\eta\tau_d} - \frac{1}{2\tau_d}. \quad (6.61)$$

It follows from equation (6.60) that

$$\sigma > \frac{2\eta}{\tau_t - \tau_d} = \sigma_a^* > 0 \quad (6.62)$$

is the precondition to case 2. The matrix of tensor $\dot{\mathbf{d}}$ is rather complicated in this case. Its presentation is omitted here.

In case 3 characterized by equation (6.56) together with $\omega_1 = -\dot{d}_{23} \neq 0$, the equations between the respective elements in positions (1,2) and (2,3) are solved for \dot{d}_{11} and \dot{d}_{22} . Thus we obtain

$$\dot{d}_{11} = \frac{\sigma\tau_t}{3\eta\tau_d} - \frac{1}{\tau_d}, \quad \dot{d}_{22} = -\frac{\sigma\tau_t}{6\eta\tau_d}, \quad (6.63)$$

and by their combination with equations (6.51), (6.52) and (6.56)

$$\omega_1^2 = \frac{1}{\tau_d^2} \left[\frac{\sigma(\tau_t - \tau_d)}{12\eta} - \frac{1}{2} \right], \quad \omega_3^2 = \frac{1}{\tau_d^2} \left[\frac{\sigma(\tau_t - \tau_d)}{6\eta} - \frac{1}{2} \right] \quad (6.64)$$

which show the precondition for case 3 as

$$\sigma > \frac{6\eta}{\tau_t - \tau_d} = \sigma_b^* > 0. \quad (6.65)$$

Introducing the variables

$$y = \tau_d \dot{d}_{11}, \quad x = \frac{\sigma\tau_t}{2\eta}, \quad x^* = \frac{\sigma^*\tau_t}{2\eta}, \quad \xi = \frac{\tau_t}{\tau_d}$$

we obtain relations for the extension rate

case	relation	x^*	$\frac{dy}{dx}$
1	$y = \frac{2}{3\xi}x$	—	$\frac{2}{3\xi}$
2	$y = \frac{3\xi+1}{6\xi}x - \frac{1}{2}$	$\frac{\xi}{\xi-1}$	$\frac{3\xi+1}{6\xi}$
3	$y = \frac{2}{3}x - 1$	$\frac{3\xi}{\xi-1}$	$\frac{2}{3}$

It should be added that both the relations (6.62) and (6.65) contain the inequality

$$\frac{\tau_t}{\tau_d} = \xi > 1. \quad (6.66)$$

From the tabulated results we see immediately that the extension rate depends linearly on the load in all the three cases; and also considering relation (6.66) we may show that the slope of the straight line is the biggest in case 3 and is the smallest in case 1. The straight lines attached to cases 1 and 2, and 2 and 3 intersect in points x_1 and x_2 , respectively, where these values are solutions of the equations

$$\frac{2}{3\xi}x_1 = \frac{3\xi+1}{6\xi}x_1 - \frac{1}{2} \quad (6.67)$$

and

$$\frac{3\xi+1}{6\xi}x_2 - \frac{1}{2} = \frac{2}{3}x_2 - 1. \quad (6.68)$$

Accordingly, the solutions

$$x_1 = \frac{\xi}{\xi-1} \quad \text{and} \quad x_2 = \frac{3\xi}{\xi-1}$$

separate the three ranges 1, 2 and 3 (shown in Figure 6.11) in terms of the variables σ and \dot{d}_{11} , i.e., load and extension rate. Figure 6.12 illustrates the situation for very high values of ξ when range 3 lies outside the picture.

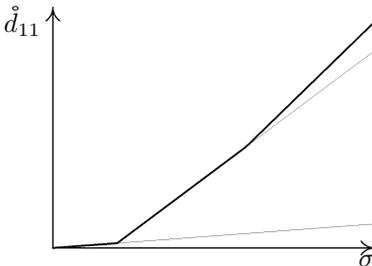


Figure 6.11

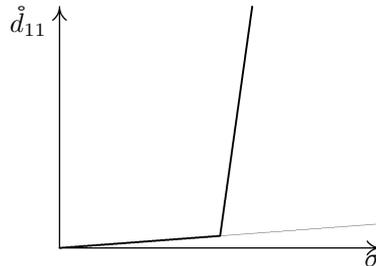


Figure 6.12

In general, the conclusion can be drawn that during stretching along a single axis, the medium definitely shows plastic behavior; and — in the range of small load — it creeps. Non-zero ω_1 in case 3 can be regarded as rotation of the angular velocity

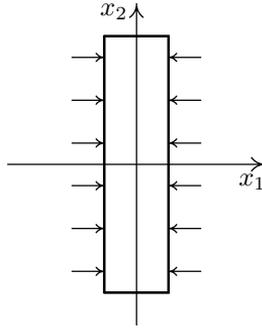


Figure 6.13

vector around the axis of the tension. This motion, however, is not stationary, and our presentation describes it in a coordinate system rotating with the angular velocity.

Let us turn now to compression along a single axis whose model is shown in Figure 6.13. The considerations used above with respect to stress can be applied, together with equation (6.45), however, with negative values of σ . The planes perpendicular to the x_1 axes are assumed not to swing; therefore, the matrix of the velocity gradient tensor is written in the form

$$\text{Grad } \mathbf{v} = \dot{\mathbf{d}} + \boldsymbol{\omega} = \begin{bmatrix} \dot{d}_{11} & 0 & 0 \\ \dot{d}_{12} + \omega_3 & \dot{d}_{22} & \dot{d}_{23} - \omega_1 \\ \dot{d}_{13} - \omega_2 & \dot{d}_{23} + \omega_1 & \dot{d}_{33} \end{bmatrix}. \quad (6.69)$$

Since ω_2 can be made zero by suitable choice of the directions of axes x_2 and x_3 , the matrices of the rotation tensor $\boldsymbol{\omega}$ and of the stretching tensor $\dot{\mathbf{d}}$ can be written in the forms

$$\boldsymbol{\omega} = \begin{bmatrix} 0 & -\omega_3 & 0 \\ \omega_3 & 0 & -\omega_1 \\ 0 & \omega_1 & 0 \end{bmatrix} \quad \text{and} \quad \dot{\mathbf{d}} = \begin{bmatrix} \dot{d}_{11} & \omega_3 & 0 \\ \omega_3 & \dot{d}_{22} & \dot{d}_{23} \\ 0 & \dot{d}_{23} & \dot{d}_{33} \end{bmatrix} \quad (6.70)$$

The matrix of tensor $-\dot{\mathbf{d}}$ will be identical with that of $\dot{\mathbf{d}}$ in equation (6.47) if we introduced the notation $\sigma = -\sigma'$. Multiplying equation (6.49) by (-1) we find the tensorial form of the equation unchanged, though with σ' , $-\dot{d}_{11}$, $-\dot{d}_{22}$, $-\dot{d}_{23}$ and $-\dot{d}_{33}$ in places of σ , \dot{d}_{11} , \dot{d}_{22} , \dot{d}_{23} and \dot{d}_{33} . The theory expounded above on plastic behavior in stretching can equally be applied to compression. Into the equations, however, we have to put compressive stress instead of tensile stress and to replace the negative value of the extension rate by the compression rate. Accordingly figures illustrating the dependence of the extension rate on the tensile stress can be applied to compressive stress as well. However, a symmetry operation is necessary.

The following important circumstances must be emphasized here. Plastic behavior is generally considered in the literature as a typical non-linear phenomenon; nevertheless, in the present work it has been derived from Onsager's strictly linear non-equilibrium thermodynamic theory. Equation (6.50) applied to determine the

velocity field is, however, not linear at all in the mathematical sense. Therefore, it is not surprising that its solutions may describe plastic properties. Most relevant, however, is the fact that non-linearity is due to the presence of rotations as factors in the objective time derivative. Thus, it is not the non-linearity of the constitutive equations that leads to non-linearity in the mathematical equations. This is a case similar to that of the Navier-Stokes equations where the classical linear constitutive equation is given while non-linearity occurs due to the almost 150 year well-known term $(\mathbf{v} \text{ grad})\mathbf{v}$ in the material time derivative

$$\frac{d\mathbf{v}}{dt} = \frac{\partial\mathbf{v}}{\partial t} + (\mathbf{v} \text{ grad})\mathbf{v}.$$

Similarly, in the case of plastic flow the terms $\tau_t(\mathbf{t}^v\boldsymbol{\omega} - \boldsymbol{\omega}\mathbf{t}^v)$ and $2\eta\tau_d(\dot{\mathbf{d}}\boldsymbol{\omega} - \boldsymbol{\omega}\dot{\mathbf{d}})$ are non-linear, and essential in the problem but do not disturb the linearity of the constitutive equations. Our conclusion that plastic behavior can be described by the linear constitutive equations of Onsagerian thermodynamics is of fundamental importance in principle and in practice.

Before proceeding, let us first examine the stability of the solutions obtained above. In case 1, a tensor $\dot{\mathbf{d}}$ deviating from the original will be substituted into equation (6.49) and the value of the time derivative of deviation $\delta\dot{\mathbf{d}}$ will be studied. From the matrix elements in position (1,2), using the relation $\dot{d}_{11} + \dot{d}_{22} + \dot{d}_{33} = 0$ as well, we obtain

$$\frac{\sigma\tau_t}{2\eta\tau_d}\delta\omega_3 = \delta\dot{\omega}_3 + \delta\omega_3 \left(\frac{1}{\tau_d} + 2\dot{d}_{11} + \dot{d}_{33} \right), \quad (6.71)$$

hence taking into account \dot{d}_{11} and \dot{d}_{22} from equations (6.57)

$$\delta\dot{\omega}_3 = \delta\omega_3 \frac{1}{\tau_d} \left[\frac{\sigma}{2\eta}(\tau_t - \tau_d) - 1 \right]. \quad (6.72)$$

As can be seen, the solution in case 1 will only be stable if the factor of $\delta\omega_3$ on the right hand side is negative. Otherwise, the solution becomes unstable. Condition of stability is therefore

$$\sigma < \frac{2\eta}{\tau_t - \tau_d}, \quad (6.73)$$

which — in coincidence with equation (6.62) — means that case 1 will not be realized, if case 2 becomes possible.

Let us turn now to the question of stability in case 2. Comparison of the elements in positions (1,3) and (2,3) of the matrices in equation (6.50) leads to

$$\delta\omega_1 + \delta\dot{d}_{23} = 0$$

and

$$-\delta\dot{\omega}_1 = \frac{1}{\tau_d}\delta\omega_1 + \delta\omega_1(2\dot{d}_{22} + \dot{d}_{11}) = 0 \quad (6.74)$$

respectively. Using equations (6.57) and (6.61), after rearrangement, we obtain

$$\delta\dot{\omega}_1 = \delta\omega_1 \left[\frac{\sigma(3\tau_t + \tau_d)}{12\eta\tau_d} - \frac{1}{2\tau_d} - \frac{\sigma}{3\eta} - \frac{1}{\tau_d} \right]. \quad (6.75)$$

Case 2 will not be stable either if the factor in brackets is positive. Condition for this relation is

$$\sigma > \frac{6\eta}{\tau_t - \tau_d}, \quad (6.76)$$

i.e. the same as the precondition of case 3 (see equation (6.65)). In other words, if case 3 becomes possible, the stability of the two other solutions are lost. Thus, the reality of plastic behavior seems to be proved.

Finally, let us examine what happens if the stress is so small that no notable angular velocity evolves. Equation (6.12) can then be written in the simpler form

$$\tau_t \dot{\mathbf{t}}^v + \mathbf{t}^v = 2\eta(\tau_d \ddot{\mathbf{d}} + \dot{\mathbf{d}}) \quad (6.77)$$

This differential equation has the solution

$$\begin{aligned} \dot{\mathbf{d}} &= \frac{1}{2\eta\tau_d} \exp\left(-\frac{t}{\tau_d}\right) \int_{-\infty}^t [\tau_t \dot{\mathbf{t}}^v(s) + \mathbf{t}^v(s)] \exp\left(\frac{s}{\tau_d}\right) ds = \\ &= \frac{1}{2\eta} \mathbf{t}^v + \frac{\tau_t - \tau_d}{2\eta\tau_d} \int_{-\infty}^t \dot{\mathbf{t}}^v(s) \exp\left(\frac{s-t}{\tau_d}\right) ds \end{aligned} \quad (6.78)$$

describing phenomenon identified above as creep, since in the case of constant stress the second integral in equation (6.77) vanishes. At very high values of η and negligible creep, the solution takes the form

$$\dot{\mathbf{d}} \approx \frac{1}{2\eta} \frac{\tau_t - \tau_d}{\tau_d} \int_{-\infty}^t \dot{\mathbf{t}}^v(s) \exp\left(\frac{s-t}{\tau_d}\right) ds \quad (6.79)$$

that is the solution of the differential equation

$$\mathbf{t}^v = \frac{2\eta}{\tau_t - \tau_d} (\tau_d \dot{\mathbf{d}} + \mathbf{d} - \delta) \quad (6.80)$$

if a suitable reference configuration is chosen. In other words, neglecting creep we arrived at the differential equation (3,20) of a Kelvin body whose constants are

$$\mu_K = \frac{\eta}{\tau_t - \tau_d}; \quad \eta_K = \frac{\eta\tau_d}{\tau_t - \tau_d} \quad (6.81)$$

which is to say that the fluid model studied here shows not only the phenomenon of plasticity, but in case of small load behaves as an elastic solid.

In summary, we may say that a fluid model that can be described by a single dynamic variable shows all properties characteristic for plastic materials with the only exception of hardening. We have found Onsagerian linear thermodynamics as an efficient tool for the analysis of deformations, since its simplest model has described a large number of phenomena and behavior hardly imagined before.

6.1.6. Extension of complex representation to plane motions. Owing to practical importance and mathematical simplicity, motion in the plane deserves special interest. If a cartesian coordinate system is found so that

$$v_1 = v_1(x_1, x_2), \quad v_2 = v_2(x_1, x_2), \quad v_3 = 0 \quad (6.82)$$

is the velocity field, the motion will be termed plane motion. All elements of the third row and third column will be zero in the matrix of the velocity-gradient. Thus, reasoning in point 6.1.3. can be applied here, too. Components of the angular velocity and stretching tensors become now

$$\begin{aligned} \dot{\mathbf{d}} &= \begin{bmatrix} v_{1,1} & \frac{1}{2}(v_{1,2} + v_{2,1}) & 0 \\ \frac{1}{2}(v_{1,2} + v_{2,1}) & v_{2,2} & 0 \\ 0 & 0 & 0 \end{bmatrix} \\ \boldsymbol{\omega} &= \begin{bmatrix} 0 & \frac{1}{2}(v_{1,2} - v_{2,1}) & 0 \\ \frac{1}{2}(v_{2,1} - v_{1,2}) & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \end{aligned} \quad (6.83)$$

For simplicity let us omit now the third row and the third column containing only zero elements and use the components of tensors and the value of the tensor-invariant of $\boldsymbol{\omega}$:

$$\dot{d}_{12} = \frac{1}{2}(v_{1,2} + v_{2,1}); \quad \dot{d}_{11} = v_{1,1}; \quad -\omega = \frac{1}{2}(v_{1,2} - v_{2,1}). \quad (6.84)$$

If we continue to restrict our study to volume preserving motions and if the matrix of $\dot{\mathbf{d}}$ is determined by its second column and by mapping it onto the complex numbers in the way described in section 3. of this chapter, we may write

$$\dot{\mathbf{d}} = \dot{d}_{12} - i\dot{d}_{11}; \quad \ddot{\mathbf{d}} = \frac{d\dot{\mathbf{d}}}{dt} - 2\omega i\dot{\mathbf{d}}. \quad (6.85)$$

From equation (6.12), we may conclude that the third row and column of the stress deviator \mathbf{t}^v also contains zero elements; thus the stress deviator and its objective time derivative may also be mapped onto the complex numbers as is shown by equation (6.85):

$$\mathbf{t}^v = t_{12}^v - it_{11}^v; \quad \dot{\mathbf{t}}^v = \dot{t}_{12}^v - i\dot{t}_{11}^v = \dot{t}_{12}^v - 2\omega t_{11}^v + i(-\dot{t}_{11}^v - 2\omega t_{12}^v). \quad (6.86)$$

By substituting them, equation (6.12) can be rewritten in the complex form

$$\tau_t \left(\frac{d\mathbf{t}^v}{dt} - 2\omega i\mathbf{t}^v \right) + \mathbf{t}^v = 2\eta \left(\tau_d \left(\frac{d\dot{\mathbf{d}}}{dt} - 2\omega i\dot{\mathbf{d}} \right) + \dot{\mathbf{d}} \right), \quad (6.87)$$

This equation is well suited for practical calculations.

Let us now determine the eigenvalues of a tensor belonging to a given complex number and the directions belonging to them. For this, let us write the complex number into the trigonometric form, and let the eigenvector be a unit vector. In this case the eigenvalue problem gives the following matrix equation:

$$z \begin{bmatrix} -\sin \varphi & \cos \varphi \\ \cos \varphi & \sin \varphi \end{bmatrix} \begin{bmatrix} \cos \alpha \\ \sin \alpha \end{bmatrix} = \lambda \begin{bmatrix} \cos \alpha \\ \sin \alpha \end{bmatrix} \quad (6.88)$$

where z is the absolute value of the complex number,

φ the angle of the complex number

λ the eigenvalue of the appropriate tensor and

α the polar angle of the eigenvector.

After trigonometric transformation we find that

$$\lambda = \pm z, \quad (6.89)$$

and

$$\alpha = \frac{\varphi}{2} \pm \frac{\pi}{4}, \quad (6.90)$$

On separating the two cases we arrive at

$$\begin{aligned} \lambda_1 &= z; & \alpha_1 &= \frac{\varphi}{2} + \frac{\pi}{4}; \\ \lambda_2 &= -z; & \alpha_2 &= \frac{\varphi}{2} - \frac{\pi}{4}. \end{aligned} \quad (6.91)$$

It is apparent that it is easy to determine the eigenvalues and directions of a tensor described by a complex number.

6.1.7. Elementary theory of streaming birefringence. Experience proves that during motion, non-newtonian liquids become optically anisotropic and show streaming birefringence. Birefringence can be observed by very sensitive methods hence, the measurement of streaming birefringence became an important experimental method for studying the dynamic structures formed by flow. A separate chapter will deal with the electromagnetic phenomena therefore, they will be discussed here only briefly [133, 143].

The optical properties of a medium are determined by the permittivity tensor. As usual, we assume the light passing through the medium does not influence the motion owing to its small amplitude. The permittivity tensor is a property of the medium in motion; thus, it is determined by the state parameters. Hence a function

$$\varepsilon = \varepsilon(u, v, \boldsymbol{\alpha}) \quad (6.92)$$

should exist, the linear approximation of which is

$$\varepsilon = \varepsilon(u, v)\boldsymbol{\delta} + \varepsilon^*(u, v)\boldsymbol{\alpha} \quad (6.93)$$

Here ε is the permittivity tensor,

ε^* a material coefficient and

$\boldsymbol{\alpha}$ the dynamic state parameter defined by equation (6.9).

In order to determine tensor α , we should turn to equation (6.10). Since the phenomenon is called streaming birefringence, a correlation is sought between tensors α and $\dot{\mathbf{d}}$. Upon eliminating \mathbf{t}^v from equation (6.10) and using the notations of equation (6.13) we obtain

$$\dot{\alpha} + \frac{1}{\tau_t} \alpha = \frac{L_{12}}{L_{11}} \dot{\mathbf{d}}, \quad (6.94)$$

which should be compared with equation (6.93). For convenience, let us introduce notation

$$\varepsilon_D = \varepsilon - \varepsilon(u, v) \delta \quad (6.95)$$

for the deviatoric part of the permittivity tensor:

$$\tau_t \dot{\varepsilon}_D + \varepsilon_D = \tau_t \varepsilon^* \frac{L_{12}}{L_{11}} \dot{\mathbf{d}} = 2\varepsilon^{**} \dot{\mathbf{d}}, \quad (6.96)$$

where ε^{**} is a new material coefficient.

By solving equation (6.96), we arrive at the description of the optical properties of flowing media. As an example, let us examine the optical behavior of the medium in shear flow. Since ε_D satisfies all the conditions necessary for the introduction of the complex notation, the solution of equation (6.96) is sought in a complex form. For simplicity, let us restrict ourselves to stationary shear flow whose velocity field is given by equation (6.23). Then $\dot{\mathbf{d}}$ corresponds to $\kappa/2$ and from the complex form of equation (6.96) we obtain that

$$\varepsilon_D = \frac{\varepsilon^{**} \kappa}{1 + i\tau_t \kappa}. \quad (6.97)$$

For the extent of birefringence, the absolute value of the complex number ε_D is characteristic:

$$|\varepsilon_D| = \frac{\varepsilon^{**} \kappa}{\sqrt{1 + \tau_t^2 \kappa^2}}. \quad (6.98)$$

On the other hand, the principal polarization directions are calculated on the basis of equation (6.90):

$$\alpha = \frac{\varphi}{2} \pm \frac{\pi}{4} \quad (6.99)$$

where

$$\tan \varphi = -\tau_t \kappa. \quad (6.100)$$

Thus, for small shear rates, the principal polarization directions point to the bisectors of axes x_1 and x_2 , which gradually turn over into the directions of x_1 and x_2 with increasing shear rate. Meanwhile, the magnitude of birefringence also increases gradually:

$$|\varepsilon_D| = \frac{\varepsilon^{**}}{\tau_t} \sin \varphi. \quad (6.101)$$

We utilized here the notation introduced in equation (6.100). Let us write the extent of birefringence for the light beam passing to the direction of axis x_3 :

$$\Delta n = \frac{1}{n} \frac{\varepsilon^{**} \kappa}{\sqrt{1 + \tau_t^2 \kappa^2}}; \quad (6.102)$$

where n is the refractivity of the medium at rest and Δn the difference in the refractivities of the two beams.

Finally, we mention that since ε_D has one positive, one negative and one zero eigenvalue, the three eigenvalues of ε are different. In the physical sense this means that the flowing medium behaves like an optically biaxial crystal, as seen from equation (6.97).

6.1.8. Deviations from linearity. Until now, we applied the strictly linear approximation of non-equilibrium thermodynamics: However, general quasi-linear theory allows for coefficients to depend also on dynamic state parameters. Let us now examine how our equations change if we allow the coefficients in equation (6.6) to depend linearly on the components of α . On utilizing the isotropy of the medium and restricting ourselves to volume preserving and isothermal motions, more general equations (instead of equation (6.10)),

$$\begin{aligned}\dot{\mathbf{d}} &= L_{11}\mathbf{t}^v - L_{12}\alpha + L'_{11} \left[\alpha\mathbf{t}^v + \mathbf{t}^v\alpha - \frac{2}{3}\delta(\alpha : \mathbf{t}^v) \right] - 2L'_{12} \left[\alpha^2 - \frac{1}{3}\delta(\alpha : \alpha) \right], \\ \dot{\alpha} &= L_{12}\mathbf{t}^v - L_{22}\alpha + L'_{12} \left[\alpha\mathbf{t}^v + \mathbf{t}^v\alpha - \frac{2}{3}\delta(\alpha : \mathbf{t}^v) \right] - 2L'_{22} \left[\alpha^2 - \frac{1}{3}\delta(\alpha : \alpha) \right],\end{aligned}\tag{6.103}$$

are obtained.

It is difficult to handle equations (6.103) mathematically; therefore, the general case will not be dealt with, only the specific case for which $L'_{22} = 0$ will be discussed. This choice has the advantage that equation (6.103b) becomes linear in the components of α . The complex representation can no longer be used since the non-linear terms lead non-zero matrix elements in position (3,3).

However, even this approximation has tremendous difficulties. If we want to calculate, e.g., the viscometric functions, then we look for tensors α and \mathbf{t}^v by knowing tensors $\dot{\mathbf{d}}$ and ω . The differential equations are not linear; thus calculations are tedious. For circumventing this difficulty, instead of writing equation (6.6) let us choose another representation. In writing the linear equations, let us consider \mathbf{J}_1 and \mathbf{X}_2 as independent variables instead of \mathbf{X}_1 and \mathbf{X}_2 . This representation has various advantages. Linear laws then have the form:

$$\begin{aligned}\mathbf{X}_1 &= \mathcal{H}_{11} : \mathbf{J}_1 + \mathcal{H}_{12} : \mathbf{X}_2, \\ \mathbf{J}_2 &= \mathcal{H}_{21} : \mathbf{J}_1 + \mathcal{H}_{22} : \mathbf{X}_2,\end{aligned}\tag{6.104}$$

where \mathcal{H}_{11} , \mathcal{H}_{21} , \mathcal{H}_{12} and \mathcal{H}_{22} are fourth order tensors satisfying Onsager-Casimir's reciprocal relations and depending on local state parameters. These equations take the following form for incompressible liquids in a quadratic approximation:

$$\begin{aligned}\mathbf{t}^v &= \mathcal{H}_{11}\dot{\mathbf{d}} - \mathcal{H}_{12}\alpha + \mathcal{H}'_{11} \left[\alpha\dot{\mathbf{d}} + \dot{\mathbf{d}}\alpha - \frac{2}{3}\delta(\alpha : \dot{\mathbf{d}}) \right] - 2\mathcal{H}'_{12} \left[\alpha^2 - \frac{1}{3}\delta(\alpha : \alpha) \right], \\ \dot{\alpha} &= -\mathcal{H}_{12}\dot{\mathbf{d}} - \mathcal{H}_{22}\alpha - \mathcal{H}'_{12} \left[\alpha\dot{\mathbf{d}} + \dot{\mathbf{d}}\alpha - \frac{2}{3}\delta(\alpha : \dot{\mathbf{d}}) \right] - 2\mathcal{H}'_{22} \left[\alpha^2 - \frac{1}{3}\delta(\alpha : \alpha) \right],\end{aligned}\tag{6.105}$$

This is essentially also a quadratic approximation but it is not equivalent to equation (6.103). The equations are not linear either. But if we assume that $\mathcal{H}_{22} = 0$,

then for a known velocity field the second equation becomes linear; from it, α can be determined and by substituting α into the first equation, the stress can be calculated.

To illustrate let us determine the viscometric functions as an example. However, let us first show that the linear partial sum of equation (6.105), i.e. the special case when $\mathcal{H}'_{11} = \mathcal{H}'_{12} = \mathcal{H}'_{22} = 0$ is equivalent to equation (6.10). To do this, let us express t^v and $\dot{\alpha}$ from equation (6.10):

$$\begin{aligned} t^v &= \frac{1}{L_{11}} \dot{\mathbf{d}} + \frac{L_{12}}{L_{11}} \alpha, \\ \dot{\alpha} &= \frac{L_{12}}{L_{11}} \dot{\mathbf{d}} - \frac{L_{11}L_{22} - L_{12}^2}{L_{11}} \alpha; \end{aligned} \quad (6.106)$$

from which expressions the coefficients \mathcal{H} are obtained as

$$\mathcal{H}_{11} = \frac{1}{L_{11}}; \quad \mathcal{H}_{12} = -\frac{L_{12}}{L_{11}}; \quad \mathcal{H}_{22} = \frac{(L_{11}L_{22} - L_{12}^2)}{L_{11}}.$$

Let us now proceed to the calculation of viscometric functions. Let the velocity field be given by equation (6.23), $\dot{\mathbf{d}}$ and ω by equation (6.24). Their substitution into the second equation of (6.105) and by the utilization of $\mathcal{H}'_{22} = 0$ give the following matrix equation:

$$\begin{aligned} -\frac{\kappa}{2} \begin{bmatrix} -2\alpha_{12} & \alpha_{11} - \alpha_{22} & -\alpha_{23} \\ \alpha_{11} - \alpha_{12} & 2\alpha_{12} & \alpha_{13} \\ -\alpha_{23} & \alpha_{13} & 0 \end{bmatrix} &= -\mathcal{H}_{12} \frac{\kappa}{2} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \\ -\mathcal{H}_{22} \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{12} & \alpha_{22} & \alpha_{23} \\ \alpha_{13} & \alpha_{23} & \alpha_{33} \end{bmatrix} - \mathcal{H}_{12} \frac{\kappa}{2} \begin{bmatrix} \frac{2}{3}\alpha_{12} & \alpha_{11} + \alpha_{22} & \alpha_{23} \\ \alpha_{11} + \alpha_{22} & \frac{2}{3}\alpha_{12} & \alpha_{13} \\ \alpha_{23} & \alpha_{13} & -\frac{4}{3}\alpha_{12} \end{bmatrix} & \quad (6.107) \end{aligned}$$

Let us first examine positions (1,3) and (2,3). The equation system obtained for the determination of α_{13} and α_{23} is linear and homogeneous; its determinant becomes zero only at a single, well-defined value of the shear rate. Disregarding this case, $\alpha_{13} = \alpha_{23} = 0$. On the basis of position (3,3), we may write that

$$\mathcal{H}_{22}\alpha_{33} = \frac{2\kappa}{3}\mathcal{H}'_{12}\alpha_{12}; \quad (6.108)$$

whereas from position (1,1) it follows that

$$\mathcal{H}_{22}\alpha_{11} = \kappa \left(1 - \frac{1}{3}\mathcal{H}'_{12} \right) \alpha_{12}, \quad (6.109)$$

Position (2,2) gives

$$\mathcal{H}_{22}\alpha_{22} = -\kappa \left(1 + \frac{1}{3}\mathcal{H}'_{12} \right) \alpha_{12}. \quad (6.110)$$

Finally, α_{12} may be calculated from position (1,2):

$$\alpha_{12} = \frac{-\frac{\mathcal{H}_{12}}{\mathcal{H}_{22}} \frac{\kappa}{2}}{1 + \frac{3 - \mathcal{H}'_{12}}{3\mathcal{H}'_{22}} \kappa^2}. \quad (6.111)$$

By knowing tensor α , the matrix of the viscous stress tensor can be calculated from the first equation of (6.105). This complex expression will not be provided here, but the viscometric functions obtained from them are the following:

$$\begin{aligned} t_{12}^v = \tau(\kappa) &= \eta \frac{\tau_d}{\tau_t} \kappa + \frac{\eta \left(1 - \frac{\tau_d}{\tau_t}\right) \kappa}{1 + \cos^2 \zeta_1 \tau_t^2 \kappa^2} \left(1 + \zeta_2 \tau_t^2 \kappa^2 + 2 \frac{\sin^2 \zeta_1 \tau_t^2 \kappa^2}{1 + \cos^2 \zeta_1 \tau_t^2 \kappa^2}\right), \\ t_{11}^v - t_{33}^v = \sigma_1(\kappa) &= \frac{\eta(\tau_t - \tau_d) \kappa^2}{1 + \cos^2 \zeta_1 \tau_t^2 \kappa^2} \left(1 - \sqrt{3} \sin \zeta_1 - \frac{\zeta_2 \sqrt{3}}{\sin \zeta_1}\right) - \\ &\quad - \frac{\eta(\tau_t - \tau_d) \kappa^2}{[1 + \cos^2 \zeta_1 \tau_t^2 \kappa^2]^2} \sqrt{3} \sin \zeta_1 \left[1 + \kappa^2 \tau_t^2 \left(\cos^2 \zeta_1 - \frac{2}{\sqrt{3}} \sin \zeta_1\right)\right], \\ t_{22}^v - t_{33}^v = \sigma_2(\kappa) &= -\frac{\eta(\tau_t - \tau_d) \kappa^2}{1 + \cos^2 \zeta_1 \tau_t^2 \kappa^2} \left(1 + \sqrt{3} \sin \zeta_1 + \frac{\zeta_2 \sqrt{3}}{\sin \zeta_1}\right) - \\ &\quad - \frac{\eta(\tau_t - \tau_d) \kappa^2}{[1 + \cos^2 \zeta_1 \tau_t^2 \kappa^2]^2} \sqrt{3} \sin \zeta_1 \left[1 + \kappa^2 \tau_t^2 \left(\cos^2 \zeta_1 + \frac{2}{\sqrt{3}} \sin \zeta_1\right)\right], \end{aligned} \quad (6.112)$$

Here correlations (6.107) and notation (6.13) are utilized and notations

$$\sin \zeta_1 = \frac{\mathcal{H}'_{12}}{\sqrt{3}}; \quad \zeta_2 = \frac{\mathcal{H}'_{11} \mathcal{H}'_{12} \mathcal{H}_{22}}{3\mathcal{H}_{12}} \quad (6.113)$$

are introduced. From equation (6.112), it is seen that in the quadratic approximation the sum of the two normal stress functions is not zero.

We only mention that birefringence can also be calculated in this approximation, but in this case it is advisable to also use a quadratic approximation instead of equation (6.93), which, for the deviatoric part of the permittivity tensor, leads to the form

$$\varepsilon_D = \varepsilon^* \alpha + \varepsilon^{***} \left[\alpha^2 - \frac{1}{3} \delta(\alpha : \alpha) \right] \quad (6.114)$$

where ε^{***} is another material constant. The calculated tensor α can be substituted into this expression, but the lengthy calculation is omitted.

Finally, we mention that the assumption $\mathcal{H}'_{22} = 0$ is reasonable. Namely, instead of the variable used so far, another variable, α , can be introduced by a topological transformation which does not change the form of the linear approximation, whose relaxation at $\dot{\mathbf{d}} = 0$ occurs strictly according to equation (6.10b). This variable has the disadvantage that the form of entropy is different from equation (6.1); thus equation (6.4) will not be strictly valid for X_2 . But this does not significantly change the form of quadratic equation (6.105).

6.1.9. Volume viscosity. Let us now turn back to the linear theory and examine the motion of a fluid whose volume changes, too. Assume again that the dynamic variable is a second order, zero trace, symmetric tensor. The choice of currents and forces should correspond to equations (6.3) and (6.4), and since we deal with a fluid, equation (6.7) may also be kept valid. Naturally, the form of linear laws will be different from equation (6.8). Utilizing the isotropy of the medium, linear constitutive equations are written as

$$\begin{aligned}\dot{\mathbf{d}}_D &= L_{11}\mathbf{t}_D^v - L_{12}\sqrt{\varrho T}\boldsymbol{\xi}; \\ \sqrt{\varrho T}\dot{\boldsymbol{\xi}} &= L_{21}\mathbf{t}_D^v - L_{22}\sqrt{\varrho T}\boldsymbol{\xi}; \\ \text{tr } \dot{\mathbf{d}} &= L_{11}^* \text{tr } \mathbf{t}^v\end{aligned}\tag{6.115}$$

where subscript D refers to the deviatoric part of the appropriate tensor. From the first two equations it is seen that the same equations hold for the deviatoric parts of $\dot{\mathbf{d}}$ and \mathbf{t}^v as in the case of constant-volume motions, and the third equation shows that the zero trace dynamic variable does not play any role in the phenomenon of volume viscosity.

The situation is completely different if the trace of the dynamic variable is not zero. Then, instead of equations (6.115), the following equations are obtained:

$$\begin{aligned}\dot{\mathbf{d}}_D &= L_{11}\mathbf{t}_D^v - L_{12}\sqrt{\varrho T}\boldsymbol{\xi}_D; \\ \sqrt{\varrho T}\dot{\boldsymbol{\xi}}_D &= L_{21}\mathbf{t}_D^v - L_{22}\sqrt{\varrho T}\boldsymbol{\xi}_D; \\ \text{tr } \dot{\mathbf{d}} &= L_{11}^* \text{tr } \mathbf{t}^v - L_{12}^*\sqrt{\varrho T} \text{tr } \boldsymbol{\xi}; \\ \sqrt{\varrho T} \text{tr } \dot{\boldsymbol{\xi}} &= L_{21}^* \text{tr } \mathbf{t}^v - L_{22}^*\sqrt{\varrho T} \text{tr } \boldsymbol{\xi}.\end{aligned}\tag{6.116}$$

The first group of the equations is unchanged; i.e., the connection between the deviatoric part remains the same. The part describing the volume change, i.e. the second group of the equations shows that the dynamic variable now influences volume changes similarly as it did earlier with respect to deformations. However, a significant difference is that in the second group of equations, the rotation of the medium does not play any role. This is easy to prove by a brief calculation. Thus, the volume changes can be followed by the method described in subsection 6.1.1. We also note that for quantities L_{11}^* , L_{12}^* , L_{21}^* and L_{22}^* in equation (6.116), the Onsager-Casimir reciprocal relations hold as well as the inequality (4.65) concerning them; but they have no relation to coefficients L_{ik} -s without asterisks as they are independent material constants. Another important difference is that the trace of the stress tensor is not zero even in equilibrium therefore, the mechanical models describing the volume viscosity of the medium characterized by equation (6.116) should be completed with a parallel spring as compared to the model given in subsection 6.1.1. The two rheological models are illustrated in Figures 6.14. and 6.15. (The former refers to an α -type, and the latter one, to a β -type dynamic variable.)

We mentioned that the deviatoric part and the trace of $\boldsymbol{\xi}$ may be regarded as two independent dynamic variables. In this case it is conceivable that the behavior of $\boldsymbol{\xi}_D$ and $\text{tr } \boldsymbol{\xi}$ is different with respect to time inversion. However, in this case

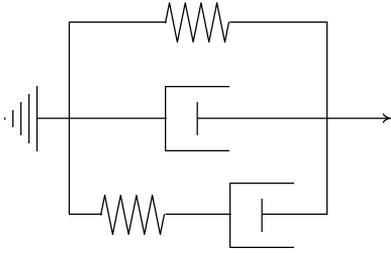


Figure 6.14

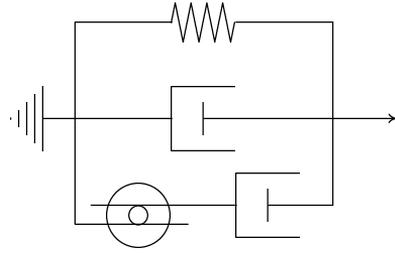


Figure 6.15

it is not appropriate to speak about a single dynamic degree of freedom; it should rather be said that two dynamic variables are needed: the one is a scalar; the other, a tensor with zero trace.

6.1.10. Motion of solid bodies. If the deformation is small for the motion of solid bodies, constitutive equations (6.115) and (6.116) may be given in an unchanged form. This means that for the deformation and volume change of solid bodies, the rheological models shown in Figures 6.14. and 6.15. can be applied. Thus this case will not be discussed here.

However, the situation is different for larger deformations, since the equilibrium state parameter \mathbf{d} representing deformation appears in linear laws (6.6). Another difference is that here the selection of the reference configuration is more restricted; hence, equation (6.7) does not hold.

With deformations, that are not too large however, we may presume about the linear laws that they are linear also in the components of $(\mathbf{d} - \delta)$. In this case due to the isotropy of the medium, linear laws — for simplicity, only their deviatoric parts — are written in the following form:

$$\begin{aligned} \frac{1}{2}(\dot{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\dot{\mathbf{d}})_D &= L_{11}\mathbf{t}^v_D - L_{12}\sqrt{\varrho T}\boldsymbol{\xi}_D + L'_{11} \left[\mathbf{t}^v\mathbf{d} + \mathbf{d}\mathbf{t}^v - \frac{2}{3}\delta(\mathbf{t}^v : \mathbf{d}) \right] - \\ &\quad - L'_{12}\sqrt{\varrho T} \left[\boldsymbol{\xi}\mathbf{d} + \mathbf{d}\boldsymbol{\xi} - \frac{1}{3}\delta(\boldsymbol{\xi} : \mathbf{d}) \right] + L^*_{11} \operatorname{tr} \mathbf{t}^v\mathbf{d}; \\ \sqrt{\varrho T}\dot{\boldsymbol{\xi}}_D &= L_{21}\mathbf{t}^v_D - L_{22}\sqrt{\varrho T}\boldsymbol{\xi}_D + L'_{21} \left[\mathbf{t}^v\mathbf{d} + \mathbf{d}\mathbf{t}^v - \frac{2}{3}(\mathbf{t}^v : \mathbf{d})\delta \right] - \\ &\quad - L'_{22}\sqrt{\varrho T} \left[\boldsymbol{\xi}\mathbf{d} + \mathbf{d}\boldsymbol{\xi} - \frac{2}{3}\delta(\mathbf{d} : \boldsymbol{\xi}) \right] + L^*_{12}(\operatorname{tr} \mathbf{t}^v)\mathbf{d}. \end{aligned} \tag{6.117}$$

Of course, these equations include also the anisotropy caused by deformation.

6.1.11. Some remarks on representation. At the beginning of this chapter the selection of X_2 in equation (6.4) might seem strange; furthermore, the introduction of variables α and β also requires explanation. The essence of the question is in the form of the entropy function and the selection of the dynamic variables. We have some freedom also in choosing the equilibrium state parameters; however, in this the traditions of thermostatics provide sufficient assurance by defining the so-called extensive variables. The situation is quite different in the choice of dynamic

variables. These are new variables necessary only out of equilibrium. If we know the quantitative physical meaning of the necessary dynamic variables and want to follow also their course, then the only problem is that the form of the entropy function differs from that given in equation (4.34) and this fact makes the calculations more difficult. Let us first examine this case. Let u be the specific internal energy; a_i the other state parameters; and ζ_j the dynamic variables which, we assume, we accurately know their physical meaning. In this case, the specific entropy may be given in the general form as

$$s = s(u, a_i, \zeta_j) \quad (6.118)$$

If we consider a small part of the medium in an environment with which there is no exchange of any chemical component, heat or work, then the values of equilibrium state parameters remains unchanged. (If this condition is not fulfilled, the selection of equilibrium state parameters has not been done well.) No similar constraints hold for the dynamic variables. If the system is under such conditions, its entropy can only increase; thus the conditions for equilibrium are provided by equations

$$\frac{\partial s}{\partial \zeta_j} = Z_j(u, a_i, \zeta_j) = 0 \quad (6.119a)$$

From these equations the equilibrium ζ_j^0 values of ζ_j are determined; if it were not so, further equilibrium state parameters would be needed that would contradict our hypothesis for choosing a_i -s. Since entropy is maximum in adiabatic equilibrium, we may write that

$$s = s(u, a_i, \zeta_j^0) - \Delta s(u, a_i, \zeta_j); \quad (6.119b)$$

where Δs is a non-negative function becoming zero only if $\zeta_j = \zeta_j^0$. In the close neighborhood of equilibrium, quadratic expansion of Δs yields

$$\Delta s = -\frac{1}{2} \left(\frac{\partial^2 s}{\partial \zeta_i \partial \zeta_j} \right)_0 (\zeta_i - \zeta_i^0)(\zeta_j - \zeta_j^0) \quad (6.120)$$

From this, correlation

$$Z_i = - \left(\frac{\partial^2 s}{\partial \zeta_i \partial \zeta_j} \right)_0 (\zeta_j - \zeta_j^0) \quad (6.121)$$

results. The use of the second derivatives in calculations is quite tedious. Thus in all cases in which the physical meaning of the dynamic variables is out of interest, we change for a new variable ξ which simplifies the calculations. An affine transformation and a subsequent continuous transformation (which does not concern the quadratic partial sum) lead to form

$$\Delta s = \frac{1}{2} \sum_i \xi_i^2 \quad (6.122)$$

which is equivalent to equation (4.34). Since between variables ζ and ξ a mutual one-to-one and continuous transformation exists, entropy may be written in the form

$$s = s_0(u, a_i) - \Delta s \quad (6.123)$$

The dynamic variables, thus transformed, may be called canonical dynamic variables belonging to the entropy. Obviously, $s_0(u, a_i)$ is the equilibrium entropy function whose value is identical with $s(u, a_i, \zeta_j^0)$ in equation (6.119).

Since orthogonal transformation carried out for canonical variables do not change the form of equation (6.122), this enables us to narrow further the definition of canonical variables. This can be done in the following way. Let us analyze the time course of dynamic variables. If the constant value of equilibrium state parameters is fixed by the environment, the entropy production is given by

$$\varrho \dot{s} = \sigma_s = -\varrho \xi_j \dot{\xi}_j, \quad (6.124)$$

from which Onsager's linear laws may be written as

$$\varrho \dot{\xi}_j = \sum_r L_{jr} \xi_r. \quad (6.125)$$

We utilize the above orthogonal transformation for bringing the symmetrical part of tensor $[L_{jr}]$ to diagonal form. Close to equilibrium, with this variables ξ_j are unambiguous except for the sign. If only Onsager's reciprocal relations hold, the mixed-index elements of matrix L_{jr} are zero; thus from equation (6.125), the simpler relations

$$\varrho \dot{\xi}_j = -L_j \xi_j \quad (6.126)$$

are obtained. (No summation has to be done for j -s.) If the medium does not rotate, the solution of the equation is

$$\xi_j = \xi_j(0) e^{-\frac{L_j}{\varrho} t} \quad (6.127)$$

By a further topological transformation, we can assume that the time course far from equilibrium (where laws (6.126) are no longer valid) would satisfy correlations

$$\frac{d}{dt} (\xi_j)^{\frac{1}{L_j}} = -(\xi_j)^{\frac{1}{L_j}} \quad (6.128)$$

Since the form of equations (6.126) is unchanged by transformations

$$|\xi_j^*| = |\xi_j|^\alpha; \quad \xi_j^* \xi_j \geq 0, \quad (6.129)$$

these can be used for ensuring the linearity of cross-effects coupling the quantities belonging to the equilibrium variables in as wide a range as possible. With this, we made the selection of canonical variables unambiguous, even far from equilibrium (aside from the sign).

Let us now proceed to energy representation. Notice that function $s_0(u, a_i)$ is a strictly increasing function of u and, thus, can be inverted with respect to u :

$$u = u_0(s + \Delta s, a_i) \quad (6.130)$$

Here $u_0(s_0, a_i)$ is a function known from thermostatics, which is a strictly increasing function of s_0 . Consequently, by utilizing the positive nature of Δs instead of equation (6.130), we may write that

$$u = u_0(s, a_i) + \Delta u \quad (6.131)$$

where Δu is zero in local equilibrium; otherwise, it is a positive quantity.

Our considerations for the selection of dynamic variables can be repeated now, and lead to

$$u = u_0(s, a_i) + \frac{1}{2} \sum_j \xi_j'^2 \quad (6.132)$$

When starting from the correlation

$$\varrho \dot{u} = 0 = \varrho \frac{\partial u_0}{\partial s} \dot{s} + \varrho \sum_j \xi_j' \dot{\xi}_j' \quad (6.133)$$

in the case of linear laws written for the canonical dynamic variables thus interpreted, then equations (6.125)-(6.129) remain valid. Note that temperature may be interpreted in entropy representation as

$$\frac{\partial s_0}{\partial u} = \frac{1}{T} \quad (6.134)$$

whereas in energy representation as

$$\frac{\partial u_0}{\partial s} = T \quad (6.135)$$

Naturally, the two interpretations are not identical, though they do not differ in linear order. The energy representation is close to the notations used traditionally; therefore, its application is often to be preferred.

It is easy to proceed from entropy representation to energy representation. On forming the objective time derivatives of both sides of equation (6.132), we obtain

$$\dot{u} = \frac{\partial u_0}{\partial s} \dot{s} + \frac{\partial u_0}{\partial a_i} \dot{a}_i + \sum_j \xi_j' \dot{\xi}_j' \quad (6.136)$$

and introducing equilibrium intensity parameters Γ_i by notations

$$\frac{\partial u_0}{\partial a_i} = \Gamma_i, \quad (6.137)$$

as well as utilizing equation (6.135) for the derivative with respect to entropy, we arrive at

$$T \dot{s} = \dot{u} - \Gamma_i \dot{a}_i - \sum_j \xi_j' \dot{\xi}_j'. \quad (6.138)$$

If we introduce entropy production repeatedly with this expression, we have to use the following transcription

$$\frac{\partial s_0}{\partial a_i} \longrightarrow -\frac{1}{T} \frac{\partial u_0}{\partial a_i}; \quad \xi_i \dot{\xi}_i \longrightarrow \frac{1}{T} \xi_j' \dot{\xi}_j'.$$

With that, we obtain an expression for $T\sigma_s$ which is easy to handle

$$T\sigma_s = \varrho T \dot{s} + T \operatorname{div} \frac{\mathbf{J}_q}{T} = \mathbf{J}_q T \operatorname{grad} \frac{1}{T} + \sigma_u - \varrho \Gamma_i \dot{a}_i - \varrho \sum_j \xi_j' \dot{\xi}_j'. \quad (6.139)$$

The selection of the representation is not a principal question; it is always made for convenience and according to personal taste.

6.2. Motion of a body with several dynamic variables.

Examine a medium whose description necessitates the use of more than one dynamic variables which is supposed to be zero trace second order tensors. In energy representation, the density of energy dissipation based on equation (4.27) by the assumption of an isothermal medium is:

$$T\sigma_s = \left(\mathbf{t} - \varrho \mathbf{d} \frac{\partial u_0}{\partial \mathbf{d}} \right) : \frac{1}{2} (\mathring{\mathbf{d}} \mathbf{d}^{-1} + \mathbf{d}^{-1} \mathring{\mathbf{d}}) - \varrho \sum_j \boldsymbol{\xi}_j : \mathring{\boldsymbol{\xi}}_j. \quad (6.140)$$

If for simplicity we consider only constant-volume motions and assume about tensor \mathbf{d}^{-1} that it is a unit tensor (either because the medium is a fluid or because the deformation is small) and introduce viscous stress tensor \mathbf{t}^v on the basis of equation (5.9), we obtain

$$T\sigma_s = \mathbf{t}^v : \mathring{\mathbf{d}} - \varrho \sum_j \boldsymbol{\xi}'_j : \mathring{\boldsymbol{\xi}}'_j. \quad (6.141)$$

Let us first examine the case when all the dynamic variables are invariant under time inversion. Then the introduction of notation

$$\sqrt{\varrho} \boldsymbol{\xi}'_j = \boldsymbol{\alpha}_j \quad (6.142)$$

is useful, as with it, the independent and dependent variables of linear laws are the following:

$$\mathbf{X}_0 = \mathring{\mathbf{d}}; \quad \mathbf{X}_j = -\boldsymbol{\alpha}_j; \quad \mathbf{J}_0 = \mathbf{t}^v; \quad \mathbf{J}_j = \mathring{\boldsymbol{\alpha}}_j. \quad (6.143)$$

By considering that \mathbf{X}_0 is a variable of the β -type, linear laws can be written as

$$\begin{aligned} \mathbf{t}^v &= L_{00} \mathring{\mathbf{d}} - \sum_j L_{0j} \boldsymbol{\alpha}_j; \\ \mathring{\boldsymbol{\alpha}}_j &= -L_{0j} \mathring{\mathbf{d}} - L_j \boldsymbol{\alpha}_j. \end{aligned} \quad (6.144)$$

These equations are similar to equation (6.10) only with more dynamic variables and $\mathring{\mathbf{d}}$ is chosen here as independent variable. This choice ensures, at the same time, that there is no coupling between individual $\boldsymbol{\alpha}_j$ -s. Initial conditions

$$\boldsymbol{\alpha}_j(0) = 0 \quad (6.145)$$

have to be considered also for a motion starting from equilibrium. If we know the velocity field, these equations are linear and relatively easy to solve. However, if we consider stress as the known quantity, our equations are non-linear and quite difficult to solve corresponding to the structure of the objective time derivative.

6.2.1. Small-amplitude oscillations. Let us now turn to small-amplitude oscillations. In this case the objective time derivatives can be regarded as identical with the partial derivatives with respect to time and the usual complex number formalism may be used. Then equation (6.144) becomes

$$\begin{aligned} \mathbf{t}^v &= L_{00} p \mathbf{d}_D - \sum_j L_{0j} \boldsymbol{\alpha}_j; \\ (L_j + p) \boldsymbol{\alpha}_j &= -L_{0j} p \mathbf{d}_D; \end{aligned} \quad (6.146)$$

from which α_j can be expressed and for the viscous stress tensor, an explicit expression is obtained:

$$\mathbf{t}^v = \left(L_{00} + \sum_j \frac{L_{0j}^2}{L_j + p} \right) p \mathbf{d}_D. \quad (6.147)$$

Let us consider, first, fluids for which $\mathbf{t}^v = \mathbf{t}_D$. If this is compared with equation (3.16), it is seen that our model for this fluid is identical with the generalized Maxwell body whose parameters are

$$\begin{aligned} \frac{1}{\mu_0} &= 0, & 2\eta_0 &= L_{00}; \\ 2\mu_i &= L_{0j}^2; & 2\eta_i &= \frac{L_{0j}^2}{L_j}. \end{aligned} \quad (6.148)$$

(Equality $1/\mu_0 = 0$ means that the spring of the 0-th Maxwell element is rigid, i.e. this is a Newton element.) Thus, in general, we may say that the behavior of a fluid model in small-amplitude oscillations can be described by a mechanical model consisting of Newton-element and as many Maxwell-elements in parallel connection as is the number of necessary α -type dynamic variables for characterizing the medium.

These results can readily be applied for solid bodies, taking into account only correlation $\mathbf{t} = \mathbf{t}^v + \mathbf{t}^e$. On using the form of Hooke's law given by equation (5.24), the stress deviator may be obtained from equation (6.147) as

$$\mathbf{t}_D = 2\mu(\mathbf{d} - \boldsymbol{\delta}) + \left(L_{00} + \sum_j \frac{L_{0j}^2}{L_j + p} \right) p \mathbf{d}_D. \quad (6.149)$$

Hence the mechanical model is given by connecting a spring with parameter μ parallel to a generalized Maxwell body.

Small changes in the volume do not significantly influence the above considerations, but the deviatoric part of the stress tensor should be substituted for stress. Simultaneously, the variation in volume and the trace of stress tensor should also be provided for which the whole chain of thought can be repeated with scalar dynamic parameters with the traces of tensors $\dot{\mathbf{d}}$ and \mathbf{t}^v . The equations thus obtained are formally analogous to equation (6.149), but with scalar variables. The number of dynamic variables and the values of parameters may, naturally, be different from those in equation (6.149). In equations describing volume changes, there is always an elastic term; thus, the mechanical models should always contain a spring in parallel connection.

6.2.2. Shear flow of liquids. Let us now examine the behavior of liquids described by equation (6.144) in the case of planar flow. The velocity field should be given then by equation (6.82). In the case of specified velocity distributions, the equations concerning the dynamic variables are solved individually; by inserting their solution into the first equation, the stress is determined.

However, this is not the task in the majority of practical cases, but mostly we look for velocity distribution in the knowledge of the stress field. In such cases the

problem is much more complex. However, solution is made easier by the fact that the third rows and third columns of matrices $\dot{\mathbf{d}}$ and $\boldsymbol{\omega}$ contain only zero elements; thus the third rows and columns of dynamic variables $\boldsymbol{\alpha}_j$ contain also only zero elements as is seen from equations (6.144). This fact enables us to use the complex formalism introduced in subsection 6.1.3. and generalized in 6.1.6. (Attention should be called to the fact that tensor \mathbf{d} has only small significance, since here the reference configuration continuously changes as is usual for liquids.) The solutions of the complex form of equations (6.144)

$$\begin{aligned} \mathbf{t}^v &= L_{00}\dot{\mathbf{d}} - \sum_j L_{0j}\boldsymbol{\alpha}_j; \\ \frac{d\boldsymbol{\alpha}_j}{dt} + 2i\boldsymbol{\omega}\boldsymbol{\alpha}_j &= -L_{0j}\dot{\mathbf{d}} - L_j\boldsymbol{\alpha}_j \end{aligned} \quad (6.150)$$

will be dealt with only for stationary shear flow, when the material derivative of dynamic variables with respect to time are zero. In this case, $\boldsymbol{\alpha}_j$ -s can easily be expressed and upon their substitution into the first equation, the correlation between stress and shear rate results in its complex form as

$$\mathbf{t}^v = L_{00}\frac{\kappa}{2} + \frac{1}{2}\sum_j \frac{L_{0j}^2\kappa}{L_j + \kappa i}; \quad (6.151)$$

where the notations introduced in subsection 6.1.2. are used.

From equation (6.151) the viscometric functions can be obtained:

$$\tau = L_{00}\frac{\kappa}{2} + \frac{1}{2}\sum_j \frac{L_j L_{0j}^2}{L_j^2 + \kappa^2}\kappa, \quad \sigma_1 = -\sigma_2 = \frac{1}{2}\sum_j \frac{L_{0j}^2\kappa^2}{L_j^2 + \kappa^2}. \quad (6.152)$$

These viscometric functions can be applied, naturally, not only for stationary shear flow, but for any viscometric flow, as well.

Though the viscometric functions thus calculated are directly suitable for practical application, cases may occur when the normal stress difference functions are necessary for a particular material about which we do not know how many dynamic variables are needed for characterizing them. The shear stress function is relatively easy to measure, and the majority of viscometers used in laboratories is applicable for this purpose. However, this is not true for the normal stress difference functions. Then the following procedure may be applied. We determine the shear stress function from the measured data in a form corresponding to equation (6.152a). This task is easy to perform by numerical methods elaborated on the basis of the constructive theory of functions. Thus σ_1 and σ_2 can be constructed from parameters L_j and L_{0j}^2 .

However, there is another method feasible for this purpose. For its application, let us rewrite equation (6.151) in a modified form:

$$\mathbf{t}^v = \left\{ L_{00} + \sum_j \frac{L_{0j}^2}{L_j + 2i\boldsymbol{\omega}} \right\} \dot{\mathbf{d}} = \eta(p)\kappa. \quad (6.153)$$

Here we introduced again the complex variable $p = 2i\omega$ and the complex viscosity $\eta(p)$ with which the viscometric functions stand in the following correlations:

$$\tau = \Re \eta \kappa, \quad \sigma_1 = -\sigma_2 = -\Im \eta \kappa. \quad (6.154)$$

Notice that the complex viscosity is a regular function of complex variable p on the closed right half plane whereas we are interested in its values only along the imaginary axis. This fact provides a possibility of determining the imaginary part of $\eta(i\kappa)$ when knowing its real part. The method used is the Hilbert transformation whose essence is the following:

Since $\eta(p)$ is regular on the closed right half plane, for any real κ the singularity of the function

$$f(p, \kappa) = \frac{\eta(p) - \eta(i\kappa)}{p - i\kappa} \quad (6.155)$$

at $p = i\kappa$ is removable. Therefore the contour of the integral of this function along any curve lying in the closed right half-plane is zero, which keeps itself away from $p = i\kappa$. By choosing the integration pathway (G) according to Figure 6.16,

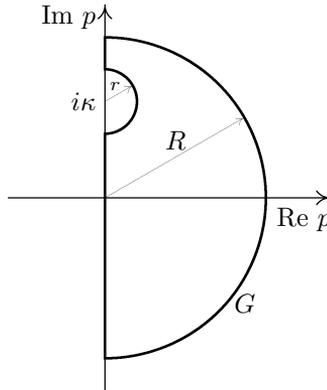


Figure 6.16

we may write:

$$\begin{aligned} \oint_S \frac{\eta(p) - \eta(i\kappa)}{p - i\kappa} dp &= \int_{-R}^{\kappa-r} \frac{\eta(it) - \eta(i\kappa)}{it - i\kappa} d(it) + \\ &+ \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{\eta(i\kappa + re^{i\varphi}) - \eta(i\kappa)}{re^{i\varphi}} d(re^{i\varphi}) + \\ &+ \int_{\kappa+r}^R \frac{\eta(it) - \eta(i\kappa)}{it - i\kappa} d(it) + \int_{\frac{\pi}{2}}^{-\frac{\pi}{2}} \frac{\eta(Re^{i\varphi}) - \eta(i\kappa)}{Re^{i\varphi} - i\kappa} d(Re^{i\varphi}) = 0. \end{aligned} \quad (6.156)$$

Let us now evaluate the limit when $r \rightarrow 0$ and $R \rightarrow \infty$ (In what follows,

$$\lim_{\varepsilon \rightarrow 0} \left(\int_{-\infty}^{\kappa - \varepsilon} \dots dt + \int_{\kappa + \varepsilon}^{\infty} \dots dt \right)$$

the so-called principal value of the integral will be denoted by $\int_{-\infty}^{\infty} \dots dt$.)

$$\int_{-\infty}^{\infty} \frac{\eta(it) - \eta(i\kappa)}{it - i\kappa} d(it) + i\pi[\eta(i\kappa) - \eta_{\infty}] = 0 \quad (6.157)$$

where it has been utilized that limit

$$\lim_{p \rightarrow \infty} \eta(p) = \eta_{\infty} \quad (6.158)$$

exists and is finite and even real as seen from equation (6.153). Upon separating the real and imaginary parts and utilizing that

$$\int_{-\infty}^{\infty} \frac{dt}{t - \kappa} = 0, \quad (6.159)$$

we arrive at expressions

$$\Im \eta(i\kappa) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Re \eta(it)}{t - \kappa} dt \quad (6.160)$$

and

$$\Re \eta(i\kappa) = \eta_{\infty} - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Im \eta(it)}{t - \kappa} dt$$

The first equation is suitable to determine the normal stress function if we know the shear stress function. On the basis of equation (6.154), the omission of complex notations gives

$$\begin{aligned} \sigma_1 = -\sigma_2 &= -\frac{\kappa}{\pi} \int_{-\infty}^{\infty} \frac{\tau(t)}{t(t - \kappa)} dt \\ \tau &= \eta_{\infty} \kappa + \frac{\kappa}{\pi} \int_{-\infty}^{\infty} \frac{\sigma_1(t)}{t(t - \kappa)} dt \end{aligned} \quad (6.161)$$

It will be shown later that these equations hold even if not all the dynamic variables are invariant under time inversion. Naturally, they cease to hold if non-linearities similar to those described in subsection 6.1.8. appear.

6.2.3. Several types of dynamic variables. It is not impossible in principle that part of the dynamic variables in equation (6.141) are even, and another part of them is odd with respect to time inversion. In this case the differential equations for the dynamic variables cannot be solved individually even if the velocity field is known. In these cases notation (6.142) loses its practicability, and the thermodynamic forces and currents may be selected as follows:

$$\begin{aligned} \mathbf{X}_0 &= \dot{\mathbf{d}}, & \mathbf{X}_j &= -\sqrt{\varrho}\dot{\xi}'_j; \\ \mathbf{J}_0 &= \mathbf{t}^v; & \mathbf{J}_j &= \sqrt{\varrho}\dot{\xi}''_j; \end{aligned} \quad (6.162)$$

Linear laws are now the following:

$$\begin{aligned} \mathbf{t}^v &= L_{00}\dot{\mathbf{d}} + \sum_j L_{0j}\mathbf{X}_j, \\ -\dot{\mathbf{X}}_k &= L_{k0}\dot{\mathbf{d}} + \sum_j L_{kj}\mathbf{X}_j, \end{aligned} \quad (6.163)$$

where the relation following from the constant volume and from equation (6.162)

$$\mathbf{J}_j = -\dot{\mathbf{X}}_j \quad (6.164)$$

is utilized. Plane motions can be described also here by complex expressions, which, for shear flow and arranging them for the unknown quantities, give

$$\begin{aligned} \mathbf{t}^v - \sum_j L_{0j}\mathbf{X}_j &= L_{00}\dot{\mathbf{d}}, \\ i\kappa\mathbf{X}_k + \sum_j L_{kj}\mathbf{X}_j &= -L_{k0}\dot{\mathbf{d}}. \end{aligned} \quad (6.165)$$

These equations are linear with respect to the quantities \mathbf{t}^v and \mathbf{X}_k . Thus, on the basis of Cramer's rule, \mathbf{t}^v may be calculated from them. Since the right-hand sides of all the equations are proportional to $\dot{\mathbf{d}}$, the result is

$$\mathbf{t}^v = 2\eta(i\kappa)\dot{\mathbf{d}} = \eta(i\kappa)\kappa, \quad (6.166)$$

where $2\eta(i\kappa)$ is the ratio of two determinants. As on the basis of the stability of thermodynamic equilibrium, it is clear that the complex function $\eta(p)$ cannot have either a pole or a zero on the closed right half-plane, correlations (6.161) between viscometric functions can be derived here, too. However, for the particular form of these functions, no general equation similar to equation (6.152) can be given; they will be different from case to case.

The attention of readers familiar with the theory of electric networks is called to the analogy existing between functions $\eta(i\kappa)$ and the impedances of electric circuits. By introducing analogies

$$\mathbf{t}^v \rightarrow U, \quad \eta \rightarrow Z, \quad \kappa \rightarrow I, \quad (6.167)$$

we may say that the viscometric functions according to correspondences

$$\Re U \rightarrow \tau, \quad \Im U \rightarrow -\sigma_1 = \sigma_2 \quad (6.168)$$

may show the same diversity as the transfer characteristics of electric two-poles. The other features of this electric analogy are also interesting, since according to equation (6.89), the absolute value of the complex stress provides the eigenvalues of the viscous stress tensor, whereas its phase gives the spatial directions of principal stresses. Another reason why this electric analogy is useful is that in this way the methods applied in the theory of linear networks may be directly employed.

6.2.4. Analogy with electric two-poles. Before elaborating the details of this analogy, let us notice that upon examining either small-amplitude oscillations or stationary shear flow, equations (6.163) may be rewritten in the form

$$\begin{aligned} \mathbf{t}^v &= L_{00} \dot{\mathbf{d}} + \sum_j L_{0j} \mathbf{X}_j; \\ -p \mathbf{X}_k &= L_{k0} \dot{\mathbf{d}} + \sum_j L_{kj} \mathbf{X}_j; \end{aligned} \quad (6.169)$$

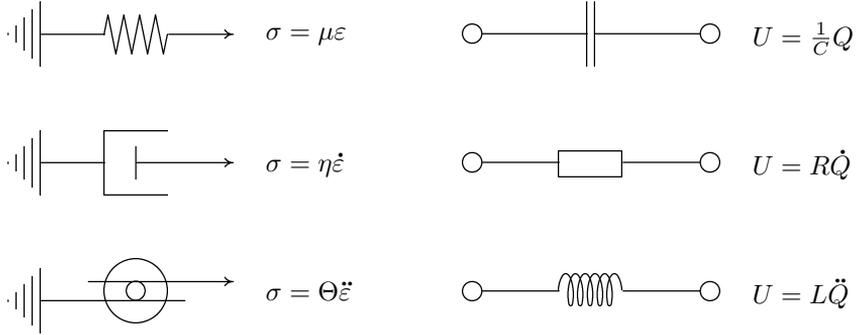
where only the meaning of the complex variable is different: for oscillations it is the complex frequency; for shear flow it is the product of shear rate and the imaginary unit. In writing the equations, we preserve the tensorial notation, since for oscillations \mathbf{t}^v , $\dot{\mathbf{d}}$ and \mathbf{X}_j are tensors with complex components; whereas for shear flow, they are complex numbers. However, this difference does not influence the formal way of calculations, thus the two cases are treated together.

In calculating \mathbf{t}^v from equations (6.169) we obtain that

$$\mathbf{t}^v = 2\eta(p) \dot{\mathbf{d}}, \quad (6.170)$$

where $2\eta(p)$ is the ratio of two determinants. Since the stability of thermodynamic equilibrium $\eta(p)$ is a positive real function. According to the theorem of Bott and Duffin [12], a two-pole consisting of capacitors, resistances and inductances can always be found whose impedance is this very function. This two-pole may be regarded as the electric model of the medium.

Let us now analyze in detail the correlation between the electrical and mechanical models. The mechanical model of the body described by equations (6.169) — though it is yet to be proved — consists of three types of elements. These are the linear spring, the dashpot and the inertia element introduced in subsection 6.1.1. Electric two-poles consist also of three types of elements: capacitors, resistors and inductors. Let us assume the analogies according to the arrangement:



It seems that analogy

$$U \leftrightarrow \sigma \quad Q \leftrightarrow \varepsilon$$

and, from this, analogies

$$\mu \leftrightarrow \frac{1}{C} \quad \eta \leftrightarrow R \quad \Theta \leftrightarrow L$$

are perfect. However, the question is not so simple. Let us examine how the partial currents, partial potentials and partial deformations correlate in the case of the serial or parallel connection of two elements:

Connection	U	Q	σ	ε
Serial	$U = U_1 + U_2$	$Q = Q_1 = Q_2$	$\sigma = \sigma_1 = \sigma_2$	$\varepsilon = \varepsilon_1 + \varepsilon_2$
Parallel	$U = U_1 = U_2$	$Q = Q_1 + Q_2$	$\sigma = \sigma_1 + \sigma_2$	$\varepsilon = \varepsilon_1 = \varepsilon_2$

It is apparent from the table that analogies only exist for the parallel connections in the mechanical model and the serial connections of the electric model and vice versa. However, due to the dual nature of electric networks, this does not cause any difficulty. We do not deal with the analogies of more complex networks, as they have not yet been applied for rheological problems. We provide two simpler (in Figure 6.17) and two more complex (in Figure 6.18) equivalent electric and mechanical models, as examples.

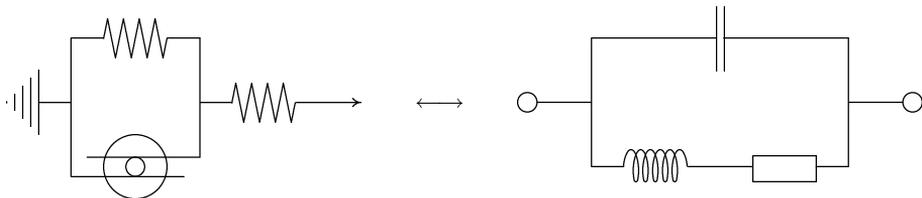


Figure 6.17

It is seen from the model that the mechanical model can be derived from the electric one as follows: Let us close the electric two-pole by a preferred edge. Construct the dual graph and place the analogous mechanical elements onto its appropriate

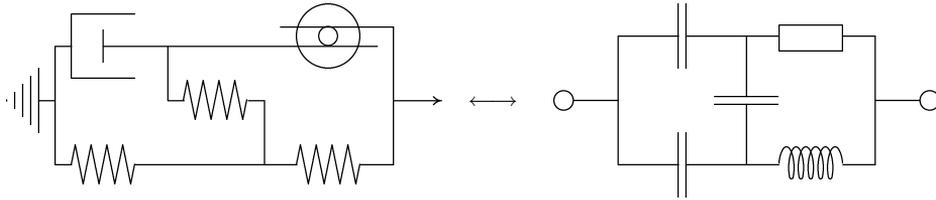


Figure 6.18

edges and finally, omit the preferred edge, fix its one end and put a load on the other. This procedure can be carried out in the reverse way, too.

The electric analogy may be generalized also for mechanical models describing plastic behavior and, thus, containing St. Venant-elements as well, only an idealized glow-discharge lamp or two oppositely connected Zener diodes should be introduced as analogies to the St. Venant-elements (Figure 6.19)

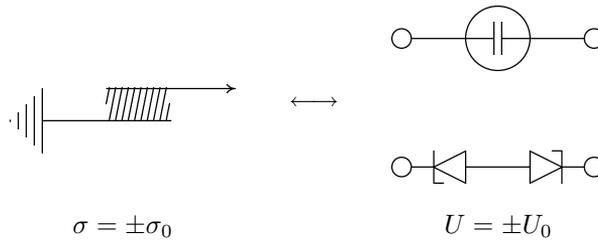


Figure 6.19

The main advantage of the above method is that the results of the theory of electric networks are easy to be transferred to mechanical problems.

6.2.5. Streaming birefringence. We turn back now to the case of pure α -type variables. The elementary theory of streaming birefringence outlined in subsection 6.1.7. can readily be generalized, only instead of equation (6.93), expression

$$\varepsilon = \varepsilon(u, v)\delta + \sum_j \varepsilon_j^*(u, v)\alpha_j \tag{6.171}$$

should be written. In the case of shear flow, the complex forms of α_j -s can be calculated from equation (6.150) and substituted into the complex form of the derivatoric part of tensor ε . Thus we arrive at the formula

$$\varepsilon_D = \sum_j \varepsilon_j^* \alpha_j = - \sum_j \frac{\varepsilon_j^* L_{0j}}{L_j + \kappa i} \frac{\kappa}{2} \tag{6.172}$$

If we introduce quantities

$$\varepsilon_j^{**} = \varepsilon_j^* \frac{L_{0j}}{2L_j}; \quad \tau_j = \frac{1}{L_j} \tag{6.173}$$

the result thus obtained is

$$\varepsilon_D = \sum_j \frac{\varepsilon_j^{**} \kappa}{1 + i\tau_j \kappa} \tag{6.174}$$

which is analogous to equation (6.97). The calculation of birefringence is now more complicated than in the case of equation (6.98), but it is feasible for particular cases.

6.2.6. Matrix representation of constitutive equations. If calculations have to be made by using several dynamic variables, matrices seem to be very useful tools for writing linear laws in a concise, symbolic way.

For the formulation of equation (6.163) in a matrix form, array the thermodynamic forces \mathbf{X}_j — which are also dynamic variables — into column matrices. The matrix obtained — which is a hypermatrix, in fact, denoted by \mathcal{X} — contains tensor \mathbf{X}_j in its j -th row. This matrix can be regarded as a second-order tensor whose components are column matrices. Correspondingly, the matrix form of equations (6.163) is:

$$\begin{aligned} \mathbf{t}^v &= L_{00}\dot{\mathbf{d}} + \mathcal{L}_{01}\mathcal{X}, \\ -\dot{\mathcal{X}} &= \mathcal{L}_{10}\dot{\mathbf{d}} + \mathcal{L}_{11}\mathcal{X}, \end{aligned} \quad (6.175)$$

where \mathcal{L}_{01} is the row matrix built of coefficients L_{0j} ; \mathcal{L}_{10} is the column matrix built of coefficients L_{k0} ; whereas the elements of quadratic matrix \mathcal{L}_{11} are coefficients L_{kj} .

The use of matrices results in an especially concise form of the complex formalism. Thus the matrix forms of complex equation (6.165) are:

$$\begin{aligned} \mathbf{t}^v &= L_{00}\dot{\mathbf{d}} + \mathcal{L}_{01}\mathcal{X}, \\ (i\kappa\delta + \mathcal{L}_{11})\mathcal{X} &= -\mathcal{L}_{10}\dot{\mathbf{d}}, \end{aligned} \quad (6.176)$$

where δ is the $n \times n$ unit matrix and n the number of complex variables. The correlation between stress and the deformation rate is easy to establish. We express, namely, \mathcal{X} from the second equation and insert it into the first one. From this,

$$\mathbf{t}^v = L_{00}\dot{\mathbf{d}} - \mathcal{L}_{01}(\mathcal{L}_{11} + i\kappa\delta)^{-1}\mathcal{L}_{10}\dot{\mathbf{d}}. \quad (6.177)$$

results. By using equality

$$(\mathcal{L}_{11} + i\kappa\delta)^{-1}(\mathcal{L}_{11} - i\kappa\delta)^{-1} = (\mathcal{L}_{11}^2 + \kappa^2\delta)^{-1}, \quad (6.178)$$

correlation

$$\mathbf{t}^v = L_{00}\dot{\mathbf{d}} - \mathcal{L}_{01}(\mathcal{L}_{11}^2 + \kappa^2\delta)^{-1}(\mathcal{L}_{11} - i\kappa\delta)\mathcal{L}_{10}\dot{\mathbf{d}} \quad (6.179)$$

is obtained. Since for shear flow $\dot{\mathbf{d}} = \kappa/2$ and the real part of \mathbf{t}^v is the shear stress function whereas its imaginary part is the (-1) -fold of normal stress function σ_1 , the separation of the real and imaginary parts leads to expressions

$$\tau(\kappa) = \frac{1}{2} [L_{00} - \mathcal{L}_{01}(\mathcal{L}_{11}^2 + \kappa^2\delta)^{-1}\mathcal{L}_{11}\mathcal{L}_{10}] \kappa. \quad (6.180)$$

and

$$\sigma_1(\kappa) = -\frac{1}{2} [\mathcal{L}_{01}(\mathcal{L}_{11}^2 + \kappa^2\delta)^{-1}\mathcal{L}_{10}] \kappa^2$$

for the viscometric functions. Provided that only α -type variables are involved in our equations, in canonical representation \mathcal{L}_{11} is a diagonal matrix and Onsager's reciprocal relations take the form

$$\mathcal{L}_{01} = -\mathcal{L}_{10}^T \quad (6.181)$$

By utilizing these, our equations transform into equations (6.152).

6.2.7. Plastic behavior. For studying the plastic properties of bodies characterized by several dynamic variables, we start from the arrangement described in subsection 6.1.5. The viscous stress tensor is given in this case also by equation (6.45), whereas the velocity gradient is sought in a form corresponding to equation (6.46). Based on this, $\boldsymbol{\omega}$ and $\dot{\boldsymbol{d}}$ can be given in the form of equation (6.47). It is not necessary now to calculate tensors \boldsymbol{t}^v and $\ddot{\boldsymbol{d}}$, as dynamic variables are not worth being eliminated from equations (6.175) now. However, we shall need the explicit form of $\dot{\boldsymbol{\mathcal{X}}}$ which in the stationary case is

$$\begin{aligned} \dot{\boldsymbol{\mathcal{X}}} &= \boldsymbol{\mathcal{X}}\boldsymbol{\omega} - \boldsymbol{\omega}\boldsymbol{\mathcal{X}} = \\ &= \begin{bmatrix} 2\omega_3\mathcal{X}_{12} & \omega_1\mathcal{X}_{13} - \omega_3(\mathcal{X}_{11} - \mathcal{X}_{22}) & \omega_3\mathcal{X}_{23} - \omega_1\mathcal{X}_{12} \\ \omega_1\mathcal{X}_{13} - \omega_3(\mathcal{X}_{11} - \mathcal{X}_{22}) & 2\omega_1\mathcal{X}_{23} - 2\omega_3\mathcal{X}_{12} & \omega_1(\mathcal{X}_{33} - \mathcal{X}_{22}) - \omega_3\mathcal{X}_{13} \\ \omega_3\mathcal{X}_{23} - \omega_1\mathcal{X}_{12} & \omega_1(\mathcal{X}_{33} - \mathcal{X}_{22}) - \omega_3\mathcal{X}_{13} & -2\omega_1\mathcal{X}_{23} \end{bmatrix} \end{aligned} \quad (6.182)$$

Concerning the possible solutions of equation (6.175), here, too, more cases may be distinguished; but now case 1 will be broken into two subcases.

In subcase 1a, let $\vec{\omega}$ be equal to zero. Then expressing $\boldsymbol{\mathcal{X}}$ from the second equation and inserting it into the first one, we obtain

$$\begin{aligned} \boldsymbol{\mathcal{X}} &= -\mathcal{L}_{11}^{-1}\mathcal{L}_{10}\dot{\boldsymbol{d}} \\ \boldsymbol{t}^v &= (L_{00} - \mathcal{L}_{01}\mathcal{L}_{11}^{-1}\mathcal{L}_{10})\dot{\boldsymbol{d}} \end{aligned} \quad (6.183)$$

By introducing notation

$$L_{00} - \mathcal{L}_{01}\mathcal{L}_{11}^{-1}\mathcal{L}_{10} = 2\eta, \quad (6.184)$$

we arrive at

$$\dot{\boldsymbol{d}} = \frac{\sigma}{6\eta} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (6.185)$$

In subcase 1b let $\omega_3 = 0$, but $\omega_1 \neq 0$. The solution of the equations remains unchanged, since $\dot{\boldsymbol{\mathcal{X}}}$ remains zero as it can be calculated from equations (6.185), (6.183) and (6.182). Hence, case 1 corresponds to a linear, viscous flow also for media characterizable with several dynamic variables. This flow is identical with the phenomenon of creep for plastic media.

By analogy to the behavior of media characterizable by one dynamic variable, the stationary solution in which $\omega_3 \neq 0$ but $\omega_1 = 0$ is considered case 2. Case 3 is when neither $\omega_3 = 0$ nor $\omega_1 = 0$. In case 2, equations are written first for tensor components (1,3) and (2,3):

$$\begin{aligned} 0 &= \mathcal{L}_{01}\mathcal{X}_{13} & -\omega_3\mathcal{X}_{23} &= \mathcal{L}_{11}\mathcal{X}_{13} \\ 0 &= L_{00}\dot{d}_{23} + \mathcal{L}_{01}\mathcal{X}_{23}; & \omega_3\mathcal{X}_{13} &= \mathcal{L}_{10}\dot{d}_{23} + \mathcal{L}_{11}\mathcal{X}_{23} \end{aligned} \quad (6.186)$$

The expression of \mathcal{X}_{23} from the second equation and its substitution into the third and fourth equations give

$$\begin{aligned} 0 &= L_{00}\dot{d}_{23} + \mathcal{L}_{01} \left(-\frac{1}{\omega_3}\mathcal{L}_{11}\mathcal{X}_{13} \right), \\ \omega_3\mathcal{X}_{13} &= \mathcal{L}_{10}\dot{d}_{23} + \mathcal{L}_{11} \left(-\frac{1}{\omega_3}\mathcal{L}_{11}\mathcal{X}_{13} \right). \end{aligned} \quad (6.187)$$

Expressing now \mathcal{X}_{13} from the second equation and inserting it into the first one we arrive at

$$0 = [L_{00} - \mathcal{L}_{01}(\mathcal{L}_{11}^2 + \omega_3^2\delta)^{-1}\mathcal{L}_{11}\mathcal{L}_{10}] \dot{d}_{23}; \quad (6.188)$$

where the coefficient of \dot{d}_{23} depends on ω_3 in the same way as the quantity in brackets in the shear stress function in equation (6.180). From this it follows that $\dot{d}_{23} = 0$, as $\tau(\kappa)$ cannot be zero and thus the coefficients of \dot{d}_{23} cannot be zero either in equation (6.188) if $\omega_3 \neq 0$. The results from the second equation of (6.187) is that $\mathcal{X}_{13} = 0$; and from the second equation of (6.186) $\mathcal{X}_{23} = 0$.

Examine now position (3,3). Then

$$\begin{aligned} -\frac{\sigma}{3} &= L_{00}\dot{d}_{33} + \mathcal{L}_{01}\mathcal{X}_{33}; \\ 0 &= \mathcal{L}_{10}\dot{d}_{33} + \mathcal{L}_{11}\mathcal{X}_{33}; \end{aligned} \quad (6.189)$$

whence for \mathcal{X}_{33} and \dot{d}_{33}

$$\begin{aligned} -\frac{\sigma}{3} &= (L_{00} - \mathcal{L}_{01}\mathcal{L}_{11}^{-1}\mathcal{L}_{10})\dot{d}_{33} = 2\eta\dot{d}_{33}; \\ \dot{d}_{33} &= -\frac{\sigma}{6\eta}; \\ \mathcal{X}_{33} &= \frac{\sigma}{6\eta}\mathcal{L}_{11}^{-1}\mathcal{L}_{10} \end{aligned} \quad (6.190)$$

is obtained. Let us now write the equation for tensor components with subscripts (1,1) and (1,2):

$$\begin{aligned} \frac{2\sigma}{3} &= L_{00}\dot{d}_{11} + \mathcal{L}_{01}\mathcal{X}_{11}; \\ -2\omega_3\mathcal{X}_{12} &= \mathcal{L}_{10}\dot{d}_{11} + \mathcal{L}_{11}\mathcal{X}_{11} \\ 0 &= -L_{00}\omega_3 + \mathcal{L}_{01}\mathcal{X}_{12} \\ \omega_3(2\mathcal{X}_{11} + \mathcal{X}_{33}) &= -\mathcal{L}_{10}\omega_3 + \mathcal{L}_{11}\mathcal{X}_{12} \end{aligned} \quad (6.191)$$

These equations are quite difficult to solve. However, the difficulties can be circumvented if we regard σ as unknown, instead of ω_3 . In this case the equations are linear and their solution for \dot{d}_{11} and σ provides the correlation between these variables in a parametric form with ω_3 as a parameter. By expressing \mathcal{X}_{12} from the second equation and substituting it into the others, the first one remains unchanged; and instead of the third and fourth, we may write

$$\begin{aligned} 0 &= 2L_{00}\omega_3^2 + \mathcal{L}_{01}\mathcal{L}_{10}\dot{d}_{11} + \mathcal{L}_{01}\mathcal{L}_{11}\mathcal{X}_{11} \\ 0 &= 4\omega_3^2\mathcal{X}_{11} + 2\omega_3^2\mathcal{X}_{33} + 2\mathcal{L}_{10}\omega_3^2 + \mathcal{L}_{11}\mathcal{L}_{10}\dot{d}_{11} + \mathcal{L}_{11}^2\mathcal{X}_{11} \end{aligned} \quad (6.192)$$

The expression of \mathcal{X}_{11} and its insertion into the first equation as well as into equation (6.191b) provides the following equations for σ and \dot{d}_{11} ;

$$\begin{aligned} \frac{\sigma}{2} + (L_{00} - a_1) \left(\frac{\sigma}{12\eta} - \dot{d}_{11} \right) &= 2\omega_3^2 a_0, \\ 2a_0 \left(\frac{\sigma}{12\eta} - \dot{d}_{11} \right) &= L_{00} - a_1, \end{aligned} \quad (6.193)$$

where notations

$$\begin{aligned} a_0 &= \mathcal{L}_{01}(\mathcal{L}_{11}^2 + 4\omega_3^2\delta)^{-1}\mathcal{L}_{10} \\ a_1 &= \mathcal{L}_{01}\mathcal{L}_{11}(\mathcal{L}_{11}^2 + 4\omega_3^2\delta)^{-1}\mathcal{L}_{10} \end{aligned} \quad (6.194)$$

have been introduced. It should be noted that functions a_0 and a_1 are in a close relationship with the viscometric functions (6.180). Let us now introduce notation

$$\kappa = 2\omega_3 \quad (6.195)$$

into equations (6.194); then a simple calculation provides for the viscometric functions the following expressions:

$$\tau(\kappa) = \frac{\kappa[L_{00} - a_1(\kappa)]}{2}; \quad \sigma_1 = -\frac{a_0(\kappa)\kappa^2}{2} \quad (6.196)$$

By preserving notation (6.195), equations (6.193) take the following form:

$$\begin{aligned} \frac{\sigma}{2} + \frac{2\tau(\kappa)}{\kappa} \left[\frac{\sigma}{12\eta} - \dot{d}_{11} \right] &= \sigma_1(\kappa), \\ \frac{\sigma}{12\eta} - \dot{d}_{11} &= -\frac{\kappa\tau(\kappa)}{2\sigma_1(\kappa)}. \end{aligned} \quad (6.197)$$

From these equations σ and \dot{d}_{11} may be determined as functions of parameter κ :

$$\begin{aligned} \sigma &= 2\frac{\sigma_1(\kappa)^2 + \tau(\kappa)^2}{\sigma_1(\kappa)}, \\ \dot{d}_{11} &= \frac{\sigma_1(\kappa)^2 + \tau(\kappa)^2 + 3\eta\kappa\tau(\kappa)}{6\eta\sigma_1(\kappa)}. \end{aligned} \quad (6.198)$$

The correlation between tensile stress and \dot{d}_{11} is, in general, non-linear. On determining the critical tensile stress from equation (6.198), we obtain

$$\sigma_{\text{crit}} = 2 \lim_{\kappa \rightarrow 0} \frac{\tau(\kappa)^2}{\sigma_1(\kappa)}. \quad (6.199)$$

By calculating the limit for \dot{d}_{11} when $\kappa \rightarrow 0$, we see that the limiting point of correlation (6.198) describing section 2 satisfies also the linear correlation (6.185) valid for creep. Calculations for case 3 will not be carried out because they would be very lengthy.

Examine now how far case 1a is stable. For components (1,2) of equations (6.175) for cases of small ω_3 and small deviations from equation (6.185), we arrive at

$$\begin{aligned} 0 &= -L_{00}\omega_3 + \mathcal{L}_{01}\mathcal{X}_{12}; \\ -\dot{\mathcal{X}}_{12} - \omega_3\mathcal{L}_{11}^{-1}\mathcal{L}_{10}\frac{\sigma}{2\eta} &= -\mathcal{L}_{10}\omega_3 - \mathcal{L}_{11}\mathcal{X}_{12}; \end{aligned} \quad (6.200)$$

in which we utilized equations (6.183) and (6.185) as well. The differential equation obtained is linear in \mathcal{X}_{12} and ω_3 . Its characteristic equation, by substitution

$$\dot{\mathcal{X}}_{12} = p\mathcal{X}_{12} \quad (6.201)$$

is as follows:

$$\begin{vmatrix} -L_{00} & \mathcal{L}_{01} \\ -\mathcal{L}_{10} + \mathcal{L}_{11}^{-1}\mathcal{L}_{10}\frac{\sigma}{2\eta} & \mathcal{L}_{11} + p\delta \end{vmatrix} = 0. \quad (6.202)$$

Critical stress is obtained by substitution $p = 0$. In calculations, by multiplying the characteristic equation from the left by the determinant of the hypermatrix

$$\begin{bmatrix} 1 & 0 \\ 0 & \mathcal{L}_{11}^{-1} \end{bmatrix}$$

and utilizing the multiplication rule of determinants, we may write that

$$\begin{vmatrix} L_{00} & \mathcal{L}_{01} \\ \mathcal{L}_{11}^{-1}\mathcal{L}_{10} - \mathcal{L}_{11}^{-2}\mathcal{L}_{10}\frac{\sigma_{crit}}{2\eta} & \delta \end{vmatrix} = 0 \quad (6.203)$$

The expansion of this determinant results in

$$L_{00} - \mathcal{L}_{01}\mathcal{L}_{11}^{-1}\mathcal{L}_{10} + \frac{\sigma_{crit}}{2\eta}\mathcal{L}_{01}\mathcal{L}_{11}^{-2}\mathcal{L}_{10} = 0 \quad (6.204)$$

whence

$$\sigma_{crit} = -\frac{(2\eta)^2}{\mathcal{L}_{01}\mathcal{L}_{11}^{-2}\mathcal{L}_{10}}. \quad (6.205)$$

The form of equation (6.180) for viscometric functions convinces us that the critical tensile stress obtained is identical with that given by equation (6.199). This means that at a certain critical stress, creep loses its stability and plastic flow starts. Naturally, these considerations do not hold for any medium: since $\sigma_{crit} < 0$ is also possible and in this case there is no creep, and case 2 cannot be called plastic flow. However, this latter case can only exist if β -type variables also occur among the dynamic variables.

Finally we note that in our previous calculations we have assumed that the root of characteristic equation (6.202) which is closest to the imaginary axis is a real number. This hypothesis is always true for cases where only α -type dynamic variables are present.

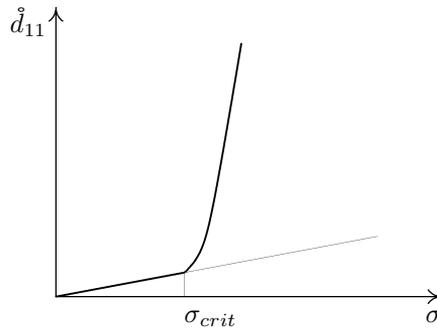


Figure 6.20

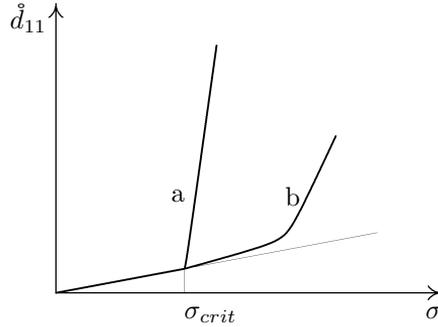


Figure 6.21

Figure 6.20 illustrates the first two sections of the correlation between tensile stress and the relative rate of stretching for a given medium characterized by two α -type dynamic variables. It should be noted that for other value of parameters it may occur that the break in the curve or its subsequent curvature is not so apparent (Figure 6.21). Finally, let us investigate the plastic behavior in plane flow. Similar to stretching along a single axis, some kinematic restrictions have to be made for the flow pattern. Let us take the axes of the coordinate system so that the matrix of the stress tensor be

$$\mathbf{t} = \begin{bmatrix} \sigma & 0 & 0 \\ 0 & -\sigma & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad (6.206)$$

i.e. motion should occur in the x_1x_2 plane. Let us assume about the flow pattern that it does not change the direction of vector

$$\mathbf{e} = \cos \alpha \mathbf{e}_1 + \sin \alpha \mathbf{e}_2 \quad (6.207)$$

Based on this, we may write:

$$\begin{bmatrix} \dot{d}_{11} & \dot{d}_{12} - \omega_3 & 0 \\ \dot{d}_{12} + \omega_3 & -\dot{d}_{11} & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \cos \alpha \\ \sin \alpha \\ 0 \end{bmatrix} = \lambda \begin{bmatrix} \cos \alpha \\ \sin \alpha \\ 0 \end{bmatrix} \quad (6.208)$$

whence

$$\tan \alpha = \frac{(\dot{d}_{12} + \omega_3) \cos \alpha - \dot{d}_{11} \sin \alpha}{\dot{d}_{11} \cos \alpha + (\dot{d}_{12} - \omega_3) \sin \alpha} \quad (6.209)$$

follows. From this, a simple calculation gives correlation

$$\omega_3 = \dot{d}_{11} \sin 2\alpha - \dot{d}_{12} \cos 2\alpha. \quad (6.210)$$

In the case of planar flow, equations (6.175) may be rewritten into the complex form by using the formalism given in subsection 6.1.6.:

$$\begin{aligned} \mathbf{t}^v &= L_{00} \dot{\mathbf{d}} + \mathcal{L}_{01} \mathcal{X}; \\ 2\omega_3 i \mathcal{X} &= \mathcal{L}_{10} \dot{\mathbf{d}} + \mathcal{L}_{11} \mathcal{X} \end{aligned} \quad (6.211)$$

The correlation between stress and the deformation rate can be obtained by eliminating \mathcal{X} :

$$\mathbf{t}^v = L_{00}\dot{\mathbf{d}} - \mathcal{L}_{01}(\mathcal{L}_{11} - 2\omega_3 i\delta)^{-1}\mathcal{L}_{10}\dot{\mathbf{d}} \quad (6.212)$$

which, after removing $i = \sqrt{-1}$ from the reciprocal matrix, becomes

$$\mathbf{t} = [L_{00} - \mathcal{L}_{01}(\mathcal{L}_{11}^2 + 4\omega_3^2\delta)^{-1}(\mathcal{L}_{11} + 2\omega_3 i\delta)\mathcal{L}_{10}] \dot{\mathbf{d}} \quad (6.213)$$

The correlation between the right side of this equation and the viscometric functions can be established by introducing the quantity

$$\kappa = -2\omega_3 \quad (6.214)$$

and utilizing the form of viscometric functions given by equation (6.180). Then, instead of equation (6.213), the very illustrative form of

$$\mathbf{t}^v = \left(\frac{2\tau}{\kappa} - i\frac{2\sigma_1}{\kappa} \right) \dot{\mathbf{d}} \quad (6.215)$$

can be written. Let us now consider the complex form of stress, $\mathbf{t} = i\sigma$, and rewrite correlation (6.210) by substituting equation (6.214). In this case

$$\begin{aligned} -i\sigma &= \frac{2}{\kappa}(\tau - i\sigma_1)(\dot{d}_{12} - i\dot{d}_{11}), \\ -\frac{\kappa}{2} &= \dot{d}_{11} \sin 2\alpha - \dot{d}_{12} \cos 2\alpha \end{aligned} \quad (6.216)$$

may be written, from where, \dot{d}_{11} , \dot{d}_{12} and κ can be determined. A more convenient solution is to regard the quantities, \dot{d}_{11} and \dot{d}_{12} as functions of κ :

$$\begin{aligned} \dot{d}_{12} &= \frac{\sigma_1}{\tau} \dot{d}_{11}; \\ \sigma &= 2\frac{\sigma_1^2 + \tau^2}{\kappa\tau} \dot{d}_{11} \\ \dot{d}_{11} &= \frac{\kappa/2}{\frac{\sigma_1}{\tau} \cos 2\alpha - \sin 2\alpha} \end{aligned} \quad (6.217)$$

When analyzing these equations we find that for $\kappa \rightarrow 0$, \dot{d}_{11} , \dot{d}_{12} , and σ also tend to zero except for the case when $\sin 2\alpha = 0$. Then, the equation for \dot{d}_{11} has the form:

$$\dot{d}_{11} = \frac{\kappa\tau}{2\sigma_1} \quad (6.218)$$

which has a finite limit for $\kappa \rightarrow 0$. Upon substituting this into the second equation, we obtain

$$\sigma = \frac{\sigma_1^2 + \tau^2}{\sigma_1} \quad (6.219)$$

On comparing this with equation (6.198) for stretching along a single axis, it can be seen that in the limiting case $\kappa \rightarrow 0$ plastic flow starts in both stretching along

a single axis and planar flow when the difference between the largest and smallest principal stresses reaches the critical value σ^* which is given by formula

$$\sigma^* = \lim_{\kappa \rightarrow 0} 2 \frac{\sigma_1^2 + \tau^2}{\sigma_1} = \lim_{\kappa \rightarrow 0} \frac{2\tau^2}{\sigma_1} \quad (6.220)$$

Summarizing, we can establish that the correlations obtained show unequivocally that the results derived by the thermodynamic theory are consistent with the yield conditions tried and proved in practice.

6.3. Some limit cases.

It has already been mentioned in subsection 6.1.8. that in the general case the coefficients in linear laws may depend on local state parameters, which are often called quasi-linear in the literature. However, the case of dynamic variables defined here ensures wide possibilities for non-linearity, since thermodynamic forces and local state parameters cannot be sharply separated.

Let us briefly analyze now what possibilities are allowed by Onsager's theory. For simplicity, we restrict our study for a single dynamic variable. The new dynamic variable has been reintroduced as it has been made in equations (6.142) and (6.143), together with thermodynamic forces and currents. Linear laws will be written now in a more general form than they are given in equation (6.144). By utilizing the isotropic nature of the medium and the canonical nature of the dynamic variable, we obtain:

$$\begin{aligned} \mathbf{t}^v &= L_{00} \dot{\mathbf{d}} + L'_{00}(\boldsymbol{\alpha}, \dot{\mathbf{d}}) - L_{01} \boldsymbol{\alpha} - L'_{01}(\boldsymbol{\alpha}, \boldsymbol{\alpha}), \\ \dot{\boldsymbol{\alpha}} &= -L_{01} \dot{\mathbf{d}} - L'_{01}(\boldsymbol{\alpha}, \dot{\mathbf{d}}) - L_1 \boldsymbol{\alpha}, \end{aligned} \quad (6.221)$$

where $L'_{00}(\boldsymbol{\alpha}, \dot{\mathbf{d}})$ and $L'_{01}(\boldsymbol{\alpha}, \dot{\mathbf{d}})$ are isotropic tensor functions of $\boldsymbol{\alpha}$ and $\dot{\mathbf{d}}$. These functions are linear for the components of $\dot{\mathbf{d}}$ and may depend almost arbitrarily on $\boldsymbol{\alpha}$. The study of these functions is rather difficult. Therefore we deal only with the case where $L'_{01}(\boldsymbol{\alpha}, \dot{\mathbf{d}}) = 0$. Then, the second equation is simplified and becomes a linear one.

Let us first suppose that L_1 is very large. Then the relaxation of the dynamic variable is relatively fast and we may say that the dynamic variable follows the changes of $\dot{\mathbf{d}}$. In this case, from equation (6.221b), it follows that

$$\boldsymbol{\alpha} = -\frac{L_{01}}{L_{11}} \dot{\mathbf{d}} \quad (6.222)$$

whose substitution into equation (6.221a) shows that \mathbf{t}^v depends on $\dot{\mathbf{d}}$ in an isotropic way; i.e., the general theory for processes that are not too fast (the dynamic variable cannot follow very fast processes) gives room for almost any $\mathbf{t}^v(\dot{\mathbf{d}})$ function which is approximately linear for small deformation rate. As a second case, let us examine how the medium behaves for small L_1 by assuming further that $L'_{01} = 0$. In this case the dynamic variable relaxes only slowly; its changes are mainly due to $\dot{\mathbf{d}}$. If, in addition, the value of L_{01} in the first equation of (6.221) can be also neglected, it can be seen that the liquid is viscous, but its viscosity depends significantly on $\boldsymbol{\alpha}$,

it may even become anisotropic. If we consider only media which do not become anisotropic, then equation (6.221) simplifies to approximation

$$\begin{aligned} \mathbf{t}^v &= L_{00}(\boldsymbol{\alpha})\dot{\mathbf{d}} \\ \dot{\boldsymbol{\alpha}} &= -L_{01}\dot{\mathbf{d}} - L_1\boldsymbol{\alpha} \end{aligned} \quad (6.223)$$

from which deviation is only observed if $\dot{\mathbf{d}} \approx 0$ and the term $-L_{01}\boldsymbol{\alpha}$ neglected so far becomes predominant. From these relations the following conclusions can be drawn: If the medium has been at rest for a long period, the value of the dynamic variable is zero. By setting the medium into motion, the value of the dynamic variable changes, which results in a change of the viscosity. Due to the slow relaxation of the dynamic variable, viscosity returns to its initial value only after a long rest.

Since function $L_{00}(\boldsymbol{\alpha})$ may have different forms, this formalism allows a wide variety of thixotropy and reopexy.

Finally, let us analyze the case where linear laws hold in their form described by equation (6.144), but L_{00} is zero and there is only a single dynamic variable. Then

$$\begin{aligned} \mathbf{t}^v &= -L_{01}\boldsymbol{\alpha}, \\ \dot{\boldsymbol{\alpha}} &= -L_{01}\dot{\mathbf{d}} - L_1\boldsymbol{\alpha}, \end{aligned} \quad (6.224)$$

By eliminating from these equations, expression

$$\dot{\mathbf{t}}^v + L_1\mathbf{t}^v = L_{01}^2\dot{\mathbf{d}} \quad (6.225)$$

results, which is the differential equation of a Maxwell-fluid.

ELECTRIC POLARIZATION IN FLOWING MEDIA

This chapter deals with two moments of interaction between electric polarization and mechanical motion. Mechanical stress caused by electric polarization will be treated first; then the basis for the theory of streaming birefringence will be outlined. No phenomena concerning ponderomotoric force will be discussed. First, the thermodynamic theory of electric polarization will be dealt with.

7.1. Thermodynamics of electric polarization.

Let us start with an insulator whose electric polarization changes, but which does not move. The equilibrium states of such a medium are determined by the internal energy and the electric dipole moment. According to equation (4.42) when local equilibrium was assumed, the density of entropy production is :

$$\sigma_s = \left[\frac{1}{T}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \frac{\partial s_0}{\partial \mathbf{p}} \right] \varrho \dot{\mathbf{p}}, \quad (7.1)$$

which suggests thermodynamic force and current

$$\mathbf{J} = \varrho \dot{\mathbf{p}}, \quad \mathbf{X} = \frac{1}{T}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \frac{\partial s_0}{\partial \mathbf{p}} \quad (7.2)$$

In a medium at rest, the condition for equilibrium is

$$\mathbf{X} = \frac{1}{T}\mathbf{E} + \frac{\partial s_0}{\partial \mathbf{p}} = 0, \quad (7.3)$$

from which the physical meaning of the derivative of the entropy with respect to the dipole moment is obtained:

$$\frac{\partial s_0}{\partial \mathbf{p}} = -\frac{1}{T}\mathbf{E}^e(u, \mathbf{p}). \quad (7.4)$$

Here $\mathbf{E}^e(u, \mathbf{p})$ means the strength of the electric field at an equilibrium belonging to the values u and \mathbf{p} . Upon using the symbols of equation (7.4) for $T\sigma_s$, we obtain

$$T\sigma_s = \varrho \dot{\mathbf{p}}(\mathbf{E} + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e). \quad (7.5)$$

Since we treat isothermal — or nearly isothermal — processes, it is expedient to use the energy representation with the force

$$\mathbf{X}' = \mathbf{E} + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e \quad (7.6)$$

In this case, the linear law has the form

$$\varrho\dot{\mathbf{P}} = L(\mathbf{E} + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e), \quad (7.7)$$

where L is Onsager's conductivity coefficient.

If the medium is not moving and, thus, its density is constant, equation (7.7) may be written in the simpler form

$$\dot{\mathbf{P}} = L(\mathbf{E} - \mathbf{E}^e), \quad (7.8)$$

where \mathbf{P} is the electric polarization as defined in equation (2.28).

If we restrict ourselves to polarization small enough and accept the linear correlation

$$\mathbf{P} = \varepsilon_0 \chi_e \mathbf{E}^e \quad (7.9)$$

usually applied in electrodynamics, then, for harmonic processes, we get

$$i\omega\mathbf{P} = L \left(\mathbf{E} - \frac{\mathbf{P}}{\varepsilon_0 \chi_e} \right) \quad (7.10)$$

and thereby obtain the dispersion relation

$$\mathbf{P} = \frac{\varepsilon_0 \chi_e}{1 + i \frac{\varepsilon_0 \chi_e \omega}{L}} \mathbf{E} \quad (7.11)$$

According to the above equation, polarization can not follow very high frequencies. (With increasing frequency, the absolute value of the denominator increases to infinity.) This may be regarded as correct if the frequency of X -rays is considered very high, though in this case the dispersion relationship (7.11) provides a too simple spectrum which does not occur in nature at all. On the other hand, if the coefficient falls into the interval of the wavenumber of X -rays, at frequencies corresponding to mechanical motion, equation (7.11) can be regarded as equal to equation (7.9). Hence the conclusion may be drawn that for describing the theoretical relationship concerning the polarization of real media, dynamic variables should be introduced.

If we think of the complex structure of optical and microwave spectra, it should be supposed that for their description several dynamic variables are needed. They can be of both α - and β -type. Fortunately, the complicated structure of spectra appears at frequencies very high from the viewpoint of mechanical motion; and, thus, they do not have to be dealt with since we do not want to describe spectra which is done better by other theories. Based on this, we shall study media whose behavior can be described satisfactorily by a few variables in the region of low frequencies. The essence of the method will be illustrated by the example of media described by a single dynamic variable. Generalization for more dynamic variables can be carried out similarly as in section 6.2.

For a medium which can be described by an α -type dynamic variable, the form of the energy dissipation function, instead of equation (7.5), becomes

$$T\sigma_s = \varrho\dot{\mathbf{P}}(E + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e) - \vec{\alpha}\vec{\alpha}, \quad (7.12)$$

where, like in equation (6.9), the dynamic variable includes also density and temperature. The dynamic variable is now a vector, since no other quantity has dynamic coupling with polarization in a isotropic material. For writing Onsager's linear law, it is expedient to choose $\varrho\dot{\mathbf{p}}$ and $\dot{\vec{\alpha}}$ as independent variables

$$\begin{aligned}\mathbf{E} + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e &= h_{00}\varrho\dot{\mathbf{p}} - h_{01}\dot{\vec{\alpha}}, \\ \dot{\vec{\alpha}} &= -h_{01}\varrho\dot{\mathbf{p}} - h_{11}\dot{\vec{\alpha}}.\end{aligned}\tag{7.13}$$

Here the Onsager coefficients are written as h_{00} , h_{01} and h_{11} , respectively, corresponding to the hybrid representation.

In a medium at rest and by accepting the validity of equation (7.9) for sinusoidal phenomena, the dispersion relation is obtained in the following form:

$$\mathbf{p} = \frac{(h_{11} + i\omega)\mathbf{E}}{\left(ih_{00}\omega + \frac{1}{\varepsilon_0\chi_e}\right)(h_{11} + i\omega) + i\omega h_{01}^2}.\tag{7.14}$$

This equation also shows that at high frequencies polarization cannot follow the electric field (the denominator is a second order polynomial of ω , whereas the numerator is linear in ω). However, if h_{00} is very small, this problem appears only at very high frequencies. This means that in the frequency ranges corresponding to mechanical phenomena, a good approximation is that h_{00} equals zero. With this simplification, equation (7.13) transforms into expression

$$\begin{aligned}\mathbf{E} + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e &= -h_{01}\dot{\vec{\alpha}}, \\ \dot{\vec{\alpha}} &= -h_{01}\varrho\dot{\mathbf{p}} - h_{11}\dot{\vec{\alpha}}\end{aligned}\tag{7.15}$$

whereas dispersion relation (7.14) becomes

$$\mathbf{P} = \varepsilon_0 \left(\chi_\infty + \frac{\chi_e - \chi_\infty}{1 + i\omega\tau_e} \right) \mathbf{E}\tag{7.16}$$

with the definitions

$$\chi_\infty = \frac{\chi_e}{1 + \varepsilon_0\chi_e h_{01}^2}, \quad \tau_e = \frac{1 + \varepsilon_0\chi_e h_{01}^2}{h_{11}}\tag{7.17}$$

Correlation (7.16) is identical with the Debye relaxation in which χ_∞ is the susceptibility belonging to the so-called displacement polarization, whereas $\chi_e - \chi_\infty$ belongs to orientation polarization. Thus the equation obtained describes well the electric polarization of a medium containing dipole molecules in the range of low frequencies, i.e. at frequencies which can be followed by the displacement polarization of atoms and molecules.

It is obvious that for the description of media containing different dipoles, more α -type vectors have to be used. Based on the knowledge of the structure of spectra at higher frequencies, it is readily seen that for their characterization more α - and β -type dynamic variables should be taken into account. Thus, though the structure of spectra does not contradict thermodynamic conclusions, their thermodynamic description is tedious.

7.2. Flow of dielectrics in an electromagnetic field.

Let us now proceed to a detailed examination of the mechanical motion of the medium. For simplicity's sake, we restrict our study to motions leaving the volume of the medium unchanged. We assumed about the medium that it has no internal momentum and the couple stress is also zero. In this case the balance of internal momentum (2.45) allows the conclusion that the electromagnetic field causes a torque on media characterized by equation (7.15); thus, Cauchy's stress tensor is not symmetric any more. However, it is also true that, as will be shown later, the electromagnetic field exerts an influence only on the antisymmetric part of the stress tensor in the case of linear order and isotropic medium. Thus, it is expedient to split the stress tensor into three parts:

$$\mathbf{t} = \mathbf{t}^e + \mathbf{t}^v + \mathbf{t}^a, \quad (7.18)$$

where \mathbf{t}^e is the equilibrium stress tensor,

\mathbf{t}^v the viscous stress tensor, which remains symmetric,

\mathbf{t}^a the antisymmetric part of the stress tensor.

As there is no coupling between a vector and a second order tensor in an isotropic medium, for the determination of \mathbf{t}^v , equation (6.144) remains valid or, for a single dynamic variable of second order tensor, equation (6.10) holds. On the other hand, the equilibrium stress is determined, also in this case, by the state parameters, but here the specific dipole moment has also to be considered. Thus the determination of \mathbf{t}^e is a task of thermostatics. The actual form of function $\mathbf{t}^e(T, \mathbf{d}, \mathbf{p})$ or the equilibrium entropy function $s^e(u, \mathbf{d}, \mathbf{p})$ reflects the phenomena of piezoelectricity and electrostriction. However, these phenomena belong to the phenomena of thermostatics, and, they will not be treated here.

What remains to be done is to determine the antisymmetric component of stress \mathbf{t}^a . Before doing this, equation (7.15) is transformed so that instead of variable $\vec{\alpha}$ the quantity

$$\mathbf{P}' = \mathbf{P} - \varepsilon_0 \chi_\infty (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (7.19)$$

is introduced. A simple calculation leads to

$$\tau_e \dot{\mathbf{P}}' + \mathbf{P}' = \varepsilon_0 (\chi_e - \xi_\infty) (\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (7.20)$$

Now we can proceed with the determination of the antisymmetric component of the stress tensor. Utilizing that $\mathbf{M} = 0$, $\mathbf{l}^i = 0$ and $\mathbf{\Pi} = 0$ and by combining equation (2.45) and (2.50), we arrive at

$$\mathbf{w}(\mathbf{t}) = -\frac{1}{2} \varrho \mathbf{m} = \frac{1}{2} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \times \mathbf{P}. \quad (7.21)$$

By a translation from the vector invariant to tensor \mathbf{t}^a and taking also equation (7.19) into account, we obtain

$$\mathbf{t}^a = \frac{1}{2} [\mathbf{P}' \circ (\mathbf{E} + \mathbf{v} \times \mathbf{B}) - (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \circ \mathbf{P}'] \quad (7.22)$$

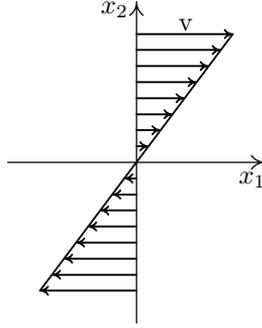


Figure 7.1
Velocity distribution
in simple shear flow.

which, together with equation (7.20), may be regarded as the equation system describing our problem.

As an application, let us study the stationary shear flow of a polar newtonian liquid in the presence of static electric and magnetic fields. In this case, the velocity field is determined by equation (6.23) (Figure 7.1), and the meaning of \mathbf{d} and $\boldsymbol{\omega}$ are given by equation (6.24). First, \mathbf{P}' will be determined from equation (7.20):

$$-\tau_e \boldsymbol{\omega} \mathbf{P}' + \mathbf{P}' = \varepsilon_0 (\chi_e - \chi_\infty) (\mathbf{E} + \mathbf{v} \times \mathbf{B}), \quad (7.23)$$

from which

$$\mathbf{P}' = \varepsilon_0 (\chi_e - \chi_\infty) (\boldsymbol{\delta} - \tau_e \boldsymbol{\omega})^{-1} (\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (7.24)$$

The inverse tensor in this equation may be rewritten by using equation (6.24). It becomes

$$(\boldsymbol{\delta} - \tau_e \boldsymbol{\omega})^{-1} = \frac{1}{2} \boldsymbol{\delta} + \frac{1}{2} \begin{bmatrix} \cos \vartheta & \sin \vartheta & 0 \\ -\sin \vartheta & \cos \vartheta & 0 \\ 0 & 0 & 1 \end{bmatrix} = \frac{1}{2} \boldsymbol{\delta} + \frac{1}{2} \boldsymbol{\Theta} \quad (7.25)$$

where, for brevity substitution

$$\frac{\tau_e \kappa}{2} = \tan \frac{\vartheta}{2} \quad (7.26)$$

has been introduced. Now \mathbf{P}' is substituted into equation (7.22). Then

$$\mathbf{t}^a = \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \{ \boldsymbol{\Theta} [(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \circ (\mathbf{E} + \mathbf{v} \times \mathbf{B})] - [(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \circ (\mathbf{E} + \mathbf{v} \times \mathbf{B})] \boldsymbol{\Theta}^T \}, \quad (7.27)$$

is obtained from which the components of \mathbf{t}^a can be calculated:

$$\begin{aligned} t_{12}^a &= \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \sin \vartheta [E_1^2 + (E_2 - vB_3)^2], \\ t_{13}^a &= \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) (E_3 + vB_2) [\sin \vartheta (E_2 - vB_3) - E_1 (1 - \cos \vartheta)], \\ t_{23}^a &= \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) (E_3 + vB_2) [(E_2 - vB_3) (1 - \cos \vartheta) + \sin \vartheta E_1] \end{aligned} \quad (7.28)$$

On comparing these equations with Cauchy's equation of motion, it is obvious that no simple shear flow may exist in a magnetic field, as \mathbf{v} depends on place. Thus, in magnetic fields, our results must be revalued. The velocity field is

$$v_1 = v(x_2); \quad v_2 = v_3 = 0 \quad (7.29)$$

instead of by equation (6.23), and the quantity

$$\kappa = \frac{dv_1}{dx_2} \quad (7.30)$$

is expedient to be introduced. In this case, equation (7.28) remains valid, and it may be used for determining function $v(x_2)$, which is, however, a difficult task.

Let us now examine what contribution is made by electric polarization to shear stress in a case where no magnetic field is present. Based on equations (7.28) and (7.26), for t_{12}^a the following equation may be written:

$$t_{12}^a = \frac{1}{4}\varepsilon_0(\chi_e - \chi_\infty) \frac{\tau_e \kappa}{1 + \left(\frac{\tau_e \kappa}{2}\right)^2} (E_1^2 + E_2^2), \quad (7.31)$$

which means that for maintaining shear flow in an electric field such an excess of shear stress is needed.

Our equations become much simpler if we consider that relaxation time τ_e of electric polarization is relatively short; hence, in shear velocities of practical importance $\tau_e \kappa \ll 1$. Then instead of equation (7.26),

$$\vartheta = \tau_e \kappa \quad (7.32)$$

may be written; and in equation (7.28), substitutions $\sin \vartheta = \vartheta$, $\cos \vartheta = 1$ may be used:

$$\begin{aligned} t_{12}^a &= \frac{1}{4}\varepsilon_0(\chi_e - \chi_\infty)(E_1^2 + E_2^2)\tau_e \kappa, \\ t_{13}^a &= \frac{1}{4}\varepsilon_0(\chi_e - \chi_\infty)E_3 E_2 \tau_e \kappa, \\ t_{23}^a &= \frac{1}{4}\varepsilon_0(\chi_e - \chi_\infty)E_3 E_1 \tau_e \kappa, \end{aligned} \quad (7.33)$$

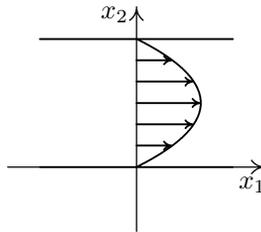


Figure 7.2
Velocity distribution
between parallel walls.

Let us apply these equations for a flow on a channel where the velocity field is described by equation (7.29) (Figure 7.2). From Cauchy's equation of motion, the stationary case is represented by

$$\text{grad } p = \eta \Delta \mathbf{v} + \text{Div } \mathbf{t}^a, \quad (7.34)$$

where it is taken into account that the equilibrium and the viscous stress is not influenced by polarization. From the detailed form of equation (7.34), for individual components

$$\frac{\partial p}{\partial x_1} = \left[\eta + \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \tau_e (E_1^2 + E_2^2) \right] \frac{d^2 v}{dx^2},$$

$$\frac{\partial p}{\partial x_2} = 0 \quad (7.35)$$

$$\frac{\partial p}{\partial x_3} = \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \tau_e E_3 E_1 \frac{d^2 v}{dx^2},$$

it is seen that the flow direction between two parallel planes does not coincide with that of pressure drop, but it forms an angle with it which can be calculated from the equations. The power needed for maintaining the flow is provided by the first equation which may be interpreted so that the viscosity of the fluid is apparently increased. This increment is

$$\eta_{e1} = \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \tau_e (E_1^2 + E_2^2), \quad (7.36)$$

and it may be called electroviscosity.

So far we presumed a time-independent electric field. Mechanical stress occurring as a consequence of such fields depends quadratically on the strength of the electric field; thus it may be expected that in quasi-stationary fields, important from the viewpoint of AC experimental techniques, similar effects are generated. For studying this problem, let us take electric and magnetic field strengths as harmonic functions of time:

$$\mathbf{E} = \mathbf{E}_0 \exp(i\omega_c t), \quad \mathbf{B} = \mathbf{B}_0 \exp(i\omega_c t) \quad (7.37)$$

and use the usual complex formalism. If we assume that the convective time derivatives are zero, then instead of equation (7.20) the following algebraic equation is obtained:

$$-\tau_e \boldsymbol{\omega} \mathbf{P}' + (1 + i\tau_e \omega_c) \mathbf{P}' = \varepsilon_0 (\chi_e - \chi_\infty) (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (7.38)$$

which, after dividing it by $(1 + i\tau_e \omega_c)$, transforms into

$$-\frac{\tau_e}{1 + i\tau_e \omega_c} \boldsymbol{\omega} \mathbf{P}' + \mathbf{P}' = \frac{\varepsilon_0 (\chi_e - \chi_\infty)}{1 + i\tau_e \omega_c} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (7.39)$$

This equation is similar to equation (7.24), only instead of τ_e and $(\chi_e - \chi_\infty)$, complex numbers $\frac{\tau_e}{1 + i\tau_e \omega_c}$, and $\frac{\chi_e - \chi_\infty}{1 + i\tau_e \omega_c}$ should be substituted. Upon assuming that the components of $\frac{\tau_e \vec{\omega}}{1 + i\tau_e \omega_c}$ are small, \mathbf{P}' may be expressed as

$$\mathbf{P}' = \frac{\varepsilon_0 (\chi_e - \chi_\infty)}{1 + i\tau_e \omega_c} \left(\boldsymbol{\delta} + \frac{\tau_e}{1 + i\tau_e \omega_c} \boldsymbol{\omega} \right) (\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (7.40)$$

Since the only factor producing torque is the component of polarization perpendicular to $(\mathbf{E} + \mathbf{v} \times \mathbf{B})$, by omitting the parallel component from \mathbf{P}' we arrive at

$$\mathbf{P}_\perp = \frac{\varepsilon_0(\chi_e - \chi_\infty)\tau_e}{(1 + i\tau_e\omega_c)^2} \boldsymbol{\omega}(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (7.41)$$

In calculating mechanical stress, \mathbf{P}_\perp should be substituted into equation (7.22); but with care as equation (7.22) has non-linear terms. A result is relatively easy to achieve if the aim is to calculate an average of mechanical stress in time. Then, the complex denominator in the coefficient in equation (7.41) means that the component \mathbf{P}_\perp of polarization is delayed relative to the electric field and the phase of this delay is

$$\tan \frac{\varphi}{2} = \tau_e\omega_c, \quad (7.42)$$

which can be readily calculated from equation (7.41).

The time average of the antisymmetric component of the mechanical stress tensor can be determined similarly as the AC power, on the basis of equation (7.22):

$$\langle t^a \rangle = \frac{1}{2} \{ \mathbf{P}_{\perp\text{rms}} \circ (\mathbf{E}_{\text{rms}} + \mathbf{v} \times \mathbf{B}_{\text{rms}}) - (\mathbf{E}_{\text{rms}} + \mathbf{v} \times \mathbf{B}_{\text{rms}}) \circ \mathbf{P}_{\perp\text{rms}} \} \cos \varphi, \quad (7.43)$$

where quantities marked by subscript ‘‘rms’’ mean effective values. The effective value of \mathbf{P}_\perp can be calculated from equation (7.41) in a direct way:

$$\mathbf{P}_{\perp\text{rms}} = \frac{\varepsilon_0(\chi_e - \chi_\infty)\tau_e}{1 + \tau_e^2\omega_c^2} \boldsymbol{\omega}(\mathbf{E}_{\text{rms}} + \mathbf{v} \times \mathbf{B}_{\text{rms}}). \quad (7.44)$$

For shear flow if no magnetic field is involved, the stress components are

$$\begin{aligned} \langle t_{12}^a \rangle &= \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \frac{1 - \tau_e^2 \omega_c^2}{(1 + \tau_e^2 \omega_c^2)^2} (E_{1\text{rms}}^2 + E_{2\text{rms}}^2) \tau_e \kappa, \\ \langle t_{13}^a \rangle &= \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \frac{1 - \tau_e^2 \omega_c^2}{(1 + \tau_e^2 \omega_c^2)^2} E_{3\text{rms}} E_{2\text{rms}} \tau_e \kappa, \\ \langle t_{23}^a \rangle &= \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \frac{1 - \tau_e^2 \omega_c^2}{(1 + \tau_e^2 \omega_c^2)^2} E_{3\text{rms}} E_{1\text{rms}} \tau_e \kappa. \end{aligned} \quad (7.45)$$

These expressions differ from those in equation (7.33) only by factor $\frac{1 - \tau_e^2 \omega_c^2}{(1 + \tau_e^2 \omega_c^2)^2}$; thus for electroviscosity, the equation analogous to equation (7.36) is derived as

$$\eta_{el} = \frac{1}{4} \varepsilon_0 (\chi_e - \chi_\infty) \tau_e \frac{1 - \tau_e^2 \omega_c^2}{(1 + \tau_e^2 \omega_c^2)^2} (E_{1\text{rms}}^2 + E_{2\text{rms}}^2) \quad (7.46)$$

7.3. Body with several dynamic variables.

If the non-equilibrium states of dielectrics moving in an electromagnetic field can be characterized by several dynamic variables, energy dissipation $T\sigma_s$ corresponding to entropy production density σ_s is

$$T\sigma_s = \mathbf{t}^v : \frac{1}{2}(\dot{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\dot{\mathbf{d}}) + \varrho\dot{\mathbf{p}}(\mathbf{E} + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e) - \varrho T \sum \vec{\xi}_i \overset{\circ}{\xi}_i \quad (7.47)$$

on the basis of equations (4.42) and (7.4). If we restrict our discussion to isothermal, volume preserving motions of isotropic materials, then there is no coupling between processes belonging to tensor and vector quantities. Upon introducing quantities

$$\varrho\dot{\mathbf{p}} = \dot{\mathbf{P}}, \quad \mathbf{X}_0 = \dot{\mathbf{P}}, \quad \mathbf{X}_i = -\sqrt{\rho T} \vec{\xi}_i \quad (7.48)$$

together with

$$\begin{aligned} \mathbf{J}_0 &= \mathbf{E} + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e, \\ \mathbf{J}_i &= \sqrt{\rho T} \overset{\circ}{\xi}_i = -\dot{\mathbf{X}}_i, \end{aligned} \quad (7.49)$$

linear laws are obtained with the matrix representation already used in subsection 6.2.6. in the following form:

$$\begin{aligned} \mathbf{E} + \mathbf{v} \times \mathbf{B} - \mathbf{E}^e &= h_{00}\dot{\mathbf{P}} + h_{01}\mathcal{X}, \\ -\dot{\mathcal{X}} &= h_{10}\dot{\mathbf{P}} + h_{11}\mathcal{X}. \end{aligned} \quad (7.50)$$

Let us investigate first the behavior of the medium at rest when the magnetic field does not contribute to the events and the objective time derivatives are identical with the partial ones. On accepting the validity of equation (7.9) for weak fields and introducing complex frequency s (p is engaged), the equations transform into

$$\begin{aligned} \mathbf{E} &= \frac{1}{\varepsilon_0\chi_e}\mathbf{P} + h_{00}s\mathbf{P} + h_{01}\mathcal{X}, \\ 0 &= h_{10}s\mathbf{P} + (h_{11} + s\delta)\mathcal{X} \end{aligned} \quad (7.51)$$

from which, after eliminating \mathcal{X} , we arrive at

$$\mathbf{E} = \left[\frac{1}{\varepsilon_0\chi_e} + h_{00}s - h_{01}(h_{11} + s\delta)^{-1}h_{10}s \right] \mathbf{P}. \quad (7.52)$$

If time dependence is given in the form of $\exp(i\omega_c t)$ and s is substituted by $i\omega_c$, the reciprocal value of complex dielectric susceptibility results as

$$\frac{1}{\varepsilon_0\chi(\omega_c)} = \frac{1}{\varepsilon_0\chi_e} - \omega_c^2 h_{01}(h_{11}^2 + \omega_c^2\delta)^{-1}h_{10} + i\omega_c [h_{00} - h_{01}h_{11}(h_{11}^2 + \omega_c^2\delta)^{-1}h_{10}]. \quad (7.53)$$

The dispersion relation theoretically describes the behavior of the medium in the whole spectral range, if a sufficient number of dynamic variables are used. In such cases, matrices are obviously very ample. Thus, equation (7.53) is not very convenient for the practical determination of complex susceptibility $\chi(\omega_c)$. This

equation becomes useful, however, for the description of dielectrics flowing in an electric field.

Let us now consider a dielectric medium with a stationary shear flow in a static electric field. The velocity field of this medium is described by equations (7.29) and (7.30). For simplicity, let us suppose that the direction of the electric field lies in the plane x_1x_2 and, further, that no magnetic field is involved. Then equation (7.50) may be written as

$$\begin{aligned}\mathbf{E} &= \frac{1}{\varepsilon_0\chi_e}\mathbf{P} + h_{00}\vec{\omega} \times \mathbf{P} + h_{01}\mathcal{X}, \\ 0 &= h_{10}\vec{\omega} \times \mathbf{P} + h_{11}\mathcal{X} + \vec{\omega} \times \mathcal{X},\end{aligned}\tag{7.54}$$

where $\vec{\omega} = \frac{\kappa}{2}\mathbf{e}_3$. The vectors in plane x_1x_2 are conveniently replaced by complex numbers since the vectorial multiplication by ω means a rotation by 90° and a stretch of $\frac{\kappa}{2}$, similar to multiplication by an imaginary number $\frac{\kappa}{2}i$. Taking this into consideration, the equations become

$$\begin{aligned}\mathbf{E} &= \frac{1}{\varepsilon_0\chi_e}\mathbf{P} + h_{00}i\frac{\kappa}{2}\mathbf{P} + h_{01}\mathcal{X} \\ 0 &= i\frac{\kappa}{2}h_{01}\mathbf{P} + \left(h_{11} + i\frac{\kappa}{2}\delta\right)\mathcal{X}\end{aligned}\tag{7.55}$$

which is identical with equation (7.51) when substitution $\frac{\kappa}{2}i = s$ is used. This means at the same time that the solutions of the equations are also identical, i.e.

$$\mathbf{E} = \frac{1}{\varepsilon_0\chi\left(\frac{\kappa}{2}\right)}\mathbf{P},\tag{7.56}$$

where $\chi\left(\frac{\kappa}{2}\right)$ is the complex susceptibility.

The antisymmetric component of Cauchy's stress tensor can be determined on the basis of equation (7.22). By providing χ in the form

$$\chi\left(\frac{\kappa}{2}\right) = \chi_1\left(\frac{\kappa}{2}\right) - i\chi_2\left(\frac{\kappa}{2}\right)\tag{7.57}$$

we may write that

$$P_1 + iP_2 = \varepsilon_0(\chi_1 - i\chi_2)(E_1 + iE_2) = \varepsilon_0(\chi_1E_1 + \chi_2E_2) + i\varepsilon_0(-\chi_2E_1 + \chi_1E_2).\tag{7.58}$$

Since according to our assumption neither \mathbf{P} nor \mathbf{E} have a third component, the only non-zero component of t^a is:

$$t_{12}^a = \frac{1}{2}(P_1E_2 - E_1P_2) = \frac{\varepsilon_0}{2}\chi_2\left(\frac{\kappa}{2}\right)(E_1^2 + E_2^2).\tag{7.59}$$

This result means that to maintain shear flow in an electric field, a shear stress larger by a factor t_{12}^a is needed. The electroviscosity coefficient is then obtained in the form

$$\eta_{el} = \frac{\varepsilon_0}{2}(E_1^2 + E_2^2)\frac{1}{\kappa}\chi_2\left(\frac{\kappa}{2}\right).\tag{7.60}$$

The peculiarity of this equation is that it contains only quantities determinable by electric measurements, i.e. no tedious and expensive mechanical techniques are required for determining $\chi\left(\frac{\kappa}{2}\right)$.

7.4. Flow and polarization of conductive media.

In a conductive medium, electric current density is also involved. Thus, on the basis of equation (4.42), energy dissipation density $T\sigma_s$ is described by

$$T\sigma_s = \mathbf{t}^v : \frac{1}{2}(\dot{\mathbf{d}}\mathbf{d}^{-1} + \mathbf{d}^{-1}\dot{\mathbf{d}}) + (\mathbf{j} + \varrho\dot{\mathbf{p}})(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \varrho T \sum_i \vec{\xi}_i \overset{\circ}{\xi}_i \quad (7.61)$$

instead of equation (7.41). Another significant difference is that here \mathbf{E}^e equals zero, since equilibrium in a conductive medium can only exist if $\mathbf{E} + \mathbf{v} \times \mathbf{B} = 0$. This means, at the same time, that electric polarization cannot be an equilibrium state parameter, but it has to be considered a dynamic variable. The situation is further complicated by the fact that the time derivative of electric polarization is included in internal energy production density, i.e. its change results in work if $\mathbf{E} + \mathbf{v} \times \mathbf{B}$ is not equal to zero.

For the sake of simplifying the mathematics involved, electric polarization is not taken a dynamic variable, it is rather considered a function of state parameters. On the other hand as the polarization is zero, in equilibrium, the vector \mathbf{p} may be given as

$$\mathbf{p} = \sum_i \sqrt{T\gamma_i} \vec{\xi}_i, \quad (7.62)$$

where close to equilibrium quantities γ_i may be regarded as independent of the dynamic state parameters. Obviously, to choose the dynamic variables canonically, polarization does not read to be kept constant for the system to approach an equilibrium as determined by the equilibrium state parameters. Besides, in order to keep the internal energy constant, condition $\mathbf{E} + \mathbf{v} \times \mathbf{B} = 0$ has also to be satisfied. Taking all this into account, thermodynamic forces belonging to vectorial processes can suitably be chosen for the motion of a conductive medium under isothermal, constant-volume conditions as

$$\mathbf{X}_0 = \mathbf{E} + \mathbf{v} \times \mathbf{B}, \quad \mathbf{X}_i = \sqrt{\rho T} \vec{\xi}_i \quad (7.63)$$

while the conjugate currents may be given on the basis of equation (7.61) in the form

$$\mathbf{J}_0 = \mathbf{j} + \dot{\mathbf{P}}, \quad \mathbf{J}_i = -\sqrt{\rho T} \overset{\circ}{\xi}_i = -\dot{\mathbf{X}}_i \quad (7.64)$$

In this case, linear laws may be written by using the matrix formalism as

$$\begin{aligned} \mathbf{j} + \dot{\mathbf{P}} &= L_{00}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \mathcal{L}_{01}\mathcal{X}, \\ -\dot{\mathcal{X}} &= \mathcal{L}_{10}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \mathcal{L}_{11}\mathcal{X} \end{aligned} \quad (7.65)$$

Using equation (7.62) for the vector of electric polarization

$$\dot{\mathbf{P}} = \gamma \dot{\mathcal{X}} = -\gamma \mathcal{L}_{10}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \gamma \mathcal{L}_{11}\mathcal{X} \quad (7.66)$$

holds and the equations are transformed to

$$\begin{aligned} \mathbf{E} + \mathbf{v} \times \mathbf{B} &= -(\gamma \mathcal{L}_{10})^{-1} \dot{\mathbf{P}} - (\gamma \mathcal{L}_{10})^{-1} \mathcal{L}_{11}\mathcal{X}, \\ -\dot{\mathcal{X}} &= -\mathcal{L}_{10}(\gamma \mathcal{L}_{10})^{-1} \dot{\mathbf{P}} - [(\gamma \mathcal{L}_{10})^{-1} \mathcal{L}_{10}(\gamma \mathcal{L}_{11}) - \mathcal{L}_{11}] \mathcal{X}. \end{aligned} \quad (7.67)$$

These equations are completely analogous to equation (7.50); only here $\mathbf{E}^e = 0$, and the notation of the coefficients is different. This result means that the equations derived for dielectrics may be used in an unchanged form also for conductive media if we take into consideration that in the latter case conductive current should also be included in the expression of entropy production. Therefore, the system of conduction coefficients in equation (7.66) does not define a necessarily positive definite form. However, the results prove that polarization phenomena taking place during the flow of conductive media may be described by the formalism elaborated for dielectrics.

7.5. Thermodynamic theory of streaming birefringence.

When studying streaming birefringence, we have to start from the solution of equations (7.50) for high frequencies. In calculating the objective time derivatives, quick variation of fields and the rotation of the medium should be taken into consideration. If a monochromatic wave is used for illumination, the objective time derivatives can be calculated as follows:

$$\begin{aligned}\dot{\mathbf{P}} &= s\mathbf{P} - \vec{\omega} \times \mathbf{P}, \\ \dot{\mathcal{X}} &= s\mathcal{X} - \vec{\omega} \times \mathcal{X}\end{aligned}\tag{7.68}$$

where s is the complex frequency of the illuminating wave and $\vec{\omega}$ is the angular velocity of the medium. In practical cases $|\vec{\omega}| \ll |s|$,

The simplest mathematical solution of our problem is obtained if matrices h_{00} , h_{10} and h_{11} are regarded as hypermatrices, the elements of which are isotropic second order tensors. Then the objective time derivatives are calculated by multiplying by tensor $s\boldsymbol{\delta} - \vec{\omega} \times \boldsymbol{\delta}$. This means that in equation (7.52), $s\boldsymbol{\delta} - \vec{\omega} \times \boldsymbol{\delta}$ should be written instead of s , and thus

$$\mathbf{P} = \varepsilon_0 \chi (s\boldsymbol{\delta} - \vec{\omega} \times \boldsymbol{\delta}) \mathbf{E}\tag{7.69}$$

results. If we consider that $|\vec{\omega}| \ll |s|$ and if we are content with expanding angular velocity components into a series up to linear order, the correlation

$$\mathbf{P} = \varepsilon_0 \chi(s) \mathbf{E} - \varepsilon_0 \frac{d\chi(s)}{ds} \vec{\omega} \times \mathbf{E}\tag{7.70}$$

is obtained which, after substitution $s = i\omega_c$ and using equation (7.57), becomes

$$\mathbf{P} = \varepsilon_0 [\chi_1(\omega_c) - i\chi_2(\omega_c)] \mathbf{E} + \varepsilon_0 \left\{ \frac{d\chi_2}{d\omega_c} + i \frac{d\chi_1}{d\omega_c} \right\} \vec{\omega} \times \mathbf{E}\tag{7.71}$$

This result may be interpreted so that for rotating media the tensor of dielectric susceptibility contains an antisymmetric component as well, which is proportional to the angular velocity of rotation.

For optical calculations, the concept of electric displacement is suitably introduced which, based on equation (7.71), may be given in the form

$$\mathbf{D} = \varepsilon(\omega_c) \mathbf{E} + i \frac{d\varepsilon(\omega_c)}{d\omega_c} \vec{\omega} \times \mathbf{E}\tag{7.72}$$

where $\varepsilon(\omega_c)$ is the complex permittivity depending on angular frequency ω_c . The above formula describes optical activity. The electric and magnetic field strengths in traveling waves are

$$\mathbf{E} = \mathbf{E}_0 \exp [i(\omega_c t - kx_1)], \quad \mathbf{H} = \mathbf{H}_0 \exp [i(\omega_c t - kx_1)]. \quad (7.73)$$

Upon substituting these expressions of \mathbf{E} and \mathbf{H} into Maxwell's equations (2.27) and taking conduction current density and electric charge density equal to zero we obtain

$$-ik\mathbf{e}_1 \times \mathbf{E} + i\omega_c\mu\mathbf{H} = 0, \quad -ik\mathbf{e}_1 \times \mathbf{H} = i\omega_c \left(\varepsilon\mathbf{E} + i\frac{d\varepsilon}{d\omega_c}\vec{\omega} \times \mathbf{E} \right), \quad (7.74)$$

where \mathbf{e}_1 is the unit vector in direction x_1 . Expressing \mathbf{H} from the first equation and substituting it into the second one we arrive at

$$-\frac{k^2}{\omega_c\mu}\mathbf{e}_1 \times (\mathbf{e}_1 \times \mathbf{E}) = \omega_c\varepsilon\mathbf{E} + i\omega_c\frac{d\varepsilon}{d\omega_c}\vec{\omega} \times \mathbf{E}. \quad (7.75)$$

If we divide both sides by $\omega_c\varepsilon$ and take the components, we obtain

$$\begin{aligned} 0 &= E_1 + i\frac{1}{\varepsilon}\frac{d\varepsilon}{d\omega_c}(\omega_2E_3 - \omega_3E_2), \\ \frac{k^2}{\omega_c^2\mu\varepsilon}E_2 &= E_2 + i\frac{1}{\varepsilon}\frac{d\varepsilon}{d\omega_c}(\omega_3E_1 - \omega_1E_3), \\ \frac{k^2}{\omega_c^2\mu\varepsilon}E_3 &= E_3 + i\frac{1}{\varepsilon}\frac{d\varepsilon}{d\omega_c}(\omega_1E_2 - \omega_2E_1). \end{aligned} \quad (7.76)$$

From the first equation the field strength component in the direction of wave propagation as a function of angular velocity components and transversal field strength components can be calculated. In the other two equations, E_1 occurs only multiplied by the angular velocity components. From the second and third equations, we arrive at

$$\frac{k^2}{\omega_c^2\mu\varepsilon}E_2 = E_2 - i\frac{\omega_1}{\varepsilon}\frac{d\varepsilon}{d\omega_c}E_3, \quad \frac{k^2}{\omega_c^2\mu\varepsilon}E_3 = E_3 + i\frac{\omega_1}{\varepsilon}\frac{d\varepsilon}{d\omega_c}E_2 \quad (7.77)$$

which is a homogeneous linear system that has a non-trivial solution only if its determinant is zero, i.e.

$$\begin{vmatrix} \frac{k^2}{\omega_c^2\mu\varepsilon} - 1 & i\frac{\omega_1}{\varepsilon}\frac{d\varepsilon}{d\omega_c} \\ -i\frac{\omega_1}{\varepsilon}\frac{d\varepsilon}{d\omega_c} & \frac{k^2}{\omega_c^2\mu\varepsilon} - 1 \end{vmatrix} = 0. \quad (7.78)$$

From this condition

$$\frac{k^2}{\omega_c^2\mu\varepsilon} = 1 \pm \frac{\omega_1}{\varepsilon}\frac{d\varepsilon}{d\omega_c} \quad (7.79)$$

results. Taking this into account, the solution of equation (7.77) is:

$$E_3 = +iE_2. \quad (7.80)$$

This result means that circularly polarized waves belong to polarization equation (7.72). Optical activity for unit length is

$$[\alpha] = \frac{\pi}{\lambda} \frac{1}{\varepsilon} \frac{d\varepsilon}{d\omega_c} \omega, \quad (7.81)$$

where λ is the wavelength of light.

On substituting particular values into our general equation, it turns out that the effect is small which means that the term originating from the rotation of the medium may be neglected in the calculation of objective time derivatives. Therefore, streaming birefringence cannot be explained by the appearance of objective time derivatives. We should notice, however, that the elements of matrices h_{00} , h_{01} , h_{10} and h_{11} in equation (7.50) may depend on state parameters, especially on dynamic state parameters as well. It should also be taken into consideration that in a weak electric field, the vectorial dynamic state parameters are small; therefore, the dependence of the conduction coefficients on them cannot be significant unless the light intensity is very high. However, important effects may result if the matrix elements in question depend on some dynamic variable of second-order tensor. As these matrix elements can be regarded as second-order tensors — they turn into numbers only due to the isotropy of the medium — the dependence may be linear, i.e. if the elements of matrices h_{00} , h_{10} , h_{01} and h_{11} are considered linear functions of dynamic variables of second-order tensor if these dynamic variables are not large. Consequently if we proceed with this linear approximation, we arrive at equation (6.171) of subsection 6.2.5.

Finally, by studying time inversion we may arrive at the conclusion that β -type dynamic variables cannot appear in equation (6.171), even if they are necessary for the description of the medium. This derivation is so simple that it is left to those who are particularly interested in it.

CHAPTER VIII

APPLICATIONS OF THE THEORY

This chapter presents some applications of the theory to problems with dynamic degrees of freedom having clear physical. On the basis of hypotheses concerning the structure of materials, constitutive equations will be derived independently of the thermodynamic theory: partly proving thereby the applicability of the thermodynamic approach and partly showing the limits of individual methods. As a first example, the motion of globular colloids will be discussed.

8.1. Viscosity of globular colloids.

The behavior of a medium consisting of a solid dispersed in a newtonian liquid will be examined first. The dispersed phase is assumed to be a Hooke body from the viewpoint of its rheological properties. It consists of homodimensional spherical particles uniformly dispersed in the continuous phase, but randomly. If the volume fraction of the dispersed phase is small enough, it may be assumed that the shape of the particles is deformed homogeneously during the motion and, meantime, the elastic medium stores mechanical energy. For simplicity let us disregard the compressibility of both phases and the temperature dependence of the viscosity of the liquid phase and that of the shear modulus of the elastic phase. From the macroscopic point of view, the colloidal solution is obviously a fluid, incompressible according to the earlier hypothesis; thus its equilibrium is determined by its specific internal energy. This is in complete accordance with the assumption that the colloidal particles in the medium at rest are spheres. The situation is totally different during motion. In this case the colloidal particles are deformed due to stress, and they store part of their energy in the form of mechanical energy. For calculating the entropy, the equilibrium entropy function based on the simplifying assumption may be used, but only stored mechanical energy should be subtracted from internal energy:

$$s = s_o \left(u - c \frac{\mu_1}{\rho} \boldsymbol{\varepsilon} : \boldsymbol{\varepsilon} \right), \quad (8.1)$$

where c is the volume fraction of dispersed phase,

μ_1 the shear modulus of the dispersed material,

ρ the average density, and

$\boldsymbol{\varepsilon}$ the deformation of the colloidal particles.

If the stored mechanical energy is small, upon expanding equation (8.1) into a series up to the linear term, we obtain:

$$s = s_0(u) - \frac{1}{T} c \frac{\mu_1}{\rho} \boldsymbol{\varepsilon} : \boldsymbol{\varepsilon}. \quad (8.2)$$

If a new variable

$$\xi = \sqrt{\frac{2c\mu_1}{T\rho}} \varepsilon \quad (8.3)$$

is introduced we arrived at

$$s = s_0(u) - \frac{1}{2} \xi : \xi \quad (8.4)$$

which is identical to equation (6.1). Thus, it is seen that in the present case the dynamic variable describes the deformation of elastic colloidal particles. From the example it is obvious why dynamic variables are unnecessary for characterizing equilibrium states.

When knowing the entropy function in the form of equation (8.4), the thermodynamic theory described in section 6.1 may be directly applied. Since the tensor ε providing the deformation of colloidal particles is even with respect to time inversion, transformation (6.9) results in

$$\sqrt{\rho T} \xi = \sqrt{2c\mu_1} \varepsilon = \alpha.$$

Thus, we arrive at constitutive equation (6.10).

It should be noted that an increase in the concentration may lead to a more complex deformation of particles. From thermodynamic aspects we may say in this case that hydrodynamic interaction between the particles necessitates the introduction of additional dynamic degrees of freedom. Later calculations prove this assumption.

8.2. Calculation of the viscosity of globular colloids based on structural considerations.

Let us now proceed to determine the viscosity of globular colloids by the mechanical method. Calculations will be performed in a more general manner than have been done with the simplifications applied so far. In what follows, the compressibility of both phases will be taken into account, and the hydrodynamic interaction between the particles will not be neglected. In the calculations, Oldroyd's method, [123] whose essential features are given below, will be used:

a. It is assumed that the particles are so small that the inertia of the medium can be neglected.

b. We introduce a complex way of writing which may be considered an operator notation. Both phases are regarded as elastic, with complex modules.

c. The hydrodynamic interaction between individual particles is taken into account so that we select one particle (with radius a) and surround it with a sphere consisting of the continuous phase whose radius b is chosen so that the volume ratio of the two concentric spheres should correspond to the composition of the colloid,

c. In short, it is assumed that

$$\frac{a^3}{b^3} = c \quad (8.5)$$

holds. The space around the outer sphere is surrounded by a medium having macroscopic properties identical with those of the colloidal solution. The parameters of

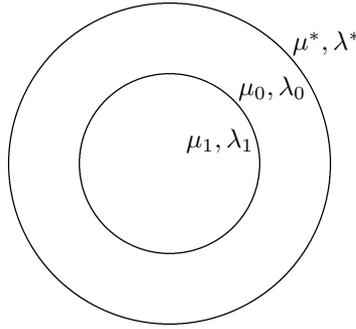


Figure 8.1

the average medium are chosen so that the structure consisting of the concentric spheres should be fitted best into the background.

The known differential equation describing the equilibrium of the elastic medium in our model is the following:

$$\mu \Delta \mathbf{l} + (\mu + \lambda) \text{grad div } \mathbf{l} = 0, \quad (8.6)$$

where

$$\mu = \begin{cases} \mu_1 & \text{if } r < a \\ \mu_0 & \text{if } a < r < b \\ \mu^* & \text{if } b < r \end{cases} \quad \text{and} \quad \lambda = \begin{cases} \lambda_1 & \text{if } r < a \\ \lambda_0 & \text{if } a < r < b \\ \lambda^* & \text{if } b < r \end{cases} \quad (8.7)$$

in which μ_1 and λ_1 are the Lamé constants of the dispersed phase; μ_0 and λ_0 those of the continuous phase; and μ^* and λ^* those of the average medium. The related boundary condition is:

$$\lim_{r \rightarrow \infty} (\mathbf{l} - \boldsymbol{\varepsilon} \mathbf{r}) = 0; \quad (8.8)$$

where $\boldsymbol{\varepsilon}$ is the deformation of the medium. In addition, function $\mathbf{l}(\mathbf{r})$ should be continuous in the whole range and the stress vector must also be continuous on all surfaces.

Since equation (8.6) and condition (8.8) are linear in \mathbf{l} , it is easy to see that solution $\mathbf{l}(\mathbf{r})$ will be homogeneous and linear in $\boldsymbol{\varepsilon}$. Hence the solution sought is :

$$\mathbf{l} = \mathbf{T}(\mathbf{r}) : \boldsymbol{\varepsilon}, \quad (8.9)$$

where $\mathbf{T}(\mathbf{r})$ is a third order tensor depending on the place. Relation (8.9) may be given also in terms of orthogonal components:

$$l_i = T_{ijk}(\mathbf{r}) \varepsilon_{jk}. \quad (8.10)$$

From this it is seen that tensor $\mathbf{T}(\mathbf{r})$ is symmetric in its second and third indices. Based on considerations of symmetry it is also easy to see that the field of tensor

$\mathbf{T}(\mathbf{r})$ is of globular symmetry. To determine it, let us choose an arbitrary point with position vector \mathbf{r} and define an auxiliary cartesian coordinate system in which this point lies on the third axis. On reflection to planes perpendicular to axes x_1 and x_2 , it can be seen that each component of tensor $\mathbf{T}(\mathbf{r})$ is zero in which an odd number of 1's or 2's occurs. By means of the mirror symmetry exchanging axes x_1 and x_2 , it is evident that an exchange of indices 1 and 2 does not alter the components of $\mathbf{T}(\mathbf{r})$. According to this, in tensor $\mathbf{T}(\mathbf{r})$ only three independent components remain:

$$T_{113} = T_{131} = T_{223} = T_{232} = \alpha, \quad T_{311} = T_{322} = \beta, \quad T_{333} = \gamma, \quad (8.11)$$

where notations α , β and γ are introduced with which we can rewrite equation (8.9) as

$$l_1 = 2\alpha\varepsilon_{13}; \quad l_2 = 2\alpha\varepsilon_{23}; \quad l_3 = \beta(\varepsilon_{11} + \varepsilon_{22}) + \gamma\varepsilon_{33}. \quad (8.12)$$

On utilizing the fact that vector r shows the direction of the third axis, equation (8.12) takes the following form:

$$\mathbf{l} = f(r)\varepsilon^0\mathbf{r} + g(r)(\mathbf{r}\varepsilon^0\mathbf{r}) + h(r)\text{tr}\varepsilon\mathbf{r}, \quad (8.13)$$

where

$$f(r) = \frac{2\alpha}{r}; \quad g(r) = \frac{\gamma - \beta - 2\alpha}{r^3}; \quad h(r) = \frac{\gamma + 2\beta}{3r}; \quad \varepsilon^0 = \varepsilon - \frac{1}{3}\text{tr}\varepsilon\delta. \quad (8.14)$$

Equation (8.13) is completely general. On the other hand, functions f , g and h are functions only of the distance from the center; in this way we eliminated the disadvantage of choosing a special coordinate system.

Let us now determine functions f , g and h . For this purpose, let us substitute equation (8.13) into differential equation (8.6). For this, we need the following expression:

$$\begin{aligned} \Delta(f\varepsilon^0\mathbf{r}) &= \left(f'' + \frac{4}{r}f'\right)\varepsilon^0\mathbf{r}, \\ \Delta[g(\mathbf{r}\varepsilon^0\mathbf{r})] &= 4g\varepsilon^0\mathbf{r} + \left(g'' + \frac{8}{r}g'\right)(\mathbf{r}\varepsilon^0\mathbf{r}) \\ \Delta[h\mathbf{r}] &= \left(h'' + \frac{4}{r}h'\right)\mathbf{r} \\ \text{grad div}(f\varepsilon^0\mathbf{r}) &= 2\frac{f'}{r}\varepsilon^0\mathbf{r} + \frac{1}{r^2}\left(f'' - \frac{1}{r}f'\right)(\mathbf{r}\varepsilon^0\mathbf{r}) \\ \text{grad div}[g(\mathbf{r}\varepsilon^0\mathbf{r})] &= (2g'r + 10g)\varepsilon^0\mathbf{r} + \left(g'' + \frac{6}{r}g'\right)(\mathbf{r}\varepsilon^0\mathbf{r}) \\ \text{grad div}(h\mathbf{r}) &= \left(h'' + \frac{4}{r}h'\right)\mathbf{r}. \end{aligned} \quad (8.15)$$

Upon using these and utilizing the fact that in the equation obtained the coefficients of $\varepsilon^0 \mathbf{r}$, $(\mathbf{r}\varepsilon^0 \mathbf{r})\mathbf{r}$ and $(\text{tr } \varepsilon)\mathbf{r}$ should individually be zero, we obtain

$$\begin{aligned} \mu \left(f'' + \frac{4}{r} f' + 4g \right) + (\mu + \lambda) \left(\frac{2}{r} f' + 2g'r + 10g \right) &= 0, \\ \mu \left(g'' + \frac{8}{r} g' \right) + (\mu + \lambda) \left(\frac{1}{r^2} f'' - \frac{1}{r^3} f' + g'' + \frac{6}{r} g' \right) &= 0, \\ \mu \left(h'' + \frac{4}{r} h' \right) + (\mu + \lambda) \left(h'' + \frac{4}{r} h' \right) &= 0. \end{aligned} \quad (8.16)$$

Our task now is to solve the set of ordinary differential equations. Since the first two equations do not involve h whereas the third contains only h , they may be solved separately. We look for solutions in the form

$$f = f_0 r^{n+2}, \quad g = g_0 r^n \quad (8.17)$$

Using them, we obtain the following homogeneous, linear equation system:

$$\begin{aligned} (n+2)[\mu(n+5) + 2(\mu + \lambda)]f_0 + 2[2\mu + (\mu + \lambda)(n+5)]g_0 &= 0, \\ (n+2)n(\mu + \lambda)f_0 + n[2\mu + (2\mu + \lambda)(n+5)]g_0 &= 0 \end{aligned} \quad (8.18)$$

It has a non-trivial solution if and only if

$$\begin{vmatrix} (n+2)[2(\mu + \lambda) + \mu(n+5)] & 2[2\mu + (\mu + \lambda)(n+5)] \\ (n+2)n(\mu + \lambda) & n[2\mu + (2\mu + \lambda)(n+5)] \end{vmatrix} = 0. \quad (8.19)$$

From this, the possible values of n are 0, -2 , -5 , -7 . The four independent particular solutions are obtained from the first equation of system (8.18):

$$\begin{aligned} f_1 &= (7\mu + 5\lambda)r^2; & g_1 &= -(7\mu + 2\lambda); \\ f_2 &= 1; & g_2 &= 0; \\ f_3 &= 2\mu r^{-3}; & g_3 &= 3(\mu + \lambda)r^{-5}; \\ f_4 &= 2r^{-5}; & g_4 &= -5r^{-7} \end{aligned} \quad (8.20)$$

Function h is obtained from the third equation of (8.16). The two particular solutions are:

$$h_1 = 1 \quad \text{and} \quad h_2 = r^{-3}. \quad (8.21)$$

The coefficients are provided by continuity conditions. However, care should be taken that μ and λ do not remain constant in the whole space; therefore, the coefficients in the solution will differ for regions $r < s$, $a < r < b$ and $b < r$.

In the first region

$$f = -A_1 f_1 - B_1; \quad g = -A_1 g_1; \quad h = -E_1. \quad (8.22)$$

Here the coefficients of f_3 , f_4 , g_3 , g_4 and h_2 are zero, since the functions sought are continuous also at $r = 0$. The negative signs will prove to be convenient later.

In the second region ($a < r < b$)

$$\begin{aligned} f &= A_2 f_1 + B_2 + C_2 f_3 + D_2 f_4; & g &= A_2 g_1 + C_2 g_3 + D_2 g_4; \\ h &= E_2 + F_2 h_2. \end{aligned} \quad (8.23)$$

In the third region ($b < r$)

$$f = -B^* - D^* f_4; \quad g = -D^* g_4; \quad h = -E^*; \quad (8.24)$$

where the coefficients of f_1 and g_1 are zero due to the behavior in infinity. For the same reason

$$B^* = -1, \quad E^* = -1/3$$

and the coefficients of f_3 , g_3 and h_2 are chosen to be zero, for the sake of a possibly faster disappearance of the perturbation caused by the two spheres. It turns out in what follows that D^* cannot be chosen freely any more, though this would have been the condition of the perfect disappearance of the perturbation outside the outer sphere.

Next the stress tensor and then the stress vector on radial surfaces are determined. They are needed when fitting the solutions on the spheres. According to Hooke's law:

$$\mathbf{t} = \mu(\mathbf{1} \circ \nabla + \nabla \circ \mathbf{1}) + \lambda \operatorname{div} \mathbf{l} \boldsymbol{\delta}; \quad (8.25)$$

from which

$$\mathbf{t} \mathbf{r} = \mu(\mathbf{r} \nabla) \mathbf{1} + \mu(\nabla \circ \mathbf{1}) \mathbf{r} + \lambda(\operatorname{div} \mathbf{1}) \mathbf{r}. \quad (8.26)$$

From equation (8.13) we get

$$\begin{aligned} \mathbf{t} \mathbf{r} &= \mu(r f' + 2f + 2gr^2) \boldsymbol{\varepsilon}^0 \mathbf{r} + \left[\mu \left(2g'r + 4g + \frac{1}{r} f' \right) + \right. \\ &\quad \left. + \lambda \left(\frac{1}{r} f' + g'r + 5g \right) \right] (\mathbf{r} \boldsymbol{\varepsilon}^0 \mathbf{r}) \mathbf{r} + [2\mu(h'r + h) + \lambda(h'r + 3h)] \operatorname{tr} \boldsymbol{\varepsilon} \mathbf{r} \end{aligned} \quad (8.27)$$

For brevity, the temporary notations defined by

$$\mathbf{t} \mathbf{r} = \alpha(r) \boldsymbol{\varepsilon}^0 \mathbf{r} + \beta(r) (\mathbf{r} \boldsymbol{\varepsilon}^0 \mathbf{r}) \mathbf{r} + \gamma(r) \operatorname{tr} \boldsymbol{\varepsilon} \mathbf{r} \quad (8.28)$$

and introduced. The particular forms of α , β and γ corresponding to equation (8.20) and (8.21) are

$$\begin{aligned} \alpha_1 &= \mu(14\mu + 16\lambda)r^2; & \alpha_2 &= 2\mu; \\ \alpha_3 &= 2\mu(2\mu + 3\lambda)r^{-3}; & \alpha_4 &= -16\mu r^{-5}; \\ \beta_1 &= -\mu(14\mu + 19\lambda); & \beta_2 &= 0; \\ \beta_3 &= -24\mu(\mu + \lambda)r^{-5}; & \beta_4 &= 40\mu r^{-7}; \\ \gamma_1 &= (2\mu + 3\lambda); & \gamma_2 &= -4\mu r^3. \end{aligned} \quad (8.29)$$

Continuity conditions say that f, g, h, α, β and γ are continuous at $r = a$ and $r = b$. First, the continuity of h and γ are written in a form reduced to zero

$$\begin{aligned} E_1 + E_2 + F_2 a^{-3} &= 0, \\ E_1(2\mu_1 + 3\lambda_1) + E_2(2\mu_0 + 3\lambda_0) - 4\mu_0 F_2 a^{-3} &= 0, \\ E_2 + F_2 b^{-3} + E^* &= 0, \\ E_2(2\mu_0 + 3\lambda_0) - 4\mu_0 F_2 b^{-3} + E^*(2\mu^* + 3\lambda^*) &= 0. \end{aligned} \quad (8.30)$$

The equations obtained may be regarded as a system of homogeneous, linear equations which has a non-trivial solution if and only if its determinant is zero:

$$\begin{vmatrix} 1 & 1 & a^{-3} & 0 \\ 3\kappa_1 & 3\kappa_0 & -4\mu_0 a^{-3} & 0 \\ 0 & 1 & b^{-3} & 1 \\ 0 & 3\kappa_0 & -4\mu_0 b^{-3} & 3\kappa^* \end{vmatrix} = 0. \quad (8.31)$$

Let us introduce the compression modulus

$$\kappa = \frac{2\mu}{3} + \lambda \quad (8.32)$$

For simplifying calculations, let us use notations

$$\xi = \frac{\kappa^*}{\kappa_0} - 1; \quad \eta = \frac{\kappa_1}{\kappa_0} - 1; \quad \zeta = \frac{3\kappa_0}{4\mu_0 + 3\kappa_0}. \quad (8.33)$$

With them, determinant (8.31) takes a simpler form

$$\begin{vmatrix} 1 & 1 & \zeta & 0 \\ \eta & 0 & -1 & 0 \\ 0 & 1 & \zeta c & 1 \\ 0 & 0 & -c & \xi \end{vmatrix} = 0. \quad (8.34)$$

If we expand it with respect to column 4 and solve the equation for ξ , we obtain:

$$\xi = \frac{c\eta}{1 + \zeta\eta(1 - c)}. \quad (8.35)$$

We proceed in the same way for f, g, α and β . With those, the determinant of the set of homogeneous linear equations is of the eighth order.

See on next page. (8.36)

The expansion of this eighth-order determinant is a tedious task. In order to simplify it, let us use the following quantities:

$$\begin{aligned} \frac{\mu_1}{\mu_0} - 1 = y; \quad \frac{\mu^*}{\mu_0} - 1 = x; \quad \frac{\mu_1}{\lambda_1} = z_1; \\ \frac{\mu_0}{\lambda_0} = z_0; \quad \frac{a}{b} = t; \end{aligned} \quad (8.37)$$

whose application and the equivalent transformation of equation (8.36) lead to the equation:

$$\text{See on next page.} \quad (8.38)$$

From the first two columns of the determinant obtained, it is apparent that the equation is quadratic with respect to the new variable x . We can select the proper root by the condition that x is necessarily zero at zero concentration and modulus μ^* is a continuous function of the concentration. The expansion of the determinant and the solution of the equation is tedious and too complex to be surveyed even by using the notations introduced; therefore, we restrict our study to incompressible media. In this case both z_1 and z_0 are zero. The situation is further simplified if we consider only low concentrations. Then, by keeping the smallest powers of t in the coefficients of the quadratic equation (even calculating the coefficient of the quadratic term at $t = 0$, since at low concentrations the root we seek is small), x^2 contributes to the value of the quadratic polynomial only to a small extent. The above simplifications lead to

$$16x^2(19y+35)(1+0.4y)+x(19y+35)[35+(14-30t^3)y]-35t^3y(19y+35)=0 \quad (8.39)$$

which become after reduction

$$16(1+0.4y)x^2+[35+(14-30c)y]x-35yc=0 \quad (8.40)$$

where we returned to notation $t^3 = c$. Since the quadratic equation obtained is only an approximation, it is not worth taking the inconvenience of accurate solution. In first approximation we are satisfied with equation

$$x = \frac{yc}{1+0.4y} \quad (8.41)$$

which is valid for very low concentrations only. It is of importance that equation (8.41) transforms into the well-known Einstein equation for rigid dispersed phase, i.e. if $y \rightarrow \infty$. In this case, namely,

$$x = 2.5c \quad (8.42)$$

which, by resolving the abbreviations, takes

$$\mu^* = \mu_0(1+2.5c). \quad (8.43)$$

As $\mu = p\eta$ for viscosity, we arrive at

$$\eta^* = \eta_0(1+2.5c) \quad (8.44)$$

which is the well-known Einstein equation.

Approximation (8.41) may be regarded as the linear expansion of the shear modulus of the colloid. The disadvantage of this form is that it provides good results only for very low concentrations. The quality of approximation may be improved if one of the factors of x^2 in equation (8.40) is substituted from equation (8.41) and

$$\begin{vmatrix}
(7\mu_1 + 5\lambda_1)a^2 & 1 & (7\mu_0 + 5\lambda_0)a^2 & 1 & 2\mu_0a^{-3} & 2a^{-5} & 0 & 0 \\
-(7\mu_1 + 2\lambda_1) & 0 & -(7\mu_0 + 2\lambda_0) & 0 & 3(\mu_0 + \lambda_0)a^{-5} & -5a^{-7} & 0 & 0 \\
\mu_1(14\mu_1 + 16\lambda_1)a^2 & 2\mu_1 & \mu_0(14\mu_0 + 16\lambda_0)a^2 & 2\mu_0 & 2\mu_0(2\mu_0 + 3\lambda_0)a^{-3} & -16\mu_0a^{-5} & 0 & 0 \\
-\mu_1(14\mu_1 + 19\lambda_1) & 0 & -\mu_0(14\mu_0 + 19\lambda_0) & 0 & -24\mu_0(\mu_0 + \lambda_0)a^{-5} & 40\mu_0a^{-7} & 0 & 0 \\
0 & 0 & (7\mu_0 + 5\lambda_0)b^2 & 1 & 2\mu_0b^{-3} & 2b^{-5} & 1 & 2b^{-5} \\
0 & 0 & -(7\mu_0 + 2\lambda_0) & 0 & 3(\mu_0 + \lambda_0)b^{-5} & -5b^{-7} & 0 & -5b^{-7} \\
0 & 0 & \mu_0(14\mu_0 + 16\lambda_0)b^2 & 2\mu_0 & 2\mu_0(2\mu_0 + 3\lambda_0)b^{-3} & -16\mu_0b^{-5} & 2\mu^* & -16\mu^*b^{-5} \\
0 & 0 & -\mu_0(14\mu_0 + 19\lambda_0) & 0 & -24\mu_0(\mu_0 + \lambda_0)b^{-5} & 40\mu_0b^{-7} & 0 & 40\mu^*b^{-7}
\end{vmatrix} = 0. \quad (8.36)$$

$$\begin{vmatrix}
x & 0 & 0 & 0 & 0 & -(2z_0 + 1)t^3 & 0 & 7(2z_0 + 1) \\
0 & 8x & 0 & 0 & 0 & 0 & 0 & -35(2z_0 + 1) \\
1 & 0 & 0 & 0 & 1 & \frac{2}{3}(4z_0 + 3)t^3 & -1.6t^5 & -7z_0 + 1 \\
0 & 1 & 0 & 0 & 0 & -(z_0 + 1)t^3 & t^5 & 7z_0 + 2 \\
0 & 0 & 1 & -3 & 1 & \frac{2}{3}z_0 & 0.4 & (7z_0 + 5)t^2 \\
0 & 0 & 0 & 7z_1 + 2 & 0 & -(z_0 + 1) & 1 & (7z_0 + 2)t^2 \\
0 & 0 & y & 7(2z_1 + 1) & 0 & -(2z_0 + 1) & 0 & 7(2z_0 + 1)t^2 \\
0 & 0 & 0 & y(14z_1 + 19) + 35(2z_1 + 1) & 0 & 0 & 0 & 35(2z_0 + 1)t^2
\end{vmatrix} = 0. \quad (8.38)$$

the improved value of x is calculated from the linear equation thus obtained. This procedure is essentially an iterative solution based on the correlation between roots and coefficients. The approximation thus obtained is

$$x = \frac{yc}{1 + 0.4y(1 - c)}; \tag{8.45}$$

which shows a perfect formal analogy to equation (8.35) valid for the compression modulus. This formal analogy, which includes also the fact that equation (8.45) gives the proper result for limiting case $c = 1$, suggests that equation (8.45) provides perhaps a better approximation for incompressible media, than the accurate solution of equation (8.38). It should be mentioned here that at the beginning of this consideration we assumed the uniformity of the colloidal particles, whereas in the results only parameter t is characteristic for concentration is involved; thus, it may be assumed that the results hold also for the simultaneous presence of particles with different sizes.

A further interesting feature of equation (8.45) is that it may be interpreted also by the mechanical models of rheology. In order to illustrate this, let us return from variables x and y to μ_1 , μ_0 and μ^* :

$$\mu^* = \mu_0 \frac{(2 + 3c)\mu_1 + 3(1 - c)\mu_0}{2(1 - c)\mu_1 + (3 + 2c)\mu_0}, \tag{8.46}$$

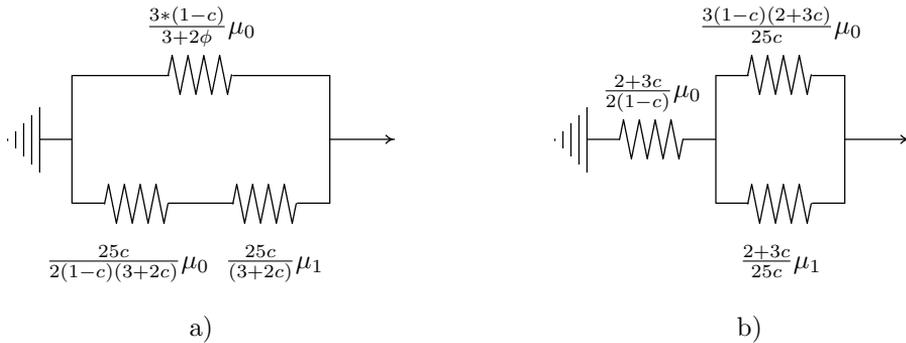


Figure 8.2

This correlation is the modulus of mechanical models shown in Figure 8.2. The mechanical models prove by their existence that for colloids consisting of viscoelastic components, the complex viscosity of the medium is always a positive real function when those of the component are positive real functions. For the medium discussed in section 8.1. when $\mu_0 = p\eta_0$, for example, by introducing symbols

$$\eta = \frac{2 + 3c}{2(1 - c)}\eta_0; \quad \tau_d = \frac{3(1 - c)}{2 + 3c} \frac{\eta_0}{\mu_1}; \quad \tau_t = \frac{3 + 2c}{2(1 - c)} \frac{\eta_0}{\mu_1} \tag{8.47}$$

correlation

$$\mu^* = \eta p \frac{\tau_d p + 1}{\tau_t p + 1} \tag{8.48}$$

is obtained which is identical with the complex modulus in equation (6.17) introduced for the medium characterized by one dynamic variable.

All this shows that the equation derived from the structure of colloids by means of classical mechanics is completely identical with the results of linear non-equilibrium thermodynamics. The thermodynamic conductivity coefficients can be determined by comparing equations (8.47) and (6.13).

Let us now examine the possibilities of calculations for the case when the concentration of the globular colloid consisting of incompressible components exceeds the limit of the applicability of equations (8.41) and (8.45). One of the possibilities is to solve the original equation (8.38). Due to incompressibility, $z_0 = z_1 = 0$. By expanding the determinant at the left side of the equation we obtain quadratic expressions for both x and y , the coefficients of which are the polynomials of parameter $t = c^{1/3}$:

$$(P_{22}y^2 + P_{21}y + P_{20})x^2 + (P_{12}y^2 + P_{11}y + P_{10})x + P_{02}y^2 + P_{01}y = 0, \quad (8.49)$$

where

$$\begin{aligned} P_{22} &= 121.6t^{10} - 760t^7 + 1276.8t^5 - 760t^3 + 121.6, \\ P_{21} &= -1480t^7 + 2352t^5 - 1400t^3 + 528, \\ P_{20} &= 560, & P_{12} &= 304t^{10} - 570t^3 + 266, \\ P_{11} &= -1050t^3 + 1155, & P_{10} &= 1225, \\ P_{02} &= -665t^3, & P_{01} &= -1225t^3. \end{aligned} \quad (8.50)$$

Quadratic equation (8.49) is suitable for numerical calculations also in the case of complex modules. We shall now illustrate how the procedure may be applied for the medium discussed in section 8.1. Corresponding to complex representation, then

$$\mu_0 = i\kappa\eta_0; \quad \mu^* = \sigma_1 + i\kappa\eta^*; \quad (8.51)$$

where η_0 is the viscosity of the continuous phase

κ the shear rate (in the case of small amplitude oscillations, it is substituted by angular frequency),

σ_1 the normal stress function,

η^* the non-newtonian viscosity belonging to stationary shear flow, or more accurately speaking, the ratio of shear stress to shear rate.

The meaning of x and y introduced in equation (8.37) is now

$$x = \frac{\eta^*}{\eta_0} - i \frac{\sigma_1}{\kappa\eta_0} - 1; \quad y = -1 - i \frac{\mu_1}{\kappa\eta_0} \quad (8.52)$$

It is obvious that in equation (8.49) only two variable parameters are included: t depending on the concentration and $\frac{\kappa\eta_0}{\mu_1}$ in y . From the two roots of the quadratic equation the one for which η^* is positive should be chosen; i.e., for which inequality

$$\frac{\eta^*}{\eta_0} - 1 = \text{Re}x > -1 \quad (8.53)$$

is fulfilled. The computer calculation is easy to perform. Figure 8.3 shows the shear stress function calculated where on the abscissa and ordinate axes, respectively, reduced variables

$$\kappa^* = \frac{\kappa\eta_0}{\mu_1}; \quad \tau^* = \frac{\tau}{\mu_1} \quad (8.54)$$

are shown.

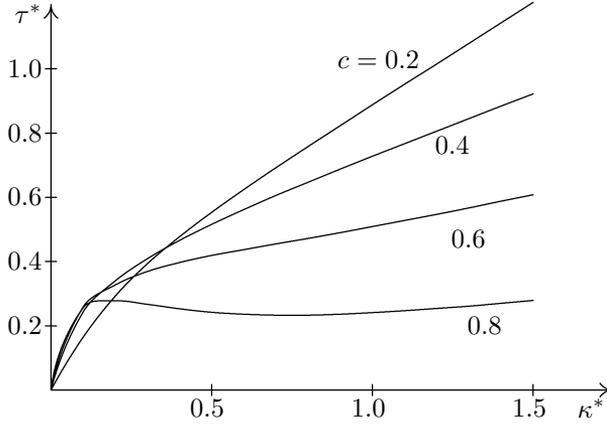


Figure 8.3

The following representation, however, provides the relations in a more refined manner. The logarithm of reduced shear rate is now on the abscissa, whereas the ordinate shows a variable defined as

$$[\eta^*] = \frac{\eta^*(\kappa^*) - \eta^*(\infty)}{\eta^*(0) - \eta^*(\infty)} \quad (8.55)$$

where

$$\eta^*(\infty) = \lim_{\kappa^* \rightarrow \infty} \eta^*. \quad (8.56)$$

A picture characteristic for the normal stress is obtained if variable

$$[\sigma_1] = \frac{\sigma_1}{\lim_{\kappa \rightarrow \infty} \sigma_1} \quad (8.57)$$

is plotted against the logarithm of κ^* .

In general, on the basis of non-equilibrium thermodynamics for bodies with more dynamic variables, functions (6.152) represented in the above-mentioned way give step-like functions if the relaxation times belonging to individual dynamic variables have different orders of magnitude. If relaxation times are close to each other, these steps merge. The curve for variable $[\eta^*]$ shows a decrease, whereas that for $[\sigma_1]$ an increase. The height of steps belonging to individual dynamic variables is connected by correlation

$$\frac{\Delta[\eta^*]_i \kappa_i^2}{\Delta[\sigma_1]_i} = const \quad (8.58)$$

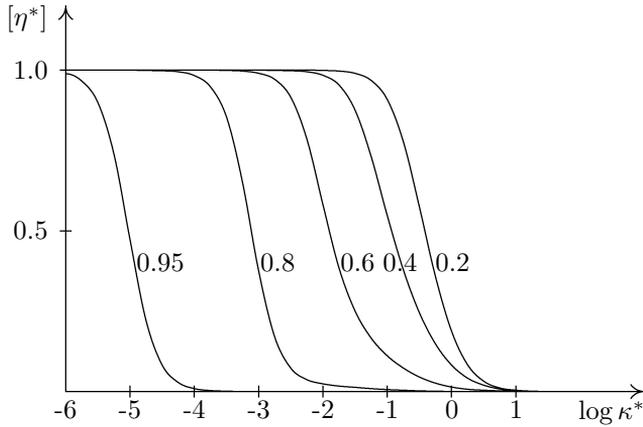


Figure 8.4

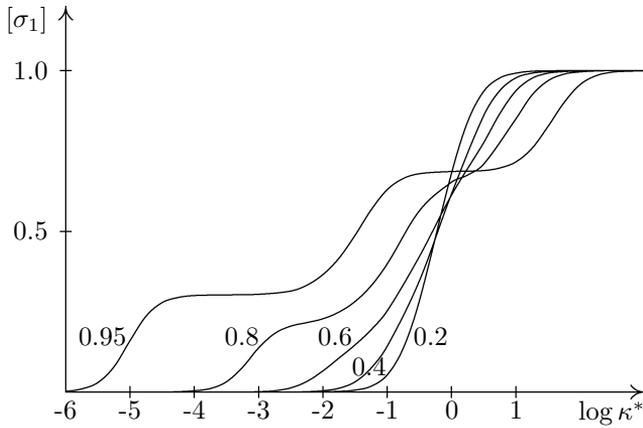


Figure 8.5

as calculated from Eq.(6.152), where $\Delta[\eta^*]_i$ and $\Delta[\sigma_1]_i$ are the heights of the i -th steps, κ corresponds to the middle of the steps.

Figures 8.4. and 8.5. show curves calculated on the basis of equations (8.49)-(8.57). The curves prove the conclusions obtained by non-equilibrium thermodynamics. However, this agreement is only of an approximate nature due to the fact that square root function obtained from the solution of equation (8.49) is not a rational fractional function of variable κ , which was true in the case of approximation (8.45).

Our problem may also be solved in another way instead of solving quadratic equation (8.49). Following the derivation of Boucher [11], we start by assuming the validity of equation (8.41) for low concentrations even when further particles are added to the colloid in low concentrations. In the case, μ_0 means the shear modulus of the starting colloid. Upon repeating this procedure frequently enough, we can arrive at any concentration we want. For elastic materials, according to Boucher, the agreement with experiments is excellent up to high concentrations.

The course of calculation is the following: Let us take a colloid with volume V_1 for the dispersed phase and volume V_0 for the continuous phase. To this colloid, let us add a volume of dV_1 (small amount) of the colloidal particles. The shear modulus of the colloid is now μ (it stands now for μ_0) and μ^* after having added the dV_1 volume of particles. Let us now apply equation (8.41) for changing the modulus so that the original colloid should be considered now to be the continuous phase:

$$\frac{\mu^*}{\mu} - 1 = \frac{\frac{\mu_1}{\mu} - 1}{1 + 0.4 \left(\frac{\mu_1}{\mu} - 1 \right)} \cdot \frac{dV_1}{V_0 + V_1 + dV}, \quad (8.59)$$

Rearranging the equation and utilizing correlations

$$c = \frac{V_1}{V_0 + V_1} \quad \text{and} \quad \mu^* - \mu = d\mu, \quad (8.60)$$

we arrive at differential equation

$$\frac{d\mu}{\mu} = \frac{\mu_1 - \mu}{\mu + 0.4(\mu_1 - \mu)} \frac{dc}{1 - c}$$

the solution of which may be performed by the separation of variables; then we obtain

$$-\ln(\mu_1 - \mu) + 0.4 \ln \mu = -\ln(1 - c) + \ln K. \quad (8.61)$$

The integration constant is determined from the condition $\mu = \mu_0$ if $c = 0$. Thus

$$-\ln(\mu_1 - \mu_0) + 0.4 \ln \mu_0 = \ln K,$$

from which the final equation is

$$\frac{\mu_1 - \mu}{\mu^{0.4}} = (1 - c) \frac{\mu_1 - \mu_0}{\mu_0^{0.4}} \quad (8.62)$$

This result is nearly identical with equation (8.45) for all cases in which μ differs only slightly from μ_0 . This becomes obvious if after rearranging equation (8.62), the function with a fractional power is expanded into a series around 1. To do this, let us substitute variables x and y from equation (8.37):

$$\frac{y - x}{y} = (1 - c)(1 + x)^{0.4} \approx (1 - c)(1 + 0.4x). \quad (8.63)$$

On solving this equation for x , we arrive at equation (8.45). This means that for low concentrations nearly the same result is obtained as from the solution of the complicated quadratic equation (8.36).

Variables in equation (8.62) are usually complex quantities; therefore, calculations with this equation are quite laborious in spite of its simple form, however, it can be conveniently used for computation. Figures 8.6 and 8.7 show results calculated by equation (8.62) for media discussed in section 8.1. On the abscissa is again

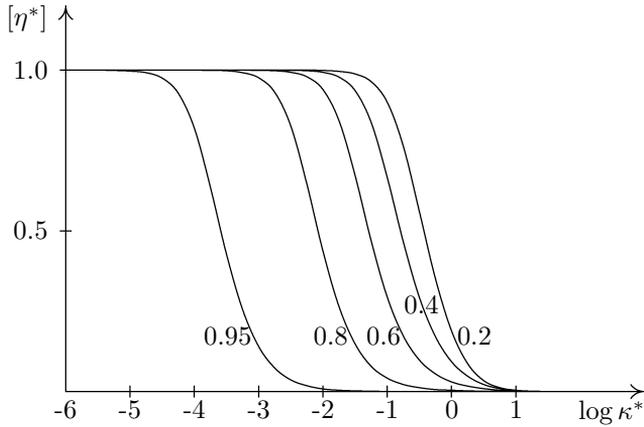


Figure 8.6

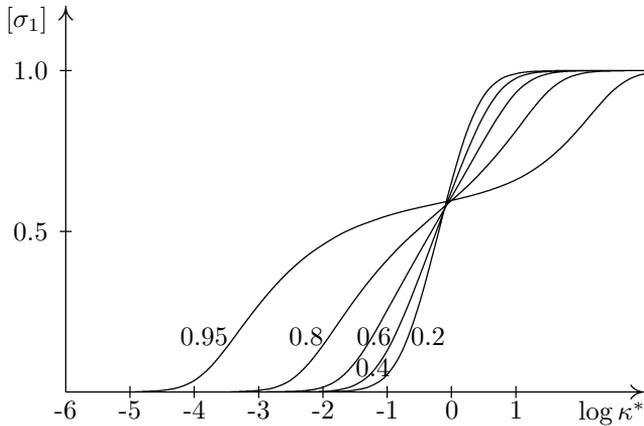


Figure 8.7

the logarithm of κ^* defined by equation (8.54), whereas on the ordinate $[\eta^*]$ defined by equation (8.55) and $[\sigma_1]$ defined by equation (8.57) are represented, respectively.

A third method for calculating the parameters of colloids with not very low concentration will also be shown. This method is essentially very similar to that of Boucher, with the only differences being that colloidal particles are not added in infinitely small steps and that parameters are calculated after individual steps by the repeated application of equation (8.45). Calculations carried out in 4 steps are shown for the medium discussed in section 8.1 in Figures 8.8 and 8.9. The repeated application of equation (8.45) ensures that the complex modulus will be a positive real function of frequency and shear stress.

The repeated application of equation (8.46) ensures that the rheological model of the result can always be obtained. This means that this method provides results completely compatible with the thermodynamic equations.

For a comparison of the three different methods, $\eta^*(0)$, $\eta^*(\infty)$ and $\lim_{\kappa \rightarrow \infty} \sigma_1$ values calculated by these methods as functions of concentration are shown in Figure 8.10.

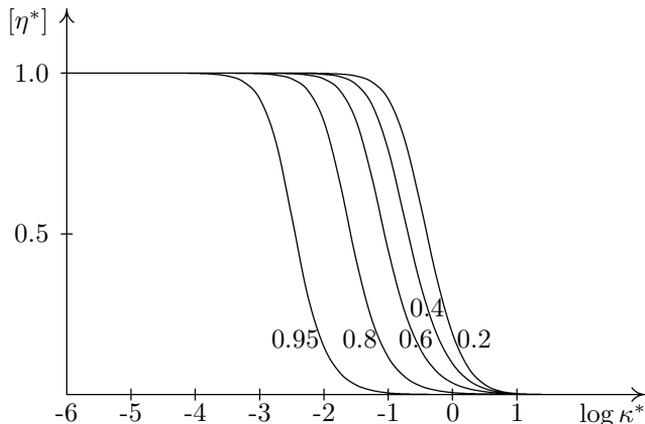


Figure 8.8

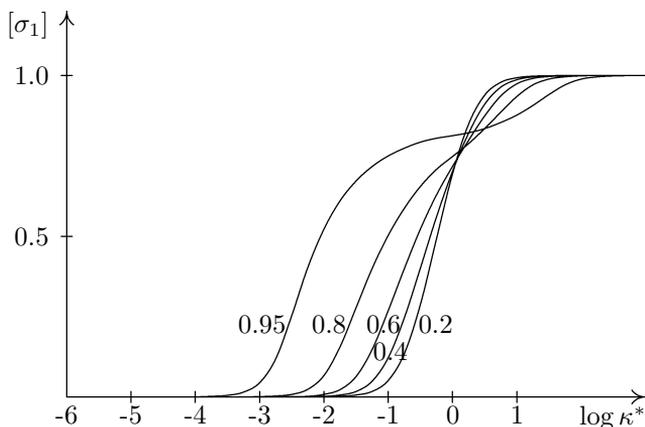


Figure 8.9

On the ordinate, a logarithmic scale is applied. It is apparent from the figure that the three methods give identical results within 10% for volume fractions not greater than 0.3 for the medium studied. A careful analysis of the curves makes it obvious that agreement is excellent even in regions of higher concentrations but not for shear rates that are too small.

Let us now proceed to compressible media. In this case, quadratic equation (8.38) should be solved for non-zero values of z and z_0 . This is a tedious task which will not be done here. The situation is considerably simpler if we restrict our study to low concentrations, in which case we arrive at

$$x = \frac{yc}{1 + 0.4y \frac{8z_0+3}{6z_0+3}} \quad (8.64)$$

analogous to equation (8.41). This equation, together with equation (8.35), is a suitable starting point for Boucher's train of thoughts shown earlier for incompressible components. Concerning details, the reader is referred to the original paper of

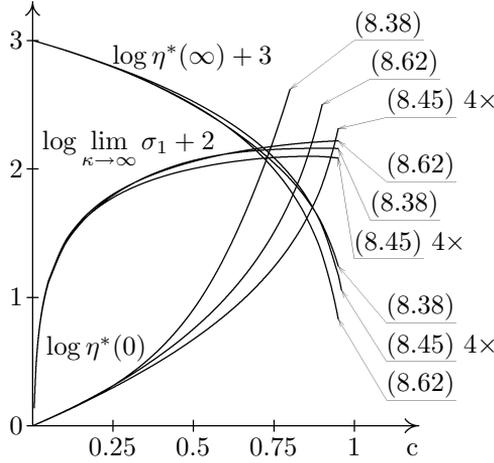


Figure 8.10

Boucher [11]; here we only mention that with the addition of colloidal particles, z_0 also changes; therefore, the procedure results in equations more complicated than those of equation (8.62).

The solution of the problem is simpler if z is considered a constant; then the result is similar to equation (8.62). The fractional power in the denominator will be $0.4 \frac{8z_0+3}{6z_0+3}$ instead of 0.4 and upon expansion into a series, leads to

$$x = \frac{yc}{1 + 0.4y \frac{8z_0+3}{6z_0+3} (1 - c)} \tag{8.65}$$

which is analogous to equation (8.45). This latter equation, together with equation (8.35), may serve as a basis for the approximation calculated in finite steps.

8.3. Effect of interfacial tension: emulsions and foams.

Correlations discussed in the previous section may be applied also when both the continuous and dispersed phases are liquid, or when one of them is gaseous and the other one is liquid. Thus, e.g., for newtonian liquids complex variables

$$\mu_1 = i\kappa\eta_1; \quad \mu_0 = i\kappa\eta_0; \quad \mu = i\kappa\eta \tag{8.66}$$

can be used. All procedures mentioned result in a real value for η , i.e. the emulsion behaves also as a newtonian liquid. However, this conclusion is premature because the effect of interfacial tension has been neglected so far.

Let us now consider the real situation. At rest, the particles in an emulsion or foam are spherical. During motion, they become deformed; and if the volume remains unchanged, their surface increases. Thus, they store excess mechanical energy due to surface tension. For simplicity, we restrict ourselves to uniform particles, and then entropy may be written by analogy to equation (8.1) as

$$s = s_0 \left(u - \frac{c}{\rho} \gamma \frac{\Delta A}{V} \right) \quad (8.67)$$

where γ is the surface tension,

ΔA the increment in the surface of the particle, and

V the volume of the particle.

Let us now determine how the change in the surface depends on the deformation. Due to spherical symmetry, the change in the surface is an isotropic function of the deformation tensor. It is expedient to introduce the deformation tensor in the form

$$\boldsymbol{\varepsilon} = d - \boldsymbol{\delta} \quad (8.68)$$

with which we may write

$$\Delta A = A_0 f(\text{tr } \boldsymbol{\varepsilon}, \text{tr } \boldsymbol{\varepsilon}^2, \text{tr } \boldsymbol{\varepsilon}^3). \quad (8.69)$$

The calculation of function f leads to elliptical integrals in the general case. However, for small deformations we stop at the quadratic term of the function expanded into a power series with respect to the components of $\boldsymbol{\varepsilon}$,

$$f \approx k \text{tr } \boldsymbol{\varepsilon} + k_1 (\text{tr } \boldsymbol{\varepsilon})^2 + k_2 \text{tr } \boldsymbol{\varepsilon}^2. \quad (8.70)$$

Constants k , k_1 and k_2 may be determined also for one-axis deformations (rotational ellipsoid). For this, let us take a rotational ellipsoid whose rotation axis coincides with the x axis of the cartesian coordinate system, and the equation of its contour is

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 \quad (8.71)$$

The surface of the ellipsoid is obtained in this case by calculating the integral

$$A = 2\pi \int_{-a}^a y \sqrt{1 + y'^2} dx. \quad (8.72)$$

which results in

$$\begin{aligned} A &= 2\pi \int_{-a}^a \sqrt{b^2 \left(1 - \frac{x^2}{a^2}\right) + \frac{b^4}{a^4} x^2} dx = 4\pi b \int_{-a}^a \sqrt{1 + \frac{x^2}{a^2} \left(\frac{b^2}{a^2} - 1\right)} dx = \\ &= 4\pi ab \int_0^1 \sqrt{1 + x^2 \left(\frac{b^2}{a^2} - 1\right)} dx. \end{aligned} \quad (8.73)$$

Though this integral may be given by elementary functions, it is more convenient for our purpose to take into account that the difference between a and b is small; thus, the square root in the integrand may be expanded into a binomial series:

$$\begin{aligned} A &\approx 4\pi ab \int_0^1 \left[1 + \frac{x^2}{2} \left(\frac{b^2}{a^2} - 1\right) - \frac{x^4}{8} \left(\frac{b^2}{a^2} - 1\right)^2 \right] dx = \\ &= 4\pi ab \left\{ 1 + \frac{1}{6} \left(\frac{b^2}{a^2} - 1\right) - \frac{1}{40} \left(\frac{b^2}{a^2} - 1\right)^2 \right\}. \end{aligned} \quad (8.74)$$

Introducing expressions

$$a = r(1 + \varepsilon_1) \quad \text{and} \quad b = r(1 + \varepsilon_2) \quad (8.75)$$

and expanding the right side of equation (8.74) again into a series with respect to the exponents of ε_1 and ε_2 and terminating it at the quadratic term, we obtain

$$A = 4\pi r^2 \left[1 + \frac{2}{3}(\varepsilon_1 + 2\varepsilon_2) + \frac{1}{15}(\varepsilon_1^2 + 6\varepsilon_2^2 + 8\varepsilon_1\varepsilon_2) \right]. \quad (8.76)$$

Utilizing that in our case

$$\text{tr } \boldsymbol{\varepsilon} = \varepsilon_1 + 2\varepsilon_2 \quad \text{and} \quad \text{tr } \boldsymbol{\varepsilon}^2 = \varepsilon_1^2 + 2\varepsilon_2^2, \quad (8.77)$$

we arrive at the following result:

$$\Delta A = 4\pi r^2 \left[\frac{2}{3} \text{tr } \boldsymbol{\varepsilon} + \frac{2}{15} (\text{tr } \boldsymbol{\varepsilon})^2 - \frac{1}{15} \text{tr } \boldsymbol{\varepsilon}^2 \right] \quad (8.78)$$

In what follows, we want to study deformations with unchanged volume. When doing this, we cannot restrict ourselves to the linear approximation of dilatation. For volume, in general, correlation

$$V = V_0(1 + \varepsilon_1)(1 + \varepsilon_2)(1 + \varepsilon_3) \quad (8.79)$$

holds the quadratic approximation of which is

$$\Delta V = V_0 \left\{ \text{tr } \boldsymbol{\varepsilon} + \frac{1}{2} [(\text{tr } \boldsymbol{\varepsilon})^2 - \text{tr } \boldsymbol{\varepsilon}^2] \right\}. \quad (8.80)$$

This means that in cases with unchanged volume (equation (8.78)) $\text{tr } \boldsymbol{\varepsilon} = \frac{1}{2} \text{tr } \boldsymbol{\varepsilon}^2$ should be used instead of linear approximation $\text{tr } \boldsymbol{\varepsilon} = 0$. Consequently, on omitting the higher order terms from equation (8.78), expression

$$\Delta A = 4\pi r^2 \frac{4}{15} \text{tr } \boldsymbol{\varepsilon}^2 = 4\pi r^2 \frac{4}{15} \boldsymbol{\varepsilon} : \boldsymbol{\varepsilon} \quad (8.81)$$

is obtained, whose substitution into equation (8.67) results for the entropy in

$$s = s_0 \left(u - \frac{c}{\rho} \frac{4\gamma}{5r} \boldsymbol{\varepsilon} : \boldsymbol{\varepsilon} \right). \quad (8.82)$$

Introducing an effective shear modulus

$$\mu_1 = \frac{4\gamma}{5r}, \quad (8.83)$$

our equation becomes identical with equation (8.1). Thus we may say that our method used in sections 8.1. and 8.2. is applicable also to emulsions; however, the effective shear modulus interpreted by equation (8.83) should be substituted.

It should be mentioned that the effective modulus of shear given by equation (8.83) depends on the size of drops; thus, the equations obtained in previous sections may be applied directly only for homodisperse emulsions. In the presence of drops with different sizes, we should proceed as if several types of colloidal particles were present simultaneously. This also means that more dynamic variables are needed for taking into account the deformation of different particles.

Let us now examine the equations in section 8.2. from the viewpoint of their generality. Equation (8.41) refers to dilute solutions and may be regarded as the linear partial sum of expansions with respect to concentration. Generalization is not difficult: on the basis of definition of y by equation (8.37), quantities

$$y_i = \frac{\mu_i}{\mu_0} - 1 \quad (8.84)$$

may be introduced use whose makes the generalization of equation (8.41) possible in the form

$$x = \sum_{i=1}^N \frac{c_i y_i}{1 + 0.4y_i}, \quad (8.85)$$

where the different colloidal particles are numbered from 1 to N .

The generalization of equation (8.45) contains, however, more arbitrary features. Let us first rearrange equation (8.45) into the form

$$\frac{x}{1 + 0.4x} = \frac{cy}{1 + 0.4y} \quad (8.86)$$

On the basis of this, generalization in the form

$$\frac{x}{1 + 0.4x} = \sum_{i=1}^N \frac{c_i y_i}{1 + 0.4y_i} \quad (8.87)$$

is obvious.

Unfortunately, generalization of the other equations in section 8.2 is much more difficult as the effect of different particles appears in the macroscopic medium in an averaged form; thus the pathway leading to equation (8.36) is not passable and no analogous equation to equation (8.36) may be written for more components present. The generalization of the derivation by Boucher is also doubtful. For more components (namely, on the basis of equation (8.59)), we arrive at correlations

$$\frac{\partial \mu}{\partial c_i} = \frac{\mu}{1 - c_i} \frac{\mu_i - \mu}{\mu + 0.4(\mu_i - \mu)} \quad (8.88)$$

which cannot hold simultaneously for all the components, since the mixed second order derivatives are identical only if $\mu_i = \mu_k$. This may be proved by a simple calculation. This fact calls attention to the shortcomings in the considerations of Boucher.

8.4. Thermal motion of rigid colloidal particles.

In the previous chapters we dealt with the behavior of globular colloids. Now we will examine how colloids behave when the particles are less symmetric. For simplicity, we assume that they are rigid: the effect of deformation had been thoroughly studied in the previous chapters and, presumably, the deformation of particles with an arbitrarily chosen shape did not result in qualitatively different behavior. The effect of the deformation of the particles is overruled by the orientational effects. The latter will be treated in this section within the framework of the linear theory.

Particles of arbitrary shape will not be discussed in what follows, as this would be too complicated; but we assume that the colloidal particles have a preferred direction around which their rotation is indifferent with respect to their properties, and even a rotation of this preferential direction by 180° is without consequences. This means that the particles may be regarded as of cylindrical symmetry. However, a lower order of symmetry would also be sufficient to reach the same results, that is, the assumption of a three-fold or higher-order rotational axis; but this would only complicate the calculation.

The orientation of particles can be given by a vector whose size may be arbitrary, but it is more expedient not to consider the size of the vector at all, i.e. vectors n and $-n$ will be regarded as identical. This assumption implies also our condition that n and $-n$ mean identical orientations.

Let us suppose that the orientation of particles is random, and in the equilibrium state of an isotropic colloid, the orientation has a distribution with spherical symmetry. During flow, obviously the continuous phase carries the particles along thereby distorting the spherical symmetry. It is also obvious that the spherical symmetry of distribution is restored by the Brownian motion of the particles after the flow stopped. This cannot take place during flow, even though the effect of Brownian motion also prevails then.

The orientation distribution of the particles will be illustrated by a closed surface whose volume is constant and whose equilibrium shape is spherical. If flow distorts the sphere, the deformed shape may be considered, up to a first approximation, an ellipsoid. This means that the deformation of the sphere can be characterized by a symmetric second-order tensor of zero trace ε , i.e. for characterizing the local state of the colloid, besides internal energy, a symmetric second-order tensor of zero trace is necessary as a dynamic variable. For small ε -s, the entropy can be expanded into a series with respect to the components of ε up to the quadratic term:

$$s = s_0(u) - \frac{s''}{2} \varepsilon : \varepsilon, \quad (8.89)$$

where s'' is a positive constant. This provides a starting point for thermodynamic treatment. If we introduce the new dynamic variable

$$\xi = \sqrt{s''} \varepsilon \quad (8.90)$$

the form of the entropy function will be identical with equation (8.4). As the shape of the sphere representing distribution does not change on time inversion, we may introduce variable

$$\sqrt{\rho T} \xi = \alpha$$

by means of which the problem can be treated in the same way as we have done for globular colloids in section 8.1.

In order to confirm the results of the thermodynamic theory, constitutive equation will also be derived on the basis of structural considerations. For this, let us first calculate the entropy for an arbitrary particle distribution. Configurational entropy s_c for one particle can be calculated from the distribution by the formula known from statistical physics

$$s_c = -k \int f \ln f d\Omega \quad (8.91)$$

where k is Boltzmann's constant,

f the density function of the probability distribution, and

$d\Omega$ the measure of the infinitesimal part of the space of events.

However, it is expedient to double the space of events and to perform integration for the total surface of the sphere. On taking the radius of the sphere to be unity,

$$s_c = -\frac{k}{2} \oint_S f \ln f dA \quad (8.92)$$

Due to the doubling of the space of events, the condition of normalization is

$$\oint_S f dA = 2$$

If distribution differs only slightly from that of spherical symmetry, notation

$$f = \frac{1}{2\pi}(1 + \varphi) \quad (8.93)$$

can be introduced; by using this, we obtain for small φ

$$\oint_S \varphi dA = 0, \quad s_c = k \ln 2\pi - \frac{k}{4\pi r^2} \oint_S \varphi^2 dA. \quad (8.94)$$

Specific entropy is now obtained in the form

$$s = s_0(u) - \frac{kN}{4\pi r^2} \oint_S \varphi^2 dA \quad (8.95)$$

where N is the number of particles in the unit mass of the colloid. If only Brownian motion is involved, the time course of the change in distribution function f can be described by the equation of diffusion on the surface of the sphere. In order to be able to use the equation of spatial diffusion, we employ relationship

$$\frac{\partial f}{\partial t} = \text{div}(Dr^2 \text{grad } f) \quad (8.96)$$

which, on the surface of the sphere with unit radius, is identical with the diffusion equation; and for solutions satisfying the initial condition

$$\left. \frac{\partial f}{\partial r} \right|_{t=0} = 0, \quad (8.97)$$

$\frac{\partial f}{\partial r} = 0$ is fulfilled forever.

Let us now examine what effect is exerted by the motion on the time dependence of the probability distribution in question. The continuous phase of the colloidal solution is a newtonian liquid for which the Navier-Stokes equation holds. We assume that the colloidal particles are very small, thus their moment of inertia may be neglected and the non-linear terms in the Navier-Stokes equation may be omitted. Based on this assumption we may say that the medium flowing around the particle does not exert any torque on the particle. However, this is only possible for a given rotation rate of the particle. The direction of the particle is denoted by n and the velocity field far from the particle should be

$$\mathbf{v} = \text{Grad } \mathbf{v} \cdot \mathbf{r} = (\dot{\mathbf{d}} + \boldsymbol{\omega})\mathbf{r}. \quad (8.98)$$

As the non-linear terms are neglected in the equations describing the motion, the time derivative of vector n characterizing orientation is a homogeneous linear function of $\text{Grad } \mathbf{v}$ if we disregard Brownian motion:

$$\frac{dn}{dt} = \mathbf{T} \text{Grad } \mathbf{v}, \quad (8.99)$$

where \mathbf{T} is a third-order tensor characteristic of the shape and orientation of the particle.

Upon writing equation (8.99) for the components:

$$\frac{dn_i}{dt} = T_{ijk} v_{j,k}, \quad (8.100)$$

we can determine tensor \mathbf{T} . For this, let us define a cartesian coordinate system whose third axis coincides with the direction of \mathbf{n} . As the size of \mathbf{n} is uninteresting, we take it for unity, from which it follows that in our coordinate system

$$\frac{dn_3}{dt} = 0, \quad \text{i.e.} \quad T_{3jk} = 0. \quad (8.101)$$

We assumed that the particle is of cylindrical symmetry; therefore, it has a symmetry plane perpendicular to axes x_1 and x_2 (among the non-zero components of \mathbf{T} cannot be involved an odd number of elements with subscripts 1 and 2). Thus the non-zero components of \mathbf{T} are T_{113} , T_{131} , T_{223} and T_{232} . As axes 1 and 2 are equivalent due to the cylindrical symmetry, correlations

$$T_{113} = T_{223}, \quad T_{131} = T_{232} \quad (8.102)$$

hold, which lead to

$$\begin{aligned}\frac{dn_1}{dt} &= T_{113}v_{1,3} + T_{131}v_{3,1}, \\ \frac{dn_2}{dt} &= T_{113}v_{2,3} + T_{131}v_{3,2}.\end{aligned}\tag{8.103}$$

Rearranging the equations and introducing notations

$$a = T_{113} + T_{131}, \quad b = T_{113} - T_{131},\tag{8.104}$$

we obtain

$$\frac{dn_1}{dt} = a\dot{d}_{31} + b\omega_{31}, \quad \frac{dn_2}{dt} = a\dot{d}_{23} + b\omega_{32}, \quad \frac{dn_3}{dt} = 0,\tag{8.105}$$

the concise, invariant form of which is:

$$\frac{dn}{dt} = a(\boldsymbol{\delta} - \mathbf{n} \circ \mathbf{n})\dot{\mathbf{d}}\mathbf{n} + b\boldsymbol{\omega}\mathbf{n}\tag{8.106}$$

by which form we dispose of the particular coordinate system.

Let us now define an arbitrary orientation vector r' of a constant size:

$$r' = \lambda n,\tag{8.107}$$

where λ is an arbitrary constant. On rearranging equation (8.106), we arrive at

$$\frac{dr'}{dt} = a\left(\boldsymbol{\delta} - \frac{\mathbf{r}' \circ \mathbf{r}'}{r'^2}\right)\dot{\mathbf{d}}\mathbf{r}' + b\boldsymbol{\omega}\mathbf{r}'.\tag{8.108}$$

If the medium rotates like a rigid body, i.e. $\dot{\mathbf{d}} = 0$, then, obviously, the orientation vector also rotates with the same angular velocity; thus $b = 1$, with which the final form of equation (8.99) becomes

$$\frac{dr'}{dt} = a\left(\boldsymbol{\delta} - \frac{\mathbf{r}' \circ \mathbf{r}'}{r'^2}\right)\dot{\mathbf{d}}\mathbf{r}' + \boldsymbol{\omega}\mathbf{r}'.\tag{8.109}$$

Thus the vector describing the orientation of the particles floats with this rate. It may be noted that the value of a can be determined by the solution of the Navier-Stokes equations and that Jeffery [81] has solved them for particles with the shape of rotational ellipsoids.

The description of the evolution of the distribution function needs the additional term

$$J_v = f \frac{d\mathbf{r}'}{dt}\tag{8.110}$$

to give account on the drift on the surface of the sphere. Taking also this into account, instead of equation (8.96) the following expression is obtained:

$$\frac{\partial f}{\partial t} = \text{div} \left[Dr^2 \text{grad} f - af \left(\boldsymbol{\delta} - \frac{\mathbf{r} \circ \mathbf{r}}{r^2} \right) \dot{\mathbf{d}}\mathbf{r} - f\boldsymbol{\omega}\mathbf{r} \right]\tag{8.111}$$

Let us now replace f by function φ defined in equation (8.93), then

$$\frac{\partial \varphi}{\partial t} = \operatorname{div} \left[Dr^2 \operatorname{grad} \varphi - a(1 + \varphi) \left(\boldsymbol{\delta} - \frac{\mathbf{r} \circ \mathbf{r}}{r^2} \right) \dot{\mathbf{d}}\mathbf{r} - \varphi \boldsymbol{\omega}\mathbf{r} \right] \quad (8.112)$$

Since φ is usually small and its integral with respect to the surface of the sphere is zero, we define it as a series with respect to spherical functions and stop at the first term:

$$\varphi = \frac{1}{2r^2} \mathbf{r}\boldsymbol{\Xi}\mathbf{r}, \quad (8.113)$$

where $\boldsymbol{\Xi}$ is a second-order tensor of zero trace. Upon substituting this into the differential equation, we arrive at

$$\frac{1}{2r^2} \mathbf{r}\dot{\boldsymbol{\Xi}}\mathbf{r} = -3D \frac{1}{r^2} (\mathbf{r}\boldsymbol{\Xi}\mathbf{r}) + 3a \frac{\mathbf{r}\dot{\mathbf{d}}\mathbf{r}}{r^2} + \frac{5a}{2r^4} (\mathbf{r}\boldsymbol{\Xi}\mathbf{r})(\mathbf{r}\dot{\mathbf{d}}\mathbf{r}) - \frac{a}{r^2} \mathbf{r}\boldsymbol{\Xi}\dot{\mathbf{d}}\mathbf{r} - \frac{1}{r^2} \mathbf{r}\boldsymbol{\Xi}\boldsymbol{\omega}\mathbf{r}. \quad (8.114)$$

As we took the first non-zero term of the series expanded with respect to spherical functions, we omit from the third term (on the right side) the part belonging to the omitted terms. Then we take the equation for tensor $\boldsymbol{\Xi}$ on the basis of the quadratic forms of coordinates r at both the left and right sides:

$$\dot{\boldsymbol{\Xi}} = -6D\boldsymbol{\Xi} + 6a\dot{\mathbf{d}} + \frac{3a}{7} \left[\boldsymbol{\Xi}\dot{\mathbf{d}} + \dot{\mathbf{d}}\boldsymbol{\Xi} - \frac{2}{3}(\boldsymbol{\Xi} : \dot{\mathbf{d}})\boldsymbol{\delta} \right] - \boldsymbol{\Xi}\boldsymbol{\omega} + \boldsymbol{\omega}\boldsymbol{\Xi}. \quad (8.115)$$

On collecting terms containing $\boldsymbol{\omega}$ on the left side and introducing the objective time derivative of $\boldsymbol{\Xi}$, we obtain

$$\dot{\boldsymbol{\Xi}} = 6a\dot{\mathbf{d}} - 6D\boldsymbol{\Xi} + \frac{3}{7}a \left[\boldsymbol{\Xi}\dot{\mathbf{d}} + \dot{\mathbf{d}}\boldsymbol{\Xi} - \frac{2}{3}(\boldsymbol{\Xi} : \dot{\mathbf{d}})\boldsymbol{\delta} \right]. \quad (8.116)$$

This equation corresponds to equation (6.105) which may readily be understood if we introduce (instead of $\boldsymbol{\Xi}$) variable $\boldsymbol{\alpha}$ proportional to $\boldsymbol{\Xi}$. As a matter of fact, if we calculate the surface integral in the expression (8.95) of entropy by utilizing also equation (8.113)

$$\frac{1}{r^2} \oint \varphi^2 dA = \frac{1}{4r^6} \oint (\mathbf{r}\boldsymbol{\Xi}\mathbf{r})^2 dA = \frac{2\pi}{15} \boldsymbol{\Xi} : \boldsymbol{\Xi}$$

we may write that

$$s = s_0(u) - \frac{kN}{30} \boldsymbol{\Xi} : \boldsymbol{\Xi}. \quad (8.117)$$

On comparing this expression with equation (6.1) and (6.9), we obtain

$$\boldsymbol{\xi} = \sqrt{\frac{kN}{15}} \boldsymbol{\Xi}, \quad \boldsymbol{\alpha} = \sqrt{\frac{\rho T k N}{15}} \boldsymbol{\Xi} \quad (8.118)$$

whose substitution into equation (8.116) leads to

$$\dot{\boldsymbol{\alpha}} = 6a \sqrt{\frac{\rho T k N}{15}} \dot{\mathbf{d}} - 6D\boldsymbol{\alpha} + \frac{3a}{7} \left[\boldsymbol{\alpha}\dot{\mathbf{d}} + \dot{\mathbf{d}}\boldsymbol{\alpha} - \frac{2}{3}(\boldsymbol{\alpha} : \dot{\mathbf{d}})\boldsymbol{\delta} \right]. \quad (8.119)$$

If we restrict ourselves to small values of \mathring{d} , the last terms on the right side may be neglected; however, in this approximation we arrive again at the equations of the linear theory.

It should be noted that the equations derived are valid primarily for small concentrations. A usable correlation for higher concentrations may be obtained by applying the considerations of Boucher.

Before finishing our analysis, it is important to note that equation (8.119) derived by microscopic considerations is perfectly identical with equation (6.105) obtained by using phenomenological thermodynamics. For coefficients \mathcal{H}'_{12} and \mathcal{H}'_{22} introduced there, we obtain correlations

$$\mathcal{H}'_{12} = -\frac{3a}{14}, \quad \mathcal{H}'_{22} = 0. \quad (8.120)$$

This agreement is partly reassuring, but calls attention partly to the fact that the partial validity of equation (8.119) does not prove that the fluid contains rigid particles of cylindrical symmetry since it has not been assumed in the phenomenological derivation of equation (6.105); hence, other microscopic models may lead to the same result. Thus, for example measured data remaining within the range of validity of linear equations cannot decide whether the colloidal particles are elastic spheres or rigid ellipsoids, since in section 8.2. we have obtained similar results. However, the hypothesis applied for microscopic structure is supported by the numerical agreement of coefficients with data calculated from measurements concerning other physical phenomena. Nevertheless, care should also be taken here, as the properties of spherical functions used in the approximation are always the same, independently of the microscopic model and the physical phenomenon discussed. In what follows, the motion of chain molecules will also be studied by applying spherical functions.

8.5. Viscosity of polymers.

This part shows that the Rouse-Bueche theory [16,140] of liquids containing chain molecules, (i.e., polymer solutions and melts) is in perfect accordance with the results of non-equilibrium thermodynamics [33, 83, 106, 107]. First, the statistical theory of liquids containing chain molecules will be summarized briefly; then the Rouse-Bueche theory will be demonstrated in a slightly generalized form. As a first step, the equilibrium configurations of chain molecules will be dealt with.

8.5.1. Equilibrium configuration of chain molecules. The simplest model of chain molecules is the so-called free chain model. According to this model, the polymer molecule consists of connected segments of uniform length which can rotate freely. The molecule will be characterized by a vector pointing from one of its ends to the other, and we assume that the segments of the molecule are randomly arranged. Vector \mathbf{a} determining the orientation of individual segments is a random variable whose distribution function is uniform on the surface of a sphere with the radius a . Vector \mathbf{r} drawn from one end to the other is the sum of vectors \mathbf{a} characterizing the segments in the chain. It is also a random variable. Supposing that the polymer molecule consists of numerous segments, the central limit theorem of probability calculus can be applied, and we may say that the vector connecting

the two ends is of normal distribution. As the distribution is three-dimensional, we have to know the variance tensor and the mean value to determine it. The latter quantities can be calculated from the mean value of vectors \mathbf{a} of individual segments and their variances by the well-known correlations

$$\mathbf{M}(\mathbf{r}) = N\mathbf{M}(\mathbf{a}), \quad \sigma^2(\mathbf{r}) = N\sigma^2(\mathbf{a}) \quad (8.121)$$

where \mathbf{M} is the mean value,

σ^2 the variance tensor, and

N the number of segments in the chain.

Quantities characteristic for individual segments are defined by the following equations of probability calculus:

$$\mathbf{M}(\mathbf{a}) = \oint \frac{\mathbf{r}}{4\pi a^2} dA \quad (8.122)$$

$$\sigma^2(\mathbf{a}) = \oint \frac{[\mathbf{r} - \mathbf{M}(\mathbf{a})] \circ [\mathbf{r} - \mathbf{M}(\mathbf{a})]}{4\pi a^2} dA \quad (8.123)$$

where integration should be carried out on the whole surface of the sphere with radius a .

The spherical integrals are easy to calculate by taking into account that the elements of a spherical surface are perpendicular to the radius belonging to them; thus,

$$\mathbf{r} dA = a d\mathbf{A}, \quad a dA = \mathbf{r} d\mathbf{A} \quad (8.124)$$

hold. By using these correlations, surface integrals can be transformed into volume integrals:

$$\mathbf{M}(\mathbf{a}) = \frac{1}{4\pi a^2} \oint \mathbf{r} dA = \frac{1}{4\pi a^2} \oint a d\mathbf{A} = \frac{1}{4\pi a} \oint d\mathbf{A} = 0 \quad (8.125)$$

and

$$\begin{aligned} \sigma^2(\mathbf{a}) &= \frac{1}{4\pi a^2} \oint r \circ r dA = \frac{1}{4\pi a} \oint \mathbf{r} \circ d\mathbf{A} = \\ &= \frac{1}{4\pi a} \int (\mathbf{r} \circ \nabla) dV = \frac{1}{4\pi a} \delta \int dV = \frac{1}{4\pi a} \delta \frac{4\pi a^3}{3} = \frac{a^2}{3} \delta. \end{aligned} \quad (8.126)$$

On substituting these into equation (8.121) we obtain:

$$\mathbf{M}(\mathbf{r}) = 0, \quad \sigma^2(\mathbf{r}) = \frac{Na^2}{3} \delta. \quad (8.127)$$

The distribution density function of the end-to-end vector can be written as

$$f(\mathbf{r}) = C \exp\left(-\frac{3r^2}{2Na^2}\right) \quad (8.128)$$

where the value of normalization factor C is:

$$C = \frac{1}{a^3} \left(\frac{3}{2\pi N}\right)^{3/2}. \quad (8.129)$$

Notice that the distribution function obtained is very similar to the Boltzmann distribution of a harmonic oscillator with thermal motion, since its distribution density is

$$f = C \exp\left(-\frac{U}{kT}\right) = C \exp\left(-\frac{\mathbf{r}\mathbf{K}\mathbf{r}}{2kT}\right), \quad (8.130)$$

where \mathbf{K} is the tensor characteristic for the quasi-elastic field,
 k the Boltzmann constant, and
 T the temperature.

This means that the vector connecting the ends of an N -member free chain behaves similarly to the position vector of a harmonic oscillator if correlation

$$\mathbf{K} = kT\boldsymbol{\sigma}^{-2}(\mathbf{r}) \quad (8.131)$$

holds.

The analogy is, as usual, not perfect, since the entropy of harmonic oscillators can be calculated from distribution function (8.130) on the basis of equation

$$s = -k \int f \ln f dV \quad (8.132)$$

while for free chains it must also be considered that to the same end-to-end vector different configurations may belong which influence significantly the entropy. The entropy of the chain is derived as follows.

Let us determine first the distribution of vector \mathbf{a} characteristic for the position of segments by assuming that the value of the vector connecting chain ends is \mathbf{R} . We suppose that the distribution functions of individual segments are identical and calculate conditional entropies and then summarize them according to

$$S = N \int s(\mathbf{a}|\mathbf{R})f(\mathbf{R})dV + S(\mathbf{R}). \quad (8.133)$$

Since on the basis of the independence of the positions of individual segments, we may say that the conditional distribution density of vector \mathbf{a} depends only on \mathbf{R}/N ; thus, we may write

$$f(\mathbf{a}|\mathbf{R}) = f\left(\mathbf{a}, \frac{\mathbf{R}}{N}\right). \quad (8.134)$$

which, for small values of \mathbf{R}/N and also considering the isotropy of space, takes the form

$$f(\mathbf{a}|\mathbf{R}) = \frac{1}{4\pi a^2} \left(1 + \lambda \frac{\mathbf{R}}{N} \mathbf{a}\right) \quad (8.135)$$

These equations are strictly valid only for small \mathbf{R}/N ; values, but on using equation (8.133), it is sufficient since large \mathbf{R}/N is highly improbable according to equation (8.128). For determining λ , we may start from

$$M(\mathbf{a}|\mathbf{R}) = \frac{\mathbf{R}}{N}, \quad (8.136)$$

whose comparison with equation (8.135) leads to correlation

$$\begin{aligned} \frac{\mathbf{R}}{N} &= \frac{1}{4\pi a^2} \oint \mathbf{r} \left(1 + \frac{\lambda \mathbf{R}}{N} \mathbf{r}\right) dA = \frac{1}{4\pi a} \oint \left(1 + \frac{\lambda \mathbf{R}}{N} \mathbf{r}\right) d\mathbf{A} = \\ &= \frac{1}{4\pi a} \int \frac{\lambda \mathbf{R}}{N} dV = \frac{\lambda}{4\pi a} \frac{\mathbf{R}}{N} \frac{4\pi a^3}{3} \end{aligned} \quad (8.137)$$

from which

$$\lambda = \frac{3}{a^2}. \quad (8.138)$$

Thus, the density function of conditional distribution sought is

$$f(\mathbf{a}|\mathbf{R}) = \frac{1}{4\pi a^2} \left(1 + \frac{3}{Na^2} \mathbf{R}\mathbf{r} \right). \quad (8.139)$$

Conditional entropy can be calculated from the equation

$$s(\mathbf{a}|\mathbf{R}) = -k \oint f(\mathbf{a}|\mathbf{R}) \ln f(\mathbf{a}|\mathbf{R}) dA. \quad (8.140)$$

However, let us also take into consideration that due to the small value of \mathbf{R}/N , the density function of conditional distribution differs only slightly from uniform distribution. Based on this, we may write that

$$f(\mathbf{a}|\mathbf{R}) = f_0(1 + f^*), \quad (8.141)$$

where

$$f_0 = \frac{1}{4\pi a^2} \quad \text{and} \quad f^* = \frac{3}{Na^2} \mathbf{R}\mathbf{r} \quad (8.142)$$

On utilizing this, instead of equation (8.140), we may write

$$\begin{aligned} s(\mathbf{a}|\mathbf{R}) &= -k \oint f_0(1 + f^*) \ln f_0 + f^* - \frac{f^{*2}}{2} dA = \\ &= -k \oint f_0 \ln f_0 + f^*(f_0 \ln f_0 + 1) + \frac{f^{*2}}{2} f_0 dA = \\ &= s(\mathbf{a}) - k \frac{1}{8\pi a^2} \oint \left(\frac{3}{Na^2} \mathbf{R}\mathbf{r} \right)^2 dA = \\ &= s(\mathbf{a}) - \frac{9k}{8\pi N^2 a^5} \oint (\mathbf{R}\mathbf{r})\mathbf{R} dA = s(\mathbf{a}) - \frac{9k}{8\pi N^2 a^5} \int \mathbf{R}^2 dV = \\ &= s(\mathbf{a}) - \frac{9k\mathbf{R}^2}{8\pi N^2 a^5} \frac{4\pi a^3}{3} = s(a) - \frac{3k}{2} \left(\frac{\mathbf{R}}{Na} \right)^2, \end{aligned} \quad (8.143)$$

where $s(\mathbf{a})$ is the entropy of uniform distribution. In the calculations it has been taken into account that f^* is small; therefore, on expanding the integrand with respect to powers of f^* , we may stop at the quadratic term. The entropy of the whole chain is obtained from equation (8.133) as

$$S = Ns(\mathbf{a}) - \frac{3k}{2Na^2} \int \mathbf{R}^2 f(\mathbf{R}) dV - k \int f(\mathbf{R}) \ln f(\mathbf{R}) dV. \quad (8.144)$$

This expression is usable also if the distribution of the vector connecting chain ends has a non-equilibrium distribution but the distribution of individual segments is of an equilibrium type. This is an obvious contradiction which will be resolved later.

We will now examine how our results are influenced by interactions between the segments. We keep further to our assumption that the vector connecting chain ends has a normal distribution. This is not a strong restriction since random variables consisting of the sum of many variables with the same distribution may be approximated in a wide range by a normal distribution. The expected value of the end-to-end vector is zero owing to the isotropy of space. The statement that the variance tensor is approximately proportional to chain length is also true in the case of interactions. We also assume that the individual segments are distributed uniformly, but now they are not independent of each other. Since their expected value is zero, the variance tensor is

$$\sigma^2(\mathbf{r}) = \sum_{i,k} \mathbf{M}(\mathbf{a}_i \circ \mathbf{a}_k), \quad (8.145)$$

where i and k denote the serial number of individual segments and summation is done over all segments. If we now assume, for simplicity, that only the distributions of neighboring segments are interrelated but those of farther ones are not, we may write

$$\sigma^2(\mathbf{r}) = \sum_i \mathbf{M}(\mathbf{a}_i \circ \mathbf{a}_{i-1} + \mathbf{a}_i \circ \mathbf{a}_i + \mathbf{a}_i \circ \mathbf{a}_{i+1}). \quad (8.145a)$$

Since the variance tensors of individual variables \mathbf{a}_i are identical, we obtain

$$\sigma^2(\mathbf{r}) = N \frac{a^2}{3} \boldsymbol{\delta} + 2(N-1) \frac{a^2}{3} \boldsymbol{\delta} \mathbb{R} = N \frac{a^2}{3} \left(1 + \frac{2(N-1)}{N} \mathbb{R} \right) \boldsymbol{\delta}, \quad (8.146)$$

where \mathbb{R} is the correlation coefficient of the distributions of neighboring segments. For large N , $1/N$ is negligible; thus

$$\sigma^2(\mathbf{r}) = N \frac{a^2}{3} (1 + 2\mathbb{R}) \boldsymbol{\delta} \quad (8.147)$$

is obtained in which the value of \mathbb{R} depends on the nature of interactions and the temperature, as well.

Finally, we mention that if we wish consider the interactions between more remote segments as well, further terms should be included in equation (8.145); but this modifies only the meaning of \mathbb{R} in equation (8.147). This problem will not be dealt with further. On the other hand, it is also remarkable that when writing conditional distribution function (8.135), we did not utilize the independence of the distributions for individual segments; hence our equations derived for entropy may also be used if interactions are considered.

8.5.2. Motion of chain molecules. When describing the motion of long chain molecules we start from the assumption that expression (8.143) of conditional entropy is applicable also when the liquid containing chain molecules is not in equilibrium and, thus, the distribution of end-to-end vector differs from that given by equation (8.128). This, as was mentioned earlier, is a contradiction, but it does not lead to erroneous results. This assumption is made on the basis of the fact that the shorter the polymer chain is, the sooner it assumes an equilibrium configuration.

Thus we are justified in supposing that the distribution of individual segments inside a short part of the chain correspond to that described by equation (8.139), although the distribution of the end-to-end vector is far from equilibrium. The contradiction may be resolved in the following way. The long polymer chain is divided into shorter sections so that individual parts should satisfy equation (8.128). The individual sections are substituted by harmonic oscillators with parameters given by equation (8.131) whose entropy is calculated by equation (8.144). The problem of coupled oscillators can be treated easily. It will be useful in later quantitative discussions if we compare the equation of conditional entropy (8.143) with the characteristics of the quasi-elastic field based on equations (8.131) and (8.147). The conditional entropy for the whole chain is determined on the basis of equation (8.143)

$$S = S_0 - \frac{3k}{2Na^2} \mathbf{r}^2 \quad (8.148)$$

where instead of \mathbf{R} we use notation \mathbf{r} . Considering equations (8.127) and (8.131), we may write that

$$S = S_0 - \frac{3k}{2Na^2} \frac{Na^2}{3} \mathbf{r} \boldsymbol{\sigma}^{-2} \mathbf{r} = S_0 - \frac{1}{T} \frac{\mathbf{r} \mathbf{K} \mathbf{r}}{2} = S_0 - \frac{1}{T} U^*, \quad (8.149)$$

where U^* is the potential energy of the substituting quasi-elastic field.

For quantitative discussion, let us divide the long chain containing N segments into M identical sections. The individual sections should be short enough for equations derived for conditional entropy to be valid to a good approximation, but long enough for the distribution of the vector connecting chain ends to be approximated by a normal distribution which is necessary for equation (8.131) to be applicable. For long enough chain molecules, these two conditions can be satisfied simultaneously.

In this case, the chain molecule may be replaced by a point system consisting of $M + 1$ particles in which subsequent points are coupled by quasi-elastic forces. The force acting on the j -th point mass is given by correlation

$$\mathbf{F}_j = K(\mathbf{r}_{j+1} + \mathbf{r}_{j-1} - 2\mathbf{r}_j) \quad (8.150)$$

where K is according to our earlier hypotheses and equations (8.131) and (8.147)

$$K = \frac{3kTM}{Na^2(1 + 2\mathbb{R})}. \quad (8.151)$$

Notice that equation (8.150) does not hold for particles at the ends of the chain. Those relationships will not be examined here, but rather approached in a different way later.

Let us first investigate classical mechanical motions determined by forces (8.150). Equations of motion for individual particles are:

$$m\ddot{\mathbf{r}}_j = K(\mathbf{r}_{j+1} + \mathbf{r}_{j-1} - 2\mathbf{r}_j). \quad (8.152)$$

Their solution will be sought in the form

$$\mathbf{r}_j = \mathbf{A} \exp[i(j\delta - \omega t)]. \quad (8.153)$$

On substituting the trial function into the differential equation we obtain

$$-m\omega^2 \mathbf{r}_j = \kappa \mathbf{r}_j (e^{i\delta} + e^{-i\delta} - 2), \quad (8.154)$$

from which

$$m\omega^2 = 2\kappa(1 - \cos \delta) = 4\kappa \sin^2 \frac{\delta}{2} \quad (8.155)$$

results. This means that the differential equation system (8.152) is satisfied by all functions in the form of equation (8.153) whose parameters ω and δ satisfy equality (8.155). Since n is an integer, we may say that the value of δ falls between $-\pi$ and π . Let us now notice the analogy between functions of the form given by equation (8.153) and traveling waves. Waves determined by $+\delta$ and $-\delta$ differ from each other only in the direction of propagation; but in solutions representing standing waves the two occur together. Thus in searching for standing waves, we may state that δ is positive. The analogy with waves also helps overcome the difficulty that the force for the chain ends has not been determined. If the chain end is free — this corresponds to the chemical freedom of chain ends, as well — the standing wave has here an antinode if the chain end is closed — e.g., if it is chemically bonded to a loose network — a node can be observed. The two cases should be distinguished. In the case when the two ends of the chain are both free or bonded, the whole chain length is an integral multiple of the half wavelength, i.e.

$$M\delta = n\pi, \quad (8.156)$$

whence

$$\delta = n \frac{\pi}{M}. \quad (8.157)$$

Thus in the case of bonded chain ends for δ , $M - 1$ different possible values are obtained. This means $2(M - 1)$ linearly independent particular solutions if we consider also the independence of $\sin \omega t$ and $\cos \omega t$, which makes a complete solution system since the two ends do not move. In the case of free chain ends, $n = M$ is also allowed; thus $2M$ particular solutions exist to which two further particular solutions are added by uniform translation.

The situation is somewhat different if one chain end is free and the other one is bonded. Then the length of the whole chain is an odd multiple of the quarter of the wavelength, i.e.

$$M\delta = (2n + 1) \frac{\pi}{2} \quad (8.158)$$

from which

$$\delta = \frac{2n + 1}{2M} \pi \quad (8.159)$$

follows. Thus $(M - 1)$ possible values can be assigned to δ which makes also a complete set of solutions. Let us notice that the number of degrees of freedom for

the oscillator chain is identical with those of the polymer chain if $N = M$. Further on, M will be chosen correspondingly.

Let us now rewrite solution (8.153) into form

$$\mathbf{r}_j = \mathbf{A}(t)e^{ij\delta}. \quad (8.160)$$

Then function $A(t)$ is defined by differential equation

$$m\ddot{\mathbf{A}} = K\mathbf{A}(e^{i\delta} + e^{-i\delta} - 2) = -4K \sin^2 \frac{\delta}{2} \mathbf{A} \quad (8.161)$$

on the basis of equation (8.152). The solutions of this equation are well known; it is shown here only for proving that the motion of the whole chain may be really substituted by a system of independent harmonic oscillators, for which the law

$$\mathbf{F}_n = -4K \sin^2 \frac{\delta_n}{2} \mathbf{A}_n \quad (8.162)$$

holds. To these, potential energy can be ascribed by the following equation

$$U_n^* = 2K \sin^2 \frac{\delta_n}{2} \mathbf{A}_n^2 = \frac{1}{2} K_n \mathbf{A}_n^2. \quad (8.163)$$

Since there is no coupling between the oscillators, their thermal motions can be treated individually. Before starting with this, we want to show that the oscillators describing the motion of chain molecules in a flowing medium are floated along.

In order to prove this, force laws (8.152) are supplemented by the linear law of the resistance of the medium by assuming that flow rate is a homogeneous linear function of position vector:

$$m\ddot{\mathbf{r}}_j = K(\mathbf{r}_{j+1} + \mathbf{r}_{j-1} - 2\mathbf{r}_j) + \beta[(\dot{\mathbf{d}} + \boldsymbol{\omega})\mathbf{r}_j - \dot{\mathbf{r}}_j]. \quad (8.164)$$

If we seek the solution in the form of equation (8.160), then for function $\mathbf{A}(t)$ equation

$$m\ddot{\mathbf{A}} = -4K \sin^2 \frac{\delta}{2} \mathbf{A} + \beta[(\dot{\mathbf{d}} + \boldsymbol{\omega})\mathbf{A} - \dot{\mathbf{A}}] \quad (8.165)$$

is obtained which proves our previous statement.

Let us now proceed to the study of the thermal motion of individual oscillators by assuming that the chain molecule is in the flow field. If neither the quasi-elastic force acts on the moving point nor does the flow carry it along, then the density function of probability distribution describing its position in space would satisfy the law of diffusion, i.e., equation

$$\dot{f} = D\Delta f \quad (8.166)$$

would be valid. This equation may be split in the usual way:

$$\dot{f} + \operatorname{div} \mathbf{J} = 0, \quad \mathbf{J} = -D \operatorname{grad} f. \quad (8.167)$$

If we consider the quasi-elastic force for current in addition to thermal motion, expression

$$\mathbf{J} = -D \text{grad } f - \frac{D}{kT} f \text{grad } U^* \quad (8.168)$$

should hold, as only this can ensure that a Boltzmann distribution would belong to the stationary case. If we take also the effect of flow into account, correlation

$$\mathbf{J} = -D \text{grad } f - \frac{D}{kT} f \text{grad } U^* + f(\dot{\mathbf{d}} + \boldsymbol{\omega})r \quad (8.169)$$

is obtained, assuming that the individual forces exert their influence independently of thermal motion. For simplifying calculations, the position vector of oscillators will be denoted by \mathbf{r} instead of \mathbf{A}_n , since no different \mathbf{A}_n -s will be needed simultaneously in the calculation.

Since f is a density function, it satisfies the partial differential equation

$$\dot{f} = D\Delta f + \frac{D}{kT} \text{div}(f \text{grad } U_n^*) - \text{div}[f(\dot{\mathbf{d}} + \boldsymbol{\omega})r]. \quad (8.170)$$

Seeking the solution in form

$$f = C \exp\left(-\frac{U^*}{kT}\right) (1 + \varphi) = f_0(1 + \varphi), \quad (8.171)$$

we obtain

$$\begin{aligned} f_0 \dot{\varphi} = f_0 D \Delta \varphi - f_0 \frac{DK_n}{kT} \mathbf{r} \text{grad } \varphi - f_0 \frac{K_n}{kT} \mathbf{r} \dot{\mathbf{r}} - \\ - f_0 \text{grad } \varphi \boldsymbol{\omega} \mathbf{r} - f_0 \text{grad } \varphi \dot{\mathbf{r}} + f_0 \frac{K_n}{kT} \varphi \mathbf{r} \dot{\mathbf{r}}. \end{aligned} \quad (8.172)$$

If $\dot{\mathbf{d}} = 0$, f_0 satisfies the equation, i.e. $\varphi = 0$. It is correct to assume that for small $\dot{\mathbf{d}}$, φ is also small; thus as a first approximation, the last two terms on the right side may be omitted as small quantities of higher order. By dividing both sides of the equation by f_0 and rearranging it slightly, we arrive at

$$\dot{\varphi} + \text{grad } \varphi \boldsymbol{\omega} \mathbf{r} = D \Delta \varphi - \frac{DK_n}{kT} \mathbf{r} \text{grad } \varphi - \frac{K_n}{kT} \mathbf{r} \dot{\mathbf{r}}, \quad (8.173)$$

whose solution is sought in form

$$\varphi = \mathbf{r} \boldsymbol{\Xi} \mathbf{r} \quad (8.174)$$

and then we obtain

$$\mathbf{r} \dot{\boldsymbol{\Xi}} \mathbf{r} + 2(\boldsymbol{\Xi} \mathbf{r})(\boldsymbol{\omega} \mathbf{r}) = 2D \text{tr} \boldsymbol{\Xi} - \frac{2DK_n}{kT} \mathbf{r} \boldsymbol{\Xi} \mathbf{r} - \frac{K_n}{kT} \mathbf{r} \dot{\mathbf{r}}. \quad (8.175)$$

Both sides of the equation are quadratic polynomials of space coordinates. Based on the identity of coefficients, it is seen that our trial function satisfies the differential equation if and only if

$$\text{tr} \boldsymbol{\Xi} = 0 \quad (8.176)$$

and

$$\dot{\Xi} + \Xi\omega - \omega\Xi = \dot{\Xi} = -\frac{2DK_n}{kT}\Xi - \frac{K_n}{kT}\dot{\mathbf{d}} \quad (8.177)$$

conditions are fulfilled. Hence equations for individual oscillators are the following:

$$\dot{\Xi}_n = -\frac{2DK_n}{kT}\Xi_n - \frac{K_n}{kT}\dot{\mathbf{d}}. \quad (8.178)$$

Ξ -s together determine the shape of the chain molecule in the statistical sense; thus, Ξ -s are dynamic state variables.

In order to arrive at state parameters ξ and α used in our thermodynamic considerations, we should determine the dependence of the entropy of chain molecules on Ξ -s. Since the distributions of individual oscillators are independent, their entropy can be determined separately and their sum is the entropy of the macromolecule. If we, for simplicity, consider only chains consisting of segments without interaction, calculations may be carried out similarly to those in equation (8.144). The conditional entropy of the oscillator is proportional to potential energy as shown in equation (8.149) and to the mean value of which tensor Ξ satisfying equation (8.176) does not contribute, as the surface integral of spherical function φ given by equation (8.174) is zero. Therefore, for entropy, we have

$$\begin{aligned} s_{\text{osc}} &= -k \int f_0(1 + \varphi)[\ln f_0 + \ln(1 + \varphi)]dV = \\ &= -k \int f_0 \ln f_0 dV - \frac{k}{2} \int f_0 \varphi^2 dV = s_{0\text{osc}} - \frac{k}{2} \int_0^\infty f_0 \oint (\mathbf{r}\Xi\mathbf{r})^2 dA dr = \\ &= s_{0\text{osc}} - \frac{k}{2} \int_0^\infty f_0 \frac{8\pi}{15} r^6 \Xi : \Xi dr = s_{0\text{osc}} - k \left(\frac{kT}{K}\right)^2 \Xi : \Xi. \end{aligned} \quad (8.179)$$

In this, we utilized the spherical function nature of φ and also that φ is small, thus, on expanding $\ln(1 + \varphi)$ into a series we stopped at the quadratic term. Thus, the entropy of the whole chain is given by

$$S = S_0 - k \sum_n \left(\frac{kT}{K_n}\right)^2 \Xi_n : \Xi_n. \quad (8.180)$$

Let now L denote the number of polymer chains in unit volume. The specific entropy is

$$s = s_0 - \frac{kL}{\varrho} \sum_n \left(\frac{kT}{K_n}\right)^2 \Xi_n : \Xi_n. \quad (8.181)$$

On comparing this expression with the general form of entropy given by equation (4.65), the connection between parameters ξ_n and Ξ_n can readily be seen:

$$\xi_n = \sqrt{\frac{2kL}{\varrho} \frac{kT}{K_n}} \Xi_n. \quad (8.182)$$

It is also easy to turn to variables

$$\alpha_n = \sqrt{\varrho T} \xi_n = \sqrt{2kTL} \frac{kT}{K_n} \Xi_n, \quad (8.183)$$

for which the equation can be obtained from equation (8.178):

$$\dot{\alpha}_n = -\frac{2DK_n}{kT} \alpha_n - \sqrt{2kTL} \dot{d}. \quad (8.184)$$

It is important to note that these equations are perfectly identical with those obtained by thermodynamic considerations (equations (6.144)). Stress equations for shear flow are obtained in the complex form on the basis of equation (6.151) and in the real form based on equation (6.152)

Let us now calculate complex shear stress for straight chain polymer molecules as an example. On comparing equations (6.144) and (8.184), we obtain the coefficients of Onsager's linear laws

$$L_{0j} = \sqrt{2kTL}, \quad L_j = \frac{2DK_j}{kT} \quad (j=1, 2, \dots, N) \quad (8.185)$$

whose substitution into equation (6.151) gives

$$t^v = \frac{L_{00}}{2} \kappa + \frac{1}{2} \sum_j \frac{2kTL\kappa}{L_j + i\kappa}. \quad (8.186)$$

For shortening the symbols, we introduce quantities:

$$\tau_j = \frac{1}{L_j} = \frac{kT}{2DK_j} \quad \text{and} \quad \eta_\infty = \frac{L_{00}}{2} \quad (8.187)$$

we may write that

$$t^v = \eta_\infty \kappa + kTL \sum_j \frac{\tau_j \kappa}{1 + i\kappa \tau_j}. \quad (8.188)$$

For examining quantities τ_j more thoroughly, let us compare equation (8.187) with equations (8.151), (8.162) and (8.157) by considering that $M = N$:

$$\tau_j = \frac{a^2(1 + 2\mathbb{R})}{24D \sin^2 \frac{j\pi}{2N}}. \quad (8.189)$$

If the number of segments (i.e., N) is large, relaxation times, τ_j , rapidly decrease for small j -s with increasing j ; hence their role becomes smaller and smaller. For small j -s, instead of equation (8.189) approximate expression

$$\tau_j = \frac{a^2 N^2 (1 + 2\mathbb{R})}{6D \pi^2 j^2} = \frac{\tau_1}{j^2} \quad (8.190)$$

is used. For large j -s the role of individual degrees of freedom becomes smaller and smaller. After comparing equations (8.189) and (8.190) it is seen that summation

may be extended up to infinity without making a significant error. Proceeding this way, we obtain

$$\mathbf{t}^v = \eta_\infty \kappa + kTL \sum_{j=1}^{\infty} \frac{\tau_1 \kappa}{j^2 + i\kappa\tau_1}, \quad (8.191)$$

where the infinite series has the interesting feature that the sum can be given in closed form based on the partial fraction expansion of the complex function $\cot(z)$:

$$\mathbf{t}^v = \eta_\infty \kappa + \frac{1}{2} kTLi \left[1 - \pi \frac{1+i}{2} \sqrt{2\kappa\tau_1} \cot \left(\pi \frac{1+i}{2} \sqrt{2\kappa\tau_1} \right) \right]. \quad (8.192)$$

On separating real and imaginary parts, for shear stress, we obtain

$$\tau = \eta_\infty \kappa + \frac{1}{4} kTL \pi \sqrt{2\kappa\tau_1} \frac{\sinh \pi \sqrt{2\kappa\tau_1} - \sin \pi \sqrt{2\kappa\tau_1}}{\cosh \pi \sqrt{2\kappa\tau_1} - \cos \pi \sqrt{2\kappa\tau_1}} \quad (8.193)$$

whereas for normal stress,

$$\sigma_1 = -\sigma_2 = kTL \left\{ \frac{1}{2} - \frac{\pi \sqrt{2\kappa\tau_1}}{4} \frac{\sinh \pi \sqrt{2\kappa\tau_1} + \sin \pi \sqrt{2\kappa\tau_1}}{\cosh \pi \sqrt{2\kappa\tau_1} - \cos \pi \sqrt{2\kappa\tau_1}} \right\}, \quad (8.194)$$

results.

8.5.3. Chemical relaxations in loose networks. When studying the chemical relaxations in loose networks, we assume that the medium consists of long chain molecules whose ends are fixed to the network by chemical bonds. These bonds are assumed to be in chemical equilibrium: i.e., from time to time the chain ends are set free. The thermal motion of free chain ends is supposed to be fast as compared to other processes; correspondingly, the vector connecting free chain ends has a normal distribution and its density function is

$$f_0 = \frac{1}{(2\pi)^{3/2} \sigma^3} \exp \left(-\frac{r^2}{2\sigma^2} \right) \quad (8.195)$$

where, according to equation (8.147),

$$\sigma^2 = N \frac{a^3}{3} (1 + 2\mathbb{R}). \quad (8.196)$$

The chains fixed to the network are carried along by the motion of the medium together with the network. Let the distribution density function of vector \mathbf{r} connecting the fixed or just liberated chain ends be denoted by $f(\mathbf{r})$, that of bonded ends by $f_1(\mathbf{r})$ and the probability of a given chain being just bound by p .

The time course of function $f_1(\mathbf{r})$ can be described by an equation analogous to equation (8.170) but it contains also a term characterizing chemical reaction:

$$\frac{\partial}{\partial t} (f_1 p L) = -\operatorname{div} [f_1 p L (\dot{\mathbf{d}} + \boldsymbol{\omega}) \mathbf{r}] - k^* f_1 p L + k^{**} (1-p) L f_0, \quad (8.197)$$

where L is the number of chains in a unit volume. The first term on the right side describes the phenomenon that flow carries along the bonded chain ends, the second term accounts for the effect of bond cleavage on chain ends, whereas the third term characterizes the process of chemical bonding of free chain ends to the network. Chemical reactions are assumed to be reversible and of first order, k^* is the reaction rate constant of the liberation of chain ends, and k^{**} is that of the opposite reaction. Corresponding to chemical equilibrium, it holds that

$$k^*pL - k^{**}(1-p)L = 0 \quad (8.198)$$

whose utilization for simplifying equation (8.197) leads to

$$\frac{\partial f_1}{\partial t} = -\text{div}[f_1(\dot{\mathbf{d}} + \boldsymbol{\omega})\mathbf{r}] - k^*(f_1 - f_0) \quad (8.199)$$

In order to determine function f_1 let us start from

$$f_1 = f_0(1 + \varphi) \quad (8.200)$$

whose substitution into the differential equation results in

$$f_0 \frac{\partial \varphi}{\partial t} = f_0 \sigma^{-2} \mathbf{r} \dot{\mathbf{d}} \mathbf{r} + f_0 \sigma^{-2} \varphi \mathbf{r} \dot{\mathbf{d}} \mathbf{r} - f_0 \nabla \varphi \dot{\mathbf{d}} \mathbf{r} - f_0 \nabla \varphi \boldsymbol{\omega} \mathbf{r} - k^* f_0 \varphi. \quad (8.201)$$

If we restrict our study to small $\dot{\mathbf{d}}$ values by neglecting the second and third terms on the right side, we obtain

$$\frac{\partial \varphi}{\partial t} = \sigma^{-2} \mathbf{r} \dot{\mathbf{d}} \mathbf{r} - \nabla \varphi \boldsymbol{\omega} \mathbf{r} - k^* \varphi. \quad (8.202)$$

Let us now seek function φ in the form of a homogeneous quadratic order polynomial:

$$\varphi = \mathbf{r} \boldsymbol{\Xi} \mathbf{r}. \quad (8.203)$$

On the basis of equation (8.202), the form of the equation for tensor $\boldsymbol{\Xi}$ is

$$\mathbf{r} \frac{\partial \boldsymbol{\Xi}}{\partial t} \mathbf{r} = \sigma^{-2} \mathbf{r} \dot{\mathbf{d}} \mathbf{r} - 2(\boldsymbol{\Xi} \mathbf{r})(\boldsymbol{\omega} \mathbf{r}) - k^* \mathbf{r} \boldsymbol{\Xi} \mathbf{r}, \quad (8.204)$$

which, after rearrangement gives

$$\dot{\boldsymbol{\Xi}} = \sigma^{-2} \dot{\mathbf{d}} - k^* \boldsymbol{\Xi}. \quad (8.205)$$

For segments moving independently of each other, variables $\boldsymbol{\xi}$ and $\boldsymbol{\alpha}$ can readily be introduced by the same method as was done earlier. The entropy for one chain is calculated as in equation (8.179):

$$s_{\text{chain}} = s_{0\text{chain}} - k\sigma^4 \boldsymbol{\Xi} : \boldsymbol{\Xi}. \quad (8.206)$$

Entropy for unit mass is:

$$s = s_0 - \frac{1}{2} \frac{2kLp}{\rho} \sigma^4 \Xi : \Xi. \quad (8.207)$$

Thus variables ξ and α are:

$$\xi = \frac{\sqrt{2kLp}}{\rho} \sigma^2 \Xi, \quad \alpha = \sqrt{2kTLp} \sigma^2 \Xi. \quad (8.208)$$

By the use of variable α the following equation is obtained instead of equation (8.205):

$$\dot{\alpha} = \sqrt{\frac{2kLpk^{**}}{k^* + k^{**}}} \dot{d} - k^* \alpha, \quad (8.209)$$

where equation (8.198) has also been utilized for calculating p .

It has to be emphasized that the existence of a dynamic variable has been derived by structural considerations and that the equations thus obtained are in a full accordance with the results of macroscopic thermodynamic theory.

8.6. Motion of liquid crystals.

Liquid crystals are anisotropic liquids. This means that motions connecting equivalent configurations are not identical with the orthogonal group even for undistorted states nor do they contain the orthogonal group as a subgroup; in short, the different directions are not equivalent.

Let us study, first, group A of motions transferring undistorted states into each other for an arbitrary material. The reader should be reminded that undistorted states are configurations in which the medium (being at rest for a long enough time) becomes stress-free. (Under usual experimental conditions, barometric pressure which is always present as an additive term is not taken into consideration.) Group A contains the orthogonal group as a subgroup since rotations do not cause essential changes in the material, and inversions should be dealt with only by convention since real media cannot be turned "inside out" as gloves. On the other hand, group A is part of the unimodular group, as a volume change always results in the appearance of a stress. From this, due to the maximality of the orthogonal group, it follows that group A may be only of two kinds: it is either identical with the orthogonal group (in which case the medium is a solid) or it is identical with the unimodular group (the medium is then called a fluid).

Let us now proceed with our study to groups A^* of motions connecting equivalent undistorted states. From the definition of group A^* , it follows that it is part of group A . If group A^* contains the orthogonal group and, thus, it is identical with group A , then the medium is isotropic. There is not much variety in an isotropic medium it is either an isotropic fluid or an isotropic solid.

The situation is completely different for anisotropic media. If the medium is a solid, group A^* is a real part of the orthogonal group and the possible structures of group A^* are discussed in the introductory text books on crystallography by taking into account also the lattice structure of solids.

For fluids, the problem is more complex. In this case, group A^* is not part of the orthogonal group and as a subgroup it contains at most only one real subgroup of it. At present, these subgroups are not yet completely known. A single example is enough to illustrate that such a subgroup really exists in the unimodular group. Let us consider a motion in space which translates an arbitrarily chosen and fixed unit vector \mathbf{e} into vector $\lambda\mathbf{e}$ parallel to it. In order to formulate the example also in components, let us take a Cartesian coordinate system whose axis x_1 points to the direction of the vector \mathbf{e} and consider motions whose matrix is

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ 0 & a_{22} & a_{23} \\ 0 & a_{32} & a_{33} \end{bmatrix}$$

and the absolute value of their determinants is unity. These motions form a group, which can easily be proved partly on the basis of the multiplication rule of determinants and partly on that of matrix multiplication, since the matrix product C of motion A and B may be given in the form

$$c_{ij} = a_{ik}b_{kj}. \quad (8.210)$$

The matrix consisting of elements c_{ij} has the desired property if $c_{ij} = 0$ in each case when $i \neq 1$ and $j = 1$. Matrices a_{ik} and b_{kj} also have these properties; thus if $i \neq 1$ and $j = 1$, then

$$c_{i1} = a_{ik}b_{k1} = a_{i1}b_{11} = 0. \quad (8.211)$$

It should also be shown that the inverse of any element has the same property. As motion has always an inverse, it is enough to prove that $a_{21}^{-1} = a_{31}^{-1} = 0$ is also true for inverse motion A^{-1} . Based on the concept of an inverse, we may write according to correlation

$$a_{ik}a_{kj}^{-1} = \delta_{ij} \quad (8.212)$$

that

$$a_{2k}a_{k1}^{-1} = 0 \quad \text{and} \quad a_{3k}a_{k1}^{-1} = 0, \quad (8.213)$$

or, in detail,

$$\begin{aligned} a_{22}a_{21}^{-1} + a_{23}a_{23}^{-1} &= 0 \\ a_{32}a_{21}^{-1} + a_{33}a_{31}^{-1} &= 0, \end{aligned} \quad (8.214)$$

which is a homogeneous linear equation system with unknowns a_{21}^{-1} and a_{31}^{-1} . The determinant D of the equation system is not zero, as

$$\det A = a_{11}D = +1 \quad (8.215)$$

and, thus, the equations have the only solution

$$a_{21}^{-1} = a_{31}^{-1} = 0. \quad (8.216)$$

Thus, the above motions form a group and this group does not contain the orthogonal group since, for example, the motion given by matrix

$$\begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$$

belongs to the orthogonal group, but it does not belong to the group in question. On the other hand, it is not part of the orthogonal group since, for example, motion represented by matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & \frac{1}{2} \end{bmatrix}$$

belongs to the group in question, but does not belong to the orthogonal group. Now we can define liquid crystals in an exact manner. Media are called liquid crystals if the group of motions connecting equivalent undistorted states A^* is not identical with the unimodular group and are not part of the orthogonal group. The group A^* is called the isotropy group of the medium. We mention that the group-theoretical classification of liquid crystals is not yet known [162].

8.6.1. Entropy of nematic liquid crystals. Media with a director \mathbf{e} (a particular direction) will be considered here; two configurations are equivalent if the directors are the same. (Directions \mathbf{e} and $-\mathbf{e}$ are regarded to be equivalent.) These requirements define nematic liquid crystals.

At first glance it seems obvious that this direction is a local state parameter; however, function $s = s(u, v, \mathbf{e})$ characterizing specific entropy cannot depend on \mathbf{e} due to the isotropy of space. From this, it follows that function $s = s(u, v)$ cannot describe anisotropic properties. In other words, we may also say that if entropy depends only on internal energy and specific volume in the liquid, no effect appears which would bring the orientations in neighboring points into harmony; thus, the direction of vector \mathbf{e} would become a random and quickly changing function of space coordinates even if the distribution of \mathbf{e} was initially homogeneous, but the medium was thoroughly stirred. Thus, the existence of a function $s = s(u, v, \mathbf{e})$ should be rejected; and instead of \mathbf{e} , another suitable variable should be sought. The solution of the problem is provided by the introduction of the entropy function in the form

$$s = s(u, v, \mathbf{e}, \text{Grad } \mathbf{e}). \quad (8.217)$$

Similarly to Frank [51] we assume that the entropy function can be well approximated by the second-order polynomial of $\text{Grad } \mathbf{e}$. For simplicity, volume changes will not be considered and, thus, variable v will not be dealt with; further, we assume local equilibrium: i.e., no further variables will be introduced. As entropy is an isotropic function of its variables, equality

$$s = s(u, \mathbf{e}, \text{Grad } \mathbf{e}) = a(u, \mathbf{Q}\mathbf{e}, \mathbf{Q}^T \text{Grad } \mathbf{e}\mathbf{Q}) \quad (8.218)$$

holds for any orthogonal tensor \mathbf{Q} . For convenience, let us take a Cartesian coordinate system whose axis x_1 points to the direction of \mathbf{e} in the chosen point; hence the matrix of tensor $\text{Grad } \mathbf{e}$ is:

$$\text{Grad } \mathbf{e} = \mathbf{E} = \begin{bmatrix} 0 & 0 & 0 \\ e_{2,1} & e_{2,2} & e_{2,3} \\ e_{3,1} & e_{3,2} & e_{3,3} \end{bmatrix} \quad (8.219)$$

(The first row contains only zero elements because the derivative of any unit vector is perpendicular to the unit vector itself.)

Let us first seek the linear expressions satisfying requirement (8.218). Though linear polynomials usually have the form

$$p_1 = a_{ik}e_{k,i}, \quad (8.220)$$

in our case the system of coefficients a_{ik} can only be of such a nature that the tensor corresponding to them should be invariant with respect to orthogonal transformations belonging to the isotropy group. On the basis of reflections onto a plane perpendicular to axis x_1 , among $a_{ik} - s$ no elements may be present in whose indices an odd number of 1-s, 2-s or 3-s occurs. Since in our coordinate system, $e_{i,k} = 0$ if $k = 1$. Therefore, a_{ik} can freely be chosen if $k = 1$; thus, let a_{ik} be zero. Hence only a_{22} and a_{33} remain as non-zero elements. By utilizing the symmetry plane and exchanging axes x_2 and x_3 , it is obvious that $a_{22} = a_{33}$ and thus for polynomial p_1 it may be written that

$$p_1 = a_{22}e_{2,2} + a_{22}e_{3,3} = a_{22} \operatorname{div} \mathbf{e}. \quad (8.221)$$

The procedure is similar for quadratic polynomials. Then

$$p_2 = a_{ijkl}e_{k,i}e_{l,j}, \quad (8.222)$$

holds, in which equalities

$$a_{ijkl} = a_{jilk} \quad (8.223)$$

are also valid. In the case of a non-zero coefficient among indices a_{ijkl} , only an even number of 1-s, 2-s and 3-s may be present; and the last two indices can only be 2 or 3 according to our convention. The value of elements does not change if we exchange indices 2 and 3. All this follows from the symmetry rules utilized, i.e. for non-zero elements we may write

$$\begin{aligned} a_{1122} &= a_{1133}, & a_{2222} &= a_{3333}, \\ a_{2233} &= a_{3322}, & a_{2323} &= a_{3232}, \\ a_{2332} &= a_{3223}. \end{aligned} \quad (8.224)$$

From a rotation around axis x_1 by an angle α , a lengthy but elementary calculation gives

$$a_{2222} = a_{2332} + a_{2323} + a_{2233}. \quad (8.225)$$

Thus polynomial p_2 may be written as

$$\begin{aligned} p_2 &= a_{1122}(e_{2,1}^2 + e_{3,1}^2) + a_{2332}(e_{2,2}^2 + e_{3,3}^2 + 2e_{2,3}e_{3,2}) + \\ &\quad + a_{2323}(e_{2,2} + e_{3,3})^2 + a_{2233}(e_{2,2}^2 + e_{3,3}^2 + e_{2,3}^2 + e_{3,2}^2). \end{aligned} \quad (8.226)$$

On writing this into an invariant form, we obtain

$$p_2 = a_{2233} \mathbf{E} : \mathbf{E} + a_{2332} \mathbf{E} : \mathbf{E}^T + a_{2323} (\operatorname{tr} \mathbf{E})^2 + (a_{1122} - a_{2233}) (\mathbf{E} \mathbf{e})^2 \quad (8.227)$$

From this, it is apparent that all terms in this equation are invariant to changing the direction \mathbf{e} into its opposite. (Here notation $\mathbf{E} = \operatorname{Grade}$ is used.) This is not

true, however, for polynomial p_1 , given by equation (8.221), which changes sign by changing the direction \mathbf{e} into its opposite. This means, at the same time, that if \mathbf{e} and $-\mathbf{e}$ are equivalent, then $a_{22} = 0$; hence the form of entropy function satisfying equation (8.218) may only be

$$s = s_0(u) - \frac{1}{2\rho T} [k_{22}\mathbf{E} : \mathbf{E} + k_{24}\mathbf{E} : \mathbf{E}^T + (k_{33} - k_{22})(\mathbf{E}\mathbf{e})^2 + (k_{11} - k_{22} - k_{24})(\text{tr } \mathbf{E})^2] \quad (8.228)$$

where notations

$$\begin{aligned} k_{11} &= -2\rho T a_{2222}, & k_{22} &= -2\rho T a_{2233}, \\ k_{33} &= -2\rho T a_{1122}, & k_{24} &= -2\rho T a_{2332} \end{aligned} \quad (8.229)$$

are introduced for uniformity with the notations of Frank [51, 127] widely accepted in the literature.

With free boundary conditions and $\mathbf{E} = 0$, the entropy should be maximum which means that in the case of homogeneous orientation the medium is at equilibrium. This also means that on the right side of equation (8.228) the expression in brackets is a positive definite form in the algebraic sense, hence, for the coefficients inequalities

$$\begin{aligned} k_{11} &\geq 0, & k_{22} &\geq 0, & k_{33} &\geq 0, \\ k_{22} &\geq |k_{24}|, & k_{11} &\geq \frac{1}{2}(k_{22} + k_{24}) \end{aligned} \quad (8.230)$$

should hold on the basis of equations (8.229) and (8.226). In the last two cases equality can only exist if both sides are equal to zero.

8.6.2. Entropy balance. The entropy balance of liquid crystals may also be given by general equation (4.35). Due to the assumption of local equilibrium, entropy current may be interpreted by equation (4.41). However, for convenience, equation (4.42) describing entropy production should be modified. One of the reasons for this is that now there are no dynamic variables among local state parameters, and the other is that tensor $\mathbf{E} = \text{Grad } \mathbf{e}$ is a state parameter which had not been considered when writing equation (4.34). For simplicity, we restrict ourselves to one-component liquid crystals which means that neither diffusion currents nor component sources have to be taken into consideration. As a further simplification, we assume that the medium is an insulator ($\mathbf{j} = 0$), isothermal ($\text{grad } 1/T = 0$) and, finally, electric and magnetic polarization is reversible, i.e. equalities

$$\frac{1}{T}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \frac{\partial s}{\partial \mathbf{p}} = 0, \quad \frac{1}{T}\mathbf{B} + \frac{\partial s}{\partial \mathbf{p}_m} = 0 \quad (8.231)$$

hold. On using these assumptions and considering also equation (8.228), for entropy production

$$T\sigma_s = \mathbf{t}^s : \mathring{\mathbf{d}} + \text{div}(\bar{\omega}^b \mathbf{\Pi}) + \mathbf{\Pi} : \text{Grad } \bar{\omega} + \rho T \frac{\partial s}{\partial \mathbf{E}} : \mathring{\mathbf{E}} + \rho T \frac{\partial s}{\partial \mathbf{e}} \dot{\mathbf{e}} \quad (8.232)$$

is obtained, where \mathbf{t}^s is the symmetric part of Cauchy's stress, $\mathring{\mathbf{d}}$ the symmetric part of the velocity gradient (a liquid crystal is also a fluid; thus the present configuration is regarded as a reference configuration) and $\bar{\omega} = \frac{1}{2} \text{rot } \mathbf{v}$.

In the previous expression of entropy production the physical meaning of $\vec{\omega}^b$, $\mathbf{\Pi}$ and \mathbf{m} should be clarified. As in liquid crystals the direction \mathbf{e} is a preferred direction and the rotation of \mathbf{e} is a result of various interactions. The hypothesis is obvious that $\vec{\omega}^b$ is connected to the rotation of vector \mathbf{e} , i.e.

$$\vec{\omega}^b = \mathbf{e} \times \dot{\mathbf{e}}. \quad (8.233)$$

An objective time derivative is used on the right side as $\vec{\omega}^b$ is the angular velocity relative to the medium which is obviously perpendicular to \mathbf{e} . Naturally, $\mathbf{\Pi}$ describes surface interactions causing the rotation of vector \mathbf{e} and, therefore, the existence of constraint

$$\mathbf{e}\mathbf{\Pi} = 0 \quad (8.234)$$

is easily understood. It should be mentioned that the moment of inertia for molecules is again neglected in the macroscopic sense, i.e., we assume that the internal moment of momentum and the rotational energy are zero in accordance with the derivation of equation (4.26) for internal energy balance.

For convenience, it is expedient to introduce the polar tensor

$$\mathbf{B} = -\mathbf{e} \times \mathbf{\Pi}. \quad (8.235)$$

($\vec{\omega}^b$ is an axial vector, whereas \mathbf{e} and $\dot{\mathbf{e}}$ are polar vectors; tensor $\mathbf{\Pi}$ is axial in its first subscript, but polar in its second subscript. This mixed character is eliminated by introducing \mathbf{B} which is a polar tensor.) After some rearrangement, we may write

$$T\sigma_s = \dot{\mathbf{e}} \left(\varrho T \frac{\partial s}{\partial \mathbf{e}} + \text{Div } \mathbf{B} \right) + \dot{\mathbf{E}} : \left(\varrho T \frac{\partial s}{\partial \mathbf{E}} + \mathbf{B} \right) + \dot{\mathbf{d}} : (\mathbf{t}^s + \mathbf{E}^T \mathbf{B}), \quad (8.236)$$

where equalities

$$\text{Grad } \dot{\mathbf{e}} = \dot{\mathbf{E}} + \mathbf{E}\dot{\mathbf{d}} + \mathbf{e} \times \text{Grad } \vec{\omega} \quad (8.237)$$

and

$$\mathbf{\Pi} = \mathbf{e} \times \mathbf{B} \quad (8.238)$$

following from equation (8.235) have been utilized.

Let us now deal with the effect of electric field. For electric fields that are not too strong, entropy given by equation (8.228) is complemented with terms describing electric polarization and thus it becomes

$$s = s(u, \mathbf{E}, \mathbf{p}) = s(u, \mathbf{E}, 0) - \frac{\varrho}{2TE_0} \left[\frac{1}{\chi_{\perp}} \mathbf{p}^2 + \left(\frac{1}{\chi_{\parallel}} - \frac{1}{\chi_{\perp}} \right) (\mathbf{p}\mathbf{e})^2 \right]; \quad (8.239)$$

where \mathbf{p} is the specific electric dipole moment, χ_{\parallel} the dielectric susceptibility in direction \mathbf{e} and χ_{\perp} the dielectric susceptibility in the perpendicular directions. This also means that the right side of equation (8.236) given for entropy production density contains term

$$\Delta(T\sigma_s) = -\frac{\varrho^2}{\varepsilon_0} \left(\frac{1}{\chi_{\parallel}} - \frac{1}{\chi_{\perp}} \right) (\mathbf{p}\mathbf{e})(\mathbf{p}\dot{\mathbf{e}}) \quad (8.240)$$

as well. Here only the term characterizing electric polarization is written, since we only want to show that equation (8.236) describes also the effect of the electromagnetic field if a suitable entropy function is used.

The expression given is readily identifiable with that of the power of torque exerted by the electric field. To this, on the one hand, the reversibility of electric polarization should be taken into account; thus,

$$\mathbf{E} + \mathbf{v} \times \mathbf{B} = -\varrho T \frac{\partial s}{\partial \mathbf{p}} = \frac{\varrho}{\varepsilon_0 \chi_{\perp}} \mathbf{p} + \frac{\varrho}{\varepsilon_0} \left(\frac{1}{\chi_{\parallel}} - \frac{1}{\chi_{\perp}} \right) (\mathbf{p}\mathbf{e})\mathbf{e}, \quad (8.241)$$

and, on the other hand, also that the power density of torque may be given in the form of $\bar{\omega}^b \varrho \mathbf{m}$. Based on this and utilizing equations (2.50) and (2.233), we obtain:

$$\begin{aligned} \bar{\omega}^b \varrho \mathbf{m} &= \varrho (\mathbf{e} \times \dot{\mathbf{e}}) \left\{ \mathbf{p} \times \left[\frac{\varrho}{\varepsilon_0} \left(\frac{1}{\chi_{\parallel}} - \frac{1}{\chi_{\perp}} \right) (\mathbf{p}\mathbf{e})\mathbf{e} \right] \right\} = \\ &= \frac{\varrho^2}{\varepsilon_0} \left(\frac{1}{\chi_{\parallel}} - \frac{1}{\chi_{\perp}} \right) (\mathbf{p}\mathbf{e})(\mathbf{e} \times \dot{\mathbf{e}})(\mathbf{p} \times \mathbf{e}) = \\ &= -\frac{\varrho^2}{\varepsilon_0} \left(\frac{1}{\chi_{\parallel}} - \frac{1}{\chi_{\perp}} \right) (\mathbf{p}\mathbf{e})(\mathbf{e} \times \dot{\mathbf{e}})(\mathbf{e} \times \mathbf{p}) = \Delta(T\sigma_s) \end{aligned} \quad (8.242)$$

where vector algebraic transformation

$$(\mathbf{e} \times \dot{\mathbf{e}})(\mathbf{e} \times \mathbf{p}) = [(\mathbf{e} \times \dot{\mathbf{e}}) \times \mathbf{e}]\mathbf{p} = \dot{\mathbf{e}}\mathbf{p} \quad (8.243)$$

has also been applied. Equality (8.242) shows that equation (8.236) is correct also in the presence of an electric field. Analogous derivation may be used for magnetic polarization.

8.6.3. Conditions of equilibrium. For establishing the conditions of equilibrium, we start again from the form of entropy production given by equation (8.236). The rate of processes is described by $\dot{\mathbf{e}}$, $\dot{\mathbf{E}}$ and $\dot{\mathbf{d}}$, and they will be regarded as generalized currents. However, coefficients are now not necessarily zero, as the currents chosen are not arbitrary since equalities following from vector \mathbf{e} being a unit vector

$$\mathbf{e}\dot{\mathbf{e}} = 0 \quad (8.244)$$

and

$$\mathbf{e}\mathbf{E} = 0 \quad (8.245)$$

hold, as well as that obtained by its derivation with respect to time,

$$\dot{\mathbf{e}}\mathbf{E} + \mathbf{e}\dot{\mathbf{E}} = 0 \quad (8.246)$$

which may be considered as constraints. To these, the symmetric nature of $\dot{\mathbf{d}}$ and the condition that only motions with unchanged volume are considered have to be added and then $\text{tr } \dot{\mathbf{d}} = 0$.

The above constraints can be utilized in different ways. The procedure is the simplest in a Cartesian frame. Then equation (8.244) means the application of one;

equation (8.246) that of three constraints. That is, among the 12 components of $\dot{\mathbf{e}}$ and $\dot{\mathbf{E}}$, only 8 are independent. We may arrive at independent currents in the following way: Multiplying the linear constraints by suitable factors and adding them to the entropy production, the coefficients of four current components can be made zero. After that, the remaining 8 current components are already linearly independent; thus, the condition of equilibrium is that their coefficients should also be zero. Hence we arrived at the result that by multiplying the constraints by suitable factors and adding them to the entropy production, the coefficients of currents became zero. Since equation (8.246) represents a vectorial constraint, the multiplier belonging to it can also be regarded as a vector. Carrying out procedures, we obtain:

$$T\sigma_s = \dot{\mathbf{e}} \left(\varrho T \frac{\partial s}{\partial \mathbf{e}} + \text{Div } \mathbf{B} + \mu \mathbf{e} - \mathbf{E} \vec{\lambda} \right) + \dot{\mathbf{E}} : \left(\varrho T \frac{\partial s}{\partial \mathbf{E}} + \mathbf{B} - \mathbf{e} \circ \vec{\lambda} \right) + \dot{\mathbf{d}} : [\mathbf{t}^s + (\mathbf{E}^T \mathbf{B})^{so}], \quad (8.247)$$

whence the conditions of equilibrium are

$$\begin{aligned} \varrho T \frac{\partial s}{\partial \mathbf{e}} + \text{Div } \mathbf{B} + \mu \mathbf{e} - \mathbf{E} \vec{\lambda} &= 0, \\ \varrho T \frac{\partial s}{\partial \mathbf{E}} + \mathbf{B} - \mathbf{e} \circ \vec{\lambda} &= 0, \\ \mathbf{t}^{so} &= -\frac{1}{2} (\mathbf{E}^T \mathbf{B} + \mathbf{B}^T \mathbf{E}) + \frac{1}{3} \text{tr}(\mathbf{E}^T \mathbf{B}) \delta. \end{aligned} \quad (8.248)$$

When writing our last equation, we took into account that $\dot{\mathbf{d}}$ is a symmetric tensor of zero trace; thus its coefficient is a symmetric and zero-trace part of tensor $\mathbf{t}^s + \mathbf{E}\mathbf{B}$. Notation \mathbf{t}^{so} refers to the symmetric zero-trace part of Cauchy's stress. In the solution of the equations obtained, constraints (8.244) and (8.246) should also be utilized. The antisymmetric part of the stress tensor can be determined from the balance equation of the moment of momentum (equation (4.25)) at the end of the calculations.

For determining the multipliers, let us carry out a scalar multiplication of the first equation by \mathbf{e} and that of the second (tensorial) equation by \mathbf{e} from the left. Also utilizing correlations $\mathbf{e}\mathbf{B} = 0$ and $\mathbf{e}\mathbf{E} = 0$, we arrive at

$$\mu = -\varrho T \mathbf{e} \frac{\partial s}{\partial \mathbf{e}} - \mathbf{e} \text{Div } \mathbf{B}, \quad \vec{\lambda} = \varrho T \mathbf{e} \frac{\partial s}{\partial \mathbf{E}}. \quad (8.249)$$

The substitution of the expression obtained for $\vec{\lambda}$ into the original equations gives

$$\begin{aligned} \varrho T \frac{\partial s}{\partial \mathbf{e}} + \text{Div } \mathbf{B} + \mu \mathbf{e} - \varrho T \mathbf{e} \frac{\partial s}{\partial \mathbf{E}} \mathbf{E}^T &= 0, \\ \mathbf{B} &= -\varrho T \frac{\partial s}{\partial \mathbf{E}} + \mathbf{e} \circ \mathbf{e} \varrho T \frac{\partial s}{\partial \mathbf{E}} \end{aligned} \quad (8.250)$$

where \mathbf{B} from the second equation can be substituted into the first one:

$$\begin{aligned} \varrho T \frac{\partial s}{\partial \mathbf{e}} - \text{Div} \left(\varrho T \frac{\partial s}{\partial \mathbf{E}} \right) + 2\mu^* \mathbf{e} &= 0, \\ 2\mu^* &= \mu + \varrho T \mathbf{E} : \frac{\partial s}{\partial \mathbf{E}} + \varrho T \mathbf{e} \text{Div} \frac{\partial s}{\partial \mathbf{E}}. \end{aligned} \quad (8.251)$$

The first equation obtained may be identified with the Euler-Lagrange equation belonging to the variation problem specified by the Lagrangian:

$$\mathcal{L} = \rho T s \quad (8.252)$$

with the condition $\mathbf{e}^2 = 1$. In fact, entropy is maximum in adiabatic equilibrium. However, if we consider also thermostatic equality

$$T \left(\frac{\partial S}{\partial X} \right)_U = - \left(\frac{\partial F}{\partial X} \right)_T \quad (8.253)$$

where F is the free energy,

U the internal energy, and

X some extensive parameter,

then equations (8.251) may be identified with the Euler-Lagrange equations belonging to the principle of minimal free energy. It should be noted that the latter procedure is the correct one, since in the former case the changes in T have been neglected.

By solving equation (8.251), function $\mathbf{e}(\mathbf{r})$ can be determined. From this, \mathbf{E} may be obtained by derivation; then by using equations (8.250) \mathbf{B} and (8.235), the actual value of $\mathbf{\Pi}$ can be calculated. When knowing quantities \mathbf{E} and \mathbf{B} , the value of \mathbf{t}^{so} may be determined by substituting into the last equation of (8.248). The function $\mathbf{w}(\mathbf{t})$ can also be calculated on the basis of equation (4.25). The calculation can, in principle, be carried out although it is very lengthy; therefore, the application of the theory will be shown by the simple example of the twisted nematic cell.

Let the nematic liquid crystal be situated between parallel planes $x_1 = 0$ and $x_1 = d$ and let us assume that its direction is everywhere perpendicular to axis x_1 and that it depends only on x_1 .

Hence,

$$\mathbf{e} = \cos \alpha \mathbf{e}_2 + \sin \alpha \mathbf{e}_3, \quad \alpha = \alpha(x_1), \quad (8.254)$$

where \mathbf{e} is the direction of the director; and \mathbf{e}_1 , \mathbf{e}_2 and \mathbf{e}_3 are unit vectors showing to the direction of x_1 , x_2 and x_3 . Let us assume the boundary conditions $\alpha(0) = 0$ and $\alpha(d) = \alpha_0$ for function $\alpha(x_1)$. For simplicity, let \mathbf{m} be zero, i.e. let us disregard the effect of electric and magnetic fields. Tensor \mathbf{E} is easy to determine, since obviously

$$\mathbf{E} = \mathbf{e} \circ \nabla = \frac{\partial \mathbf{e}}{\partial x_1} \circ \mathbf{e}_1 = \alpha' (-\sin \alpha \mathbf{e}_2 + \cos \alpha \mathbf{e}_3) \circ \mathbf{e}_1 = \alpha' (\mathbf{e}_1 \times \mathbf{e}) \circ \mathbf{e}_1 \quad (8.255)$$

where α' is the derivative of function $\alpha(x_1)$. As \mathbf{e} and \mathbf{e}_1 are perpendicular to each other at every point, therefore

$$\mathbf{E}\mathbf{e} = 0, \quad \text{tr} \mathbf{E} = 0, \quad \mathbf{E} : \mathbf{E}^T = 0. \quad (8.256)$$

Hence, the equation of entropy (8.238) simplifies into

$$s = s_0(u) - \frac{k_{22}}{2\rho T} \mathbf{E} : \mathbf{E} = s_0(u) - \frac{k_{22}}{2\rho T} \alpha'^2 \quad (8.257)$$

Whence

$$\varrho T \frac{\partial s}{\partial \mathbf{E}} = -k_{22} \mathbf{E} \quad \text{and} \quad \varrho T \frac{\partial s}{\partial \mathbf{e}} = 0 \quad (8.258)$$

are obtained, the substitution of which into equation (8.250) results in the following form for \mathbf{B} :

$$\mathbf{B} = k_{22} \mathbf{E} = k_{22} \alpha' (\mathbf{e}_1 \times \mathbf{e}) \circ \mathbf{e}_1. \quad (8.259)$$

For determining function $\alpha(x_1)$, expressions of $\varrho T \frac{\partial s}{\partial \mathbf{E}}$ and \mathbf{E} are substituted into equation (8.251). This gives

$$\begin{aligned} k_{22} \frac{\partial}{\partial x_1} [\alpha' (\mathbf{e}_1 \times \mathbf{e})] + 2\mu^* \mathbf{e} &= k_{22} \alpha'' \mathbf{e}_1 \times \mathbf{e} + k_{22} \alpha'^2 \mathbf{e}_1 \times (\mathbf{e}_1 \times \mathbf{e}) + 2\mu^* \mathbf{e} = \\ &= k_{22} \alpha'' \mathbf{e}_1 \times \mathbf{e} - k_{22} \alpha'^2 \mathbf{e} + 2\mu^* \mathbf{e} = 0, \end{aligned} \quad (8.260)$$

from which

$$k_{22} \alpha'' = 0 \quad \text{and} \quad 2\mu^* - k_{22} \alpha'^2 = 0 \quad (8.261)$$

results as \mathbf{e} and $\mathbf{e}_1 \times \mathbf{e}$ are perpendicular to one another. The solution of the differential equation obtained for function $\alpha(x_1)$, satisfying also the former boundary conditions is

$$\alpha(x_1) = \frac{\alpha_0}{d} x_1. \quad (8.262)$$

Let us now determine tensors \mathbf{t} and $\mathbf{\Pi}$. The symmetric part of the stress tensor may be calculated from equation (8.248) as

$$\mathbf{t}^{so} = -k_{22} \alpha'^2 \left(\mathbf{e}_1 \circ \mathbf{e}_1 - \frac{1}{3} \boldsymbol{\delta} \right). \quad (8.263)$$

The evaluation of the antisymmetric part starts with the determination of tensor $\mathbf{\Pi}$ according to equation (8.238):

$$\mathbf{\Pi} = k_{22} \mathbf{e} \times \mathbf{E} = k_{22} \alpha' [\mathbf{e} \times (\mathbf{e}_1 \times \mathbf{e})] \circ \mathbf{e}_1 = k_{22} \alpha' \mathbf{e}_1 \circ \mathbf{e}_1. \quad (8.264)$$

This tensor is constant as is seen from equation (8.262). Thus its divergence is zero; consequently, $\mathbf{w}(\mathbf{t}) = 0$ according to equation (4.25), and Cauchy's stress is symmetric in this case.

Our results can be summarized, as follows: The rotation of the director of the twisted nematic cell is stationary in the absence of external fields, and the liquid crystals exert a torque of $k_{22} \alpha'$ per unit surface on the boundary planes of the cell and a pressure of $k_{22} \alpha'^2$.

8.6.4. Motion of liquid crystals. In determining the laws of motion for liquid crystals we start from expression (8.236) of entropy production. However, care should be taken in writing Onsager's linear laws, since quantities $\dot{\mathbf{e}}$, $\dot{\mathbf{E}}$ and $\dot{\mathbf{d}}$ describing the rate of processes are not independent: relations (8.244) and (8.246) hold for them in each point. Neither are the coefficients in the expression of entropy production independent forces.

In solving this problem, several methods can be used. One of them is that we apply linearly independent currents. The disadvantage of this method is that it spoils the covariant formalism.

The other method is based on the fact that Onsager's linear laws can be given by virtual forces also for linearly not independent currents; in such a case, the fulfillment of constraints has to be ensured by correlations between coefficients L_{ik} . The shortcoming of this method is that numerous L_{ik} parameters have to be introduced which make calculations unnecessarily complicated.

In what follows we shall use a third approach which is based on the direct application of the local form of Gyarmati's variational principle given by equation (4.68).

First, we take the local form of Gyarmati's principle in energy picture and then look for the extrema with constraints (8.244) and (8.246) by varying $\dot{\mathbf{e}}$, $\dot{\mathbf{E}}$ and $\dot{\mathbf{d}}$. For the formulation and solution of the variational problem, first, determine the possible form of dissipation potential $\Phi(\dot{\mathbf{e}}, \dot{\mathbf{E}}, \dot{\mathbf{d}})$. Dissipation potential is a homogeneous quadratic function of the above variables where the coefficients depend in some way on local state parameters. In our case, this means that in addition to these variables, Φ may depend also on the temperature, \mathbf{e} and \mathbf{E} . In the simplest case — if we restrict ourselves to small deformations — the dependence on tensor \mathbf{E} is negligible for nematic liquid crystals; hence

$$\Phi = \Phi(\dot{\mathbf{e}}, \dot{\mathbf{E}}, \dot{\mathbf{d}}, \mathbf{e}, T) \quad (8.265)$$

may be written.

In the following we restrict our study to isothermal motions; therefore, we disregard variable T . Since the above dissipation potential is an isotropic, scalar function of its variables, which also shows the symmetry relations of the medium, it obviously holds that

$$\Phi(\mathbf{Q}\dot{\mathbf{e}}, \mathbf{Q}\dot{\mathbf{E}}\mathbf{Q}^T, \mathbf{Q}\dot{\mathbf{d}}\mathbf{Q}^T, \mathbf{Q}\mathbf{e}) = \Phi(\dot{\mathbf{e}}, \dot{\mathbf{E}}, \dot{\mathbf{d}}, \mathbf{e}) \quad (8.266)$$

where \mathbf{Q} is an arbitrary orthogonal tensor. (We note that in colesteric liquid crystals, equation (8.266) is valid only if $\det \mathbf{Q} = 1$.) Since the selection between \mathbf{e} and $-\mathbf{e}$ is completely arbitrary, the relationship

$$\Phi(-\dot{\mathbf{e}}, -\dot{\mathbf{E}}, \dot{\mathbf{d}}, -\mathbf{e}) = \Phi(\dot{\mathbf{e}}, \dot{\mathbf{E}}, \dot{\mathbf{d}}, \mathbf{e}) \quad (8.267)$$

should also necessarily hold.

Thus the quadratic form of the dissipation potential may have the following form:

$$\Phi = \frac{1}{2} \dot{\mathbf{e}} \mathbf{R}^{11} \dot{\mathbf{e}} + \dot{\mathbf{e}} \mathbf{R}^{12} : \dot{\mathbf{E}} + \dot{\mathbf{e}} \mathbf{R}^{13} : \dot{\mathbf{d}} + \frac{1}{2} \dot{\mathbf{E}} : \mathbf{R}^{22} : \dot{\mathbf{E}} + \dot{\mathbf{E}} : \mathbf{R}^{23} : \dot{\mathbf{d}} + \dot{\mathbf{d}} : \mathbf{R}^{33} : \dot{\mathbf{d}}, \quad (8.268a)$$

where \mathbf{R}^{11} is a second order,

\mathbf{R}^{12} and \mathbf{R}^{13} third order, and

\mathbf{R}^{22} , \mathbf{R}^{23} and \mathbf{R}^{33} fourth order tensors.

For clarity, let us write our equation also in orthogonal components:

$$\begin{aligned} \Phi = \frac{1}{2} \mathbf{R}_{ij}^{11} \dot{e}_i \dot{e}_j + \mathbf{R}_{ijk}^{12} \dot{e}_i \dot{E}_{jk} + \mathbf{R}_{ijk}^{13} \dot{e}_i \dot{d}_{jk} + \frac{1}{2} \mathbf{R}_{ijkl}^{22} \dot{E}_{ij} \dot{E}_{kl} + \\ + \mathbf{R}_{ijkl}^{23} \dot{E}_{ij} \dot{d}_{kl} + \mathbf{R}_{ijkl}^{33} \dot{d}_{ij} \dot{d}_{kl}, \end{aligned} \quad (8.268b)$$

where i, j, k, l denote subscript 1, 2 and 3, and summation should be carried out for all of them from 1 to 3. It is important to emphasize that this equation is completely general: it does not show any symmetry, and coefficients \mathbf{R} are functions of \mathbf{e} .

Let us now examine which conditions should be satisfied by tensors \mathbf{R} for function Φ , corresponding to constraints (8.266) and (8.267). It is apparent from equation (8.266) that every orthogonal transformation leaving the vector \mathbf{e} unchanged leaves tensors \mathbf{R} also unchanged. Orthogonal transformations converting vector \mathbf{e} into vector $-\mathbf{e}$ leave tensors \mathbf{R}^{11} , \mathbf{R}^{12} , \mathbf{R}^{22} and \mathbf{R}^{23} unchanged, but they transform tensors \mathbf{R}^{13} and \mathbf{R}^{23} into their -1 -fold.

To establish the form of the tensors, let us temporarily define a Cartesian coordinate system whose axis x_1 points to direction \mathbf{e} . Calculations will be carried out with the subscripts; this method is based on the rule that the components transform in the same way as do the product of vector components. Individual tensors will not be given now, only subscripts will be provided in parentheses.

The following transformations will be used:

Q_1 : reflection with respect to the plane perpendicular to axis x_1 :

$$x'_1 = -x_1, \quad x'_2 = x_2, \quad x'_3 = x_3,$$

which may be written in short forms as

$$(1)' = -(1), \quad (2)' = (2), \quad (3)' = (3).$$

Q_2 : reflection with respect to the plane perpendicular to axis x_2 :

$$(1)' = (1), \quad (2)' = -(2), \quad (3)' = (3).$$

Q_3 : reflection with respect to the plane perpendicular to axis x_3 :

$$(1)' = (1), \quad (2)' = (2), \quad (3)' = -(3).$$

Q_4 : reflection with respect to the plane passing through axis x_1 and the bisector of axes x_2 and x_3 :

$$(1)' = (1), \quad (2)' = (3), \quad (3)' = (2).$$

Q_5 : elementary rotation (by a very small angle α) around axis x_1 :

$$(1)' = (1), \quad (2)' = (2) + \alpha(3), \quad (3)' = (3) - \alpha(2).$$

Transformations Q_2 , Q_3 , Q_4 and Q_5 leave the direction of \mathbf{e} unchanged, whereas Q_1 reverses it. (We note that for colesteric materials only Q_4 is allowed for calculations instead of reflections; rotations by 180° should be used.)

For a deeper understanding of the application of our method, we show as an example how the components (123) and (233) of a third-order tensor transform. Obviously:

$$\begin{aligned} Q_1: & \quad (123)' = -(123), & (233)' &= (233), \\ Q_2: & \quad (123)' = -(123), & (233)' &= -(233), \end{aligned}$$

$$\begin{aligned}
\mathbf{Q}_3: & \quad (123)' = -(123), & (233)' &= (233), \\
\mathbf{Q}_4: & \quad (123)' = (132), & (233)' &= (322), \\
\mathbf{Q}_5: & \quad (123)' = (1)[(2) + \alpha(3)][(3) - \alpha(2)] = (123) + \alpha[(133) - (122)], \\
& \quad (233)' = (233) + \alpha[(333) - (223) - (232)].
\end{aligned}$$

Let us first examine the effect of transformation \mathbf{Q}_2 . Since \mathbf{Q}_2 multiplies every subscript 2 by -1 , the non-disappearing tensor components may have only an even number of subscript 2. In the case of transformation \mathbf{Q}_3 , the same is true for subscript 3; i.e., invariance with respect to transformations \mathbf{Q}_2 and \mathbf{Q}_3 means those components of tensor \mathbf{R} are zero that have an odd number of subscripts 2 or 3. Transformation \mathbf{Q}_4 changes subscripts 2 to 3 and vice versa; this means that those tensor components obtained from one another so that their subscripts 2-s are interchanged with 3-s and vice versa are identical.

From this, tensor \mathbf{R}^{11} can readily be given. Since the subscripts of non-zero components are

$$(11), \quad (22) = (33),$$

we may write term $\mathbf{\hat{e}}\mathbf{R}^{11}\mathbf{\hat{e}}$ in equation (8.268) in the following form:

$$\mathbf{\hat{e}}\mathbf{R}^{11}\mathbf{\hat{e}} = \mathbf{R}_{11}^{11}\mathbf{\hat{e}}_1\mathbf{\hat{e}}_1 + \mathbf{R}_{22}^{11}(\mathbf{\hat{e}}_2\mathbf{\hat{e}}_2 + \mathbf{\hat{e}}_3\mathbf{\hat{e}}_3).$$

However, as $\mathbf{\hat{e}}\mathbf{e} = 0$, i.e. $\mathbf{\hat{e}}_1$ is zero, we have

$$\mathbf{\hat{e}}\mathbf{R}^{11}\mathbf{\hat{e}} = R^{11}\mathbf{\hat{e}}^2, \quad (8.269)$$

where the subscripts of R_{22}^{11} are omitted.

Let us now analyze third-order tensors \mathbf{R}^{12} and \mathbf{R}^{13} whose non-zero components are:

$$(111), \quad (122) = (133), \quad (212) = (313), \quad (221) = (331).$$

Transformation \mathbf{Q}_1 changes them into their -1 -fold, since there are an odd number of 1-s in all of them. Consequently, $\mathbf{R}^{12} = 0$, and \mathbf{R}^{13} can also be determined. Since in the form of expression $\mathbf{\hat{e}}\mathbf{R}^{13} : \mathbf{\hat{d}}$ written in terms of components the first subscript is that of $\mathbf{\hat{e}}$, we may write

$$\begin{aligned}
\mathbf{\hat{e}}\mathbf{R}^{13} : \mathbf{\hat{d}} &= \mathbf{R}_{212}^{13}(\mathbf{\hat{e}}_2\mathbf{\hat{d}}_{12} + \mathbf{\hat{e}}_3\mathbf{\hat{d}}_{13}) + \mathbf{R}_{221}^{13}(\mathbf{\hat{e}}_2\mathbf{\hat{d}}_{21} + \mathbf{\hat{e}}_3\mathbf{\hat{d}}_{31}) = \\
&= R_{212}^{13}\mathbf{e}\mathbf{\hat{d}}\mathbf{\hat{e}} + R_{221}^{13}\mathbf{\hat{e}}\mathbf{e}\mathbf{\hat{d}} = R^{13}\mathbf{e}\mathbf{\hat{d}}\mathbf{\hat{e}}, \quad (8.270)
\end{aligned}$$

in which we utilized that $\mathbf{\hat{d}}$ is symmetric.

Let us now proceed to the analysis of fourth-order tensors \mathbf{R}^{22} , \mathbf{R}^{23} and \mathbf{R}^{33} . Since the number of subscripts is now 4 and the numbers of both the 2-s and 3-s are even (the number of 1-s is necessarily even), transformation \mathbf{Q}_1 leaves every fourth order tensor invariant which are unchanged by \mathbf{Q}_2 and \mathbf{Q}_3 . This also means that \mathbf{R}^{23} is zero, since it should be transformed by \mathbf{Q}_1 into its (-1) -fold. We have to study \mathbf{R}^{22} and \mathbf{R}^{33} . Now the subscript combinations of non-zero elements are the following as calculated from \mathbf{Q}_1 , \mathbf{Q}_2 , \mathbf{Q}_3 and \mathbf{Q}_4 :

$$\begin{aligned}
(1111), & \quad (2121) = (3131), & (2233) &= (3322), \\
(1122) &= (1133), & (1221) &= (1331), & (2323) &= (3232), \\
(1212) &= (1313), & (2211) &= (3311), & (2332) &= (3223), \\
(2112) &= (3113), & (2222) &= (3333),
\end{aligned}$$

which means 11 different elements. However, we did not utilize \mathbf{Q}_5 so far. (We have not needed it until now, since the formulae derived by the simpler transformations and given in an invariant form are invariant also under \mathbf{Q}_5 .) Let us now calculate the behavior of element $(2223)=0$.

$$(2223)' = (2223) + \alpha[(2222) - (2233) - (2323) - 3223]$$

whence

$$(2222) = (2233) + (2323) + (2332)$$

results. Thus the number of independent elements is reduced to 10.

It would be quite a difficult task to write the equations with the subscript combinations obtained and then transform them into the invariant form; but this latter can be determined also in the simpler way, as follows: A fourth-order tensor maps a second order tensor to another second order tensor in a homogeneous, linear way. The fourth order tensor of interest depends on \mathbf{e} . Let us try to assign second-order tensors homogeneous and linear in \mathbf{X} to a second order tensor \mathbf{X} and to \mathbf{e} . These are the following:

$$\begin{aligned} \mathbf{X}, \quad \mathbf{X}^T, \quad \mathbf{e} \circ \mathbf{X} \mathbf{e}, \quad \mathbf{e} \circ \mathbf{X}^T \mathbf{e}, \quad \mathbf{X} \mathbf{e} \circ \mathbf{e}, \quad \mathbf{X}^T \mathbf{e} \circ \mathbf{e}, \quad \text{tr } \mathbf{X} \delta, \\ \text{tr } \mathbf{X} \mathbf{e} \circ \mathbf{e}, \quad (\mathbf{e} \mathbf{X} \mathbf{e}) \delta, \quad (\mathbf{e} \mathbf{X} \mathbf{e}) \mathbf{e} \circ \mathbf{e}. \end{aligned}$$

There are just ten in number; thus, bilinear forms in \mathbf{X} and \mathbf{Y} are the following:

$$\begin{aligned} \mathbf{X} : \mathbf{Y}, \quad \mathbf{X}^T : \mathbf{Y}, \quad \mathbf{e} \mathbf{Y} \mathbf{X} \mathbf{e}, \quad \mathbf{e} \mathbf{Y} \mathbf{X}^T \mathbf{e}, \quad \mathbf{e} \mathbf{X}^T \mathbf{Y} \mathbf{e}, \quad \mathbf{e} \mathbf{X} \mathbf{Y} \mathbf{e}, \quad \text{tr } \mathbf{X} \text{tr } \mathbf{Y}, \\ \text{tr } \mathbf{X} \mathbf{e} \mathbf{Y} \mathbf{e}, \quad \text{tr } \mathbf{Y} \mathbf{e} \mathbf{X} \mathbf{e}, \quad \mathbf{e} \mathbf{X} \mathbf{e} \mathbf{e} \mathbf{Y} \mathbf{e}. \end{aligned}$$

In the case of \mathbf{R}^{22} , $\mathbf{X} = \mathbf{Y} = \mathbf{E}$; hence, expressions 3, 6 and 8, 9 are identical. For \mathbf{R}^{33} , $\mathbf{X} = \mathbf{Y} = \mathbf{d}$; thus the first and second expressions are identical, but also expressions 3, 4, 5 and 6 are equal, whereas expressions 7, 8 and 9 are zero. Thus we may write that

$$\begin{aligned} \mathbf{E} : \mathbf{R}^{22} : \mathbf{E} &= R_1^{22} \mathbf{E} : \mathbf{E} + R_2^{22} \mathbf{E} : \mathbf{E}^T + R_3^{22} \mathbf{e} \mathbf{E}^2 \mathbf{e} + R_4^{22} (\mathbf{e} \mathbf{E})^2 + R_5^{22} (\mathbf{E} \mathbf{e})^2 + \\ &\quad + R_6^{22} (\text{tr } \mathbf{E})^2 + R_7^{22} \text{tr } \mathbf{E} \mathbf{e} \mathbf{E} \mathbf{e} + R_8^{22} (\mathbf{e} \mathbf{E} \mathbf{e})^2, \quad (8.271) \\ \mathbf{d} : \mathbf{R}^{33} : \mathbf{d} &= R_1^{33} \mathbf{d} : \mathbf{d} + R_2^{33} \mathbf{e} \mathbf{d}^2 \mathbf{e} + R_3^{33} (\mathbf{e} \mathbf{d} \mathbf{e})^2, \end{aligned}$$

by means of which the dissipation function can be written as follows:

$$\begin{aligned} \Phi &= \frac{1}{2} R^{11} \mathbf{e}^2 + R^{13} \mathbf{e} \mathbf{d} \mathbf{e} + \frac{1}{2} R_1^{22} \mathbf{E} : \mathbf{E} + \frac{1}{2} R_2^{22} \mathbf{E} : \mathbf{E}^T + \frac{1}{2} R_3^{22} \mathbf{e} \mathbf{E}^2 \mathbf{e} + \\ &\quad + \frac{1}{2} R_4^{22} (\mathbf{e} \mathbf{E})^2 + \frac{1}{2} R_5^{22} (\mathbf{E} \mathbf{e})^2 + \frac{1}{2} R_6^{22} (\text{tr } \mathbf{E})^2 + \frac{1}{2} R_7^{22} (\text{tr } \mathbf{E}) \mathbf{e} \mathbf{E} \mathbf{e} + \\ &\quad + \frac{1}{2} R_8^{22} (\mathbf{e} \mathbf{E} \mathbf{e})^2 + \frac{1}{2} R_1^{33} \mathbf{d} : \mathbf{d} + \frac{1}{2} R_2^{33} \mathbf{e} \mathbf{d}^2 \mathbf{e} + \frac{1}{2} R_3^{33} (\mathbf{e} \mathbf{d} \mathbf{e})^2. \quad (8.272) \end{aligned}$$

The equations of motion for liquid crystals are obtained from the actual form of Gyarmati's local principle

$$\mathcal{L}^* = T \sigma_s - \Phi + \mu \mathbf{e} \dot{\mathbf{e}} - (\dot{\mathbf{e}} \mathbf{E} + \mathbf{e} \dot{\mathbf{E}}) \vec{\lambda} \quad (8.273)$$

by seeking the maximum of its Lagrangian, where μ and $\vec{\lambda}$ are Lagrange multipliers. The extremum problem means now that we search for values of $\dot{\mathbf{e}}$, $\dot{\mathbf{E}}$, $\dot{\mathbf{d}}$, μ and $\vec{\lambda}$ for which \mathcal{L}^* is maximum when the values of \mathbf{E} , \mathbf{B} and \mathbf{e} are given in accordance with section 4.6. In calculations it must not be forgotten that $\dot{\mathbf{d}}$ is a symmetric tensor of zero trace. Equations describing the motion are the following:

$$\begin{aligned} \varrho T \frac{\partial s}{\partial \mathbf{e}} + \text{Div } \mathbf{B} + \mu \mathbf{e} &= \mathbf{E} \vec{\lambda} + R^{11} \dot{\mathbf{e}} + R^{13} \dot{\mathbf{d}}\mathbf{e}, \\ \varrho T \frac{\partial s}{\partial \mathbf{E}} + \mathbf{B} &= \mathbf{e} \circ \vec{\lambda} + R_1^{22} \dot{\mathbf{E}} + R_2^{22} \dot{\mathbf{E}}^T + \frac{1}{2} R_3^{22} (\mathbf{e} \circ \dot{\mathbf{E}}\mathbf{e} + \mathbf{e} \dot{\mathbf{E}} \circ \mathbf{e}) + R_4^{22} \mathbf{e} \circ \mathbf{e} \dot{\mathbf{E}} + \\ &+ R_5^{22} \dot{\mathbf{E}}\mathbf{e} \circ \mathbf{e} + R_6^{22} \text{tr } \dot{\mathbf{E}} \boldsymbol{\delta} + \frac{1}{2} R_7^{22} (\mathbf{e} \dot{\mathbf{E}} \mathbf{e} \boldsymbol{\delta} + \text{tr } \dot{\mathbf{E}} \mathbf{e} \circ \mathbf{e}) + R_8^{22} (\mathbf{e} \dot{\mathbf{E}} \mathbf{e}) \mathbf{e} \circ \mathbf{e} \\ \mathbf{t}^{so} + (\mathbf{E}^T \mathbf{B})^{so} &= \frac{1}{2} R^{13} (\dot{\mathbf{e}} \circ \mathbf{e} + \mathbf{e} \circ \dot{\mathbf{e}}) + R_1^{33} \dot{\mathbf{d}} \\ &+ \frac{1}{2} R_2^{33} \left[\mathbf{e} \circ \dot{\mathbf{d}}\mathbf{e} + \dot{\mathbf{d}}\mathbf{e} \circ \mathbf{e} - \frac{2}{3} (\mathbf{e} \dot{\mathbf{d}} \mathbf{e}) \boldsymbol{\delta} \right] + R_3^{33} (\mathbf{e} \dot{\mathbf{d}} \mathbf{e}) \left(\mathbf{e} \circ \mathbf{e} - \frac{1}{3} \boldsymbol{\delta} \right), \\ \mathbf{e} \dot{\mathbf{e}} &= 0, \quad \mathbf{e} \mathbf{E} = 0, \end{aligned} \tag{8.274}$$

which include 13 kinetic coefficients of the resistance type. If we take also into account the 4 Frank coefficients, it is apparent that 17 material constants are needed for describing nematic liquid crystals.

Owing to the large number of material constants the equations of motion are very complicated; efforts to eventually simplify the equations, even at the expense of their range of validity, are understandable. One possible way of reduction is that we restrict ourselves to cases in which the dimensions of the liquid crystal cell are not too thin. In fact, when assuming large enough cells, $\dot{\mathbf{E}}$ is small as compared to $\dot{\mathbf{e}}$; thus, in dissipation potential the terms quadratic in the components of $\dot{\mathbf{E}}$, which correspond to approximation $\mathbf{R}^{22} = 0$ can be neglected. In this approximation the number of material constant reduces to 9; however, in this case the theory provides correct results only for sufficiently thick samples.

It is very important to note that the thermodynamic theory presented becomes, for approximation $\mathbf{R}^{22} = 0$, identical with the Ericksen-Leslie-Parodi theory well-known in the literature [40, 100, 131]. In order to illustrate the comparison, we tabulated the notations used here and by the above authors.

Leslie	here	Leslie	here	Leslie	here
\mathbf{d}	\mathbf{e}	\mathbf{G}	$-\mathbf{e} \times \mathbf{m}$	μ_1	R_3^{33}
σ	\mathbf{t}^T	\mathbf{N}	$\dot{\mathbf{E}} + \mathbf{E} \mathbf{d}$	μ_2	$\frac{1}{2} (R^{13} - R^{11})$
$\vec{\beta}$	$\vec{\lambda}$	\mathbf{A}	$\dot{\mathbf{d}}$	μ_3	$\frac{1}{2} (R^{13} + R^{11})$
\mathbf{N}	$\dot{\mathbf{e}}$	\mathbf{g}	$-\mathbf{e} \times \varrho \mathbf{m} - \text{Div } \mathbf{B}$	μ_4	R_1^{33}
$\mathbf{\Pi}$	\mathbf{B}^T	λ_1	$-R^{11}$	μ_5	$\frac{1}{2} (R_2^{33} - R^{13})$
γ	μ	λ_2	$-R^{13}$	μ_6	$\frac{1}{2} (R_2^{23} + R^{13})$
\mathbf{w}	$\dot{\mathbf{e}}$				

8.6.5. An example. We show now an example for the application of equations (8.274). Consider a liquid crystal cell which is set between parallel planes. The director at the boundary should be fixed parallel with the planes, in the same sense on both sides. Take a Cartesian frame so that axis x_1 should be perpendicular to the boundary planes of the cell. At the boundary the direction of \mathbf{e} should coincide with that of axis x_2 .

Suppose that for some reason inside the cell, the director has turned around x_1 . Let us examine the restoration of the equilibrium.

If we assume that the quantities describing the processes depend only on x_1 and time, they may be given in the form

$$\begin{aligned} \mathbf{e} &= \cos \alpha \mathbf{e}_2 + \sin \alpha \mathbf{e}_3, & \dot{\mathbf{e}} &= \frac{\partial \alpha}{\partial t} \mathbf{e}_1 \times \mathbf{e}, \\ \mathbf{E} &= \frac{\partial \alpha}{\partial x} (\mathbf{e}_1 \times \mathbf{e}) \circ \mathbf{e}_1, & \dot{\mathbf{E}} &= \frac{\partial^2 \alpha}{\partial x_1 \partial t} (\mathbf{e}_1 \times \mathbf{e}) \circ \mathbf{e}_1 - \frac{\partial \alpha}{\partial x_1} \frac{\partial \alpha}{\partial t} \mathbf{e} \circ \mathbf{e}_1. \end{aligned} \quad (8.275)$$

From these expressions it is easy to see in our case $\mathbf{E} : \mathbf{E}^T = 0$, $\mathbf{E}\mathbf{e} = 0$ and $\text{tr} \mathbf{E} = 0$; thus the expression of entropy given by equation (8.228) is simplified to

$$s = s_0(u) - \frac{1}{2T\varrho} k_{22} \mathbf{E} : \mathbf{E} = s_0(u) - \frac{1}{2T\varrho} k_{22} \left(\frac{\partial \alpha}{\partial x_1} \right)^2 \quad (8.276)$$

Similarly, it is apparent that

$$\begin{aligned} \dot{\mathbf{E}} : \dot{\mathbf{E}}^T &= 0, & \dot{\mathbf{E}}\mathbf{e} &= 0, \\ \mathbf{e}\dot{\mathbf{E}} &= -\frac{\partial \alpha}{\partial x_1} \frac{\partial \alpha}{\partial t} \mathbf{e}_1, & \text{tr} \dot{\mathbf{E}} &= 0, \end{aligned} \quad (8.277)$$

and, hence, the actual expression for dissipation potential is

$$\begin{aligned} \Phi &= \frac{1}{2} R^{11} \dot{\mathbf{e}}^2 + \frac{1}{2} R_1^{22} \dot{\mathbf{E}} : \dot{\mathbf{E}} + \frac{1}{2} R_4^{22} (\mathbf{e}\dot{\mathbf{E}})^2 = \frac{1}{2} R^{11} \left(\frac{\partial \alpha}{\partial t} \right)^2 + \\ &+ \frac{1}{2} R_1^{22} \left(\frac{\partial^2 \alpha}{\partial t \partial x_1} \right)^2 + \frac{1}{2} (R_1^{22} + R_4^{22}) \left(\frac{\partial \alpha}{\partial x_1} \right)^2 \left(\frac{\partial \alpha}{\partial t} \right)^2. \end{aligned} \quad (8.278)$$

If we also assume that the medium does not flow ($\dot{\mathbf{d}} = 0$), by utilizing these formulae our equations of motion become

$$\begin{aligned} \text{Div} \mathbf{B} + \mu \mathbf{e} &= \mathbf{E} \vec{\lambda} + R^{11} \dot{\mathbf{e}}, \\ -k_{22} \mathbf{E} + \mathbf{B} &= \mathbf{e} \circ \vec{\lambda} + R_1^{22} \dot{\mathbf{E}} + R_4^{22} \mathbf{e} \circ (\mathbf{e}\dot{\mathbf{E}}). \end{aligned} \quad (8.279)$$

We did not write the third equation since we are only looking for the equation determining $\alpha(x_1, t)$. Now we determine $\vec{\lambda}$ by multiplying the second equation by \mathbf{e} from the left, and utilizing correlations $\mathbf{e}\mathbf{E} = \mathbf{e}\mathbf{B} = 0$ and equation (8.277):

$$\vec{\lambda} = (R_1^{22} + R_4^{22}) \frac{\partial \alpha}{\partial x_1} \frac{\partial \alpha}{\partial t} \mathbf{e}_1, \quad (8.280)$$

then also tensor \mathbf{B} :

$$\mathbf{B} = \left(k_{22} \frac{\partial \alpha}{\partial x_1} + R_1^{22} \frac{\partial^2 \alpha}{\partial x_1 \partial t} \right) (\mathbf{e}_1 \times \mathbf{e}) \circ \mathbf{e}_1. \quad (8.281)$$

On substituting these expressions into the first equation of (8.279), we arrive at

$$\begin{aligned} & \left(k_{22} \frac{\partial^2 \alpha}{\partial x_1^2} + R_1^{22} \frac{\partial^3 \alpha}{\partial t \partial x_1^2} \right) \mathbf{e}_1 \times \mathbf{e} - \left(k_{22} \frac{\partial \alpha}{\partial x_1} + R_1^{22} \frac{\partial^2 \alpha}{\partial x_1 \partial t} \right) \frac{\partial \alpha}{\partial x_1} \mathbf{e} + \mu \mathbf{e} = \\ & = (R_1^{22} + R_4^{22}) \left(\frac{\partial \alpha}{\partial x_1} \right)^2 \frac{\partial \alpha}{\partial t} \mathbf{e}_1 \times \mathbf{e} + R^{11} \frac{\partial \alpha}{\partial t} \mathbf{e}_1 \times \mathbf{e}, \end{aligned} \quad (8.282)$$

whence, by identifying the coefficients of $\mathbf{e}_1 \times \mathbf{e}$, equation

$$k_{22} \frac{\partial^2 \alpha}{\partial x_1^2} + R_1^{22} \frac{\partial^3 \alpha}{\partial t \partial x_1^2} = R^{11} \frac{\partial \alpha}{\partial t} + (R_1^{22} + R_4^{22}) \left(\frac{\partial \alpha}{\partial x_1} \right)^2 \frac{\partial \alpha}{\partial t} \quad (8.283)$$

is obtained.

Moreover, we deal with the solution of equation (8.283) only for small α -s. In this case, the last term on the right side being of third degree may be neglected and a solution is sought in the form

$$\alpha = \sum_n A \exp \left(-\frac{t}{\tau_n} \right) \sin \frac{n\pi}{d} x_1 \quad (8.284)$$

where d is the thickness of the cell. The solution is obtained in the form of a Fourier series. The relaxation times for individual terms are determined from equation (8.283):

$$\tau_n = \frac{R_1^{22}}{k_{22}} + \frac{R^{11}}{k_{22}} \frac{d^2}{n^2 \pi^2}. \quad (8.285)$$

From this equation it is seen that the relaxation times of establishing equilibrium are quadratic functions of the thickness and on decreasing this thickness beyond all limits they approach a finite, non-zero limiting value. Since \mathbf{R}^{22} is zero in Leslie's theory, it leads to a relaxation time proportional to the square of cell thickness [54].

Let us finally show that the direct application of Gyarmati's variation principle simplifies significantly the solution of this task. Since only dissipation potential Φ has been calculated, it is expedient to use the space-integrated partial form of the variational principle, the so-called current representation

$$\delta_J \int_0^d T \sigma_s - \Phi dx_1 = 0. \quad (8.286)$$

This partial form is written in energy representation and may also be written in an alternative form by utilizing entropy balance

$$\delta_J \int_0^d \rho T \dot{s} - \Phi dx_1 = 0 \quad (8.287)$$

whose Lagrange function $\mathcal{L} = \rho T \dot{s} - \Phi$ can be obtained directly from equations (8.276) and (8.278):

$$\begin{aligned} \rho T \dot{s} - \Phi = & -k_{22} \left(\frac{\partial \alpha}{\partial x_1} \right) \left(\frac{\partial^2 \alpha}{\partial x \partial t} \right) - \frac{1}{2} R^{11} \left(\frac{\partial \alpha}{\partial t} \right)^2 + \frac{1}{2} R_1^{22} \left(\frac{\partial^2 \alpha}{\partial x_1 \partial t} \right)^2 + \\ & + \frac{1}{2} (R_1^{22} + R_4^{22}) \left(\frac{\partial \alpha}{\partial x_1} \right)^2 \left(\frac{\partial \alpha}{\partial t} \right)^2. \end{aligned} \quad (8.288)$$

The Euler-Lagrange equation of variation problem (8.287) is obtained so that $\frac{\partial \alpha}{\partial t}$ characteristic for the rate of the process is regarded as an unknown function depending on place. It is easy to see that the equation obtained is identical with equation (8.283).

8.6.6. Shear flow of nematic liquid crystals. The medium studied is situated also in the present case between planes $x_1 = 0$ and $x_1 = d$. The director is assumed to be perpendicular to axis x_3 . Flow rate is defined by

$$\mathbf{v} = v(x_1) \mathbf{e}_2. \quad (8.289)$$

If we suppose that the quantities describing the processes depend only on x_1 and time, they may be given in the following form:

$$\begin{aligned} \mathbf{e} &= \cos \alpha \mathbf{e}_1 + \sin \alpha \mathbf{e}_2, & \dot{\mathbf{d}} &= \frac{1}{2} \frac{\partial v}{\partial x_1} (\mathbf{e}_2 \circ \mathbf{e}_1 + \mathbf{e}_1 \circ \mathbf{e}_2), \\ \boldsymbol{\omega} &= \frac{1}{2} \frac{\partial v}{\partial x_1} (\mathbf{e}_2 \circ \mathbf{e}_1 - \mathbf{e}_1 \circ \mathbf{e}_2), & \dot{\mathbf{e}} &= \left(\frac{\partial \alpha}{\partial t} - \frac{1}{2} \frac{\partial v}{\partial x_1} \right) \mathbf{e}_3 \times \mathbf{e}, \\ \mathbf{E} &= \frac{\partial \alpha}{\partial x_1} (\mathbf{e}_3 \times \mathbf{e}) \circ \mathbf{e}_1, \end{aligned} \quad (8.290)$$

$$\begin{aligned} \dot{\mathbf{E}} &= \frac{\partial^2 \alpha}{\partial x_1 \partial t} (\mathbf{e}_3 \times \mathbf{e}) \circ \mathbf{e}_1 + \frac{1}{2} \frac{\partial \alpha}{\partial x_1} \frac{\partial v}{\partial x_1} (\mathbf{e}_3 \times \mathbf{e}) \circ \mathbf{e}_2 - \\ & - \frac{\partial \alpha}{\partial x_1} \left(\frac{\partial \alpha}{\partial t} - \frac{1}{2} \frac{\partial v}{\partial x_1} \right) \mathbf{e} \circ \mathbf{e}_1. \end{aligned}$$

We can check by a simple calculation that conditions $\mathbf{e} \dot{\mathbf{e}} = 0$ and $\dot{\mathbf{e}} \mathbf{E} + \mathbf{e} \dot{\mathbf{E}} = 0$ are fulfilled.

In what follows, for simplicity, we restrict ourselves to Leslie's theory, i.e. we assume that $\mathbf{R}^{22} = 0$. The forms of entropy and dissipation potential are calculated by using equations (8.290):

$$s = s_0 - \frac{1}{2\rho T} \left(\frac{\partial \alpha}{\partial x_1} \right)^2 (k_{11} \sin^2 \alpha + k_{33} \cos^2 \alpha) \quad (8.291)$$

and

$$\begin{aligned} \Phi &= \frac{1}{2} R^{11} \left(\frac{\partial \alpha}{\partial t} \right)^2 + \frac{1}{2} (R^{13} \cos 2\alpha - R^{11}) \frac{\partial \alpha}{\partial t} \frac{\partial v}{\partial x_1} + \\ & + \frac{1}{8} \left(\frac{\partial v}{\partial x_1} \right)^2 (R^{11} + 2R_1^{33} + R_2^{33} + 4R_3^{33} \sin^2 \alpha \cos^2 \alpha - 2R^{13} \cos 2\alpha). \end{aligned}$$

Equations of motion are obtained in the simplest way by utilizing Gyarmati's variational principle in its form given by equation (8.287). If function

$$f(\alpha) = k_{11} \sin^2 \alpha + k_{33} \cos^2 \alpha \quad (8.292)$$

is introduced for simplifying notations, then the Lagrange function of the variational problem is described by

$$\mathcal{L} = \rho T \dot{s} - \Phi = -\frac{\partial \alpha}{\partial x_1} \frac{\partial^2 \alpha}{\partial x_1 \partial t} f(\alpha) - \frac{1}{2} \frac{\partial \alpha}{\partial t} \left(\frac{\partial \alpha}{\partial x_1} \right)^2 \frac{df}{d\alpha} - \Phi \quad (8.293)$$

The unknown functions with respect to which variation has to be carried out (rates of processes) are $\mathbf{v}(x_1)$ and $\frac{\partial \alpha(x_1)}{\partial t}$, whereas $\alpha(x_1)$ is fixed.

The Euler-Lagrange equations belonging to the variational problem can be written directly as

$$\begin{aligned} \frac{1}{2} \left(\frac{\partial \alpha}{\partial x_1} \right)^2 \frac{df}{d\alpha} + R_{11} \frac{\partial \alpha}{\partial t} + h(\alpha) \frac{\partial v}{\partial x_1} &= \frac{\partial}{\partial x_1} \left(\frac{\partial \alpha}{\partial x_1} f(\alpha) \right), \\ \frac{\partial}{\partial x_1} \left(h(\alpha) \frac{\partial \alpha}{\partial t} + \frac{\partial v}{\partial x_1} g(\alpha) \right) &= 0, \end{aligned} \quad (8.294)$$

where notations

$$\begin{aligned} g(\alpha) &= \frac{1}{4} [R^{11} + 2R_1^{33} + R_2^{33} + 4R_3^{33} \sin^2 \alpha \cos^2 \alpha - 2R^{13} \cos 2\alpha] \\ h(\alpha) &= \frac{1}{2} (R^{13} \cos 2\alpha - R^{11}) \end{aligned} \quad (8.295)$$

have been introduced.

It is obvious that in a stationary state the equations take the simpler forms

$$\begin{aligned} \frac{dv}{dx_1} g(\alpha) &= C, \\ 2f(\alpha) &= \frac{d^2 \alpha}{dx_1^2} + \frac{df}{d\alpha} \left(\frac{d\alpha}{dx_1} \right)^2 - \frac{2h(\alpha)C}{g(\alpha)} = 0 \end{aligned} \quad (8.296)$$

which are identical with those derived by Leslie from a non-thermodynamic theory [100].

About the practical application of equations (8.296), it should be noted they are quite difficult to solve accurately, especially if we consider that different boundary conditions may exist. In the simplest case, when the director is perpendicular to the surface at the boundaries, boundary conditions may be given as

$$\alpha(0) = \alpha(d) = 0, \quad v(0) = 0, \quad v(d) = v_0 \quad (8.297)$$

We cannot deal here with the different methods for solving these equations, but we mention that for a given problem, especially if we are satisfied with approximate solutions, we may start from the actual form of Gyarmati's variational principle

in both the stationary (equation (8.296)) and the general case corresponding to equation (8.294); by applying some direct methods of variational calculus (Ritz method, etc.), we can arrive at good approximate solutions very quickly [145-147].

Before finishing the study of liquid crystals, we shall calculate the general form of stress tensor for the case of approximation corresponding to the Ericksen-Leslie-Parodi theory when $\mathbf{R}^{22} = 0$ substitution is applied in equation (8.274). The equations provide the symmetric part of the stress tensor in an explicit form. The antisymmetric part can be determined by utilizing the balance of moment of momentum described by equation (4.66) in the form

$$2\mathbf{w}(\mathbf{t}) + \text{Div}(\mathbf{e} \times \mathbf{B}) + \varrho \mathbf{m} = 0 \quad (8.298)$$

From the scalar nature of entropy and the second equation of (8.274) and by also utilizing correlation $\mathbf{e}\mathbf{E} = 0$, we obtain

$$-\varrho \mathbf{m} + \mathbf{e} \times \varrho T \frac{\partial s}{\partial \mathbf{e}} + 2\mathbf{w}(\mathbf{E}^T \mathbf{B} - \mathbf{B}\mathbf{E}^T) = \mathbf{e} \times \mathbf{E}\vec{\lambda}. \quad (8.299)$$

Let us now also utilize the first equation of (8.274) whose vectorial multiplication from the left by \mathbf{e} leads to

$$\mathbf{e} \times \varrho T \frac{\partial s}{\partial \mathbf{e}} + \mathbf{e} \times \text{Div} \mathbf{B} = \mathbf{e} \times \mathbf{E}\vec{\lambda} + \mathbf{e} \times \frac{\partial \Phi}{\partial \dot{\mathbf{e}}}. \quad (8.300)$$

If equality

$$\text{Div}(\mathbf{e} \times \mathbf{B}) = 2\mathbf{w}(\mathbf{B}\mathbf{E}^T) + \mathbf{e} \times \text{Div} \mathbf{B} \quad (8.301)$$

is added to the above relationships, then the latter four equations give

$$2\mathbf{w}(\mathbf{t} + \mathbf{E}^T \mathbf{B}) = -\mathbf{e} \times \frac{\partial \Phi}{\partial \dot{\mathbf{e}}} = -\mathbf{e} \times (R^{11} \dot{\mathbf{e}} + R^{13} \dot{\mathbf{d}}\mathbf{e}). \quad (8.302)$$

From this correlation and the third equation of (8.274), the traceless part of \mathbf{t} can already be determined:

$$\mathbf{t} = -\mathbf{E}^T \mathbf{B} - p\delta + \frac{\partial \Phi}{\partial \dot{\mathbf{d}}} + \frac{1}{2} \left[\mathbf{e} \circ \frac{\partial \Phi}{\partial \dot{\mathbf{e}}} - \frac{\partial \Phi}{\partial \dot{\mathbf{e}}} \circ \mathbf{e} \right]. \quad (8.303)$$

Here p is an undefined scalar quantity. It can be obtained only by the solution of Cauchy's equation of motion. Due to its relatively simple form, expression (8.303) can be used in numerous important cases.

APPENDIX.

(Mathematical notations and definitions.)

The reader is supposed to be familiar with the elements of the vector and tensor calculus, nevertheless, a concise recapitulation makes the book easier to read. Our aim is to give a report on the nomenclature and notation used throughout.

A 1. The Basic Operations. A scalar is written with *italics*:

a scalar (tensor of zero order).

a vector with **bold**:

v vector, the components are v_i ($i=1, 2, 3$)

(tensor of first order).

while the tensors of second or higher order are printed with *slanted bold* as for example in

d second order tensor

with components d_{ik} ($i,k=1, 2, 3$)

The operations are given here both in invariant form and with indices joined by the sign \longleftrightarrow referring equivalence. Here, as throughout the book, we use Einstein's summation convention if an index in a formula appears twice, it means that summation is carried out over all possible values; i.e. the sign of summation \sum is omitted. Neither do we list the possible values of the other indices, as they are always 1, 2 or 3 in a Cartesian frame. The Greek letter δ stands for the unit tensor, which has the components δ_{ik} , for which

$$\delta_{ik} = \begin{cases} 1 & \text{if } i = k \\ 0 & \text{if } i \neq k. \end{cases}$$

Two tensors are equal

$$\mathbf{A} = \mathbf{B} \quad \text{if} \quad A_{ik} = B_{ik}.$$

Analogous relations are valid for higher-order tensors.

The sum (difference) of two tensors is defined in components

$$\mathbf{C} = \mathbf{A} \pm \mathbf{B} \longleftrightarrow C_{ik} = A_{ik} \pm B_{ik}.$$

Similarly, **B** equals **A** multiplied by a scalar *a* if

$$\mathbf{B} = a\mathbf{A} \longleftrightarrow B_{ik} = aA_{ik}.$$

A 2. Symmetric and Antisymmetric Tensors. One obtains the transposed tensor \mathbf{A}^T when transposing its indices:

$$A_{ik}^T = A_{ki}.$$

A tensor is called symmetric if

$$\mathbf{A} = \mathbf{A}^T \longleftrightarrow A_{ik} = A_{ki}$$

and antisymmetric if

$$\mathbf{A} = -\mathbf{A}^T \longleftrightarrow A_{ik} = -A_{ki}$$

Any tensor can be split up into a symmetric

$$\mathbf{A}^s = \frac{1}{2}(\mathbf{A} + \mathbf{A}^T) \longleftrightarrow A_{ik}^s = \frac{1}{2}(A_{ik} + A_{ki})$$

and an antisymmetric (skew-symmetric)

$$\mathbf{A}^a = \frac{1}{2}(\mathbf{A} - \mathbf{A}^T) \longleftrightarrow A_{ik}^a = \frac{1}{2}(A_{ik} - A_{ki})$$

part, i.e.

$$\mathbf{A} = \mathbf{A}^s + \mathbf{A}^a.$$

Sometimes the alternating epsilon gives convenience;

$$\boldsymbol{\varepsilon} \longleftrightarrow \varepsilon_{ijk}.$$

It has the components

$$\varepsilon_{123} = \varepsilon_{231} = \varepsilon_{312} = 1$$

$$\varepsilon_{321} = \varepsilon_{213} = \varepsilon_{132} = -1$$

while all the others equal zero.

A 3. Tensor products. The exterior product of two tensors of order m and n is a tensor of order $m + n$. In the case of two vectors, the product

$$\mathbf{c} = \mathbf{a} \circ \mathbf{b} \longleftrightarrow c_{ik} = a_i b_k$$

is called a dyad.

The vector product of two polar vectors defines an axial vector

$$\mathbf{c} = \mathbf{a} \times \mathbf{b} \longleftrightarrow c_i = \varepsilon_{ijk} a_j b_k.$$

An axial vector can be obtained from any antisymmetric tensor

$$\mathbf{c} = \mathbf{w}(\mathbf{A}) \longleftrightarrow c_i = \frac{1}{2} \varepsilon_{ijk} A_{kj}.$$

The interior product of two tensors is often called a scalar product. It is obtained from the external product by putting two indices equal and summing over the resulting “dummy” index. We indicate the interior product with a dot (\cdot) inserted between the symbols of the tensors, which can be omitted without the danger of misunderstanding. The most frequent products are

$$\begin{aligned}\mathbf{a} \cdot \mathbf{b} &= \mathbf{ab} \longleftrightarrow a_i b_i \\ \mathbf{v} \cdot \mathbf{T} &= \mathbf{vT} \longleftrightarrow (\mathbf{vT})_i = v_k T_{ki} \\ \mathbf{T} \cdot \mathbf{v} &= \mathbf{Tv} \longleftrightarrow (\mathbf{Tv})_i = T_{ik} v_k\end{aligned}$$

The second-order tensor defined by

$$\mathbf{A} \cdot \mathbf{B} = \mathbf{AB} \longleftrightarrow (\mathbf{AB})_{ik} = A_{ij} B_{jk}$$

is called simply the product of the tensors \mathbf{A} and \mathbf{B} .

The scalar product of two second-order tensors can also be defined, which is indicated by colon

$$\mathbf{A} : \mathbf{B} = \mathbf{B} : \mathbf{A} \longleftrightarrow (\mathbf{A} : \mathbf{B}) = A_{ik} B_{ik}.$$

The trace of the tensor \mathbf{A} is the scalar product

$$\text{tr } \mathbf{A} = \mathbf{A} : \boldsymbol{\delta} \longleftrightarrow \text{tr } \mathbf{A} = A_{ik} \delta_{ik} = A_{kk}.$$

The following identities hold

$$\begin{aligned}\mathbf{a} \times \mathbf{b} &= \boldsymbol{\varepsilon} : (\mathbf{a} \circ \mathbf{b}) \longleftrightarrow (\mathbf{a} \times \mathbf{b})_i = \varepsilon_{ijk} a_j b_k \\ \mathbf{c}(\mathbf{a} \times \mathbf{b}) &= \mathbf{a}\boldsymbol{\varepsilon} : (\mathbf{a} \circ \mathbf{b}) \longleftrightarrow \mathbf{c}(\mathbf{a} \times \mathbf{b}) = \varepsilon_{ijk} c_i a_j b_k \\ \mathbf{a} \times (\mathbf{b} \times \mathbf{c}) &= \mathbf{b}(\mathbf{ac}) - \mathbf{c}(\mathbf{ab}) \\ \varepsilon_{ijk} \varepsilon_{klm} &= \delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}.\end{aligned}$$

A 4. Eigenvalues and Invariants. The eigenvalues and eigenvectors are rather important in the theory of second-order tensors. A number λ is called an eigenvalue and a non-zero vector is said to be an eigenvector of the tensor \mathbf{A} if they are connected by the equation

$$\mathbf{ae} = \lambda \mathbf{e} \longleftrightarrow A_{ik} e_k = \lambda e_i = \lambda \delta_{ik} e_k.$$

The scalar numbers defined as

$$\begin{aligned}I_1 &= \varepsilon_{ijk} (A_{1i} \delta_{2j} \delta_{3k} + \delta_{1i} A_{2j} \delta_{3k} + \delta_{1i} \delta_{2j} A_{3k}) = \\ &= \varepsilon_{i23} A_{1i} + \varepsilon_{1i3} A_{2i} + \varepsilon_{12i} A_{3i} = A_{11} + A_{22} + A_{33} = \text{tr } \mathbf{A}, \\ I_2 &= \varepsilon_{ijk} (A_{1i} A_{2j} \delta_{3k} + A_{1i} \delta_{2j} A_{3k} + \delta_{1i} A_{2j} A_{3k}) = \\ &= \varepsilon_{ij3} A_{1i} A_{2j} + \varepsilon_{i2j} A_{1i} A_{3j} + \varepsilon_{1ij} A_{2i} A_{3j} =\end{aligned}$$

$$= A_{11}A_{22} - A_{12}A_{21} + A_{11}A_{33} - A_{14}A_{31} + A_{22}A_{33} - A_{23}A_{32}$$

and

$$I_3 = \varepsilon_{ijk}A_{1i}A_{2j}A_{3k} = \det \mathbf{A}$$

are called the first (I_1), the second (I_2) and the third (I_3) scalar invariants of the tensor \mathbf{A} , respectively.

Any symmetric second-order tensor can be given in the form

$$\mathbf{A} = \lambda_1 \mathbf{e}_1 \circ \mathbf{e}_1 + \lambda_2 \mathbf{e}_2 \circ \mathbf{e}_2 + \lambda_3 \mathbf{e}_3 \circ \mathbf{e}_3,$$

where λ_1 , λ_2 and λ_3 are real numbers, while \mathbf{e}_1 , \mathbf{e}_2 and \mathbf{e}_3 are mutually orthogonal unit vectors.

The eigenvalues and the scalar invariants are related by

$$I_1 = \lambda_1 + \lambda_2 + \lambda_3; \quad I_2 = \lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1; \quad I_3 = \lambda_1\lambda_2\lambda_3$$

The scalar invariants can be expressed by interior products

$$I_1 = \text{tr } A = \boldsymbol{\delta} : \mathbf{A},$$

$$I_2 = \frac{1}{2}(\text{tr } \mathbf{A})^2 - \frac{1}{2}\text{tr}(\mathbf{A}^2),$$

$$I_3 = \frac{1}{3}\text{tr}(\mathbf{A}^3) - \frac{1}{2}\text{tr}(\mathbf{A}^2)\text{tr } A + \frac{1}{6}(\text{tr } \mathbf{A})^3.$$

In the case of antisymmetric tensors, the vector invariant is often useful

$$\mathbf{w}(\mathbf{A}) = -\frac{1}{2}\boldsymbol{\varepsilon} : \mathbf{A} \longleftrightarrow w_i(\mathbf{A}) = \frac{1}{2}\varepsilon_{ijk}A_{kj},$$

From here the identity

$$\mathbf{A} = w(\mathbf{A}) \times \boldsymbol{\delta} \longleftrightarrow A_{ik} = \varepsilon_{ijl}w_j(\mathbf{A})\delta_{kl} = \varepsilon_{ijk}w_j(\mathbf{A})$$

follows.

A 5. Orthogonal Tensors. A special kind of second-order tensors are the orthogonal ones, for which the relation

$$(\mathbf{R}\mathbf{a})(\mathbf{R}\mathbf{b}) = \mathbf{a} \cdot \mathbf{b} \longleftrightarrow R_{ij}R_{ik}a_jb_k = a_ib_i$$

holds. From here, the equivalent relation

$$\mathbf{R}^T \mathbf{R} = \boldsymbol{\delta} \longleftrightarrow R_{ij}R_{ik} = \delta_{jk}$$

follows. A second-order tensor \mathbf{R} is orthogonal if and only if the above identity holds. An eigenvalue of an orthogonal tensor equals 1 or -1 .

For any orthogonal tensor \mathbf{R} , there exists a frame the basis vector \mathbf{e}_1 of which is an eigenvector of the tensor \mathbf{R} . In this case we get

$$\begin{aligned} \mathbf{R}\mathbf{e}_1 &= \pm\mathbf{e}_1 \\ \mathbf{R}\mathbf{e}_2 &= \cos\alpha\mathbf{e}_2 + \sin\alpha\mathbf{e}_3 \\ \mathbf{R}\mathbf{e}_3 &= \pm\sin\alpha\mathbf{e}_2 \mp \cos\alpha\mathbf{e}_3 \end{aligned}$$

An orthogonal tensor describes a rotation if its determinant is +1 and a rotation combined with a reflection the plain of which is perpendicular to the axis of the former if the determinant is -1.

The set of the orthogonal tensors is a group, as any one has an inverse, the unit tensor is also orthogonal; moreover, the product of two orthogonal tensors is also orthogonal.

The set of tensors with determinant +1 or -1 is also a group, which is called the unimodular group. The orthogonal group is a maximal subgroup in the unimodular group. In continuum mechanics, Cauchy's polar decomposition theorem is important. It says that any tensor of second-order is the product of a symmetric and an orthogonal tensor

$$\mathbf{A} = \mathbf{S}\mathbf{R} = \mathbf{R}\mathbf{S}' \iff A_{ij} = S_{ik}R_{kj} = R_{ik}S'_{kj}$$

where

$$\mathbf{S} = \mathbf{S}^T, \quad \mathbf{R}^T\mathbf{R} = \delta \quad \text{and} \quad \mathbf{S}' = \mathbf{R}^T\mathbf{S}\mathbf{R}$$

If the eigenvalues of \mathbf{S} and \mathbf{S}' are declared positive, Cauchy's decomposition is unique.

A 6. Isotropic Tensors. The so-called isotropic tensors, the components of which are invariant under the change of frame, play an important role in the description of the material properties of isotropic bodies. It is obvious that the only isotropic vector is the zero vector. The isotropic tensors of second-order are proportional to the unit tensor; and those of third-order, to the alternating epsilon. The higher-order isotropic tensors are external products of some power of the second-order unit tensor and of the alternating epsilon. Keeping the identity

$$\varepsilon_{ijk}\varepsilon_{lmn} = \begin{vmatrix} \delta_{il} & \delta_{im} & \delta_{in} \\ \delta_{jl} & \delta_{jm} & \delta_{jn} \\ \delta_{kl} & \delta_{km} & \delta_{kn} \end{vmatrix}$$

in mind, we see that the alternating epsilon is on the first power or does not enter the formula at all. For further details, we refer to the work of Smith and Rivlin [134]. For illustration, let the form of the fourth and the fifth order isotropic tensors stand here:

$$\begin{aligned} I_{ijkl}^{(4)} &= a_1\delta_{ij}\delta_{kl} + a_2\delta_{ik}\delta_{jl} + a_3\delta_{il}\delta_{jk} \\ I_{ijklm}^{(5)} &= a_1\varepsilon_{ijk}\delta_{lm} + a_2\varepsilon_{ijl}\delta_{km} + a_3\varepsilon_{ikl}\delta_{jm} + a_4\varepsilon_{jkl}\delta_{im} + \\ & \quad a_5\varepsilon_{ijm}\delta_{kl} + a_6\varepsilon_{ikm}\delta_{jl} + a_7\varepsilon_{jkm}\delta_{il} + a_8\varepsilon_{ilm}\delta_{jk} + \\ & \quad a_9\varepsilon_{jlm}\delta_{ik} + a_{10}\varepsilon_{klm}\delta_{ij} \end{aligned}$$

Finally, we mention that the sign of the isotropic tensors of an even order remain unchanged under reflection while that of odd order changes.

A 7. Derivatives. Here we list the most important spatial derivatives using the so-called nabla operator.

$$\nabla = \frac{\partial}{\partial \mathbf{r}} \longleftrightarrow \nabla_i = \frac{\partial}{\partial x_i}$$

The gradient of a scalar:

$$\nabla a = \text{grad } a \longleftrightarrow (\nabla a)_i = \frac{\partial a}{\partial x_i} = a_{,i}$$

The gradient of a vector:

$$\mathbf{v} \circ \nabla = \text{Grad } \mathbf{v} \longleftrightarrow (v \circ \nabla)_{ij} = \frac{\partial v_i}{\partial x_j} = v_{i,j}$$

The divergence of a vector

$$\nabla \cdot \mathbf{v} = \text{div } \mathbf{v} \longleftrightarrow \nabla \cdot \mathbf{v} = \frac{\partial v_i}{\partial x_i} = v_{i,i}$$

The rotation of a vector

$$\nabla \times \mathbf{v} = \text{rot } \mathbf{v} \longleftrightarrow (\nabla \times \mathbf{v})_i = \varepsilon_{ijk} \frac{\partial v_k}{\partial x_j} = \varepsilon_{ijk} v_{k,j}$$

The divergence of a tensor

$$\mathbf{T} \cdot \nabla = \text{Div } \mathbf{T} \longleftrightarrow (\mathbf{T} \nabla)_i = \frac{\partial T_{ij}}{\partial x_j} = T_{ij,j}$$

The Laplacian

$$\nabla \cdot \nabla = \Delta \longleftrightarrow \sum_{i=1}^3 \frac{\partial^2}{\partial x_i^2}$$

A 8. Integral Theorems.. The Gauss theorem for vectors

$$\int \text{div } \mathbf{v} \, dV = \oint \mathbf{v} \, d\mathbf{A} \longleftrightarrow \int V_{i,i} \, dV = \oint v_i \, dA_i$$

The Gauss theorem for higher-order tensors

$$\int \mathbf{T} \nabla \, dV = \oint \mathbf{T} \, d\mathbf{A} \longleftrightarrow \int T_{i\dots l,l} \, dV = \oint T_{i\dots l} \, dA_l,$$

The Stokes theorem

$$\int \nabla \times \mathbf{T} \, d\mathbf{A} = \oint \mathbf{T} \, d\mathbf{r} \longleftrightarrow \int \varepsilon_{ijk} T_{\dots k,j} \, dA_i = \oint T_{\dots i} \, dx_i$$

Green's formulae

$$\oint a \cdot \text{grad } b \, d\mathbf{A} = \int (a \Delta b + \text{grad } a \cdot \text{grad } b) \, dV$$

and

$$\oint (a \cdot \text{grad } b - b \cdot \text{grad } a) \, d\mathbf{A} = \int (a \Delta b - b \Delta a) \, dV$$

We stress once more that the only aim of this appendix is to declare the nomenclature and the notation used. It is completely unsuitable to learn the essentials of vector and tensor calculus from it.

REFERENCES

- [1] Alfrey, T., *Mechanical Behaviour of High Polymers*, Interscience Publ. Co., New York, 1948.
- [2] Bampi, F., Morro, A., *Found. of Phys.* **10** (1980), 905..920; *J. Non-Equilib. Thermodyn.* **6** (1981), 1..14.
- [3] Bartlett, A. C., *Phyl. Mag.* **49** (1925), 728..739.
- [4] Bataille, J., Kestin, J., *Jour de Mecanique* **14** (1975), 365..384; *J. Non-Equilib. Thermodyn.* **1** (1976), 25..31; **2** (1977), 49..65.
- [5] Becker, E., Burger, W., *Kontinuums mechanik*, B. G. Teubner, Stuttgart, 1975.
- [6] Bednarczyk, H., *J. Appl. Math. Phys. (ZAMP)* **19** (1968), 140..141.
- [7] Bhattacharya, D. K., *The Application of Governing Principle of Dissipative Processes to Incompressible Fluid Flow and Heat Transfer* (1978), Thesis, Kharagpur, (India); *Ann. d. Phys.* **7.39** (1982), 325..332; *Acta Mechanica* **47** (1983), 87..94.
- [8] Biot, M. A., *Phys. Rev.* **97** (1955), 1463..1469.
- [9] Biot, M. A., *Variational principles in heat transfer*, Oxford Univ. Press, London, 1970.
- [10] Bosnjakovic, F., *Technische Thermodynamik*, Steinkopf, Leipzig, 1960.
- [11] Boucher, S., *Revue M.* **21** (1975), 243..249; **22** (1976), 31..36.
- [12] Bott, R., Duffin, R. J., *J. Appl. Phys.* **20** (1949), 816.
- [13] Böröcz, Sz., *Z. Phys. Chem.* **234** (1967), 26..32.
- [14] Brune, V., *J. Math. Phys.* **10** (1931), 191..235.
- [15] Buchheim, W., Stuart, H. A., Menz, H., *Z. Physik.* **112** (1939), 407..419.
- [16] Bueche, F., *J. Chem. Phys.* **22** (1954), 603..609; **22** (1954), 1570..1576.
- [17] Callen, H. B., *Found. Phys.* **4** (1974), 423..443.
- [18] Casimir, H. G. B., *Rev. Mod. Phys.* **17** (1945), 343..350.
- [19] Cauer, W., *Arch. f. Elektrotechnik* **17** (1927), 355.
- [20] Chapman, S., Cowling T. G., *The Mathematical Theory of Non-Uniform Gases*, Cambridge Univ. Press, 1952.
- [21] Chue, S. H., *Thermodynamics*, John Wiley and Sons, New York, 1977.
- [22] Ciancio, V., Verhás, J., *Atti Academia Peloritania dei Pericolanti (Messina)* **68** (1990), 41..53; *J. Non-Equilib. Thermodyn.* **17** (1990), 33..43; **16** (1991), 57..65; **18** (1993), 39..50; *Acta Physica Hungarica.* **69** (1991), 63..70; *Le Matematiche (Catania)* **46** (1991), 77..83; *Physica A* **189** (1992), 665..675.
- [23] Coleman, B. D., *Arch. Rat. Mech. Anal.* **17** (1964), 1..46.
- [24] Coleman, B. D., Dill, E. H., Toupin, R. A., *Arch. Rat. Mech. Anal.* **39** (1970), 358..399.
- [25] Coleman, B. D., Gurtin, M. E., *J. Chem. Phys.* **47** (1967), 597..613.
- [26] Coleman, B. D., Markovitz, H., Noll, W., *Viscometric Flows of Non-Newtonian Fluids*, Springer, Berlin, 1966.
- [27] *Continuum Physics I-II*. Ed. A. C. Eringen., Academic Press, New York London 1971/1975.
- [28] Cox, W. P., Merz, E. H., *J. Polym. Sci.* **28** (1958), 619..622; *Am. Soc. Testing Material Spec. Techn. Publ.* **247** (1958), 178..188.
- [29] Currie, P. K., *Rheol Acta* **16** (1977), 205..212.
- [30] Darlington, S., *J. Math. Phys.* **18** (1939), 257..353.
- [31] Day, W. A., Silhavy, M., *Arch. Rat. Mech. Anal.* **66** (1977), 73..81.
- [32] Dickel, G., *Electro-Mechanical Equilibrium in Membranes*, Topics in Bioelectrochemistry and Bioenergetics (G. Milazzo., eds.), vol. 4, John Wiley and Sons, New York, 1981.
- [33] Drouod, R., Maugin, G. A., *Constitutive Laws and Microstructure* (Axelrad, D. R., Muschik, W., eds.), Springer, Berlin, New York, 1988, pp. 1366.
- [34] Eckart, C., *Phys. Rev.* **58** (1940), 267..269; **58** (1940), 269..275; **58** (1940), 919..924; **73** (1948), 373..382.
- [35] Edelen, D. G. B., *Int. J. Engng. Sci.* **12** (1974), 397..411; **14** (1976), 1013..1032; *Arch. of Mech.* **26** (1974), 251..261.
- [36] Ehrlich, P., *Am. J. Phys.* **49** (1981), 622..632.
- [37] Eichenwald, A., *Ann. d. Phys.* **11(316)** (1903), 421..441.
- [38] Einstein, A., de Haas, W. J., *Naturwiss.* **3** (1915), 237..238.
- [39] Eisenschitz R., *Statistical Theory of Irreversible Processes*, Oxford Univ Press., London, 1958.

- [40] Ericksen, J. L., Arch. Rat. Mech. Anal. **9** (1962), 371..378.
- [41] Eringen, A. C., Phys. Rev. **117** (1960), 1174..1183.
- [42] Eringen, A. C., *Nonlinear Theory of Continuous Media*, McGraw-Hill, New York, 1962.
- [43] Farkas, H., Z. f. Phys. Chemie **239** (1968), 124..132; Int. J. Engng. Sci. **13** (1975), 1035..1053; **13** (1975), 1029..1033.
- [44] Farkas, H., Noszticzius, Z., Ann. d. Phys. **27** (1971), 341..348.
- [45] Fedosyev, V., *Strength of Materials*, Mir Publ, Moscow, 1968.
- [46] Fekete, D., Phys. Stat. Sol.(b) **105** (1981), 161..174.
- [47] Ferry, J. D., *Viscoelastic Properties of Polymers*, John Wiley and Sons, New York, 1970.
- [48] Fitts, D. D., *Nonequilibrium Thermodynamics*, McGraw-Hill, New York, 1962.
- [49] Fixman, M., J. Chem. Phys. **42** (1965), 3831..3837.
- [50] Foster, R. M., Trans. A.I.E.E. (1932 jun.), 309..317.
- [51] Frank, F. C., Disc. Faraday Soc. **25** (1958), 19..28.
- [52] Gambár, K., Márkus, F., Nyíri, B., J. Non-Equilib. Thermodyn. **16** (1991), 217..224.
- [53] Gambár, K., Márkus, F., J. Non-Equilib. Thermodyn. **18** (1993), 51..57.
- [54] De Gennes, P. G., *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1974.
- [55] Glansdorff, P., Prigogine, I., *Thermodynamic Theory of Structure, stability and Fluctuations*, Wiley-Interscience, London, 1971.
- [56] Gray, G. W., *Molecular Structure and Properties of Liquid Crystals.*, Acad. Press, London, New York, 1962.
- [57] Green, A. E., Adkins, J. E., *Large Elastic Deformations and Non-linear Continuum Mechanics.*, Oxford Univ. Press, London, 1960.
- [58] Green, A. E., Naghdi, P. M., Acta Mechanica **30** (1978), 157..162.
- [59] De Groot, S. R., Physica **88A** (1977), 172..182; **88A** (1977), 183..189.
- [60] De Groot, S. R., *Thermodynamics of Irreversible Processes*, North-Holland Publ. Co., Amsterdam, 1951.
- [61] De Groot, S. R., Mazur P., *Non-equilibrium Thermodynamics*, North-Holland Publ. Co., Amsterdam, 1962.
- [62] De Groot, S. R., Suttorp, L. G., *Foundations of Electrodynamics*, North-Holland Publ. Co., Amsterdam, 1972.
- [63] Guillemin, E. A., *Communication Networks. I-II*, Wiley-Chapman, London, 1935.
- [64] Guillemin, E. A., *Mathematics of Circuit Analysis*, Wiley-Chapman, London, 1935.
- [65] Gyarmati, I., *A termodinamika elveiről. (in Hungarian)*, Thesys, Budapest, 1958.
- [66] Gyarmati, I., Periodica Polytechnica Ser. Chem. Engng. Budapest **5** (1961), 219..243, 321..339.
- [67] Gyarmati, I., Acta Chim. Hung. **30** (1962), 147..206.
- [68] Gyarmati, I., Acta Chim. Hung. **43** (1964), 353..377.
- [69] Gyarmati, I., Z. Phys. Chemie **234** (1967), 371..378.
- [70] Gyarmati, I., *Non-equilibrium Thermodynamics*, Springer, Berlin, 1970.
- [71] Gyarmati, I., Z. f. Phys. Chemie **239** (1968), 133..137.
- [72] Gyarmati, I., Ann. d. Phys. **23** (1969), 353..378.
- [73] Gyarmati, I., Ann. d. Phys. **7/31** (1974), 18..32.
- [74] Gyarmati, I., J. Non-Equilib. Thermodyn. **2** (1977), 233..260.
- [75] Hamel, G., *Theoretische Mechanik*, Springer, Berlin, 1949.
- [76] Hess, S., Physica A **87** (1977), 273..287.
- [77] Hill, R., J. Mech. Phys. Solids **12** (1964), 199..212, 213..218; **13** (1965), 89..101, 189..198, 213..222.
- [78] Hofelich, F., Z. Physik **226** (1969), 395..408; **229** (1969), 192.
- [79] Hurley, J., Garrod, C., Phys. Rev. Lett. **48** (1982), 1575..1577.
- [80] Hutter, K., Acta Mechanica **27** (1977), 1..54.
- [81] Jeffery, G. B., Proc. Roy. Soc. London **A102** (1922-23), 161..179.
- [82] Jou, D., Rubi, J. M., Casas-Vazquez, J., J. Phys. A **12** (1979), 2515..2520.
- [83] Jou, D., Casas-Vázquez, J., Lebon, G., Rep. Prog. Phys. **51** (1988), 1105..1179; J. Non-Equilib. Thermodyn. **17** (1992), 383..396; *Extended Irreversible Thermodynamics*, Springer, Berlin, New York, 1993.
- [84] Kafka, V., J. Appl. Math. Mech. (ZAMM) **54** (1974), 649..657.

- [85] Kästner, S., *Ann. d. Phys.* **(7)1** (1958), 377..399; **(7)2** (1958), 146..162; **(7)3** (1959), 82..93.
- [86] Kaye, A., *Rheol. Acta* **12** (1973), 206..211.
- [87] Keller, J. U., *Thermodynamik der Irreversiblen Prozesse*, W. de Guyter, Berlin, New York 1977.
- [88] Kirschner, I., *Acta Phys. Hung.* **30** (1971), 61..71.
- [89] Kluitenberg, G. A., *Physica* **28** (1962), 217..232, 561..568, 1173..1183; **29** (1963), 633..652; **30** (1964), 1945..1972; **35** (1967), 177..192; **38** (1968), 513..548; **68** (1973), 75..92; **87A** (1977), 302..330; **88A** (1977), 122..134; **109A** (1981), 91..122.
- [90] Kluitenberg, G. A., Ciancio, V., *Physica* **93A** (1978), 273..286; **99A** (1979), 592..600.
- [91] Kluitenberg, G. A., De Groot, S. R., *Physica* **20** (1954), 199..209; **21** (1955), 148..168, 169..192.
- [92] Kluitenberg, G.A., De Groot, S. R., Mazur, P., *Physica* **19** (1953), 689..704, 1079..1094.
- [93] Kubo, R., *Thermodynamics*, North-Holland Publ. Co., Amsterdam, 1966.
- [94] Lam, L., *Z. Physik* **B27** (1977), 349..356.
- [95] Lamprecht, I., Zotin, A. I. (eds.), *Thermodynamics of Biological Processes*, W. de Guyter, Berlin, 1978..
- [96] Lebon, G., Perzyna, P., *Recent development in thermomechanics of solids*, Springer, Wien, 1980.
- [97] Lebon, G., *Extended Thermodynamics.*, Non-Equilibrium Thermodynamics with Applications to Solids. (W. Muschik, eds.), vol. CISM Courses and Lectures 336, Springer, Wien, New York, 1993.
- [98] Leigh, D. C., *Nonlinear Continuum Mechanics*, McGraw-Hill, New York, 1968.
- [99] Lengyel, S., Gyarmati, I., *J. Chem. Phys.* **75** (1981), 2384..2389.
- [100] Leslie, F. M., *Arch. Rat. Mech. Anal.* **28** (1968), 265..283.
- [101] Li, J. C. M., *J. Chem. Phys.* **29** (1958), 747..754; *Phys. Rev.* **127** (1962), 1784..1786; *J. Phys. Chem.* **66** (1962), 1414..1420; *J. Appl. Phys.* **33** (1962), 616..624.
- [102] Lorentz, H. A., *Maxwells electromagnetische Theorie*, Encyklopadie der Mathematischen Wissenschaften, vol. Band V2 Heft 1, Teubner, Leipzig, 1904, pp. 63..144; *Elektronentheorie*, Encyklopadie der Mathematischen Wissenschaften, vol. Band V2 Heft 1, Teubner, Leipzig, 1904, pp. 145..280.
- [103] Macvean, D. B., *J. Appl. Math. Phys. (ZAMP)* **19** (1968), 157..185.
- [104] Machlup, S., Onsager, L., *Phys. Rev.* **91** (1953), 1512..1515.
- [105] Márkus, F., Gambár, K., *J. Non-Equilib. Thermodyn.* **14** (1989), 355..362; **16** (1991), 27..32; **18** (1993), 288..292.
- [106] Maugin, G. A., *Thermomechanics of Plasticity and Fracture*, Cambridge University Press, Cambridge, 1992; *J. Non-Equilib. Thermodyn.* **15** (1990), 173..192; W. Muschik (eds.), *Non-Equilibrium Thermodynamics of Electromagnetic Solids*, Non-Equilibrium Thermodynamics with Applications to Solids., vol. CISM Courses and Lectures 336, Springer, Wien, New York, 1993; *Theoretical and Applied Mechanics*, Bulgarian Acad. Sci., Sofia, 1981, pp. 671..676.
- [107] Maugin, G. A., Drouod, R., *Int. J. Engng. Sci.* **21**, 705..724.
- [108] Maxwell, J. C., *Phyl. Trans. Roy. Soc.* **157** (1867), 49.
- [109] Meixner, J., *Ann. d. Phys.* **39** (1941), 333..356; **40** (1941), 165..180; **41** (1942), 409..425; **43** (1943), 244..270; **43** (1943), 470..487; *Z. f. Physik* **131** (1952), 456..469; **139** (1954), 30..43; **164** (1961), 145..155; *Arch. Rat. Mech. Anal.* **17** (1964), 278..296; *J. Appl. Mech.* **33E** (1966), 481..188; *Rheol. Acta* **7** (1968), 8..13; *Arch. Rat. Mech. Anal.* **33** (1969), 33..53; *Z. f. Physik* **219** (1969), 79..104; **229** (1969), 352..364; *Arch. Rat. Mech. Anal.* **39** (1970), 108..130; *Physica* **59** (1972), 305..313; *Adv.Molecular Relax. Proc.* **5** (1973), 319..331; *Rheol. Acta* **12** (1973), 465..467; *Pep. on Math. Phys.* **7** (1975), 37..57; *Arch. Rat. Mech. Anal.* **57** (1975), 281..290.
- [110] Meixner, J., Reik, H. G., *Thermodynamik der Irreversiblen Prozesse*, Handbuch der Physik, vol. III./2., Springer, Berlin, 1959, pp. 413.
- [111] Morse, M., *Trans. Am. Math. Soc.* **27** (1925), 345..396.
- [112] Müller, I., *Thermodynamics*, Pitman Publ. Co., London, 1985; *Arch. Rat. Mech. Anal.* **28** (1968), 1..39; **40** (1971), 1..36.
- [113] Müller, I., Ruggeri, T., *Extended Thermodynamics*, Springer, Berlin, New York, 1993.

- [114] Muschik, W., Z. Naturforschung **23a** (1968), 1446..1451; Arch. Rat. Mech. Anal. **66** (1977), 379..401.
- [115] Muschik, W., Kunz, E., Brunk, G., J. Appl. Math. Mech. (ZAMM) **56** (1976), 134..136.
- [116] Muschik, W., Szer, J., J. Non-Equilib. Thermodyn. **1** (1976), 61..65.
- [117] Muschik, W., *Fundamentals of Non-Equilibrium Thermodynamics, Non-Equilibrium Thermodynamics with Applications to Solids.* (W. Muschik, eds.), vol. CISM Courses and Lectures 336, Springer, Wien, New York, 1993.
- [118] Müser, H. E., Petterson, J., Fortschritte der Physik **19** (1971), 559..612.
- [119] Nettleton, R. E., Physica **30** (1964), 1989..2002; Ann. d. Phys. **2** (1993), 490..499; J. Chem. Phys. **99**, 3059..3066.
- [120] Noll, W., Arch. Rat. Mech. Anal. **18** (1965), 100..102.
- [121] Noll, W., *The Foundations of Mechanics and Thermodynamics. (Selected Papers)*, Springer, Berlin, 1974.
- [122] Nyíri, B., Acta Physica Hungarica. **60** (1986), 245..260; **63** (1988), 13..16; J. Non-Equilib. Thermodyn. **16** (1991), 39..56, 179..186.
- [123] Oldroyd, J. G., Proc. Roy. Soc. London **A200** (1949), 523; **A218** (1953), 122..132; R. Gramel (eds.), *The Effect of Small Viscous Inclusions on the Mechanical Properties of an elastic Solid*, Deformation and Flow of Solids, Springer, Berlin, 1956.
- [124] Onsager, L., Phys. Rev. **37** (1931), 405..426.
- [125] Onsager, L., Phys. Rev. **38** (1931), 2265..2279.
- [126] Onsager, L., Maclup, S., Phys. Rev. **91** (1953), 1505..1512.
- [127] Oseen, C. W., Trans. Faraday Soc. **29** (1933), 883..899.
- [128] Oster, G. F., Perelson, A. S., Izrael J. of Chem. **11** (1973), 445..478.
- [129] Ostwald, Wo., Kolloid Z. **36** (1925), 99..117, 157..167, 248..250.
- [130] Ostwald, W., Auerbach, Kolloid Z. **38** (1926), 261.
- [131] Parodi, O., Le J. de Phys. **31** (1970), 581..584.
- [132] Perzyna, P., Plochocki, Z., Valanis, K. C., *Thermodynamical Problems of Continuous Media*, Ossolineum, Warszawa, 1970.
- [133] Peterlin, A., J. Polym. Sci. **8** (1952), 621..632.
- [134] Peterlin, A., Stuart, H. A., Z. f. Physik, **112** (1939), 129..147.
- [135] Prigogine I., *Introduction to Thermodynamics of Irreversible Processes*, Interscience, New York, 1961.
- [136] Raats, P. A. C., Arch. Rat. Mech. Anal. **44** (1972), 267..280.
- [137] Reiner, M., *Deformation, Strain and Flow*, Interscience, New York, 1960.
- [138] Reuss, E., Z. angew. Math. Mech. **10** (1930), 266..274.
- [139] Roscoe, R., Rheol. Acta **12** (1973), 404..411.
- [140] Rouse, P. E., J. Chem. Phys. **21** (1953), 1272..1280.
- [141] Sándor, J., Acta Chim. Hung. **67** (1971), 303..320; Electrochimica Acta **17** (1972), 673..782.
- [142] Schapery, R. A., J. Appl. Phys. **35** (1964), 1451..1465; Q. Appl. Math. **22** (1964), 207..215.
- [143] Scheraga, H. A., Edsall, J. T., Gadd, J. O., J. Chem. Phys. **19** (1951), 1101..1108.
- [144] Schowalter, W. R., *Mechanics of Non-Newtonian Fluids*, Pergamon Press, New York, 1978.
- [145] Singh, P., J. Non-Equilib. Thermodyn. **1** (1976), 105..116; Acta Phys. Hung. **43** (1977), 59..63, 133..140.
- [146] Singh, P., Bhattacharya, D. K., Indian J. pure appl. Math. **9** (1978), 407..416; Acta Mechanica **30** (1978), 137..144.
- [147] Singh, P., Srivastrava, K. K., Acta Phys. Hung. **45** (1978), 201..211.
- [148] Smith, G. F., Rivlin, R. S., Q. Appl. Math. **15** (1957), 308..314.
- [149] Stark, A., Ann. d. Phys. **7/31** (1974), 53..75; **5** (1975), 481..490.
- [150] Stuart, E. B., Gal-Or, B., Brainard, A. J. (eds.), *A Critical Review of Thermodynamics*, Mono Book Corp., Baltimore, 1970.
- [151] Trouton, F., Proc. Roy. Soc. A **77** (1906), 326..
- [152] Truesdell, C., *Rational Thermodynamics*, McGraw-Hill, New York, 1969.
- [153] Truesdell, C., Noll, W., *The Non-linear Field Theories of Mechanics.*, Handbuch der Physik, vol. . III/3., Springer, Berlin, 1965.
- [154] Truesdell, C., Toupin, R., *The Classical Field Theories.*, Handbuch der Physik, vol. . III/1., Springer, Berlin, 1960.

- [155] Valanis, K. C., *Irreversible Thermodynamics of Continuous Media*, Springer, Wien, 1971.
- [156] van Veenendaal, W., Kluitenberg, G. A., *Physica* **109A** (1981), 123..127.
- [157] Verhás, J., *Z. f. Phys. Chemie* **234** (1967), 226..234; *Ann. d. Phys.* **20** (1967), 90..94; *Z. f. Phys. Chemie* **249** (1972), 119..122; *Periodica Polytechnica Ser. Chem. Engng. Budapest* **21** (1977), 319..332; **25** (1981), 53..61; *Ann. d. Phys.* **7/40** (1983), 189..193; *Int. J. Heat Mass Transfer* **30** (1987), 1001; *Liquid Crystals (London)*. **3** (1988), 1183; *J. Non-Equilib. Thermodyn* **8** (1983), 201..206; **18** (1993), 311..335; *Acta Mechanica* **38** (1981), 127..128; **53** (1984), 125..139; *Acta Phys. Hung.* **55** (1984), 275..291; **66** (1989), 95..97; *Atti Academia Peloritania dei Pericolanti (Messina)* **67** (1989), 32..43; **67** (1989), 45..64; **67** (1989), 73..79; **67** (1989), 65..72; *On the Mechanism of Cell Division.*, 6th Liquid Crystal Conference of Socialist Countries, Halle, August 26-30,, Halle, 1985., pp. (E 14); Kröner, E., Kirchgässner, K. (eds.), *Linear Thermodynamics and Non-Linear Phenomena in Fluids.*, Lecture Notes in Physics 249. Trends in Applications of Pure Mathematics to Mechanics., Springer-Verlag, Berlin Heidelberg New York Tokyo, 1986., pp. 359; Eckhaus, W., Besseling, J. F. (eds.), *A Thermodynamic Model for Turbulence*, Lecture Notes in Physics, Trends in Applications of Pure Mathematics to Mechanics. Proceedings, Wassenaar, The Netherlands, 1987., Springer-Verlag, Berlin Heidelberg New York Tokyo, 1988., pp. 321; Schneider, W., Troger, H., Zigler, F. (eds.), *Liquid Crystal Membranes with Morphogenetic Relevances.*, Lecture Notes in Physics, Trends in Applications of Pure Mathematics to Mechanics. Proceedings, Hollabrunn, Austria. 1989., Longman, London, 1991; Sieniutycz, S., Salamon, P. (eds.), *The Governing Principle of Dissipative Processes; Theory, Applications and Generalizations.*, Nonequilibrium Thermodynamics., Taylor and Francis, London, Philadelphia, 1990.; Ebeling, W., Muschik, W. (eds.), *The Steps of Modeling in Non-Equilibrium Thermodynamics.*, Statistical Physics and Thermodynamics of Nonlinear Nonequilibrium Systems., World Scientific, Singapore, New Jersey, London, Hong Kong, 1993, pp. 132..136.
- [158] J. Verhás- C. Papenfuss - W. Muschik, *A Simplified Thermodynamic Theory for Biaxial Nematics Using Gyarmati's Principle.*, *Mol. Cryst. Liq. Cryst.* **215** (1992), 313..321.
- [159] Vernotte, P., *Compt. Rend.* **246** (1958), 3154..3155.
- [160] Vincze, Gy., *Ann. d. Phys.* **27** (1971), 225..136; *Acta Chim. Hung.* **75** (1972), 33..43.
- [161] Vojta, G., *Acta Chim. Hung.* **54** (1967), 55..64.
- [162] Wang, C. C., *Arch. Rat. Mech. Anal.* **20** (1965), 1..40.