Chapters in thermodynamics

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Lecture notes

BME (Budapest University of Technology and Economics)

Contents

1 Before reading

1.1 Prerequisites

This material intends to serve as a background source for advanced thermodynamics courses at BME. Accordingly, it is assumed that the Reader understands and can recall/reproduce

- the surface area and volume of a sphere in terms of its radius,
- $a^2 - b^2 = (a-b)(a+b), \qquad a^4 - b^4 = (a-b)(a+b)(a^2+b^2),$
- $a^3 - b^3 = (a-b)(a^2+ab+b^2), \qquad a^3 + b^3 = (a+b)(a^2-ab+b^2),$
- $x^2+px+q=0 \quad \Longrightarrow \quad x_\pm = -\frac{p}{2} \pm \sqrt{(\frac{p}{2})^2 - q}, \quad x^2+px+q = (x-x_+)(x-x_-),$
- $\exp(a \ln b) = e^a b,$
- $\det \left(\begin{smallmatrix} 1 & 2 \\ 3 & 4 \end{smallmatrix}\right) = -2,$
- $e^{-x} \approx 1 - x, \quad \sin x \approx x \quad (|x| \ll 1), \qquad \sin 180 = -0.8011526,$
- $\mathrm{d}\big(\frac{1}{x^2}\big)/\mathrm{d}x = -\frac{2}{x^3}, \qquad \mathrm{d}\big(\ln\frac{x}{c}\big)/\mathrm{d}x = \frac{1}{x}, \qquad \mathrm{d}\big(\ln\frac{c}{x}\big)/\mathrm{d}x = -\frac{1}{x}, \qquad \frac{\partial e^{uv}}{\partial u}\Big|_v = ve^{uv},$
- $(fg)' = f'g + fg', \qquad \big(\frac{f}{g}\big)' = \frac{f'g - fg'}{g^2}, \qquad \frac{\mathrm{d}f(g(x))}{\mathrm{d}x} = f'\big(g(x)\big) \cdot g'(x),$
- $\frac{\partial f(x(u),y)}{\partial u}\Big|_y = \frac{\partial f}{\partial x}\Big|_y \cdot \frac{\mathrm{d}x}{\mathrm{d}u}, \qquad \frac{\mathrm{d}f(x(u),y(u))}{\mathrm{d}u} = \frac{\partial f}{\partial x}\Big|_y \cdot \frac{\mathrm{d}x}{\mathrm{d}u} + \frac{\partial f}{\partial y}\Big|_x \cdot \frac{\mathrm{d}y}{\mathrm{d}u},$
- $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x},$
- $\int \frac{\mathrm{d}x}{x^3} = -\frac{1}{2x^2} + C$, $\int \frac{\mathrm{d}x}{x} = \ln|x| + C$ and $\int_a^b \frac{\mathrm{d}x}{x} = \ln\frac{b}{a}$ (why is there no need for $\left|\frac{b}{a}\right|$?),
- that the solution of $\mathrm{d}y/\mathrm{d}x = -3y(x)$ with $y(0) = 4$ is $y(x) = 4e^{-3x}$,
- how to treat 3×3 matrices, and how three-dimensional Euclidean vectors,
- what an ideal gas is,
- what isothermal and adiabatic processes are,
- what heat and work are, and what the specific heats c_v and c_p are,
- what a Carnot cycle is and what its properties are,
- that mass, volume, and internal energy are extensive state quantities,
- that temperature and pressure are intensive state quantities.

1.2 Suggested literature on thermodynamics

Standard: Callen: Thermodynamics and an introduction to thermostatistics
Kondepudi – Prigogine: Modern thermodynamics
Gyftopoulos – Beretta: Thermodynamics: foundations and applications
Környey: Termodinamika (in Hungarian)
Harmatha: Termodinamika műszakiaknak (in Hungarian)

Temporal: Matolcsi: Ordinary thermodynamics
("`Matolcsi_Ordinary_Thermodynamics_2017-04-26.pdf`"
open-access version available on the internet)
Matolcsi: Közönséges termodinamika (in Hungarian)

Continuum: De Groot – Mazur: Non-equilibrium thermodynamics
Verhás: Thermodynamics and rheology
("`Verhas_Thermodynamics_and_Rheology_2017-05-17.pdf`"
open-access version available on the internet)

1.3 On notations

Equations are numbered in the form (pagenumber.whichequationonthatpage), like (15.2). Figures and tables are numbered analogously. $A \overset{(15.2)}{=} B$ means that (15.2) can be used to find $A = B$. Similarly, $\overset{\textcircled{3}}{\left.\frac{\partial e}{\partial v}\right|_T}$ indicates that identity ③ has been utilized to obtain $\left.\frac{\partial e}{\partial v}\right|_T$.

In better pdf viewers, if you move the mouse pointer over an equation number, section number, figure number *etc.*, a floating window will show that equation/*etc.* In parallel, if you click on the number, you can jump there. You can then return by a 'Go back'-like menu item / icon / hot key. Alternatively, you can view this pdf in two windows.

2 Four types of thermodynamical modelling

2.1 On modelling in general

Before speaking about modelling in thermodynamics, it is worth speaking about modelling in general. Furthermore, before modelling in general, it is worth speaking about theories in general.

Theories have three benefits:

- power to explain,
- power to predict, and
- power to motivate action.

The first is not only for science but is a general need of humans in their everyday life. The world around us is infinitely complicated, and if we have an explanation for something that happened then – even if the explanation comes too late to change anything – somehow the soul gets relieved. Therefore, this first benefit is, to large extent, emotional. An explanation may give only *the illusion of* rationality.

The second benefit is much more the field for a scientist. Actually, a 'good' scientist stops here, and is satisfied if the theoretical prediction is fulfilled.

The third benefit is the point where the engineer gets most excited. It's nice if a theory works – now let us make some use of it, let us use it for creating something new that is useful for the society. "Scientists study the world as it is; engineers create the world that never has been." (Theodore von Kármán)

For illustration, we can consider the example of electromagnetic waves. Maxwell, based partly on a cogwheel-like picture in mind and to make the then-known electromagnetic equations consistent with the conservation with electric charge, suggested a new term in one of the electromagnetic equations. This led him to predict electromagnetic waves, and to explain light as a special case. At this level, this theory had only the first benefit guaranteed (explanation of light). The second one was realized when Hertz experimentally confirmed the existence of the predicted electromagnetic waves. This has triggered vivid activity worldwide on constructing systems that can transmit signals via this new type of wave (leading to the radio, the television, and the whole area of telecommunication), as an example for the third benefit.

Now, any theory is a model. In fact, all our thoughts are models, created by our brain, they are rude approximations of certain parts/aspects of the terribly complicated universe. Even when we speak or write about experiments and natural phenomena, all that is also just a bunch of models of the brain.

All models are severely simplifying approximations of reality.[1] Although theories of

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[1] According to sayings, physics studies horses/cows/chickens of spherical shape in vacuum.

physics get gradually generalized and unified, we can never reach a level of ‘perfect description’.

In parallel, already the existing level of physical theories poses very tough problem if we want to calculate how a certain concrete setting behaves.[2] Solving the equations is very demanding so not only the theory but also its application means a massive compromise: we have to apply various further simplifications and approximations to reach a result with acceptable effort.

Fortunately, many problems of engineering we have to solve include a level of tolerance and robustness. Answers are needed only to some finite precision – sometimes even the questions are specified up to an amount of tolerance. It also happens frequently that the sources we can use for obtaining the solution are imperatively limited and we must accept the type of result that is allowed by these constraints.

We also have to bear in mind that when we devotedly and perseveringly increase the amount of invested effort, the impact on the outcome will gradually get more and more minute. We will need a cost–benefit consideration.

In science and engineering, the language of models is mathematics. This means much more than using mathematical formulae here or there. It is also a typical mistake to use a mathematical theorem/rule without ensuring that the conditions required for its validity hold in our case. When those conditions are violated then expect surprises – physical/engineering ones.

Actually, the methodologically proper way of modelling is when *all* our notions are given a precise mathematical meaning. In practice this means that any notion must be characterized by a set, an element of a set or a function (mapping from a set to a set). Experience shows that, whenever we are not able to give a notion a precise mathematical meaning, we actually do not understand that notion in the physical/engineering sense.

This level of modelling is not easy to achieve and practice. We, in the present lecture notes material, won’t fully follow it, either. Nevertheless, warnings will be issued at important places. Moreover, since the birth of computer programs with the capability for analytical calculations and manipulations, there is a – directly practical – version of the preciseness criterion. Namely, we should be able to realize the model in such software. If we are not able to do this then we actually don’t know what we want. (Since these softwares have limitations, we have to accept compromises, but the level of preciseness is quite well indicated via this latter criterion version.)

The final comment related to the general level is that, at university, one has to learn three levels of thinking. The first is the level of recipes. One learns that ‘in this and this situation do this and this’. The second level is that of examples/analogies. At

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[2] Present physical (quantum field theoretical) knowledge says that even a point mass possesses infinitely many degrees of freedom.

that level there is no single recipe given but a variety of recipes is shown and it is you who will have to decide which one to use at a given situation. Finally, at the third level, overview is in action, which seizes the essence that connects the various examples and could create new examples if needed.

Partly in connection to this, when we sit at a university lecture, there are three types of information we can take notes about. The first one is all the formulae and text appearing on the blackboard or whiteboard or screen. The second type is the explanation told around those formulae and texts. At last, the third type is the interpretation and overview that is behind.

Consequently, when you sit at a university lecture, try to take notes according the following order: do not concentrate on the first type of information but more on the second, and extremely concentrate on the third type. It is easy to complete the part you happened to miss from the first type of information – from your neighbour's notes, from lecture notes and books etc. – while it is much harder to reproduce an explanation you missed. At last, be extremely sensitive to grab the third type because those are the most valuable moments in your university study, lasting for decades and becoming the ground of your knowledge and thinking at your field.

2.2 The table with the four cells

Although thermodynamics started as the theory of temperature and of heat (thermal interaction), it gradually incorporated mechanical interaction, mass / particle number interaction, electric and magnetic interaction (and counting). Besides the historical perspective, it is also possible to approach a field along some organizing/reorganizing idea, some system in which the collected knowledge is arranged. Here follows an organized presentation of thermodynamics, which is originally an application-oriented arrangement along a practical modelling viewpoint. Nevertheless, it turns out to be a successful analysis of various principal aspects as well.

The classification considered here is the following table.

		space dependence considered	
		no	yes
time dependence considered	no	1	3
	yes	2	4

Table 10.1 Four types of modelling.

Hereafter, cells 1–4 will be denoted in short by $\boxed{1}$, $\boxed{2}$, $\boxed{3}$, $\boxed{4}$, respectively.

The subsequent sections provide an analysis of each of these cells, addressing the following aspects:

- the state describing quantities,
- time dependence,
- space dependence,
- interactions,
- irreversibility,
- processes,
- the equations determining processes,
- equilibrium,
- stability.

For a first reading, this analysis may appear vague here and there – if you return here after reading the whole lecture notes material then those points will prove much clearer.

2.3 Cell 1 – thermostatics

$\boxed{1}$ will be named here thermostatics but it is also called classical/quasistatic/reversible/equilibrium thermodynamics.

Thermostatics studies what state quantities describe a system when it is stationary or near enough to it, and what relationships – so-called constitutive relations – hold among them.

Consequently, time dependence is not considered, and according to the assumption that circumstances are ‘quiet’ and quantities are homogeneous enough, space dependence is not assumed, either. (Behind this is the observation that inhomogeneities typically induce processes, such ones that govern the system towards homogeneity.) What is allowed is discrete space dependence, i.e., to have more than one system, each homogeneous in itself, but different systems are allowed to be consisting of different materials, and to have different extensive state quantities and densities. Intensive state quantities are assumed to be the same for two systems in interaction. The simplest arrangement is when one has one system and a ‘very large’ other one called environment / reservoir / heat bath. Here, ‘very large’ means the limit when the intensive quantities of the environment do not change if its extensive quantities change due of interaction with the ‘small’ system.

A system with space independent state quantities is also called a lumped parameter system – here, ‘parameter’ refers to state quantities, not coefficient constants nor prescribed external quantities – while a system with space dependence is also referred to as a distributed parameter system.

The work-type interaction is described by $đW = -p\,\mathrm{d}V$ (the so-called inexact differential notation $đW$ intends to indicate that this is not a change of a state quantity – see more in Sect. 3.2 on exact and inexact differentials) but no similar formula is used for heat. More closely, a formula $đQ = T\,\mathrm{d}S$ exists but is of little use since one cannot govern, nor even measure, the change of entropy S. In practice, the problem is circumvented by using $đQ = \mathrm{d}E - đW$.

In $\boxed{1}$, systems are governed, by externally prescribed interactions. Related to that intensive quantities are equal for systems in interaction, there is no trace of irreversibility,[3] *e.g.,* heat can flow in either direction – we have no means in $\boxed{1}$ of deducing this direction from the state quantities.

Processes are also not results of the interactions but are prescribed externally. There are no equations whose solutions would be the processes.

Concerning equilibrium, if you ever meet the word ‘equilibrium’, always identify whether that person speaks about external equilibrium or internal equilibrium. *External equilibrium* is when two systems are in equilibrium with one another (the intensive quantities are the same for the two systems, they don’t modify one another’s state *etc.*). *Internal equilibrium* is when a system is in equilibrium in itself

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[3] As a rare exception, internal efficiency of turbines and compressors is related to irreversibility, but internal efficiency is still not an intrinsic process determining principle but something prescribed externally ‘by brute force’.

(for example, you can visualize your system as a collection of small subsystem parts, and those subsystems are in equilibrium with each other). Now, in $\boxed{1}$, both external equilibrium and internal equilibrium are assumed.[4]

Finally, stability (stability of equilibrium) is a meaningless notion in $\boxed{1}$. See the next section for what stability is.

2.4 Cell 2 – temporal thermodynamics

$\boxed{2}$ will be called here temporal thermodynamics. Related names or approaches are: ordinary thermodynamics, endoreversible thermodynamics, finite-time thermodynamics, control theory.

In $\boxed{2}$, one can have state describing quantities that are missing from the scope of $\boxed{1}$: time-derivative velocity-like quantities (like volume change rate), space-derivative type ones, and so-called nonequilibrium/internal variables.

Processes are parametrized by time explicitly, while we still use the lumped parameter description.

Interactions between thermodynamical bodies are expressed via interaction functions – which are analogous to forces in mechanics – as functions of state variables. An example is the heat-type interaction between two bodies where heating rate is proportional to the difference of the two temperatures. This example immediately shows as well that irreversibility is present – and is completely common – in $\boxed{2}$.

Processes are results of the interactions, and the equations determining processes are ordinary differential equations. This is again a similarity to Newton's equation in mechanics. Here we already do thermoDYNAMICS.

The mathematical notion of equilibrium is definable in the model, as the stationary solution of the process determining equations. The equilibrium solution proves to be (asymptotically) stable. This mathematical notion of equilibrium embodies both external and internal physical equilibrium. Nonstationary solutions do not exhibit external equilibrium but may express internal equilibrium (endoreversible systems). However, $\boxed{2}$ is capable of describing internal nonequilibrium phenomena as well, like viscosity and non-Newtonian rheology.

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[4] In $\boxed{1}$, there is isothermal heat transfer, *i.e.,* two systems have the same temperature but heat flows from one system to the other (why not vice versa?). Yes, $\boxed{1}$ is neither too consistent nor too realistic.

2.5 Cell 4 – continuum thermodynamics

In $\boxed{4}$ (called, *e.g.,* continuum/nonequilibrium/irreversible thermodynamics, which is a distributed parameter description), quantities – temperature, density etc. – have both time and space dependence[5]; in other terminology, they are fields. Spatial inhomogeneities bring in further possible interactions, inducing internal nonequilibrium, and 'more' irreversibility. For example, gradient of temperature induces heat conduction (transfer of internal energy), which acts towards homogenizing temperature, towards internal equilibrium regarding temperature, and this is an irreversible process (it always decreases temperature differences, never increases).

Processes are determined by partial differential equations. Partial differential equations are much harder to solve than ordinary differential equations so whenever possible, we try to utilize or assume geometric symmetries to decrease the spatial dimension 3 to lower. For example, a spherically symmetric situation allows to eliminate the two angle-type coordinates of a spherical coordinate system, leaving the radial coordinate the only one on which spatial dependence is expressed.

2.6 Cell 3 – stationary continuum thermodynamics

$\boxed{3}$, a special case of $\boxed{4}$, is interesting not because of principal reasons but more because of practical reasons. Namely, these are the stationary, time independent – but space dependent – situations. Recall that stationary situations are very convenient and advantageous for technology, reliability, calculability *etc.* Another practical reason is that eliminating the time variable is also an example of when we have reduced the number of independent variables, the spacetime dimension 4, to 3.[6]

In engineering practice, $\boxed{3}$ is a frequent target for optimization since stationary processes 'take a long time' so a large gain can be achieved. On the other side, one also has to be able to reach that optimal stationary state – via a nonstationary, transient process – safely, and a swith-off (including the case of an accidental abrupt stop) should also happen under safe circumstances.[7]

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[5] More properly saying: they have spacetime dependence.

[6] Time independence is also a case of symmetry – spacetime symmetry –: it's invariance under time translation.

[7] Danger may be added to the cost function used for the optimization.

3 Thermostatics

3.1 Quantities, variables, functions, states

From introductory thermodynamics about ideal gases and similar, we are acquainted with the following, so-called extensive, quantities: mass (m), volume (V), and internal energy (E). From these, let us form densities:

$$\varrho \equiv \varrho_m = \frac{m}{V}\,, \qquad \varrho_E = \frac{E}{V}\,. \tag{14.1}$$

It is worth mentioning that, in certain situations, one must take into consideration that internal energy is not purely proportional to volume but a term proportional to surface area is present (think of surface tension):

$$E = \varrho_E V + \eta_E A\,. \tag{14.2}$$

Nevertheless, in what follows we neglect such additional contributions.

Similarly can we define mass-specific – or, simply, specific – quantities, where we relate to mass:

$$v = \frac{V}{m}\,, \qquad e = \frac{E}{m}\,. \tag{14.3}$$

In parallel, we know so-called intensive quantities: pressure (p) and [absolute] temperature (T).

In a number of books on thermodynamics, the question of the existence of temperature is an extensively discussed topic. In the meantime, in some treatments of thermodynamics, the existence of entropy is not investigated (later, we will investigate it) but is postulated, with various properties. On the practical side, however, you can buy a device measuring temperature (i.e., a thermometer) at any hypermarket. For a device measuring pressure, you need to find a much more specialized store. Measuring internal energy (changes) requires an appropriate laboratory setting. At last, if you ever meet an entropy meter, please let me know[8].

For an ideal gas, we know the following two relationships among these quantities:

$$pV = mRT\,, \qquad E = \frac{f}{2}RmT, \tag{14.4}$$

where

$$R = \frac{\mathcal{R}}{M} \tag{14.5}$$

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[8] `mailto:fulop.tamas@gpk.bme.hu`

is the specific gas constant, the universal gas constant $\mathcal{R} = 8.31446\,\frac{\mathrm{J}}{\mathrm{mol\,K}}$ divided by the molar mass M, and the constant f denotes the *energy storing degrees of freedom of one molecule*, which is the number of statistically independent energy storing possibilities of one (atom or) molecule. Namely, according to the microscopic picture behind the ideal gas model, molecules change energy via random collisions, and what we perceive macroscopically as temperature is proportional to the average of microscopic energy changes (average of energy change absolute values). Now, a spherically symmetric molecule with mass m_1 and Cartesian velocity components v_x, v_y, v_z has $f = 3$ possibilities corresponding to the three parts of kinetic energy

$$\frac{1}{2}m_1\mathrm{v}_x^2, \quad \frac{1}{2}m_1\mathrm{v}_y^2, \quad \frac{1}{2}m_1\mathrm{v}_z^2. \tag{15.1}$$

A rod-like molecule[9] has, in addition, two rotation related degrees of freedom, $f = 5$ (according to quantum mechanics, rotations can store energy only in finite amounts, the allowed energy values being inversely proportional to the moment of inertia, hence, rotation around the axis of the "rod", with its too small moment of inertia, is practically forbidden at room temperature – collisions cannot provide enough energy for it). Molecules with other, more extended, shape have three rotational degrees of freedom ($f = 6$). At temperatures above, *e.g.,* 1000 K, so-called vibrational (roughly speaking: elastic) energy storing modes may also become available, raising f above 6. For longer molecules and for molecules containing less tight chemical bonds, this may occur at a considerably lower temperature.

From introductory thermodynamics, we remember the formulae

$$c_v = \frac{f}{2}R, \qquad c_p = \frac{f+2}{2}R \tag{15.2}$$

for the isochoric and isobaric specific heats[10] of an ideal gas, respectively. These specific heats are constants as long as f is constant – now, we can see that f may be T dependent so, consequently, c_v and c_p may also be T dependent. Then the combination

$$E = c_v m T \tag{15.3}$$

of (14.4b) and (15.2a) is also to be replaced by a more general T dependence of E.[11]

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[9] Important examples are O_2 (with $M = 32$ g), N_2 (with $M = 28$ g), and, therefore, effectively, air, too (with $M = 29.3$ g) since air contains 78 % N_2, 21 % O_2, "and 1 % poison".

[10] 'Specific heat' also runs under the more correct but longer name 'specific heat capacity'.

[11] As one step from (14.4) towards more realistic models, some people allow *any* (strictly monotonously increasing) general temperature dependence of E under the name 'ideal gas', and the special case of *linear* temperature dependence is termed 'perfect gas'. Throughout this Lecture Notes, for simplicity, the meaning of 'ideal gas' will include constant f, unless explicitly mentioned. (Anyway, is 'perfect' more perfect than ideal, or 'ideal' is more ideal than perfect?)

These two expressions in (14.4) are called the *thermal* and *caloric* equations of state – in other words, constitutive relations –, respectively. Hereafter, we write them in the form of two functions,

$$p(T,V,m) = \frac{mRT}{V}\,, \qquad E(T,V,m) = \frac{f}{2}RmT\,, \tag{16.1}$$

which are called *constitutive functions.* In what follows, it will turn important what quantity is treated as a *function* and what quantities its *variables* are (important both for the topic of thermodynamical potentials, Sect. 3.4, and for the topic of phases).

From (16.1) we obtain

$$p(T,v) = \frac{RT}{v}\,, \qquad e(T,v) = \frac{f}{2}RT \qquad \text{with positive constants } R, f\,. \tag{16.2}$$

We can observe that these two functions are independent of the extent (mass, volume) of the gas, and are therefore characteristic to the material. Hereafter, we distinguish *materials* and *bodies* because many of the forthcoming considerations will be specific to materials themselves – then we will not have to specify a body and bother with more variables than needed. We will, accordingly, distinguish when we speak about air and when we speak about the air in the room.

Some other well-known material models, being qualitatively and/or quantitatively closer to reality than (16.2), are[12,13] the Van der Waals model

$$p(T,v) = \frac{RT}{v-b} - \frac{a}{v^2}\,, \qquad e(T,v) = \frac{f}{2}RT - \frac{a}{v} \qquad \text{with constants } a, b \geq 0\,, \tag{16.3}$$

the Berthelot model,

$$p(T,v) = \frac{RT}{v-B} - \frac{A}{Tv^2}\,, \qquad e(T,v) = \frac{f}{2}RT - \frac{2A}{Tv} \qquad \text{with constants } A, B \geq 0\,, \tag{16.4}$$

the Clausius model,

$$p(T,v) = \frac{RT}{v-\beta} - \frac{\alpha}{T(v+\gamma)^2}\,, \quad e(T,v) = \frac{f}{2}RT - \frac{2\alpha}{T(v+\gamma)} \quad (\text{constants } \alpha, \beta, \gamma \geq 0), \tag{16.5}$$

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[12] In sources like Wikipedia, you may find these models under the term ‘real gases’. Fortunately, by now you already know that all these are mere models, too, just maybe somewhat better approximations to reality. (Better examples for real gases are cow belching and fart.)

[13] Beware that, frequently, *e.g.,* in chemistry, specific volume and other specific quantities are defined as particle number specific or molar specific, rather than mass specific. For those purposes, the constants a, b, ... here have to be adapted accordingly (multiplying them by appropriate powers of M).

the Dieterici, the Redlich–Kwong, the Martin, the Peng–Robinson, the Wohl, the Beattie–Bridgeman, the Benedict–Webb–Rubin, the Starling *etc.* models with more and more constants (high-precision models like IAPS1984 for water/steam[14] have more than 60 constants), and, finally, the virial expansion formula (which is a series in powers of $\frac{1}{v}$),

$$p(T,v) = \frac{RT}{v}\left(1 + \frac{c_1(T)}{v} + \frac{c_2(T)}{v^2} + \cdots\right), \tag{17.1}$$

$$e(T,v) = \frac{f}{2}RT - RT^2\left(\frac{c_1'(T)}{v} + \frac{c_2'(T)}{v^2} + \cdots\right) \tag{17.2}$$

with prime denoting derivative, with respect to temperature, of the coefficient functions $c_1(T)$, $c_2(T)$, ...

A microscopic argument for the Van der Waals model, (16.3), is that molecules have not only *kinetic energy* – which explains the first term in $e(T,v)$ – but also *potential energy* coming from distance dependent attraction between any two molecules – hence the distance related (thus v related) second term in $e(T,v)$. In pressure, which is the macroscopic manifestation of microscopic *forces*, this attraction is also visible. In addition, molecules have some finite volume, and a rigid-body collision occurs whenever two of them get too close to one another; correspondingly, the available volume for their flight is decreased by their own volume, hence the difference $v - b$ in the motion related term of pressure [but b has no role in $e(T,v)$ – the macroscopic manifestation of microscopic *energies* – as long as kinetic energy conservation holds for the rigid-body collisions].

This microscopic picture is appealing but reality is more complex.[15] The complexities are reflected in the historically subsequent material models, with more and more coefficients in more and more complicated formulae.

It is important to note that, just like in the ideal gas case (cf. Footnote 11 on page 15), the purely temperature dependent term $\frac{f}{2}RT$ in all of the above models can be replaced by any function $\varepsilon(T)$ that satisfies $\mathrm{d}\varepsilon/\mathrm{d}T > 0$.

Remarkably, in most books and other sources, for each such model, only the thermal constitutive function $p(T,v)$ is provided. As we will see in Sect. 3.3, $e(T,v)$ can then be derived, due to a consistency condition, (26.5), which stems from the existence and properties of entropy.[16] However, this derivation does not provide $e(T,v)$ uniquely, and the ambiguity proves to be just the freedom in choosing the solely temperature dependent term $\varepsilon(T)$. The uncertainty in $\varepsilon(T)$ [in case of $\varepsilon(T) = \frac{f}{2}RT$: the

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[14] J. Kestin and J. V. Sengers: New international formulations for the thermodynamic properties of light and heavy water, *J. Phys. Chem. Ref. Data* **15** (1986) 305–320.

[15] As always.

[16] It is this condition that determines the second term of $e(T,v)$ in each of the models above from the corresponding $p(T,v)$.

uncertainty in f] has important engineering consequences. Namely, entropy and all other thermodynamical potentials, and thus all related phenomena, depend on this ambiguity, as we will see in Sect. 3.3. One such phenomenon is whether a material is 'wet' or 'dry'[17] : dry ones are much more advantageous in turbines. Now, a Van der Waals model with $f > 10$ turns out to be dry.[17] Therefore, a material model is properly given only if both the thermal constitutive function $p(T, v)$ and the caloric one $e(T, v)$ are fully specified.

There is not only an equality-type condition [the above already mentioned (26.5)] that any $p(T, v)$, $e(T, v)$ must satisfy. In parallel, two inequalities must also hold, which we call hereafter *material stability conditions*:

$$\left.\frac{\partial e}{\partial T}\right|_v > 0\,, \tag{18.1}$$

$$\left.\frac{\partial p}{\partial v}\right|_T < 0\,. \tag{18.2}$$

These inequalities[18] are historically present in the Le Chatelier–Braun principle, which, roughly speaking, says that quantities of a system change under any external action in a way that decreases the extent of that action. Actions–interactions, processes, and stability will be discussed first within $\boxed{2}$ in Sect. 4 but one aspect can already be realized here in $\boxed{1}$: if something holds for *any* type of interaction of a material then it may be a property of the *material*, not of the possible *interactions*. This happens here where the conditions (18.1)–(18.2) are formulated for the material itself [actually without any need for speaking about interactions between systems]. While the full role of (18.1)–(18.2) will be recognized within $\boxed{2}$, the existence of more than one phase will be one consequence of them already in $\boxed{1}$.

While the above-seen range of modelling capabilities seems quite broad, this may not be enough. Namely, the quantities T and v may or may not be able to describe the thermodynamical state of a material. For example, electric or magnetic interactions are related to some further state characterizing quantities of vectorial type. Furthermore, even within the scope of heat and work type interactions, materials in solid state are not characterized fully via T and v since a solid body with fixed temperature, mass, and volume can have various different geometric shapes with different (elasticity-originated) internal energy values, which a volume variable is not enough to characterize. In fact, solid materials require a symmetric tensor, rather than a scalar, geometric variable. (See more on it in Sect. 3.14.) In addition, even when v is

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[17] Wikipedia: Working fluids (as of 2019-02-19); A. Groniewsky, G. Györke, and A. R. Imre: Description of wet-to-dry transition in model ORC working fluids, *Applied Thermal Engineering* **125** (2017) 963–971; DOI:10.1016/j.applthermaleng.2017.07.074.

[18] which, equivalently, say that isochoric specific heat and isothermal compressibility are positive – see more on them later

enough to describe the relevant aspects of geometry, its time derivative $\mathrm{d}v/\mathrm{d}t$ may also be needed as a state variable – as we will see in Sect. 4.4.[19] In what follows, we speak about a *simple material* when the variables T, v suffice to characterize the thermodynamical state of a given material. In other words, the *state space* – denoted by $\mathcal{Z}$ hereafter – of a simple material is parametrizable by the quantities T, v.[20]

In the $\boxed{1}$ approach, a process of a material is a continuous sequence of states.[21] As indicated in Sect. 2.3, in $\boxed{1}$ processes are treated in a half-hearted way, and one manifestation of this is that, in $\boxed{1}$, processes are usually parametrized by some state quantity, rather than by time. Sometimes it is only a part of a process within which a state quantity characterizes the states uniquely. For example, during a Carnot cycle, temperature cannot parametrize the two isothermal parts. Then one needs to switch to some other quantity as parameter. (Or to switch to parametrizing by time, in the spirit of $\boxed{2}$.)

In many applications, such processes are considered during which some state quantity remains constant. Such examples are isothermal (constant-temperature), isochoric (constant-volume), isobaric (constant pressure) processes [and, with quantities to be introduced later, isentropic and isenthalpic processes, too]. Restrictions that some quantity must stay constant during a process are either suggested by the circumstances or are introduced by us as (hopefully) good enough approximations.

For a simple material, a state ζ in the state space $\mathcal{Z}$ can also be uniquely identified via the quantities e, v.[22] Actually, for certain purposes the latter characterization is more convenient, and there are situations when even more different variable pairs come useful. Hence, the topic of variable transformations – applied for the constitutive and other state dependent functions – is very important in thermodynamics. The next section contains a collection of related mathematical rules we are going to apply hereafter.

3.2 Necessary mathematical ingredients

We start with a list of **identities concerning partial derivatives,** all derivable from rules mentioned on page 5. We assume that all required mathematical conditions hold. The notation applied here will be oversimplifying, convenient for application but hiding the fact that one has composite functions here. Never forget

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[19] In such a case, we must unavoidably move outside of $\boxed{1}$.

[20] Note that, while the value of T can be anything non-negative, some models forbid v to take arbitrarily small positive values. For example, the Van der Waals model forbids $v \leq b$. This is actually realistic if we consider b to be related to the volume of the molecules themselves (see more on this in Sect. 3.10.)

[21] In other words, a process is an oriented curve in the state space.

[22] This follows from the material stability inequality (18.1).

that we differentiate not “quantities with respect to quantities” but functions with respect to variables. For example, $\frac{\partial z}{\partial x}\big|_y$ indicates that z is a function with variables x and y. For composite functions, this has to be treated mutatis mutandis.

Identity ① :
$$\left.\frac{\partial z}{\partial y}\right|_x = \frac{1}{\left.\dfrac{\partial y}{\partial z}\right|_x}\,, \tag{20.1}$$

Identity (2a) :
$$\left.\frac{\partial u}{\partial z}\right|_x = \left.\frac{\partial u}{\partial y}\right|_x \cdot \left.\frac{\partial y}{\partial z}\right|_x\,, \tag{20.2}$$

Identity (2b) :
$$\left.\frac{\partial u}{\partial y}\right|_x = \frac{\frac{\partial u}{\partial z}\big|_x}{\frac{\partial y}{\partial z}\big|_x}\,, \tag{20.3}$$

Identity ③ :
$$\left.\frac{\partial z}{\partial x}\right|_y \cdot \left.\frac{\partial x}{\partial y}\right|_z \cdot \left.\frac{\partial y}{\partial z}\right|_x = -1\,, \tag{20.4}$$

Identity (4a) :
$$\left.\frac{\partial u}{\partial x}\right|_z = \left.\frac{\partial u}{\partial x}\right|_y + \left.\frac{\partial u}{\partial y}\right|_x \cdot \left.\frac{\partial y}{\partial x}\right|_z\,, \tag{20.5}$$

Identity (4b) :
$$\left.\frac{\partial u}{\partial x}\right|_y = \left.\frac{\partial u}{\partial x}\right|_z - \frac{\left.\dfrac{\partial u}{\partial z}\right|_x}{\left.\dfrac{\partial y}{\partial z}\right|_x} \cdot \left.\frac{\partial y}{\partial x}\right|_z\,. \tag{20.6}$$

Second, let us briefly summarize the topic of **potentials**. A vector field

$$\mathbf{v}\left(x,y,z\right) = \begin{pmatrix} \mathrm{v}_x \\ \mathrm{v}_y \\ \mathrm{v}_z \end{pmatrix} \tag{20.7}$$

in a three-dimensional Euclidean[23] vector space, expressed in Cartesian coordinates,

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[23] If the vector space is not Euclidean then we must consider a covector field here. In a Euclidean space, the scalar product provides a natural identification between vectors and covectors (elements of the vector space and elements of the dual space). For our purposes of thermodynamics below, the vector space will not be Euclidean but will be the Cartesian product of one-dimensional vector spaces – thus, the dual space is the Cartesian product of the one-dimensional dual spaces, and a one-dimensional dual space is the set of reciprocal values – so the treatment of covectors is so natural that we will not need to emphasize the difference from vectors.

is said to *have a potential* if there is a scalar field function $u(x, y, z)$ such that[24]

$$\mathbf{v} = \operatorname{grad} u\,, \qquad \textit{i.e.,} \qquad \begin{pmatrix} \mathrm{v}_x \\ \mathrm{v}_y \\ \mathrm{v}_z \end{pmatrix} = \begin{pmatrix} \frac{\partial u}{\partial x} \\ \frac{\partial u}{\partial y} \\ \frac{\partial u}{\partial z} \end{pmatrix}. \tag{21.1}$$

The following four statements are equivalent (up to mathematical assumptions):

- to a vector field $\mathbf{v}$, there exists a scalar field u satisfying $\operatorname{grad} u = \mathbf{v}$,
- $\operatorname{curl} \mathbf{v} = \mathbf{0}$,
- the line integral $\int_{\mathbf{r}=\mathbf{r}_0}^{\mathbf{r}} \mathbf{v}(\tilde{\mathbf{r}})\, \mathrm{d}\tilde{\mathbf{r}}$ is independent of the path connecting $\mathbf{r}_0$ and $\mathbf{r}$,
- the closed line integral $\oint \mathbf{v}(\tilde{\mathbf{r}})\, \mathrm{d}\tilde{\mathbf{r}}$ is zero along any closed line.

Among these, the second one is the easiest to check:

$$\operatorname{curl} \mathbf{v} = \begin{pmatrix} \frac{\partial \mathrm{v}_z}{\partial y} - \frac{\partial \mathrm{v}_y}{\partial z} \\ \frac{\partial \mathrm{v}_x}{\partial z} - \frac{\partial \mathrm{v}_z}{\partial x} \\ \frac{\partial \mathrm{v}_y}{\partial x} - \frac{\partial \mathrm{v}_x}{\partial y} \end{pmatrix} \overset{?}{=} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{21.2}$$

Notably, if $\mathbf{v}$ has a potential u then $u + \text{const.}$ is also a potential for $\mathbf{v}$ [since an additive constant drops out when checking (21.1)].

If $\mathbf{v}$ has a potential u then one can determine it via

$$u(\mathbf{r}) = u(\mathbf{r}_0) + \int_{\mathbf{r}=\mathbf{r}_0}^{\mathbf{r}} \mathbf{v}(\tilde{\mathbf{r}})\, \mathrm{d}\tilde{\mathbf{r}} \tag{21.3}$$

along any path that connects $\mathbf{r}_0$ and $\mathbf{r}$. Here, $u(\mathbf{r}_0)$ remains undetermined because of the mentioned ambiguity in an additive constant. Frequently, a convenient choice is a path that consists of three segments, the first in the x direction, the second in the y direction, and the third in the z direction:

$$u(x, y, z) = u_0 + \int_{\tilde{x}=x_0}^{x} \mathrm{v}_x(\tilde{x}, y_0, z_0)\, \mathrm{d}\tilde{x} + \int_{\tilde{y}=y_0}^{y} \mathrm{v}_y(x, \tilde{y}, z_0)\, \mathrm{d}\tilde{y} + \int_{\tilde{z}=z_0}^{z} \mathrm{v}_z(x, y, \tilde{z})\, \mathrm{d}\tilde{z} \tag{21.4}$$

with the shorthand $u_0 = u(x_0, y_0, z_0)$.

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[24] For the purpose of potential energy related to a force field, and for some similar applications, physics puts a minus sign before the grad in the definition (21.1). In mathematics and in thermodynamics, that minus sign would be an unnatural choice.

In two dimensions, there is only one condition to check:

$$\frac{\partial \mathrm{v}_y}{\partial x} - \frac{\partial \mathrm{v}_x}{\partial y} \overset{?}{=} 0\,, \qquad \text{or, written more simply,} \qquad \frac{\partial \mathrm{v}_y}{\partial x} \overset{?}{=} \frac{\partial \mathrm{v}_x}{\partial y}\,. \tag{22.1}$$

Finally, staying closely related to both partial derivatives and potentials, let us collect a few facts about **differentials,** without precisely explaining what they are[25]; here in thermodynamics you can think of the small change of a state quantity as we move from a state ζ in the state space $\mathcal{Z}$ to a "nearby" other state $\tilde{\zeta}$. For example, you can think of $\mathrm{d}p$ as the small pressure difference

$$\mathrm{d}p \approx p\left(\tilde{\zeta}\right) - p(\zeta)\,. \tag{22.2}$$

The Leibniz rule for the derivative of products has an analogous version for differentials:

$$\mathrm{d}(\mathtt{f}\mathtt{g}) = \mathtt{g}\,\mathrm{d}\mathtt{f} + \mathtt{f}\,\mathrm{d}\mathtt{g}\,. \tag{22.3}$$

Similarly, the analogy of the rule of differentiation of multivariate composite functions (see Sect. 1.1) is

$$\mathrm{d}z = \left.\frac{\partial z}{\partial x}\right|_y \mathrm{d}x + \left.\frac{\partial z}{\partial y}\right|_x \mathrm{d}y\,, \quad \textit{i.e.,} \quad \mathrm{d}z(x,y) = \left.\frac{\partial z}{\partial x}\right|_y (x,y)\,\mathrm{d}x + \left.\frac{\partial z}{\partial y}\right|_x (x,y)\,\mathrm{d}y\,. \tag{22.4}$$

Intuitively, this says that, if x changes a bit and y also changes a bit, then a function z depending on them also changes a bit, according to (22.4).

One important and convenient application of (22.4) is that, whenever we see a formula

$$\mathrm{d}z = \mathtt{f}\,\mathrm{d}x + \mathtt{g}\,\mathrm{d}y\,, \tag{22.5}$$

this formula is actually a compact way of displaying two things:

$$\mathtt{f} = \left.\frac{\partial z}{\partial x}\right|_y, \qquad \mathtt{g} = \left.\frac{\partial z}{\partial y}\right|_x. \tag{22.6}$$

A so-called Pfaffian[26],

$$\mathtt{a}(x,y)\,\mathrm{d}x + \mathtt{b}(x,y)\,\mathrm{d}y \tag{22.7}$$

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[25] Exterior derivatives of scalar functions on a differentiable manifold (here, on $\mathcal{Z}$).

[26] Under other names: a covector field, a one-form.

is, in general, only a so-called inexact differential[27], *i.e.,* it is not the differential of a function. Expression (22.7) is a differential of a function $u(x,y)$,

$$\mathtt{a}(x,y)\,\mathrm{d}x+\mathtt{b}(x,y)\,\mathrm{d}y=\mathrm{d}u(x,y)\,,\qquad \textit{i.e.,}\qquad \mathtt{a}(x,y)=\left.\frac{\partial u}{\partial x}\right|_y \text{ and } \mathtt{b}(x,y)=\left.\frac{\partial u}{\partial y}\right|_x \tag{23.1}$$

if and only if

$$\left.\frac{\partial \mathtt{a}}{\partial y}\right|_x=\left.\frac{\partial \mathtt{b}}{\partial x}\right|_y\,. \tag{23.2}$$

Let us observe that, here, we actually ask whether the two-dimensional vector field

$$\begin{pmatrix}\mathtt{a}(x,y)\\ \mathtt{b}(x,y)\end{pmatrix} \tag{23.3}$$

has a potential [cf. (22.1)], in other words, whether there is a $u(x,y)$ for which

$$\left.\frac{\partial u}{\partial x}\right|_y=\mathtt{a}\quad\text{and}\quad\left.\frac{\partial u}{\partial y}\right|_x=\mathtt{b}\,;\qquad\text{or, in other form,}\quad\begin{pmatrix}\mathtt{a}\\ \mathtt{b}\end{pmatrix}=\begin{pmatrix}\left.\frac{\partial u}{\partial x}\right|_y\\ \left.\frac{\partial u}{\partial y}\right|_x\end{pmatrix}. \tag{23.4}$$

If a potential exists then it can be reconstructed from $\mathtt{a}$ and $\mathtt{b}$, for example via the line integral [cf. (21.4)]

$$u(x,y)=u(x_0,y_0)+\int_{\tilde{x}=x_0}^{x}\mathtt{a}(\tilde{x},y_0)\,\mathrm{d}\tilde{x}+\int_{\tilde{y}=y_0}^{y}\mathtt{b}(x,\tilde{y})\,\mathrm{d}\tilde{y}\,, \tag{23.5}$$

where, as already mentioned, the initial point (x_0,y_0) is arbitrary, and $u(x,y)$ is undetermined up to a constant, hence the arbitrary value $u(x_0,y_0)$. Note that, in the first integral, not y but y_0 appears, while in the second one not x_0 but x.

Differentials are convenient and effective since many steps one would instinctively perform are actually valid steps. For example, expressing $\mathrm{d}x$ from $\mathrm{d}z=\mathtt{f}\,\mathrm{d}x+\mathtt{g}\,\mathrm{d}y$,

$$\mathrm{d}x=-\frac{\mathtt{g}}{\mathtt{f}}\,\mathrm{d}y+\frac{1}{\mathtt{f}}\,\mathrm{d}z \tag{23.6}$$

does indeed say that the meanings (22.6) of $\mathtt{f}$, $\mathtt{g}$ are compatible with

$$-\frac{\mathtt{g}}{\mathtt{f}}=\left.\frac{\partial x}{\partial y}\right|_z,\qquad\frac{1}{\mathtt{f}}=\left.\frac{\partial x}{\partial z}\right|_y, \tag{23.7}$$

---

[27] Recall the inexact differentials known from basic thermodynamics, $đQ=T\mathrm{d}S$ and $đW=-p\mathrm{d}V$, invoked in Sect. 2.3.

the properties following from (22.4) applied to $x(y, z)$. In other words, the rules for derivatives during variable transformations (including identities ① – (4b)) are reflected automatically when manipulating with differentials.

Another convenient notion is that of *restricted differentials.* For example, one can think of $\mathrm{d}p|_T$ as representing a small change in pressure during an isothermal process.[28] The ratio of two restricted differentials can be meaningful and useful: *e.g.,*

$$\frac{\mathrm{d}p|_T}{\mathrm{d}v|_T} = \left.\frac{\partial p}{\partial v}\right|_T , \tag{24.1}$$

just as one would heuristically think. Analogously, one can speak about restriction along a process. As an important application, specific heat along any given process is defined as

$$c_{\text{process}} = \frac{\text{đ}q|_{\text{process}}}{\mathrm{d}T|_{\text{process}}} , \tag{24.2}$$

a small amount of mass-specific heat along a process, divided by the corresponding small temperature change (recall Sect. 2.3 for the notation đ). As examples,

$$c_v = \frac{\text{đ}q|_v}{\mathrm{d}T|_v} , \qquad c_p = \frac{\text{đ}q|_p}{\mathrm{d}T|_p} \qquad \textit{etc.} \tag{24.3}$$

Apparently, specific heats are, in general, both state dependent and process dependent. It is only some special material models and some special processes when the corresponding specific heat is constant. For ideal gases with constant c_v, the so-called polytropic processes – the ones during which $c_{\text{process}} = \text{const.}$ – prove to be the ones for which $pv^\alpha = \text{const.}$ with arbitrary $-\infty \leq \alpha \leq \infty$ (called *polytropic index*[29]), and the corresponding constant specific heat is (see Problem 3) $c_\alpha = c_v + \frac{R}{1-\alpha}$.

In parallel, if a process is parametrized by time then a ratio of time derivatives can be expressed via restricted differentials, *e.g.,*

$$\frac{\mathrm{d}p/\,\mathrm{d}t}{\mathrm{d}v/\,\mathrm{d}t} = \frac{\mathrm{d}p|_{\text{process}}}{\mathrm{d}v|_{\text{process}}} . \tag{24.4}$$

For example, along an isothermal process,

$$\frac{\mathrm{d}p/\,\mathrm{d}t}{\mathrm{d}v/\,\mathrm{d}t} = \frac{\mathrm{d}p|_T}{\mathrm{d}v|_T} \overset{(24.1)}{=} \left.\frac{\partial p}{\partial v}\right|_T . \tag{24.5}$$

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[28] A side remark: the mathematically more informative notation would be $\mathrm{d}p|_{\mathrm{Ker}\,\mathrm{d}T}$ where Ker denotes the kernel: we restrict the domain of definition of $\mathrm{d}p$ to a subset, in our case, to a linear subspace.

[29] Frequently, the polytropic index is denoted by n, which notation falsely suggests that its value could only be some integer, however, in fact, it can be $-\sqrt{\pi}$ as well.

3.3 The entropic property of simple materials

A simple material will be called *entropic* if the vector field

$$\begin{pmatrix} \frac{1}{T(e,v)} \\ \\ \frac{p(e,v)}{T(e,v)} \end{pmatrix} = \begin{pmatrix} \frac{1}{T} \\ \\ \frac{p}{T} \end{pmatrix} (e,v) \tag{25.1}$$

has a potential. By (23.2)–(23.4), this is equivalent to[30]

$$\left.\frac{\partial \frac{1}{T}}{\partial v}\right|_e = \left.\frac{\partial \frac{p}{T}}{\partial e}\right|_v . \tag{25.2}$$

In such a case, the potential, called *specific entropy*, calculated using (23.5), is

$$s(e,v) = s(e_0, v_0) + \int_{\tilde{e}=e_0}^{e} \frac{1}{T}(\tilde{e}, v_0)\,\mathrm{d}\tilde{e} + \int_{\tilde{v}=v_0}^{v} \frac{p}{T}(e, \tilde{v})\,\mathrm{d}\tilde{v}\,. \tag{25.3}$$

For instance, for the ideal gas with constant $c_v = \frac{f}{2}R$, (16.2), we find

$$\begin{pmatrix} \frac{1}{T(e,v)} \\ \\ \frac{p(e,v)}{T(e,v)} \end{pmatrix} = \begin{pmatrix} \frac{\frac{f}{2}R}{e} \\ \\ \frac{R}{v} \end{pmatrix} ; \qquad \left.\frac{\partial \frac{1}{T}}{\partial v}\right|_e = \left.\frac{\partial \frac{p}{T}}{\partial e}\right|_v = 0 \tag{25.4}$$

so this material is entropic, and its specific entropy is [cf. (25.3)]

$$s(e,v) = s_0 + \int_{\tilde{e}=e_0}^{e} \frac{\frac{f}{2}R}{\tilde{e}}\,\mathrm{d}\tilde{e} + \int_{\tilde{v}=v_0}^{v} \frac{R}{\tilde{v}}\,\mathrm{d}\tilde{v} = s_0 + \frac{f}{2}R\ln\frac{e}{e_0} + R\ln\frac{v}{v_0} \tag{25.5}$$

[with the abbreviation $s_0 = s(e_0, v_0)$].

Probably all known simple materials are entropic.

For entropic simple materials, we have[31]

$$\mathrm{d}s = \frac{1}{T}\,\mathrm{d}e + \frac{p}{T}\,\mathrm{d}v\,, \tag{25.6}$$

rearranging which gives the so-called *Gibbs relation*,

$$\mathrm{d}e = T\,\mathrm{d}s - p\,\mathrm{d}v\,, \tag{25.7}$$

---

[30] In order to check (25.2) for a given simple material, one has to express T from $e(T,v)$, obtaining thus $T(e,v)$. Then, substituting $T(e,v)$ into $p(T,v)$ yields the other ingredient, $p(e,v)$.

[31] Actually, the historically raised question was more like this: can $\mathrm{d}e + p\,\mathrm{d}v$ be made an exact/total differential – the differential of a function – via dividing by an appropriate function $T(e,v)$? Such a factor, here $\frac{1}{T}$, is called an integrating factor in general.

which, as seen in (22.5)–(22.6), is a concise encoding of

$$T = \left.\frac{\partial e}{\partial s}\right|_v , \qquad -p = \left.\frac{\partial e}{\partial v}\right|_s . \tag{26.1}$$

Interactions will be possible to describe seriously in $\boxed{2}$ but, nevertheless, the inexact differentials

$$\text{đ}w = -p\,\mathrm{d}v\,, \qquad \text{đ}q = \mathrm{d}e - \text{đ}w = \mathrm{d}e + p\,\mathrm{d}v \overset{(25.7)}{=} T\,\mathrm{d}s\,, \tag{26.2}$$

can already be treated here, with our present tools, and can be utilized. For example, the definition of specific heat seen in (24.2)–(24.3) can be rewritten in forms advantageous for applications, as

$$c_{\text{process}} = \frac{\text{đ}q|_{\text{process}}}{\mathrm{d}T|_{\text{process}}} = \frac{\mathrm{d}e|_{\text{process}} + p\ \mathrm{d}v|_{\text{process}}}{\mathrm{d}T|_{\text{process}}}, \quad \textit{e.g.}, \quad c_v = \frac{\mathrm{d}e|_v}{\mathrm{d}T|_v} = \left.\frac{\partial e}{\partial T}\right|_v , \tag{26.3}$$

$$c_{\text{process}} = \frac{\text{đ}q|_{\text{process}}}{\mathrm{d}T|_{\text{process}}} = T\left.\frac{\partial s}{\partial T}\right|_{\text{process}} , \quad \textit{e.g.}, \quad c_v = T\left.\frac{\partial s}{\partial T}\right|_v , \quad c_p = T\left.\frac{\partial s}{\partial T}\right|_p . \tag{26.4}$$

Again as a reminder: here, we treat a generic simple material so we have, in general, $c_{\text{process}}(T, v),\ c_v(T, v),\ c_p(T, v)$.

A convenient reformulation of condition (25.2), in terms of $p(T, v)$ and $e(T, v)$ – the functions we usually have directly, such as in (16.2)–(17.2) – is

$$\left.\frac{\partial e}{\partial v}\right|_T = T\left.\frac{\partial p}{\partial T}\right|_v - p\,. \tag{26.5}$$

The outline of obtaining (26.5) from (25.2) is

$$-\frac{1}{T^2}\left.\frac{\partial T}{\partial v}\right|_e = \frac{T\left.\frac{\partial p}{\partial e}\right|_v - p\left.\frac{\partial T}{\partial e}\right|_v}{T^2}\,, \qquad \Bigg|\ \cdot T^2 \left.\tfrac{\partial e}{\partial T}\right|_v \tag{26.6}$$

$$-\left.\frac{\partial T}{\partial v}\right|_e \left.\frac{\partial e}{\partial T}\right|_v = T\left.\frac{\partial p}{\partial e}\right|_v \left.\frac{\partial e}{\partial T}\right|_v - p\left.\frac{\partial T}{\partial e}\right|_v \left.\frac{\partial e}{\partial T}\right|_v , \tag{26.7}$$

$$\overset{\text{③}}{\left.\frac{\partial e}{\partial v}\right|_T} = T\,\overset{\text{(2a)}}{\left.\frac{\partial p}{\partial T}\right|_v} - \overset{\text{①}}{p}\ . \tag{26.8}$$

Using the Maxwell relations we meet in Sect. 3.5, this calculation can be considerably shortened [see (31.1)], serving thus as an example why the Maxwell relations are beneficial.

It is a good exercise to check that the material models (16.2)–(17.2) are entropic, *i.e.,* each satisfy (26.5).

In fact, as anticipated in Sect. 3.1, (26.5) enables us to determine $e(T,v)$ from $p(T,v)$ to a certain extent. Namely, indefinite integration of (26.5) in v gives

$$e(T,v) = \int \left(T \left. \frac{\partial p}{\partial T} \right|_v - p(T,v) \right) \mathrm{d}v + C(T) , \tag{27.1}$$

where $C(T)$ is a constant of integration with respect to variable v but can depend on the other variable, T.

As an example, for the Van der Waals thermal constitutive function $p(T,v) = \frac{RT}{v-b} - \frac{a}{v^2}$,

$$T \left. \frac{\partial p}{\partial T} \right|_v - p = \frac{a}{v^2} , \tag{27.2}$$

and (27.1) yields

$$e(T,v) = \int \frac{a}{v^2} \, \mathrm{d}v + C(T) = -\frac{a}{v} + C(T) \tag{27.3}$$

so $e(T,v)$ in (16.3) is recovered up to a solely temperature dependent term – which was denoted by $\varepsilon(T)$ on page 17. For fixing the ambiguity, we need extra information or requirement – *e.g.,* that, in the ideal gas limit $a \to 0$, $b \to 0$, (16.2) is obtained.

This is the method to (partially) determine $e(T,v)$ whenever only $p(T,v)$ is provided.

In parallel, this method prevents us from running into trouble regarding measurements. That is, all measurements are burdened with errors. Now, if reconstruct both $p(T,v)$ and $e(T,v)$ separately, from measurement data and some fitting procedure, (26.5) will be violated almost surely. Avoid measuring too much: you will save time, effort, and money while you also avoid running into such an inconsistency.[32]

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[32] Nevertheless, some extra measurements are useful for checking. Also, you might discover a nonentropic material, and get a Nobel prize.

3.4 Thermodynamical potentials

One reason why the entropic property is remarkable is as follows. Let us take a look at (25.6): it says us that

$$\left.\frac{\partial s}{\partial e}\right|_v = \frac{1}{T}\,, \qquad \left.\frac{\partial s}{\partial v}\right|_e = \frac{p}{T}\,. \tag{28.1}$$

The first of these two equalities enables us to determine $T(e,v)$ from $s(e,v)$ [*i.e.,* from its partial derivative w.r.t.[33] its first variable]. By expressing e from $T(e,v)$, we recover the caloric constitutive function $e(T,v)$. In parallel, from the second of the equalities (28.1) and the already known $T(e,v)$ we can deduce $p(e,v)$. With the aid of the also already determined $e(T,v)$, we end up with $p(T,v)$, the thermal constitutive function. In summary, we have been able to extract all constitutive information (in our case: the two constitutive functions) from one function, $s(e,v)$.

Whenever a function contains, via its derivatives, all thermodynamical information about a material, we call it a *thermodynamical potential function.*[34] $s(e,v)$ is therefore an example of a thermodynamical potential function. Also, we will call s a *thermodynamical potential quantity*, and e,v *its natural variables.* To restate, a thermodynamical potential quantity as a function of its natural variables forms a thermodynamical potential function.

Another example can be observed when inspecting (26.1). That is, $T(s,v)$ is provided by the first equality, from which s can be expressed as the function of (T,v). Next, the second equality delivers $p(s,v)$, which, with $s(T,v)$, yields $p(T,v)$, which is the thermal constitutive function. In parallel, $s(T,v)$ substituted into $e(s,v)$ itself gives us $e(T,v)$, *i.e.,* the caloric constitutive function. In consequence, $e(s,v)$ is also a thermodynamical potential function, and e is a thermodynamical potential quantity, with s,v as its natural variables.

Entropy (specific entropy), with its above-seen properties, makes it possible to define further thermodynamical potentials as well. One of them is *specific free energy*,

$$f = e - Ts \tag{28.2}$$

for which we find, from (25.7) and (22.3),

$$\mathrm{d}f = -s\,\mathrm{d}T - p\,\mathrm{d}v\,, \qquad \text{which encodes} \quad -s = \left.\frac{\partial f}{\partial T}\right|_v, \quad -p = \left.\frac{\partial f}{\partial v}\right|_T \tag{28.3}$$

and that the natural variables of f are T, v. Similarly defined are *specific enthalpy*,

$$h = e + pv \tag{28.4}$$

---

[33] with respect to

[34] Recall Sect. 3.2: at the general level, a potential is always such a function that encodes, via its derivatives, more than one function. So to say, it is an effective lossless data compression method.

with

$$\mathrm{d}h = T\,\mathrm{d}s + v\,\mathrm{d}p, \qquad T = \left.\frac{\partial h}{\partial s}\right|_p, \qquad v = \left.\frac{\partial h}{\partial p}\right|_s \tag{29.1}$$

and having natural variables s, p, and *specific Gibbs potential* (also called *specific free enthalpy*),

$$g = e - Ts + pv \tag{29.2}$$

with

$$\mathrm{d}g = -s\,\mathrm{d}T + v\,\mathrm{d}p, \qquad -s = \left.\frac{\partial g}{\partial T}\right|_p, \qquad v = \left.\frac{\partial g}{\partial p}\right|_T \tag{29.3}$$

with natural variables T, p.[35] To anticipate some benefits of these further thermodynamical potential quantities, f proves useful for isothermal and isochoric processes, h for adiabatic and isobaric ones, while g proves important in the topic of phases and for chemical reactions. As another example, the measurement-based high-precision IAPS1984 model for water/steam (cf. Footnote 14 on page 16) offers $f(T, v)$ only, and everything else – constitutive functions, specific heats *etc.* – has to be derived from it. As further and immediate advantages,

$$đq \overset{(26.2)}{=} \mathrm{d}e + p\,\mathrm{d}v \overset{\substack{(28.4),\\(22.3)}}{=} \mathrm{d}h - v\,\mathrm{d}p, \qquad \left.đq\right|_p = \left.\mathrm{d}h\right|_p, \qquad c_p = \frac{\left.đq\right|_p}{\left.\mathrm{d}T\right|_p} = \left.\frac{\partial h}{\partial T}\right|_p . \tag{29.4}$$

Without going into details, a separate remark is that the way how (28.2), (28.4), and (29.2) introduce new quantities and corresponding new variables, are special examples of the so-called Legendre transform. In mechanics, the Legendre transform also appears, connecting the Hamiltonian with the Lagrangian. For nice properties of the Legendre transform, convexity is required – see more on this in Sect. 3.7.

Closing this section with an important note, it is not enough to speak about thermodynamical potential quantities – we also have to ensure that they are given in their natural variables. Otherwise they are not thermodynamical potential functions: they do not encode all constitutive information. As an example, in Sect. 3.6 we will determine $s(T, v)$ for the Van der Waals model, and find explicitly that it does not contain all information about the material.

---

[35] Actually, the existence of liquid and gas phases of simple materials is related to that describing states in variables T, p is nontrivial, which is thus ‘a feature rather than a bug’.

3.5 Maxwell relations and Gibbs–Helmholtz relations

As already mentioned in the last paragraph of Sect. 3.3 in page 27, whenever we have some relationship among quantities then we have to measure less, as well as we avoid inconsistency among measurement data. With the aid of the thermodynamical potential functions f, h, and g, it is possible to derive/reveal such relationships, analogous to (26.5).

In the light of (22.5)–(22.6) and Young's theorem on the arbitrary order of mixed derivatives, $\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x}$ (recall page 5), we find the *Maxwell relations*,

$$\mathrm{d}e = T\,\mathrm{d}s - p\,\mathrm{d}v \quad \Longrightarrow \quad \left.\frac{\partial T}{\partial v}\right|_s = \left.\frac{\partial(-p)}{\partial s}\right|_v, \quad \textit{i.e.,} \quad \left.\frac{\partial T}{\partial v}\right|_s = -\left.\frac{\partial p}{\partial s}\right|_v, \tag{30.1}$$

$$\mathrm{d}f = -s\,\mathrm{d}T - p\,\mathrm{d}v \quad \Longrightarrow \quad \left.\frac{\partial(-s)}{\partial v}\right|_T = \left.\frac{\partial(-p)}{\partial T}\right|_v, \quad \textit{i.e.,} \quad \left.\frac{\partial s}{\partial v}\right|_T = \left.\frac{\partial p}{\partial T}\right|_v, \tag{30.2}$$

$$\mathrm{d}h = T\,\mathrm{d}s + v\,\mathrm{d}p \quad \Longrightarrow \quad \left.\frac{\partial T}{\partial p}\right|_s = \left.\frac{\partial v}{\partial s}\right|_p, \tag{30.3}$$

$$\mathrm{d}g = -s\,\mathrm{d}T + v\,\mathrm{d}p \quad \Longrightarrow \quad \left.\frac{\partial(-s)}{\partial p}\right|_T = \left.\frac{\partial v}{\partial T}\right|_p, \quad \textit{i.e.,} \quad \left.\frac{\partial s}{\partial p}\right|_T = -\left.\frac{\partial v}{\partial T}\right|_p. \tag{30.4}$$

So far, the thermodynamical potential quantities have been considered in their natural variables. The *Gibbs–Helmholtz relations* provide them in natural variables of another such quantity. As an example, let us determine $e(T, v)$: T, v are the natural variables of f so we proceed as

$$e = f + Ts = f - T\left.\frac{\partial f}{\partial T}\right|_v, \qquad \textit{i.e.,} \qquad e(T, v) = f(T, v) - T\left.\frac{\partial f}{\partial T}\right|_v, \tag{30.5}$$

bearing in mind $s = -\left.\frac{\partial f}{\partial T}\right|_v$, as seen in (28.3).

For instance, such tasks arise when constitutive information about a simple material is provided in the form of $f(T, v)$, like for the IAPS1984 model for water/steam (cf. Footnote 14 in page 16): then the other thermodynamical potential quantities e, h, g can be derived using the appropriate Gibbs–Helmholtz relation.

3.6 Utilizing the relationships among derivatives

As the first application, let us prove (26.5) from the consequences of the properties of $s(e, v)$ in a much shorter way:

$$\left.\frac{\partial e}{\partial v}\right|_T \overset{\text{(4a)}}{=} \left.\frac{\partial e}{\partial v}\right|_s + \left.\frac{\partial e}{\partial s}\right|_v \left.\frac{\partial s}{\partial v}\right|_T = \overset{(26.1)}{-p} + \overset{(26.1)}{T} \overset{(30.2)}{\left.\frac{\partial p}{\partial T}\right|_v} . \tag{31.1}$$

In the second example, let us determine $s(T, v)$ of a simple material if its thermal constitutive function $p(T, v)$ is given while, concerning caloric information, we don't know $e(T, v)$ but only its isochoric specific heat $c_v(T, v_0)$ for any T but only a single fixed v_0. [This is quite a realistic scenario: for example, we have measured c_v for various temperature values but we had time to do this for only one value of specific volume.]

Integrating the differential

$$\mathrm{d}s(T, v) \overset{(22.4)}{=} \left.\frac{\partial s}{\partial T}\right|_v \mathrm{d}T + \left.\frac{\partial s}{\partial v}\right|_T \mathrm{d}v = \overset{(26.3)}{\frac{c_v(T, v)}{T}} \mathrm{d}T + \overset{(30.2)}{\left.\frac{\partial p}{\partial T}\right|_v} \mathrm{d}v \tag{31.2}$$

from a T_0 and *the given* v_0 distinguished in our problem, we obtain

$$\begin{aligned} s(T, v) &\overset{(23.5)}{=} s(T_0, v_0) + \int_{\tilde{T}=T_0}^{T} \left.\frac{\partial s}{\partial T}\right|_v (\tilde{T}, v_0)\, \mathrm{d}\tilde{T} + \int_{\tilde{v}=v_0}^{v} \left.\frac{\partial s}{\partial v}\right|_T (T, \tilde{v})\, \mathrm{d}\tilde{v} \\ &\overset{(31.2)}{=} s(T_0, v_0) + \int_{\tilde{T}=T_0}^{T} \frac{c_v(\tilde{T}, v_0)}{\tilde{T}} \mathrm{d}\tilde{T} + \int_{\tilde{v}=v_0}^{v} \left.\frac{\partial p}{\partial T}\right|_v (T, \tilde{v})\, \mathrm{d}\tilde{v}\,, \end{aligned} \tag{31.3}$$

which is, as a matter of fact, the answer to our problem since, fortunately, it does not demand anything more than we have. The trick was actually that we calculate the integral along such a path that, during its first part, v does not change but remains the value v_0 at which we have c_v. During the second part, we have freedom: the thermal constitutive function we had at all values T, v.

For the ideal gas model (16.2), with its constant $c_v = \frac{f}{2}R$, (31.3) yields

$$s(T, v) = s_0 + \int_{\tilde{T}=T_0}^{T} \frac{\frac{f}{2}R}{\tilde{T}} \mathrm{d}\tilde{T} + \int_{\tilde{v}=v_0}^{v} \frac{R}{\tilde{v}} \mathrm{d}\tilde{v} = s_0 + \frac{f}{2} R \ln \frac{T}{T_0} + R \ln \frac{v}{v_0} \tag{31.4}$$

[with the abbreviation $s_0 = s(T_0, v_0)$], in accord with (25.5) [recall the relationship (16.2) between T and e].

Similarly, for the Van der Waals model (16.3), we again have $c_v = \frac{f}{2}R = \text{const.}$ but now $\left.\frac{\partial p}{\partial T}\right|_v = \frac{R}{v-b}$ and, therefore,

$$s(T,v) = s_0 + \int_{\tilde{T}=T_0}^{T} \frac{\frac{f}{2}R}{\tilde{T}}\,\mathrm{d}\tilde{T} + \int_{\tilde{v}=v_0}^{v} \frac{R}{\tilde{v}-b}\,\mathrm{d}\tilde{v} = s_0 + \frac{f}{2}R\ln\frac{T}{T_0} + R\ln\frac{v-b}{v_0-b}. \tag{32.1}$$

A remarkable thing to observe here is that this result is independent of a. Consequently, $s(T,v)$ does not contain *all* constitutive information about the material. This is an apparent example of that, though s is a thermodynamical potential quantity, it is a thermodynamical potential function only in its natural variables e, v – it encodes all material properties only in its natural variables. [Reassuringly, when expressing T from the caloric $e(T,v) = \frac{f}{2}RT - \frac{a}{v}$ and substituting this $T(e,v) = \frac{2}{fR}\left(e + \frac{a}{v}\right)$ into $s(T,v)$, the resulting $s(e,v)$ will contain a.]

As the third problem, let us express $c_p - c_v$ of a simple material only using $p(T,v)$. Why this task is relevant is that, concerning *caloric* information, we may have experimental knowledge or some model expectation on $c_v(T,v)$, but we only know the *thermal* constitutive function in addition; and from these we try to gain some further *caloric* information [namely, $c_p(T,v)$] without any further measurement or assumption.[36]

$$\frac{c_p - c_v}{T} \overset{(26.3)}{=} \left.\frac{\partial s}{\partial T}\right|_p - \left.\frac{\partial s}{\partial T}\right|_v \overset{\textcircled{\scriptsize 4b}}{=} -\frac{\left.\frac{\partial s}{\partial v}\right|_T}{\left.\frac{\partial p}{\partial v}\right|_T}\left.\frac{\partial p}{\partial T}\right|_v \overset{(30.2)}{=} -\frac{\left.\frac{\partial p}{\partial T}\right|_v}{\left.\frac{\partial p}{\partial v}\right|_T}\left.\frac{\partial p}{\partial T}\right|_v, \tag{32.2}$$

$$c_p - c_v = -T\frac{\left(\left.\frac{\partial p}{\partial T}\right|_v\right)^2}{\left.\frac{\partial p}{\partial v}\right|_T} = T\frac{\left(\left.\frac{\partial p}{\partial T}\right|_v\right)^2}{-\left.\frac{\partial p}{\partial v}\right|_T}. \tag{32.3}$$

Here, the second version of the outcome is also informative since, due to the material stability inequality $\left.\frac{\partial p}{\partial v}\right|_T < 0$ again, it emphasizes that

$$c_p - c_v \geq 0\,, \qquad c_p \geq c_v \overset{\substack{(29.4),\\(18.1)}}{>} 0 \tag{32.4}$$

for any simple material.

As always, it is a good idea again to check the result for some well-known special case so let us check it for the ideal gas $\left[p(T,v) = \frac{RT}{v},\ c_v = \frac{f}{2}R,\ c_p = \frac{f+2}{2}R\right]$:

$$c_p - c_v = -T\frac{\left(\frac{R}{v}\right)^2}{-\frac{RT}{v^2}} = -T\frac{\frac{R^2}{v^2}}{-\frac{RT}{v^2}} = R\,:\ \checkmark \tag{32.5}$$

---

[36] Don't forget that, here, we consider *any* simple material so both c_v and c_p are T, v dependent in general.

The fourth application deals with the speed of sound $\mathrm{v}_{\text{sound}}$ in simple materials, for which a continuum mechanical derivation has found (expressed using density ϱ)[37]

$$\mathrm{v}_{\text{sound}} = \sqrt{\left.\frac{\partial p}{\partial \varrho}\right|_s} \,. \tag{33.1}$$

Our task is to prove that (33.1) can be rewritten in the more practical form

$$\mathrm{v}_{\text{sound}} = \sqrt{-v^2 \frac{c_p}{c_v} \left.\frac{\partial p}{\partial v}\right|_T} \,. \tag{33.2}$$

The initial step is simple: let us change the variable ϱ to $v = \frac{1}{\varrho}$:

$$\left.\frac{\partial p}{\partial \varrho}\right|_s = \left.\frac{\partial p}{\partial v}\right|_s \cdot \frac{\mathrm{d}v}{\mathrm{d}\varrho} = \left.\frac{\partial p}{\partial v}\right|_s \cdot \frac{-1}{\varrho^2} = -v^2 \left.\frac{\partial p}{\partial v}\right|_s \,. \tag{33.3}$$

From this point we continue in two ways. First, let us see an advanced usage of restricted differentials. Analogously to (31.2) leading to

$$\mathrm{d}s = \frac{c_v}{T}\,\mathrm{d}T + \left.\frac{\partial p}{\partial T}\right|_v \mathrm{d}v \,, \tag{33.4}$$

we find[38]

$$\mathrm{d}s \overset{(22.4)}{=} \left.\frac{\partial s}{\partial T}\right|_p \mathrm{d}T + \left.\frac{\partial s}{\partial p}\right|_T \mathrm{d}p = \overset{(26.3)}{\frac{c_p}{T}}\,\mathrm{d}T - \overset{(30.4)}{\left.\frac{\partial v}{\partial T}\right|_p} \mathrm{d}p \,. \tag{33.5}$$

Now, along an isentropic process, $\mathrm{d}s = 0$, (33.4) and (33.5) give, respectively,

$$0 = \frac{c_v}{T}\,\mathrm{d}T|_s + \left.\frac{\partial p}{\partial T}\right|_v \mathrm{d}v|_s \qquad \Longrightarrow \qquad \mathrm{d}v|_s = -\frac{c_v}{T \left.\frac{\partial p}{\partial T}\right|_v}\,\mathrm{d}T|_s \,, \tag{33.6}$$

$$0 = \frac{c_p}{T}\,\mathrm{d}T|_s - \left.\frac{\partial v}{\partial T}\right|_p \mathrm{d}p|_s \qquad \Longrightarrow \qquad \mathrm{d}p|_s = \frac{c_p}{T \left.\frac{\partial v}{\partial T}\right|_p}\,\mathrm{d}T|_s \,. \tag{33.7}$$

---

[37] The physical idea is that waves are small density and pressure oscillations – and, correspondingly, temperature oscillations – that are usually fast enough (high-frequency enough) so heat can be neglected: heat conduction induced by the space dependence of temperature does not have enough time to modify anything before the oscillation reverses the sign of temperature difference between two neighboring volumes of the material. Neglected $đq = T\,\mathrm{d}s$ [recall (26.2)] means $\mathrm{d}s = 0$.

[38] Using variables T, p works only within one phase, as foreshadowed in Footnote 35 on page 29.

Dividing the two outcomes yields

$$\frac{\mathrm{d}p|_s}{\mathrm{d}v|_s} \overset{\substack{\text{like in}\\(24.1)}}{=} \left.\frac{\partial p}{\partial v}\right|_s = -\frac{c_p}{c_v}\frac{\left.\frac{\partial p}{\partial T}\right|_v}{\left.\frac{\partial v}{\partial T}\right|_p} \overset{\textcircled{1}}{=} \frac{c_p}{c_v}\frac{-1}{\left.\frac{\partial T}{\partial p}\right|_v \left.\frac{\partial v}{\partial T}\right|_p} \overset{\textcircled{3}}{=} \frac{c_p}{c_v}\left.\frac{\partial p}{\partial v}\right|_T, \tag{34.1}$$

which, in light of (33.3), proves (33.2).

Alternatively, we 'attack' $\left.\frac{\partial p}{\partial v}\right|_s$ directly:

$$\left.\frac{\partial p}{\partial v}\right|_s \overset{\textcircled{3}}{=} \frac{-1}{\left.\frac{\partial v}{\partial s}\right|_p \left.\frac{\partial s}{\partial p}\right|_v} \overset{\textcircled{1}}{=} -\frac{\left.\frac{\partial s}{\partial v}\right|_p}{\left.\frac{\partial s}{\partial p}\right|_v} \overset{\frac{\textcircled{2b}}{\textcircled{2b}}}{=} -\frac{\frac{\left.\frac{\partial s}{\partial T}\right|_p}{\left.\frac{\partial v}{\partial T}\right|_p}}{\frac{\left.\frac{\partial s}{\partial T}\right|_v}{\left.\frac{\partial p}{\partial T}\right|_v}} \overset{\textcircled{1}}{=} \frac{\left.\frac{\partial s}{\partial T}\right|_p}{\left.\frac{\partial s}{\partial T}\right|_v} \frac{-1}{\left.\frac{\partial v}{\partial T}\right|_p \left.\frac{\partial T}{\partial p}\right|_v} \overset{(26.3)\ \textcircled{3}}{=} \frac{\frac{c_p}{T}}{\frac{c_v}{T}} \left.\frac{\partial p}{\partial v}\right|_T \tag{34.2}$$

so we arrive at the rhs[39] of (34.1).

It is enlighting to reformulate (33.2) as

$$\mathrm{v}_{\text{sound}} = \sqrt{v^2 \frac{c_p}{c_v}\left(-\left.\frac{\partial p}{\partial v}\right|_T\right)}. \tag{34.3}$$

Namely, it reflects how unphysical it would be if one of the material stability inequalities, $\left.\frac{\partial p}{\partial v}\right|_T < 0$ [seen in (18.2)], were violated: it[40] would make the speed of sound imaginary, which would mean, instead of oscillations sinusoidal in time, exponential blow-up of any small disturbance – an obvious sign of material instability.

Result (33.2) proves particularly simple for the ideal gas model $\left[p(T,v) = \frac{RT}{v},\ c_v = \frac{f}{2}R,\ c_p = \frac{f+2}{2}R\right]$:

$$\mathrm{v}_{\text{sound}} = \sqrt{-v^2 \frac{c_p}{c_v}\left.\frac{\partial p}{\partial v}\right|_T} = \sqrt{-v^2 \frac{f+2}{f}\frac{(-RT)}{v^2}} = \sqrt{\kappa RT} \tag{34.4}$$

with the customary notation

$$\kappa = \frac{f+2}{f}. \tag{34.5}$$

This result says that, for ideal gases, the speed of sound is independent of v – in other words, independent of density –, and increases with the square root of temperature. For example, for room-temperature air ($f = 5$, see Footnote 9 on page 15),

$$\mathrm{v}_{\text{sound}} = 341\,\frac{\mathrm{m}}{\mathrm{s}}, \tag{34.6}$$

---

[39] Right-hand side.

[40] The other factors under the square root are positive, cf. (32.4).

in 1% agreement with measurement (343.5 $\frac{\mathrm{m}}{\mathrm{s}}$). For models differing from the ideal gas one, $\mathrm{v}_{\text{sound}}$ depends on v (depends on density). This indicates that, for gases where molecules have more considerable interactions, prediction (34.4) is somewhat worse. Indeed, for CO_2 for example, it has 4% relative error.

3.7 Concavity of $s(e,v)$

For the stability of thermodynamical equilibrium, which will be discussed in $\boxed{2}$ in Sect. 4.2, an important ingredient coming from $\boxed{1}$ is the concavity property of $s(e,v)$. Therefore, let us now discuss this property.

If the second derivative (matrix) is strictly negative definite then the function is concave from above. To this end, let us calculate the second derivative of $s(e,v)$. The first derivative has already been seen to be [cf. (28.1)]

$$\mathrm{D}s\,(e,v) = \begin{pmatrix} \left.\frac{\partial s}{\partial e}\right|_v \\ \left.\frac{\partial s}{\partial v}\right|_e \end{pmatrix} = \begin{pmatrix} \frac{1}{T} \\ \frac{p}{T} \end{pmatrix} (e,v)\,. \tag{35.1}$$

Then the second derivative proves to be

$$\mathrm{D}^2 s\,(e,v) = \begin{pmatrix} \left.\frac{\partial^2 s}{\partial e^2}\right|_v & \frac{\partial^2 s}{\partial e\,\partial v} \\ \frac{\partial^2 s}{\partial v\,\partial e} & \left.\frac{\partial^2 s}{\partial v^2}\right|_e \end{pmatrix} = \begin{pmatrix} \left.\frac{\partial \frac{1}{T}}{\partial e}\right|_v & \left.\frac{\partial \frac{1}{T}}{\partial v}\right|_e \\ \left.\frac{\partial \frac{p}{T}}{\partial e}\right|_v & \left.\frac{\partial \frac{p}{T}}{\partial v}\right|_e \end{pmatrix} = \begin{pmatrix} -\frac{1}{T^2}\left.\frac{\partial T}{\partial e}\right|_v & -\frac{1}{T^2}\left.\frac{\partial T}{\partial v}\right|_e \\ \left.\frac{\partial \frac{p}{T}}{\partial e}\right|_v & \left.\frac{\partial \frac{p}{T}}{\partial v}\right|_e \end{pmatrix}. \tag{35.2}$$

It is equivalent but will be more convenient to investigate whether the matrix

$$-\mathrm{D}^2 s\,(e,v) = \begin{pmatrix} \frac{1}{T^2}\left.\frac{\partial T}{\partial e}\right|_v & \frac{1}{T^2}\left.\frac{\partial T}{\partial v}\right|_e \\ -\left(\frac{1}{T}\left.\frac{\partial p}{\partial e}\right|_v - \frac{p}{T^2}\left.\frac{\partial T}{\partial e}\right|_v\right) & -\left(\frac{1}{T}\left.\frac{\partial p}{\partial v}\right|_e - \frac{p}{T^2}\left.\frac{\partial T}{\partial v}\right|_e\right) \end{pmatrix} = \frac{1}{T^2}A \tag{35.3}$$

is strictly positive definite, where

$$A \equiv \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} = \begin{pmatrix} \left.\frac{\partial T}{\partial e}\right|_v & \left.\frac{\partial T}{\partial v}\right|_e \\ p\left.\frac{\partial T}{\partial e}\right|_v - T\left.\frac{\partial p}{\partial e}\right|_v & p\left.\frac{\partial T}{\partial v}\right|_e - T\left.\frac{\partial p}{\partial v}\right|_e \end{pmatrix}. \tag{35.4}$$

Then it is actually enough to check whether A is strictly positive definite.

A necessary and sufficient criterion to ensure this is Sylvester's criterion, which in our case says that $A_{11} > 0$ and $\det A > 0$ are the conditions to be fulfilled. $A_{11} > 0$ is easily seen via (18.1) and ①. Regarding $\det A > 0$, both material stability inequalities (18.1)–(18.2) play a role:

$$
\begin{aligned}
\det A &= \left.\frac{\partial T}{\partial e}\right|_v \left(p \left.\frac{\partial T}{\partial v}\right|_e - T \left.\frac{\partial p}{\partial v}\right|_e \right) - \left.\frac{\partial T}{\partial v}\right|_e \left(p \left.\frac{\partial T}{\partial e}\right|_v - T \left.\frac{\partial p}{\partial e}\right|_v \right) \\
&= -T \left(\left.\frac{\partial T}{\partial e}\right|_v \left.\frac{\partial p}{\partial v}\right|_e - \left.\frac{\partial p}{\partial e}\right|_v \left.\frac{\partial T}{\partial v}\right|_e \right) = -T \left.\frac{\partial T}{\partial e}\right|_v \left(\left.\frac{\partial p}{\partial v}\right|_e - \frac{\left.\frac{\partial p}{\partial e}\right|_v \left.\frac{\partial T}{\partial v}\right|_e}{\left.\frac{\partial T}{\partial e}\right|_v} \right) \\
&\overset{\textcircled{\scriptsize 4b}}{=} - \underbrace{T}_{>0} \underbrace{\left.\frac{\partial T}{\partial e}\right|_v}_{>0} \underbrace{\left.\frac{\partial p}{\partial v}\right|_T}_{<0} > 0 \; : \; \checkmark
\end{aligned}
\tag{36.1}
$$

It is to be noted that a similar argumentation proves that $e(s, v)$ is convex from above (see Problem 5).

3.8 The consequence of the entropic property on bodies

For a thermodynamical body made of a simple material, the extensive quantities can be obtained from the specific ones as

$$
V = mv\,, \quad E = me\,, \quad S = ms\,, \quad F = mf\,, \quad H = mh\,, \quad G = mg\,. \tag{36.2}
$$

The relationships among quantities of the *material* help in giving relationships among quantities of the *body*. For instance, if we aim at $E(S, V, m)$, we can proceed as

$$
E(S, V, m) = me(s, v) = me\left(\tfrac{S}{m}, \tfrac{V}{m}\right). \tag{36.3}
$$

With the aid of (25.7)–(26.1) recalled,

$$
\mathrm{d}e = T\,\mathrm{d}s - p\,\mathrm{d}v\,, \qquad T = \left.\frac{\partial e}{\partial s}\right|_v, \quad -p = \left.\frac{\partial e}{\partial v}\right|_s, \tag{36.4}
$$

we find, via differentiating composite functions,

$$
\left.\frac{\partial E}{\partial S}\right|_{V,m} = m \cdot \left.\frac{\partial e}{\partial s}\right|_v \cdot \frac{1}{m} = T\,, \qquad \left.\frac{\partial E}{\partial V}\right|_{S,m} = m \cdot \left.\frac{\partial e}{\partial v}\right|_s \cdot \frac{1}{m} = -p\,, \tag{36.5}
$$

and for the third partial derivative, usually denoted by μ and called *chemical potential*,

$$\mu = \left.\frac{\partial E}{\partial m}\right|_{S,V} \overset{(36.3)}{=} \left.\frac{\partial\left[me\left(\frac{S}{m},\frac{V}{m}\right)\right]}{\partial m}\right|_{S,V}$$

$$= e\left(\tfrac{S}{m},\tfrac{V}{m}\right) + m\left.\frac{\partial e}{\partial s}\right|_{v}\left.\frac{\partial \frac{S}{m}}{\partial m}\right|_{S} + m\left.\frac{\partial e}{\partial v}\right|_{s}\left.\frac{\partial \frac{V}{m}}{\partial m}\right|_{V}$$

$$= e + mT\cdot\left(-\frac{S}{m^2}\right) + m\,(-p)\cdot\left(-\frac{V}{m^2}\right),$$

$$\mu = e - Ts + pv \overset{(29.2)}{=} g\,. \tag{37.1}$$

Having already seen (29.3),[41] now we also have the so-called Gibbs–Duhem relation,

$$\mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p\,. \tag{37.2}$$

In parallel, (36.5)–(37.1) can be summarized as

$$\mathrm{d}E = \left.\frac{\partial E}{\partial S}\right|_{V,m}\mathrm{d}S + \left.\frac{\partial E}{\partial V}\right|_{S,m}\mathrm{d}V + \left.\frac{\partial E}{\partial m}\right|_{S,V}\mathrm{d}m\,,$$

$$\mathrm{d}E = T\,\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}m\,, \tag{37.3}$$

which is the Gibbs relation for a body.

Moreover,

$$m\,(e - Ts + pv) \overset{(37.1)}{=} m\mu\,, \qquad E - TS + pV = m\mu\,,$$

$$E = TS - pV + m\mu\,. \tag{37.4}$$

Beware that (37.4) is quite different from the similarly-looking (37.3). From (37.4), we also have

$$S = \frac{1}{T}E + \frac{p}{T}V - \frac{\mu}{T}m\,. \tag{37.5}$$

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[41] Yes, historically, two different names and notations have been introduced for the same quantity. And yes, like the two other partial derivatives of $E(S,V,m)$, μ is considered an intensive quantity – with good reason [cf. (38.8)] – and g is considered a specific extensive quantity – also with good reason [$g = G/m$].

Rearranging (37.3) provides the differential of $S(E, V, m)$,

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{p}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}m\,. \tag{38.1}$$

Again, note the essential difference between (38.1) and (37.5).

If we have two bodies – of the same material – that can exchange energy, volume[42] and mass while they are insulated from the environment then, along any allowed process, the totals are constant,

$$E_1 + E_2 = E_\mathrm{t} = \text{const.}, \qquad \Longrightarrow \qquad \mathrm{d}E_2|_\mathrm{pr} = -\,\mathrm{d}E_1|_\mathrm{pr}\,, \tag{38.2}$$

$$V_1 + V_2 = V_\mathrm{t} = \text{const.}, \qquad \Longrightarrow \qquad \mathrm{d}V_2|_\mathrm{pr} = -\,\mathrm{d}V_1|_\mathrm{pr}\,, \tag{38.3}$$

$$m_1 + m_2 = m_\mathrm{t} = \text{const.}, \qquad \Longrightarrow \qquad \mathrm{d}m_2|_\mathrm{pr} = -\,\mathrm{d}m_1|_\mathrm{pr}\,. \tag{38.4}$$

Then the change of total entropy

$$S_1(E_1, V_1, m_1) + S_2(E_2, V_2, m_2) = S_\mathrm{t}(E_1, V_1, m_1, E_2, V_2, m_2) \tag{38.5}$$

is

$$\begin{aligned}
\mathrm{d}S_\mathrm{t}|_\mathrm{pr} = \mathrm{d}S_1|_\mathrm{pr} + \mathrm{d}S_2|_\mathrm{pr} &\overset{(38.1)}{=} \frac{1}{T_1}\,\mathrm{d}E_1|_\mathrm{pr} + \frac{p_1}{T_1}\,\mathrm{d}V_1|_\mathrm{pr} - \frac{\mu_1}{T_1}\,\mathrm{d}m_1|_\mathrm{pr} \\
&+ \frac{1}{T_2}\,\mathrm{d}E_2|_\mathrm{pr} + \frac{p_2}{T_2}\,\mathrm{d}V_2|_\mathrm{pr} - \frac{\mu_2}{T_2}\,\mathrm{d}m_2|_\mathrm{pr} \\
= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\mathrm{d}E_1|_\mathrm{pr} &+ \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\mathrm{d}V_1|_\mathrm{pr} - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\mathrm{d}m_1|_\mathrm{pr}\,.
\end{aligned} \tag{38.6}$$

As one consequence of this, total entropy does not change if

$$\frac{1}{T_1} = \frac{1}{T_2}\,, \qquad \frac{p_1}{T_1} = \frac{p_2}{T_2}\,, \qquad \frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}\,. \tag{38.7}$$

This fact will come later handy, when discussing processes in $\boxed{2}$, in Sect. 4. Note that (38.7) is equivalent to

$$T_1 = T_2\,, \qquad p_1 = p_2\,, \qquad \mu_1 = \mu_2\,, \tag{38.8}$$

i.e., each of the three intensive quantities is the same for the two bodies.

Without proof, we mention here that (38.5) with restrictions (38.2)–(38.4), in other words,

$$S_\mathrm{t}|_\mathrm{pr}(E_1, V_1, m_1) \equiv S_\mathrm{t}(E_1, V_1, m_1, E_\mathrm{t} - E_1, V_\mathrm{t} - V_1, m_\mathrm{t} - m_1) \tag{38.9}$$

is concave from above, with a single maximum described by (38.7). It will be proved for a special limiting case in Sect. 4 where we are going to make use of it.

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[42] Think of a rigid piston separating two gases: if the piston moves then the increase of V_1 equals the decrease of V_2.

3.9 Switch to dimensionless quantities – in general and for VdW

Similarly to how, in fluid mechanics, rescaling quantities by constants to make them dimensionless and forming dimensionless combinations of constants are beneficial for various purposes – realizing similarity among different setups and establishing the appropriate rescaling of one setup to another, finding a universal common behaviour of systems with different sizes, and reducing the number of free parameters to the *essentially independent/free* parameters for reducing the dimension of the parameter space to scan for numerical calculations and diagrams –, the effort to reduce the number of free parameters and to have dimensionless quantities is similarly advantageous in thermodynamics. Before considering the example of the Van der Waals gas, let us summarize what dimensionful quantities are and how to practically treat them.

When we walk in a forest, we can find sticks and rods of various size. Similarly, at home we find pens, pencils, pieces of thread etc. of various size. Then we gradually invent the abstraction of *the set of possible length values.* We find that lengths can be compared whether they are of the same lengths or one is larger than the other. We can add lengths (one stick as the continuation of the other), subtract them (backward continuation), multiply them by numbers[43], with natural operation rules (associativity, distributivity *etc.*). Altogether, we find that the set of possible length values, denoted here by $\mathbb{L}$, is a one-dimensional real oriented vector space.[44] Hereafter, a one-dimensional real oriented vector space is called a *measure line*, which is a much shorter and friendlier name[45].

For the possible time interval values, we introduce another measure line, denoted by $\mathbb{T}$. For the possible mass values, yet another measure line, $\mathbb{M}$ is needed; and we will use a fourth measure line, $\mathbb{\Theta}$, for temperature values.[46] Adding a length l and a time interval t is meaningless (physically, as well as mathematically you cannot add elements coming from different sets). However, their product and their quotient are meaningful – mathematically, the product lt lives in the tensorial product of $\mathbb{L}$ and $\mathbb{T}$, $\mathbb{L}\mathbb{T}$, which is also a measure line[47], and the quotient lives in the tensorial quotient

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[43] Multiplication by integers: repeating a length n times; division by integers: folding a piece of thread into two, three *etc.*; multiplication by rational numbers: a multiplication and a division; irrational numbers: as a limit of rational ones.

[44] Initially, the set of possible length values contains only positive values but, since we frequently find it convenient to use space coordinates like $x = -3.2\,\mathrm{m}$, we extend it to negative values, too. ‘Oriented’ means here that we have distinguished one half of the vector space as positive, the other half being the negative one.

[45] A line used for quantities, that is, for measurement purposes.

[46] A more classic typography is L, T, M, and Θ – the present typographic choice reflects that, similarly to the famous mathematical sets $\mathbb{R}, \mathbb{C}, \mathbb{Z}, \mathbb{N}, \mathbb{Q}$, the measure lines $\mathbb{L}, \mathbb{T}, \mathbb{M}, \mathbb{\Theta}$ are also famous sets.

[47] The tensorial or dyadic product is usually denoted in the way $\mathbb{L} \otimes \mathbb{T}$ or $\mathbb{L} \circ \mathbb{T}$ but usually there

of $\mathbb{L}$ and $\mathbb{T}$, another measure line $\frac{\mathbb{L}}{\mathbb{T}}$. The notions of tensorial product and quotient may sound new but no need to worry: they embody just the rules we have been accustomed to since elementary school, *e.g.,* $(2l)(4t) = 8lt$ and $(6l)/(2t) = 3l/t$.[48] A quotient l/t is an example of a velocity value.[49] Similarly, a force value lives in $\mathbb{M}\frac{\mathbb{L}}{\mathbb{T}^2}$, where $\mathbb{T}^2$ abbreviates $\mathbb{T}\mathbb{T}$.[50] A tensorial power can be any real number so quantities like $l^{\frac{1}{2}}$, $l^{7.38}$, $l^{\sqrt{2}}$, l^{π}, $l^{-\pi}$ are meaningful. Negative powers satisfy $\mathbb{L}^{-p} = \mathbb{R}/\mathbb{L}^p$ and $\mathbb{L}^p\mathbb{L}^{-p} = \mathbb{R}$, just as expected since, *e.g.,* for two lengths l_1, l_2, their quotient l_1/l_2 is a real number.[51] For any positive quantity, *e.g.,* a length l, one finds $l^0 = 1$.

Functions like sin, cos, exp, and ln are not meaningful for dimensionful quantities. For example, when we try to extend the definition of exp,

$$\exp x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots , \tag{40.1}$$

to dimensionful x – *e.g.,* a length l – then each term on the rhs (see Footnote 39 on page 34) lives in different vector spaces: the first one in $\mathbb{R}$, the second in $\mathbb{L}$, the third in $\mathbb{L}^2$ *etc.* so the sum is meaningless. Only combinations

$$e^{\frac{l}{l_0}}, \qquad \ln\frac{l}{l_0} \qquad \textit{etc.} \tag{40.2}$$

are meaningful, where l_0 is also some length value.[52]

Now comes a notation we are going to find particularly useful. The fact that a length value l lives in measure line $\mathbb{L}$ will be denoted as $⟪l⟫ = \mathbb{L}$. Accordingly, with $⟪t⟫ = \mathbb{T}$ and $⟪m⟫ = \mathbb{M}$, $⟪\frac{l}{t}⟫ = \frac{⟪l⟫}{⟪t⟫} = \frac{\mathbb{L}}{\mathbb{T}}$ and $⟪m\frac{l}{t^2}⟫ = ⟪m⟫\frac{⟪l⟫}{⟪t^2⟫} = ⟪m⟫\frac{⟪l⟫}{⟪t⟫^2} = \mathbb{M}\frac{\mathbb{L}}{\mathbb{T}^2}$.

In vector spaces, one practically (*e.g.,* for numerical purposes) convenient characterization of vectors happens with the aid of a basis. Namely, any vector v of an n dimensional vector space can be uniquely characterized, with the aid of linearly independent vectors v_i $(i = 1, \ldots, n)$ by n real numbers c_i that are the coefficients

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is no danger of misunderstanding so we can simply write $\mathbb{L}\mathbb{T}$.

[48] Actually, it is just these rules that *define* the tensorial product and quotient of vector spaces.

[49] For velocity *vectors*, and for dimensionful vectors and tensors in general, the generalization is natural, see the details in the book T. Matolcsi: *Spacetime without reference frames,* Society for the Unity of Science and Technology, Budapest, 2018, ISBN 978-615-80157-3-8 (open access, `"Matolcsi_Spacetime_without_Reference_Frames_2018-07-31.pdf"` or `"Matolcsi_Spacetime_without_Reference_Frames_2018-07-31_two-page_format.pdf"` anywhere on the internet).

[50] Mathematics customarily uses such a power notation for the *Cartesian product* of sets, *e.g.,* $\mathbb{R}^2 = \mathbb{R} \times \mathbb{R}$, which contains pairs of values, like $(3.2, 1.84)$. When distinction is needed, one may write $\mathbb{T}^{\langle 2\rangle}$ for $\mathbb{T}\mathbb{T}$ but, as long as misunderstanding is unlikely, we'll follow the established style $\mathbb{T}^2$.

[51] As a special case, $\mathbb{L}^{-1}$ is actually the dual space $\mathbb{L}^*$ of $\mathbb{L}$.

[52] Accordingly, "$\log p$" of a "$\log p$–h diagram" is also meaningless, only versions like $\log(p/p_{\text{reference}})$, $\log(p/1\,\text{Pa})$, $\log(p/\text{bar})$ are meaningful.

in the expansion $\sum_{i=1}^{n} c_i v_i$. Now, a measure line is a one-dimensional vector space. Correspondingly, only one basis vector is needed to have a basis. For example, any length l can be uniquely expressed, with the aid of a nonzero length l_u as $l = c l_\mathrm{u}$. Customarily, a basis vector in a measure line is called a unit of measurement. According to the international standard, the notations { }, [ ] are introduced as

$$\{l\} = c\,, \qquad [l] = l_\mathrm{u}\,. \tag{41.1}$$

As an example, for a length $l = 3.2\,\mathrm{m}$, $\{l\} = 3.2$ and $[l] = \mathrm{m}$. Unfortunately, other usages of [ ] can also be found in the context of dimensionful quantities, putting the unit into the brackets as $[\mathrm{m}]$, or putting the measure line into the brackets as $[\mathbb{L}]$ (or $[\mathrm{L}]$) – sometimes two such different (hence, contradictory) meanings of the bracket are used on the same page of a book. Here, it will be used only as in (41.1).

Confusing, *e.g.,* the number $\{l\} = 3.2$ with l itself – assuming tacitly what the unit, say, $[l] = \mathrm{m}$, is – is a frequent type of mistake that has resulted[53] in death of people (catastrophe of a Korean Air flight, 1999) and in the waste of 300 million USD and of substantial scientific and technological effort (loss of the NASA Mars Climate Orbiter, just in the same year). Everyone should always specify the unit as well; a quantity is meaningless (and dangerous) without the unit.

As a brief repetition:

- Any dimensionful quantity lives in a one-dimensional vector space.
- A unit of measurement is a basis vector in such a one-dimensional vector space.
- The customary rules of product and quotient of dimensionful quantities also apply for the corresponding one-dimensional vector spaces (measure lines).

Units, though hopefully being standardized well enough, are arbitrary in a sense[54]. For a given specific problem, however, there may be some distinguished units, defined by the relevant constants at present. In such a case it is beneficial to use them as units (and to form, from them, units for other measure lines involved) since these embody self-scales (characteristic scales or natural scales) for the given situation. In the lucky case, we can make all our quantities dimensionless via these distinguished units.

Let us consider the example of the thermal constitutive relationship of the Van der

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[53] `https://en.wikipedia.org/wiki/Unit_of_measurement#Real-world_implications` (as of 2019-03-02)

[54] Why is the second defined as the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom, at a temperature of 0K? [Wikipedia: Second (as of 2019-03-03).]

Waals simple material,

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \tag{42.1}$$

with positive constants a, b, R. This will actually be directly useful for our later purposes like in the topic of phases.

A generally applicable strategy is to identify all the appearing quantities and constants as products of powers of the elementary measure lines $\mathbb{L}$, $\mathbb{T}$, $\mathbb{M}$, and $\mathbb{\Theta}$. For example, the specific volume v lives in $\frac{\mathbb{L}^3}{\mathbb{M}}$,

$$\langle\!\langle v \rangle\!\rangle = \frac{\mathbb{L}^3}{\mathbb{M}}\,. \tag{42.2}$$

Then a unit v_u is sought in the form

$$v_\mathrm{u} = a^{\alpha_v} \cdot b^{\beta_v} \cdot R^{\gamma_v}\,, \qquad \langle\!\langle v_\mathrm{u} \rangle\!\rangle \equiv \frac{\mathbb{L}^3}{\mathbb{M}} = \langle\!\langle a \rangle\!\rangle^{\alpha_v} \langle\!\langle b \rangle\!\rangle^{\beta_v} \langle\!\langle R \rangle\!\rangle^{\gamma_v}\,, \tag{42.3}$$

where the powers α_v, β_v, γ_v are determined from the requirement that the total of powers of $\mathbb{L}$ on the rhs be 3 (the power of $\mathbb{L}$ on the lhs), that the total of powers of $\mathbb{M}$ be -1, the total of powers of $\mathbb{T}$ be 0, and the total of powers of $\mathbb{\Theta}$ be also 0. Hence, we solve a set of linear equations for α_v, β_v, γ_v. The same procedure is to apply for $p_\mathrm{u} = a^{\alpha_p} \cdot b^{\beta_p} \cdot R^{\gamma_p}$ and for $T_\mathrm{u} = a^{\alpha_T} \cdot b^{\beta_T} \cdot R^{\gamma_T}$.

Yes, this is lengthy and tiring. Therefore, let us now see an alternative route that is much shorter. It is shorter partly because we won't need to identify the $\mathbb{L}$, $\mathbb{T}$, $\mathbb{M}$, and $\mathbb{\Theta}$ content of the measure lines of the constants and of the quantities.

Let us start by recognizing the difference $v - b$ in (42.1). Such a difference is meaningful only if

$$\langle\!\langle v \rangle\!\rangle = \langle\!\langle b \rangle\!\rangle\,. \tag{42.4}$$

This immediately suggests the straightforward choice

$$v_\mathrm{u} = b\,. \tag{42.5}$$

Next, an analogous consistency requirement tells us that

$$\langle\!\langle p \rangle\!\rangle = \left\langle\!\!\left\langle \frac{a}{v^2} \right\rangle\!\!\right\rangle. \tag{42.6}$$

We can exploit this as

$$\langle\!\langle p_\mathrm{u} \rangle\!\rangle = \langle\!\langle p \rangle\!\rangle = \left\langle\!\!\left\langle \frac{a}{v^2} \right\rangle\!\!\right\rangle = \frac{\langle\!\langle a \rangle\!\rangle}{\langle\!\langle v^2 \rangle\!\rangle} = \frac{\langle\!\langle a \rangle\!\rangle}{\langle\!\langle v \rangle\!\rangle^2} \overset{(42.4)}{=} \frac{\langle\!\langle a \rangle\!\rangle}{\langle\!\langle b \rangle\!\rangle^2} = \frac{\langle\!\langle a \rangle\!\rangle}{\langle\!\langle b^2 \rangle\!\rangle} = \left\langle\!\!\left\langle \frac{a}{b^2} \right\rangle\!\!\right\rangle, \tag{42.7}$$

$$p_\mathrm{u} = \frac{a}{b^2}\,. \tag{42.8}$$

Finally,

$$\langle\!\langle p\rangle\!\rangle = \left\langle\!\!\left\langle \frac{RT}{v-b} \right\rangle\!\!\right\rangle, \tag{43.1}$$

$$\frac{\langle\!\langle a\rangle\!\rangle}{\langle\!\langle b\rangle\!\rangle^2} = \left\langle\!\!\left\langle \frac{a}{b^2} \right\rangle\!\!\right\rangle = \langle\!\langle p_\mathrm{u}\rangle\!\rangle = \langle\!\langle p\rangle\!\rangle = \frac{\langle\!\langle RT\rangle\!\rangle}{\langle\!\langle v-b\rangle\!\rangle} = \frac{\langle\!\langle R\rangle\!\rangle\langle\!\langle T\rangle\!\rangle}{\langle\!\langle b\rangle\!\rangle} = \frac{\langle\!\langle R\rangle\!\rangle\langle\!\langle T_\mathrm{u}\rangle\!\rangle}{\langle\!\langle b\rangle\!\rangle}, \tag{43.2}$$

$$\langle\!\langle T_\mathrm{u}\rangle\!\rangle = \frac{\langle\!\langle a\rangle\!\rangle}{\langle\!\langle b\rangle\!\rangle^2}\frac{\langle\!\langle b\rangle\!\rangle}{\langle\!\langle R\rangle\!\rangle} = \frac{\langle\!\langle a\rangle\!\rangle}{\langle\!\langle b\rangle\!\rangle\langle\!\langle R\rangle\!\rangle} = \left\langle\!\!\left\langle \frac{a}{bR} \right\rangle\!\!\right\rangle, \qquad T_\mathrm{u} = \frac{a}{bR}. \tag{43.3}$$

Having obtained the distinguished units in either way, we continue with introducing the nondimensionalized quantities as[55]

$$\check{v} = \frac{v}{v_\mathrm{u}}, \qquad \check{p} = \frac{p}{p_\mathrm{u}}, \qquad \check{T} = \frac{T}{T_\mathrm{u}}. \tag{43.4}$$

In terms of them, the dimensionless counterpart of (42.1) by replacing v with $\check{v}v_\mathrm{u}$, p with $\check{p}p_\mathrm{u}$, and T with $\check{T}T_\mathrm{u}$ is[56]

$$\check{p}p_\mathrm{u} = \frac{R\check{T}T_\mathrm{u}}{\check{v}v_\mathrm{u} - b} - \frac{a}{(\check{v}v_\mathrm{u})^2}, \qquad \Bigg|\ \cdot\frac{1}{p_\mathrm{u}} \tag{43.5}$$

$$\begin{aligned}\check{p} &= \frac{1}{p_\mathrm{u}}RT_\mathrm{u}\frac{\check{T}}{\check{v}b - b} - \frac{1}{p_\mathrm{u}}\frac{a}{v_\mathrm{u}^2}\frac{1}{\check{v}^2} = \frac{b^2}{a}R\frac{a}{bR}\frac{\check{T}}{b(\check{v}-1)} - \frac{b^2}{a}\frac{a}{b^2}\frac{1}{\check{v}^2} \\ &= \frac{\check{T}}{\check{v}-1} - \frac{1}{\check{v}^2}.\end{aligned} \tag{43.6}$$

The result does not contain any dimensionful constant, thus being of a universal form. Accordingly, instead of plotting p–v diagrams for various values of a, b, R, it is enough to plot only a single $\check{p}$–$\check{v}$ diagram. Similarly, instead of running a numerical calculation many times for various values of a, b, R, you need only a single run (and then to transform the dimensionless result back to the level of dimensionful quantities).

In Sect. 3.10, we will see that, for Van der Waals-like models of simple materials – and, according to measurements in real life as well –, there is a distinguished thermodynamical state called the critical point, and then the corresponding critical

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[55] In the paper mentioned in Footnote 14 on page 16, a similar notation is used: there, the dimensionless counterparts are denoted by overbar.

[56] A general suggestion for such transformations: replace the *old* objects *in terms of the new* (and then rearrange), not vice versa: do not try starting with the new ones and attempting to apply the old expressions here or there. And it's not a waste of effort to calculate the inverse transformation: you will anyway need the inverse direction at the end, *i.e.,* when translating anything you obtained at the dimensionless level back to the initial level.

values v_c, p_c, T_c (which are, for the Van der Waals model, $v_\mathrm{c} = 3b$, $p_\mathrm{c} = \frac{1}{27}\frac{a}{b^2}$, $T_\mathrm{c} = \frac{8}{27}\frac{a}{bR}$) provide distinguished units. The corresponding dimensionless quantities are usually called *reduced quantities*. In thermodynamics, one usually encounters this latter way of nondimensionalizing since it can be performed in any model (that has a critical point) as well as for any real material (whose critical values are known precisely enough).

As we have seen, all Van der Waals models admit the same nondimensional *thermal* constitutive relationship.[57] When making their *caloric* constitutive relationship

$$e = \frac{f}{2}RT - \frac{a}{v} \tag{44.1}$$

[see (16.3)] nondimensional with these units[58] then the result is

$$\check{e} = \frac{f}{2}\check{T} - \frac{1}{\check{v}}\,. \tag{44.2}$$

One can see that no dimensionful parameters have remained in (44.2), as expected. However, we can also observe that there remained a free dimensionless parameter, f. As a consequence, Van der Waals models with different f prove to be inequivalent in the dimensionless form: the thermal parts are equivalent while the caloric parts not. Accordingly, not states (see Footnote 57) but only some of their quantities may correspond to one another. Different f leads to even qualitatively different behaviour, as seen in Footnote 17 in page 18.

Here, one can draw a general moral, actually. Namely, just because you made all your quantities and equations dimensionless, it does not mean that you have eliminated all free parameters and obtained one universal model. You may have just made the free parameters dimensionless.[59]

Nevertheless, nondimensionalization is useful: we can reduce ourselves to the *truly free* and *truly different* parameters.

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[57] This universality has led, in thermodynamics, to the “principle of corresponding states”, which can be used for models and real-life materials both, and states the expectation that the reduced thermal constitutive functions be the same for different models/materials. Among Van der Waals models, this exactly holds, as we have seen. With appropriate care, it can also be used for comparing other models, and for comparing different real-life materials, within some reasonable approximation.

[58] In case one uses the critical values v_c, p_c, T_c for nondimensionalization, it is tempting to use $e_\mathrm{c} = e(T_\mathrm{c}, v_\mathrm{c})$ for making e dimensionless – don’t do it. Instead, realize that $\langle\!\langle e \rangle\!\rangle = \langle\!\langle pv \rangle\!\rangle = \langle\!\langle p_\mathrm{c} v_\mathrm{c} \rangle\!\rangle$ and use $p_\mathrm{c} v_\mathrm{c}$ as the unit for e. All quantities must be nondimensionalized with respect to the same set of units. Otherwise you can lose consistency. For example, the entropic property related $\left.\frac{\partial e}{\partial v}\right|_T = T \left.\frac{\partial p}{\partial T}\right|_v - p$ [(26.5), (31.1)] can be violated at the dimensionless level. (True story!)

[59] Remember these words when doing fluid dynamics.

Finally, some useful formulae: how derivatives can be made dimensionless is illustrated in the following two examples.

$$\left.\frac{\partial p}{\partial v}\right|_T = \left.\frac{\partial(p_\mathrm{u}\check{p})}{\partial v}\right|_T = \left.\frac{\partial(p_\mathrm{u}\check{p})}{\partial \check{v}}\right|_T \cdot \frac{\mathrm{d}\check{v}}{\mathrm{d}v} = p_\mathrm{u}\left.\frac{\partial \check{p}}{\partial \check{v}}\right|_T \cdot \frac{1}{v_\mathrm{u}} = \frac{p_\mathrm{u}}{v_\mathrm{u}}\left.\frac{\partial \check{p}}{\partial \check{v}}\right|_T = \frac{p_\mathrm{u}}{v_\mathrm{u}}\left.\frac{\partial \check{p}}{\partial \check{v}}\right|_{\check{T}}, \tag{45.1}$$

$$\begin{aligned}\left.\frac{\partial^2 p}{\partial v^2}\right|_T &= \left.\frac{\partial\left(\left.\frac{\partial p}{\partial v}\right|_T\right)}{\partial v}\right|_T = \left.\frac{\partial\left(\frac{p_\mathrm{u}}{v_\mathrm{u}}\left.\frac{\partial \check{p}}{\partial \check{v}}\right|_{\check{T}}\right)}{\partial v}\right|_T = \left.\frac{\partial\left(\frac{p_\mathrm{u}}{v_\mathrm{u}}\left.\frac{\partial \check{p}}{\partial \check{v}}\right|_{\check{T}}\right)}{\partial \check{v}}\right|_T \cdot \frac{\mathrm{d}\check{v}}{\mathrm{d}v} \\ &= \frac{p_\mathrm{u}}{v_\mathrm{u}}\left.\frac{\partial\left(\left.\frac{\partial \check{p}}{\partial \check{v}}\right|_{\check{T}}\right)}{\partial \check{v}}\right|_{\check{T}} \cdot \frac{1}{v_\mathrm{u}} = \frac{p_\mathrm{u}}{v_\mathrm{u}^2}\left.\frac{\partial^2 \check{p}}{\partial \check{v}^2}\right|_{\check{T}}.\end{aligned} \tag{45.2}$$

3.10 The Van der Waals model in closer detail

In case of the Van der Waals model (16.3), repeated here for convenience,

$$p(T,v) = \frac{RT}{v-b} - \frac{a}{v^2}, \qquad e(T,v) = \frac{f}{2}RT - \frac{a}{v} \tag{45.3}$$

one of the material stability conditions, $\left.\frac{\partial p}{\partial v}\right|_T < 0$ [recall (18.1)–(18.2)] is not automatically satisfied. If temperature is below a so-called *critical value* T_c then there are two specific volume values, determined as the two roots of $\left.\frac{\partial p}{\partial v}\right|_T = 0$, between which $\left.\frac{\partial p}{\partial v}\right|_T > 0$. This region is therefore physically forbidden. Right at the critical temperature, these two specific volume values merge into one, the critical specific value v_c. T_c and v_c can be obtained from the set of equations

$$\left.\frac{\partial p}{\partial v}\right|_T = 0, \qquad \left.\frac{\partial^2 p}{\partial v^2}\right|_T = 0, \tag{45.4}$$

the latter expressing that the two $\left.\frac{\partial p}{\partial v}\right|_T = 0$ specific volume values, *i.e.*, the local minimum and the local maximum, have merged into a point of inflection. The solution is not hard to obtain:

$$v_\mathrm{c} = 3b, \qquad T_\mathrm{c} = \frac{8}{27}\frac{a}{bR}, \qquad p_\mathrm{c} \equiv p(T_\mathrm{c}, v_\mathrm{c}) = \frac{1}{27}\frac{a}{b^2}. \tag{45.5}$$

For a given $T < T_\mathrm{c}$, there is not a single v for a given p. Rather, there is one v value to the left of the local minimum, there is one between the local minimum and the local maximum, and there is one to the right of the local maximum. The second of these three possibilities is unphysical but the other two are valid – and describe two different phases of the same material. To the left of the local minimum is the liquid phase and to the right of the local maximum is the vapour phase. *One phase is such a (largest connected) domain of the state space of the material within which T and p together determine a state uniquely.* (Hence, determine a v uniquely.)

3.11 Thermoelasticity of solids – 1D variables and mechanical aspects

Solids – as the name suggests – are, as our experience since childhood shows, "solid". As a kind of zeroth order approximation, they do not change their size and shape (think of the table, the wall, the pavement *etc.*). As a next, first order, approximation, we recognize that they can exhibit small size and shape changes. The change of volume is not sufficient to describe the related phenomena: the necessary forces and power depend on directions as well. For example, if you press or twist a sponge in various ways, its response will be direction dependent. As a special case, twisting may leave the volume invariant but will nevertheless require force and power to exert. For characterizing the shape changes – the geometric state changes, to which mechanical changes correspond – volume, a scalar quantity, is not enough but a tensor is needed – to which a tensorial description of forces corresponds.

Here, we start with a simplified special treatment applicable for a practically important class of processes: the so-called uniaxial ones. If you elongate a rubber thread, it demonstrates that, in a uniaxial process, it is the length of the rubber thread that's important (the orthogonal directions and size changes not). In the subsequent few sections, we consider a given straight solid sample of cylindrical or prismatic shape, pulled/pressed only longitudinally (uniaxial loading). (The full, 3D, treatment will follow in Sect. 3.14.)

We intend to remain in $\boxed{1}$ so space independence of quantities is assumed along the sample.

Although being in $\boxed{1}$, we frequently parametrize changes of solids by time (*i.e.*, in applications, measurement data are usually parametrized by time). Moreover, parametrizing by time will be a good occasion for practicing for the forthcoming $\boxed{2}$ aspects and for preparing ourselves to describe inherently $\boxed{2}$ phenomena.

Accordingly, along a process, length will be treated as a function of time: $l = l(t)$, and will be called the *instantaneous length* (or *current length*).

With overdot denoting the time derivative $\frac{\mathrm{d}}{\mathrm{d}t}$, let us introduce

$$L = \dot{l}/l\,, \tag{46.1}$$

the *relative length change rate* (or strain rate).[60]

A difference between solids and liquids–gases is that solids have an own structure, somehow (microscopically-mesoscopically) encoded in the material: there is a distinguished length, size, shape: if undisturbed, unstressed, relaxed, then the body takes

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[60] The 3D generalization of this quantity is the velocity gradient tensor, see Sect. 3.14 for its use in $\boxed{2}$ and Sect. 5 for its full understanding in $\boxed{4}$.

this *relaxed length* l_{R}. For example, an elongated and then released rubber thread returns to its distinguished, preferred, favourite, length.

In many situations of solids, $l(t) \approx l_{\mathrm{R}}$, in other words, $|l(t) - l_{\mathrm{R}}|/l_{\mathrm{R}} \ll 1$. This is the so-called *small-deformation regime.* Hereafter, we will frequently remain in this regime. Then $L \approx \dot{l}/l_{\mathrm{R}}$, the cross-section area A is nearly constant, $A \approx A_{\mathrm{R}}$, and mass density is also approximately constant, $\varrho \approx \varrho_{\mathrm{R}}$.

Elasticity, explained in the uniaxial framework, is a phenomenon when a force is needed to keep l at an $l \neq l_{\mathrm{R}}$, which force depends on the relationship between l and l_{R}. For example, larger elongation of a rubber thread requires larger force. *Elastic deformedness* is the geometric state variable

$$D = \ln \frac{l}{l_{\mathrm{R}}} \tag{47.1}$$

(this is a Hencky-like definition).

A consequence is

$$L \overset{(46.1)}{=} \frac{\dot{l}}{l} \overset{(47.1)}{=} \frac{\left(e^{D} l_{\mathrm{R}}\right)^{\cdot}}{l} = \frac{\dot{D} e^{D} l_{\mathrm{R}}}{l} \overset{(47.1)}{=} \dot{D} : \quad L = \dot{D}. \tag{47.2}$$

In the small-deformation regime, because of the first-order Taylor expansion

$$\ln(1+\delta) \approx \delta \qquad (|\delta| \ll 1), \tag{47.3}$$

$$D = \ln \frac{l_{\mathrm{R}} + (l - l_{\mathrm{R}})}{l_{\mathrm{R}}} = \ln\left(1 + \frac{l - l_{\mathrm{R}}}{l_{\mathrm{R}}}\right) \approx \frac{l - l_{\mathrm{R}}}{l_{\mathrm{R}}}. \tag{47.4}$$

For small deformedness, the linear (in D) or Hooke model of elasticity reads

$$\sigma_{\mathrm{el}} = ED \qquad (|D| \ll 1) \tag{47.5}$$

for the *elastic stress* $\sigma_{\mathrm{el}} = F_{\mathrm{el}}/A$ (Cauchy stress), where F_{el} is the elastic force, and E is Young's modulus. In words, the Hooke model says that elastic stress depends on $l - l_{\mathrm{R}}$ linearly.

A good[61] finite deformedness extension of (47.5) is Hencky's elasticity model, writable in our notations as

$$\sigma_{\mathrm{el}} = \frac{\varrho}{\varrho_{\mathrm{R}}} ED. \tag{47.6}$$

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[61] It (and its 3D version) is frequently a quite good model up to $\frac{l}{l_{\mathrm{R}}} \approx 1.4$ [here, think of rubber and elastomer polymers, not metals or rocks], according to Anand and others (Anand 1979, `http://doi.org/10.1115/1.3424532`; Beatty–Stalnaker 1986, `http://doi.org/10.1115/1.3171862`; Horgan–Murphy 2009, `http://doi.org/10.1016/j.mechmat.2009.03.001`).

Mostly, we will stay in the small deformation regime. There the cross-section is approximately constant, thus $\sigma_{\mathrm{el}} \approx F_{\mathrm{el}}/A_{\mathrm{R}}$.

Next, let us introduce some quantities related to measurements:

displacement is

$$u_{t_0}(t) = l(t) - l(t_0)\,, \tag{48.1}$$

where t_0 is an initial time chosen by the experimenter (called reference time).

Strain is[62]

$$\varepsilon_{t_0}(t) = \frac{u_{t_0}(t)}{l(t_0)}\,. \tag{48.2}$$

More closely, this is called the Cauchy strain, and many other versions of strain[63] have also been introduced historically. Nevertheless, none of them are thermodynamical state variables, since they depend on an arbitrary auxiliary quantity, t_0. Both displacement and strain belong to the same class as work and heat: they are *change quantities*, related to a part of the process corresponding to a time interval – while a state quantity corresponds to a single instant.

Usually and tacitly it is assumed that $l(t_0) = l_{\mathrm{R}}$, in other words, $D(t_0) = 0$, but this is not always true. In fact, in most uniaxial experiments, a (small but non-negligible) initial pre-stress is applied to ensure that subsequent loading of the sample will be uniform across the cross-section of the sample. And, more remarkably, the measurement method ASR (Anelastic Strain Recovery) is just based on the fact that a rock sample is prestressed at, say, 600 m depth and when, by drilling, it is brought to Earth surface, its expansion towards the relaxed state is measured, from which the original stress condition at the 600 m depth is recovered.

In the small-deformation approximation,

$$L(t) \overset{(46.1)}{=} \frac{\dot{l}(t)}{l(t)} \approx \frac{\dot{l}(t)}{l(t_0)} = \frac{\dot{u}_{t_0}(t)}{l(t_0)} = \dot{\varepsilon}_{t_0}(t)\,, \tag{48.3}$$

$$\varepsilon_{t_0}(t) = \int_{t_0}^{t} \dot{\varepsilon}_{t_0}\big(\tilde{t}\big)\,\mathrm{d}\tilde{t} = \int_{t_0}^{t} L\big(\tilde{t}\big)\,\mathrm{d}\tilde{t} \overset{(47.2)}{=} \int_{t_0}^{t} \dot{D}\big(\tilde{t}\big)\,\mathrm{d}\tilde{t} = D(t) - D(t_0) : \tag{48.4}$$

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[62] Usually, t_0 is not displayed. Here, we will find it important to display it.

[63] Like the Green–Lagrange one, $\frac{1}{2}\frac{l(t)^2-l(t_0)^2}{l(t_0)^2} = \frac{1}{2}\frac{l(t)+l(t_0)}{l(t_0)}\frac{l(t)-l(t_0)}{l(t_0)} \overset{\substack{\text{small}\\ \text{def.}}}{\approx} \frac{l(t)-l(t_0)}{l(t_0)} = \varepsilon_{t_0}(t)$, and the Hencky one, $\ln\frac{l(t)}{l(t_0)} = \ln\frac{l(t_0)+\left[l(t)-l(t_0)\right]}{l(t_0)} = \ln\!\left[1+\frac{l(t)-l(t_0)}{l(t_0)}\right] \overset{\substack{\text{small}\\ \text{def.}}}{\approx} \frac{l(t)-l(t_0)}{l(t_0)} = \varepsilon_{t_0}(t)$.

$$\boxed{\varepsilon_{t_0}(t) = D(t) - D(t_0)} \tag{49.1}$$

is the small-deformation relationship between strain and elastic deformedness.

Thermal expansion is the next-level observation when we realize in practice that l_R is temperature dependent: $l_\mathrm{R} = l_\mathrm{R}(T)$.

$$\alpha = \frac{\mathrm{d}l_\mathrm{R}/\,\mathrm{d}T}{l_\mathrm{R}(T)} \tag{49.2}$$

is the *linear thermal expansion coefficient.* It's not necessarily constant, but, for small temperature changes, it can usually be assumed constant.[64]

Then, a consequence is the generalization of (47.2),

$$L = \frac{\dot{l}}{l} \overset{(47.1)}{=} \frac{\left(\mathrm{e}^D l_\mathrm{R}\right)^{\boldsymbol{\cdot}}}{l} = \frac{\dot{D}\mathrm{e}^D l_\mathrm{R}}{l} + \frac{\mathrm{e}^D \dot{l_\mathrm{R}}}{l} \overset{(47.1)\,\text{twice}}{=} \dot{D} + \frac{1}{l_\mathrm{R}}\dot{l_\mathrm{R}} = \dot{D} + \frac{1}{l_\mathrm{R}}\frac{\mathrm{d}l_\mathrm{R}}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t}\,,$$

$$L = \dot{D} + \overset{(49.2)}{\alpha\dot{T}}\ . \tag{49.3}$$

As can be seen, this is valid for finite deformation and nonconstant α in general. However, beware: in 3D, the generalization of this result is similarly simple only for small deformation: for finite deformation, it has a quite more complicated form [because, for tensors, a product is not commutative: $\mathbf{AB} \neq \mathbf{BA}$ in general so, for example, $\mathbf{A}\dot{\mathbf{A}} \neq \dot{\mathbf{A}}\mathbf{A}$ and $\left(\mathrm{e}^\mathbf{D}\right)^{\boldsymbol{\cdot}} \neq \dot{\mathbf{D}}\mathrm{e}^\mathbf{D}$].

In the small-deformation approximation, the generalization of (48.3)–(49.1) is

$$L(t) = \frac{\dot{l}(t)}{l(t)} \approx \frac{\dot{l}(t)}{l(t_0)} = \frac{\dot{u}_{t_0}(t)}{l(t_0)} = \dot{\varepsilon}_{t_0}(t)\,, \tag{49.4}$$

$$\varepsilon_{t_0}(t) = \int_{t_0}^{t} \dot{\varepsilon}_{t_0}(\tilde{t})\,\mathrm{d}\tilde{t} \approx \int_{t_0}^{t} L(\tilde{t})\,\mathrm{d}\tilde{t} \overset{(49.3)}{=} \int_{t_0}^{t}\left(\dot{D} + \alpha\dot{T}\right)(\tilde{t})\,\mathrm{d}\tilde{t}\,, \tag{49.5}$$

$$\varepsilon_{t_0}(t) = \left[D(t) - D(t_0)\right] + \alpha\left[T(t) - T(t_0)\right]\,, \tag{49.6}$$

$$\varepsilon_{t_0}(t) = D(t) - D(t_0) + \alpha\Delta T_{t_0}(t) \tag{49.7}$$

with the deviation of temperature

$$\Delta T_{t_0}(t) = T(t) - T(t_0) \tag{49.8}$$

from the *reference temperature* $T(t_0)$.

To summarize:

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[64] Analogously, Young's modulus E can also be temperature dependent, and it's our decision whether we neglect this temperature dependence.

- elastic deformedness D
  - is a thermodynamical state variable,
  - is not directly measurable (unfortunately);
- strain ε_{t_0}
  - is not a thermodynamical state variable (since it's reference time dependent),
  - is directly measurable,
  - contains an elasticity related change as well as a thermal expansion part.[65]

If – but only if – $D(t_0) = 0$, *i.e.,* $l(t_0) = l_{\mathrm{R}}$, then one can write

$$D(t) = \varepsilon_{t_0}(t) - \alpha \Delta T_{t_0}(t)\,, \tag{50.1}$$

$$\sigma_{\mathrm{el}} \overset{(47.5)}{=} E\varepsilon_{t_0} - E\alpha\Delta T_{t_0}\,, \tag{50.2}$$

expression (50.2) being known as the *Duhamel–Neumann* formula. It is usually interpreted as an extension to Hooke's law, however, in the language of D we do not need to extend anything in Hooke's law. It seems to be an extension only in the language of ε_{t_0}.

On the other side, internal energy does need a – thermal expansion induced – temperature dependent extension of elastic energy, as shown in the next section.

Actually, in the literature, the Hooke, the Hencky, and other elasticity models are also written in terms of ε_{t_0}, assuming tacitly that the initial state is the relaxed one [in other words, $D(t_0) = 0$]. Here, we work in terms of D, a thermodynamical state variable. Thus we do not need any such auxiliary assumption.

3.12 Thermoelasticity of solids – 1D thermodynamical aspects

The formula for 'infinitesimal' work is, as known from mechanics:

$$đW = F\,\mathrm{d}l\,. \tag{50.3}$$

Its density version is

$$đW/V = (F\,\mathrm{d}l)/V = (F\,\mathrm{d}l)/(Al) = (F/A)(\,\mathrm{d}l/l) = (F/A)\left(\dot{l}\,\mathrm{d}t/l\right) \overset{(46.1)}{=} \sigma L\,\mathrm{d}t\,; \tag{50.4}$$

---

[65] When plastic changes also occur then there is a plasticity related expansion part as well in ε_{t_0}, as will be seen in Sect. 4.11.

and the specific version is

$$\text{đ}w = \frac{1}{\varrho}\sigma L \, \mathrm{d}t \, . \tag{51.1}$$

As a comment, by (49.4), we also have

$$\text{đ}w = \frac{1}{\varrho}\sigma \, \mathrm{d}\varepsilon_{t_0} \tag{51.2}$$

although, as we have seen, this is misleading since, although one could use ε_{t_0} as a variable, it is not a state variable.

Hereafter, we stay in the small-deformation regime.

Let us make a comparison with the formula of ‘infinitesimal’ specific work seen for simple materials, $\text{đ}w = -p\,\mathrm{d}v$: σ here is $-p$ there; moreover, here

$$\mathrm{d}v = \frac{\mathrm{d}V}{m} = \frac{\mathrm{d}V}{\varrho V} = \frac{1}{\varrho}\frac{\mathrm{d}V}{V} = \frac{1}{\varrho}\frac{A_\mathrm{R}\,\mathrm{d}l}{A_\mathrm{R} l} = \frac{1}{\varrho}\frac{\mathrm{d}l}{l} = \frac{1}{\varrho}\frac{\dot{l}\,\mathrm{d}t}{l} = \frac{1}{\varrho}L\,\mathrm{d}t \tag{51.3}$$

so the correspondence with $\text{đ}w = -p\,\mathrm{d}v$ is accurate.[66]

The specific working rate is

$$\overset{*}{w} \equiv \frac{\text{đ}w}{\mathrm{d}t} = \frac{1}{\varrho}\sigma L \, . \tag{51.4}$$

Here, we consider stress of elastic origin only. Then

$$\overset{*}{w} = \frac{1}{\varrho}\sigma_\mathrm{el} L = \frac{1}{\varrho}\overset{(47.5)}{ED}\overset{(49.3)}{\left(\dot{D} + \alpha\dot{T}\right)} = \frac{E}{\varrho}D\dot{D} + \frac{1}{\varrho}\alpha E D\dot{T} = \dot{e}_\mathrm{el}(D) + \frac{\alpha E}{\varrho}D\dot{T} \tag{51.5}$$

with specific elastic energy

$$e_\mathrm{el}(D) = \frac{E}{2\varrho}D^2 \, . \tag{51.6}$$

In parallel, we hope to have (26.2) of simple materials, repeated here for convenience,

$$\text{đ}q = T\,\mathrm{d}s \, , \tag{51.7}$$

to be valid for solids as well. This, put together with (51.5) and the expectation (for any process)

$$\mathrm{d}e = \text{đ}q + \text{đ}w \tag{51.8}$$

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[66] In fact, the correspondence can be found perfect for finite deformation, too, in the framework shown in Sect. 3.14.

determines $e(T, D)$ and $s(T, D)$ essentially uniquely[67] if, in order to have a simple model, we wish a constant specific heat $c_{\sigma=0} = c_{D=0}$ (denoted hereafter in short by c), which is an analogue of c_p, more closely, of $c_{p=0}$:

$$e(T, D) = cT + \frac{\alpha E}{\varrho} TD + e_{\mathrm{el}}(D) = cT + \frac{\alpha E}{\varrho} TD + \frac{E}{2\varrho} D^2 \,, \tag{52.1}$$

$$s(T, D) = c \ln \frac{T}{T_{\mathrm{aux}}} + \frac{\alpha E}{\varrho} D \,, \tag{52.2}$$

where T_{aux} is an arbitrary auxiliary constant with the dimension of temperature, $\langle\!\langle T_{\mathrm{aux}} \rangle\!\rangle = \langle\!\langle T \rangle\!\rangle = \theta$ – recall that s is undetermined up to an additive constant and choosing another T_{aux} is equivalent to shifting s by an additive constant.

Therefore, we have (52.1) as the caloric constitutive function, (47.5) as the thermal one, and (52.2) as the specific entropy with which this model for solids is entropic.

It is a good idea to check[68] whether c above is $c_{D=0}$, as promised:

$$c_{D=0} = \left.\frac{đq}{\mathrm{d}T}\right|_{D=0} \overset{(51.7)}{=} T \left.\frac{\partial s}{\partial T}\right|_{D=0} \overset{(52.2)}{=} T \frac{c}{T} = c \,:\, \checkmark \,. \tag{52.3}$$

Moreover, it is worth verifying whether (52.1)–(52.2) fulfil (51.8):

$$\mathrm{d}e \overset{(51.8)}{\overset{?}{=}} T \mathrm{d}s + \overset{*}{w} \mathrm{d}t \,, \tag{52.4}$$

$$c\mathrm{d}T + \frac{\alpha E}{\varrho} D\mathrm{d}T + \frac{\alpha E}{\varrho} T\mathrm{d}D + \frac{E}{\varrho} D\mathrm{d}D \overset{?}{=} T\underbrace{\left(\frac{c}{T}\mathrm{d}T + \frac{\alpha E}{\varrho}\mathrm{d}D\right)}_{}\!\!{}^{(52.2)} + \frac{E}{\varrho} D\mathrm{d}D + \frac{\alpha E}{\varrho} D\mathrm{d}T \,{}^{(51.5)}, \tag{52.5}$$

which is an equality indeed.

Thermal expansion is a phenomenon, or special process type, when a solid is in stressless state during a time interval but changes its size because of change in temperature. In virtue of (47.5), $\sigma = 0$ imposes $D = 0$ during the time interval, implying $\dot{D} = 0$, (49.3) tells

$$L = \frac{\dot{l}}{l} = \alpha \dot{T} \,, \tag{52.6}$$

size changes due to temperature change. In fact, $l = l_{\mathrm{R}}$ during such a process. In small-deformation approximation, if t_1, t_2 are two instants within the time interval

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[67] Uniquely except for the usual unavoidable additive freedom in s, covered here by the freedom in T_{aux} (see below); the freedom in e up to an additive constant is fixed by choosing $e(0, 0) = 0$.

[68] Checking is always a good idea.

of free expansion (or contraction, naturally), then

$$\alpha[T(t_2) - T(t_1)] = \int_{t_1}^{t_2} \alpha\dot{T}(t)\,\mathrm{d}t \overset{(52.6)}{=} \int_{t_1}^{t_2} \frac{\dot{l}}{l}(t)\,\mathrm{d}t \approx \int_{t_1}^{t_2} \frac{\dot{l}(t)}{l(t_1)}\,\mathrm{d}t = \frac{l(t_2) - l(t_1)}{l(t_1)} \,: \tag{53.1}$$

a finite length change is proportional to temperature change.

Thermal stress is when length change is prohibited but temperature changes. Prohibited length change imposes $L = 0$, with which (49.3) yields

$$\dot{D} = -\alpha\dot{T}\,, \tag{53.2}$$

$$E\dot{D} = -\alpha E\dot{T}\,, \tag{53.3}$$

$$\dot{\sigma} \overset{(47.5)}{=} -\alpha E\dot{T}\,, \tag{53.4}$$

integrating which between any two instants during the process relates the change of stress to change of temperature:

$$\Delta\sigma = -\alpha E\Delta T\,. \tag{53.5}$$

Hence, change of temperature induces stress if initially there was no stress. This stress is actually of elastic nature: the body cannot take its relaxed, preferred, size so elastic stress emerges.

The Joule–Thomson effect is the third special type of process we consider here. This happens when the process is adiabatic, in other words, isentropic [see (51.7)].[69] By (52.2), while stress changes [or, while D changes, cf. (50.4)], that is necessarily accompanied by temperature change: in change rate form,

$$\dot{s}\big|_s = 0\,, \qquad c\frac{\dot{T}\big|_s}{T} \overset{(52.2)}{=} -\frac{\alpha E}{\varrho}\dot{D}\Big|_s\,, \qquad \dot{T}\Big|_s = -\frac{\alpha E}{\varrho c}T\dot{D}\Big|_s\,, \tag{53.6}$$

and in change form,

$$s(T_2, D_2) = s(T_1, D_1)\,, \tag{53.7}$$

$$c\ln\frac{T_2}{T_{\mathrm{aux}}} + \frac{\alpha E}{\varrho}D_2 \overset{(52.2)}{=} c\ln\frac{T_1}{T_{\mathrm{aux}}} + \frac{\alpha E}{\varrho}D_1\,, \tag{53.8}$$

$$c\ln\frac{T_2}{T_1} = -\frac{\alpha E}{\varrho}\left(D_2 - D_1\right)\,, \tag{53.9}$$

$$T_2 = T_1 e^{-\frac{\alpha E}{\varrho c}(D_2 - D_1)} = T_1 e^{-\frac{\alpha}{\varrho c}(\sigma_2 - \sigma_1)} \tag{53.10}$$

---

[69] For instance, fast enough mechanical experiments on a sample surrounded by nonmoving air can be quite such processes.

or, approximately,

$$T_2 - T_1 = T_1 \frac{T_2 - T_1}{T_1} \overset{(47.3)}{\approx} T_1 \ln\left(1 + \frac{T_2 - T_1}{T_1}\right) = T_1 \ln \frac{T_2}{T_1} \overset{(53.9)}{=} -T_1 \frac{\alpha E}{\varrho c}(D_2 - D_1)$$
$$= -T_1 \frac{\alpha}{\varrho c}(\sigma_2 - \sigma_1). \qquad (54.1)$$

In words, stretching induces cooling and pressing induces warming. Observe that this is a completely reversible process: by going back to initial stress, temperature returns to the initial value. This temperature change is not related to heat but to mechanical power.

As seen later, this is only one possible cause of warming during pressing: rheological changes and plastic changes also lead to warming. The two latter effects are irreversible, as it turns out. In practice, it is hard to distinguish / separate the three possible sources of warming. On the other side, if the constants ϱ, c, E, α are known then we can separate the Joule–Thomson part from temperature change, thus being able to observe the presence of rheology or the starting of plastic change by monitoring temperature. *Measuring temperature* of the sample during a process, and determining the thermodynamics-related quantities c, α, are therefore very valuable parts of *mechanical experiments.*

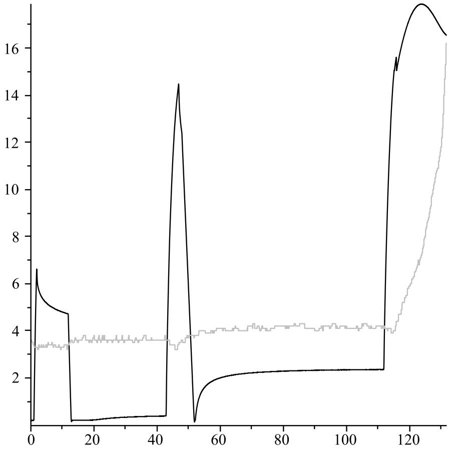

Figure 54.1 Stress (black) and temperature (grey) as functions of time, measured during uniaxial stretching of a plastic sample. During the second loading-unloading part (sharp up and down in stress), temperature decreases and then returns (Joule–Thomson effect). During the third – and final – loading, temperature decreases initially again, but when plastic change begins (when the stress curve shows a small 'hesitation' and continues less steeply), temperature starts to increase: plasticity induced dissipative warming is much stronger than Joule–Thomson related cooling. (For further details on the experiment, consult paper `https://doi.org/10.3311/PPci.8628` .)

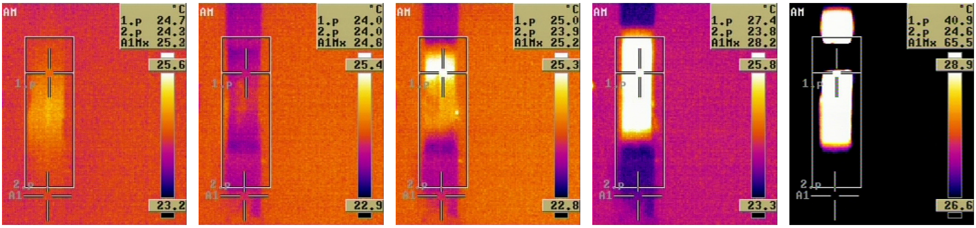

Figure 55.2 Snapshots taken by a thermal camera about the sample during the same experiment. The sample is vertical and its – somewhat thinner – medium part is monitored by the standing rectangle. Temperature values at the crosshairs are displayed numerically with labels "1.p" and "2.p". The first figure shows the initial state of essentially homogeneous temperature. In the second, the Joule–Thomson cooling is observable. In the third snapshot, heat dissipation appears due to plastic change, and in the fourth the plastic change reaches the whole thinner part of the sample. Finally, failure occurs.

3.13 Thermoelasticity of solids – the effective Young's modulus

A typical measurement of Young's modulus is to start from unstressed, *i.e.*, relaxed, state[70] and, by governing either stress σ or strain ε_{t_0}, the ratio of measured changes in stress and in strain approximates

$$E|_{\mathrm{pr}} = \frac{\mathrm{d}\sigma|_{\mathrm{pr}}}{\mathrm{d}\varepsilon_{t_0}|_{\mathrm{pr}}}\,. \tag{55.1}$$

The notation $|_{\mathrm{pr}}$ is to remind us that the outcome – called hereafter *effective Young's modulus* – is process dependent. For example, the two most important cases are the isothermal process and the adiabatic (here, equivalently: isentropic) one. A slow enough process is expected to be approximately isothermal – there is enough time for temperature to equilibrate with the environment – while a fast enough one may be nearly adiabatic.

For any type of process,

$$E|_{\mathrm{pr}} = \frac{\mathrm{d}\sigma|_{\mathrm{pr}}}{\mathrm{d}\varepsilon_{t_0}|_{\mathrm{pr}}} \overset{(47.5)}{=} E\frac{\mathrm{d}D|_{\mathrm{pr}}}{\mathrm{d}\varepsilon_{t_0}|_{\mathrm{pr}}} \overset{(50.1)}{=} E\frac{\mathrm{d}\varepsilon_{t_0}|_{\mathrm{pr}} - \alpha\,\mathrm{d}T|_{\mathrm{pr}}}{\mathrm{d}\varepsilon_{t_0}|_{\mathrm{pr}}} = E\left(1 - \frac{\alpha\,\mathrm{d}T|_{\mathrm{pr}}}{\mathrm{d}\varepsilon_{t_0}|_{\mathrm{pr}}}\right). \tag{55.2}$$

The isothermal special case is easy to evaluate: $\mathrm{d}T|_{\mathrm{pr}} = \mathrm{d}T|_{T} = 0$ so

$$E|_{T} = E\,. \tag{55.3}$$

---

[70] Some pre-stress is usually applied but let us now generously forget about that.

The adiabatic/isentropic case requires a longer calculation: we need to determine $\mathrm{d}T|_{\mathrm{pr}} \equiv \mathrm{d}T|_s$ in terms of $\mathrm{d}\varepsilon_{t_0}|_{\mathrm{pr}} \equiv \mathrm{d}\varepsilon_{t_0}|_s$. In an isentropic process, $\mathrm{d}s|_{\mathrm{pr}} = 0$, which, in light of (53.6), gives

$$\frac{c\,\mathrm{d}T|_s}{T} = -\frac{E\alpha}{\varrho}\,\mathrm{d}D|_s \overset{(50.1)}{=} -\frac{E\alpha}{\varrho}\left(\mathrm{d}\varepsilon_{t_0}|_s - \alpha\,\mathrm{d}T|_s\right) = -\frac{E\alpha}{\varrho}\,\mathrm{d}\varepsilon_{t_0}|_s + \frac{E\alpha^2}{\varrho}\,\mathrm{d}T|_s\,,$$

$$\left(\frac{c}{T} - \frac{E\alpha^2}{\varrho}\right)\mathrm{d}T|_s = -\frac{E\alpha}{\varrho}\,\mathrm{d}\varepsilon_{t_0}|_s\,, \qquad \frac{\mathrm{d}T|_s}{\mathrm{d}\varepsilon_{t_0}|_s} = \frac{-\frac{E\alpha}{\varrho}}{\frac{c}{T} - \frac{E\alpha^2}{\varrho}} = \frac{-\frac{E\alpha T}{\varrho c}}{1 - \frac{E\alpha^2 T}{\varrho c}}\,. \tag{56.1}$$

Hence,

$$E|_s \overset{(55.2)}{=} E\left(1 - \frac{\alpha\,\mathrm{d}T|_s}{\mathrm{d}\varepsilon_{t_0}|_s}\right) = E\left(1 + \frac{\frac{E\alpha^2 T}{\varrho c}}{1 - \frac{E\alpha^2 T}{\varrho c}}\right) = E\frac{1 - \frac{E\alpha^2 T}{\varrho c} + \frac{E\alpha^2 T}{\varrho c}}{1 - \frac{E\alpha^2 T}{\varrho c}}$$

$$= \frac{E}{1 - \frac{E\alpha^2 T}{\varrho c}}\,. \tag{56.2}$$

Therefore, the effective Young's modulus is process dependent (T dependent).

The process dependent dimensionless correction term $\frac{E\alpha^2 T}{\varrho c}$ is, at room temperature $T = 293\,\mathrm{K}$, well below 1 % for many solids (steel: $2.5 \cdot 10^{-3}$, granite: $3.5 \cdot 10^{-4}$, polyamide-6 plastic: $2.4 \cdot 10^{-3}$), making the adiabatic and isothermal Young's moduli approximately equal.

It can be shown that, if $\frac{E\alpha^2 T}{\varrho c} \ll 1$, $|\Delta T_{t_0}| \ll T$, and $D(t_0) = 0$, then

$$\sigma|_s = ED \approx E|_s\,\varepsilon_{t_0}|_s \qquad \text{and} \qquad e|_s \approx cT(t_0) + \frac{E|_s}{2\varrho}\left(\varepsilon_{t_0}|_s\right)^2. \tag{56.3}$$

Here, the first result is in accord with that $E|_s$ is the isentropic effective Young's modulus. In parallel, the second result says that, up to an additive constant[71], specific internal energy looks like specific *elastic* energy, written with $E|_s$ and ε_{t_0} rather than E and D [cf. (51.6)].

Note that, in the isothermal case, with $D(t_0) = 0$,

$$\varepsilon_{t_0}|_T \overset{(50.1)}{=} D|_T \qquad \Longrightarrow \qquad e|_T \overset{(52.1)}{=} cT(t_0) + \frac{\alpha E}{\varrho}T(t_0)\,\varepsilon_{t_0}|_T + \frac{E}{2\varrho}\left(\varepsilon_{t_0}|_T\right)^2. \tag{56.4}$$

This expression is of the form 'constant plus quadratic' only if the middle term is negligible, requiring $\left|\varepsilon_{t_0}|_T\right| \gg \alpha T(t_0)$. Remarkably, in the isothermal case, energy

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[71] If one dares to consider $T(t_0)$ a 'constant'.

changes not only in the form of mechanical work but, to compensate the Joule–Thomson effect originated temperature change, in form of heat as well. We can see that, in mechanics, some consequences of $\alpha \neq 0$ are negligible while some others are more relevant.

3.14 Thermoelasticity of solids – 3D variables

In the forthcoming three-dimensional treatment, we consider isotropic solid materials only, meaning that there are no direction dependent material properties.

Tensors in a three-dimensional Euclidean vector space are linear vector-to-vector functions.[72] With the aid of an orthonormal basis in the Euclidean vector space, a tensor can be represented as a 3×3 matrix. For example, during uniaxial processes, taking the first basis vector in the direction of the loading (in the *longitudinal/axial direction*) – then the two other basis vectors are orthogonal to the direction of the loading (*transversal/lateral directions*). In this basis, the tensors involved have particularly simple and convenient matrix form:

$$\{\boldsymbol{\sigma}\}_{\text{uniax}} = \begin{pmatrix} \sigma^{\parallel} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad \{\boldsymbol{\varepsilon}_{t_0}\}_{\text{uniax}} = \begin{pmatrix} \varepsilon^{\parallel}_{t_0} & 0 & 0 \\ 0 & \varepsilon^{\perp}_{t_0} & 0 \\ 0 & 0 & \varepsilon^{\perp}_{t_0} \end{pmatrix}, \tag{57.1}$$

where $\sigma^{\parallel}$ is what was simply σ in the 1D treatment (Sect. 3.11) and there are no other stress components as there is pulling/pressing in one direction only; while in strain transversal components are also possible – but are equal because of isotropy of the material and the lack of transversal forces/actions. Similarly,

$$\{\mathbf{D}\}_{\text{uniax}} = \begin{pmatrix} D^{\parallel} & 0 & 0 \\ 0 & D^{\perp} & 0 \\ 0 & 0 & D^{\perp} \end{pmatrix}, \qquad \{\mathbf{L}\}_{\text{uniax}} = \begin{pmatrix} L^{\parallel} & 0 & 0 \\ 0 & L^{\perp} & 0 \\ 0 & 0 & L^{\perp} \end{pmatrix}, \tag{57.2}$$

Without entering the technical details of the general-level definitions of $\boldsymbol{\varepsilon}_{t_0}$, $\mathbf{D}$, and $\mathbf{L}$, the uniaxial case is easy to present:

$$D^{\parallel} \overset{\text{see }(47.1)}{=} \ln \frac{l^{\parallel}}{l^{\parallel}_{\text{R}}}, \qquad L^{\parallel} \overset{\text{see }(46.1)}{=} \frac{\dot{l}^{\parallel}}{l^{\parallel}}, \qquad \varepsilon^{\parallel}_{t_0}(t) \overset{\text{see }(48.2)}{=} \frac{u^{\parallel}_{t_0}(t)}{l^{\parallel}(t_0)}, \tag{57.3}$$

$$D^{\perp} \overset{\text{see }(47.1)}{=} \ln \frac{l^{\perp}}{l^{\perp}_{\text{R}}}, \qquad L^{\perp} \overset{\text{see }(46.1)}{=} \frac{\dot{l}^{\perp}}{l^{\perp}}, \qquad \varepsilon^{\perp}_{t_0}(t) \overset{\text{see }(48.2)}{=} \frac{u^{\perp}_{t_0}(t)}{l^{\perp}(t_0)}, \tag{57.4}$$

where $l^{\parallel}$, $l^{\parallel}_{\text{R}}$, $l^{\parallel}(t_0)$, $u^{\parallel}_{t_0}(t)$ are the longitudinal counterparts of the corresponding 1D quantities, and $l^{\perp}$, $l^{\perp}_{\text{R}}$, $l^{\perp}(t_0)$, $u^{\perp}_{t_0}(t)$ are understood in any fixed transversal direction

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[72] Please refresh your knowledge concerning the mathematical notions appearing in this section.

– the definitions (57.3)–(57.4) are independent of the chosen transversal direction as being dependent only on *ratios* of transversal quantities.

As in the 1D treatment, here we also stay in the small-deformation regime.[73] The 3D generalizations of (49.3) and (49.4) are

$$\mathbf{L}^{\mathsf{S}} = \dot{\mathbf{D}} + \alpha \dot{T} \mathbf{1}\,, \tag{58.1}$$

$$\dot{\boldsymbol{\varepsilon}}_{t_0} = \mathbf{L}^{\mathsf{S}}\,, \tag{58.2}$$

where

$$\mathbf{L}^{\mathsf{S}} = \frac{\mathbf{L} + \mathbf{L}^{\mathsf{T}}}{2} \tag{58.3}$$

is the *symmetric part* of $\mathbf{L}$, defined using its transpose $\mathbf{L}^{\mathsf{T}}$, and $\mathbf{1}$ is the 3D unit tensor to which thermal expansion is proportional – as part of all material properties, thermal expansion has also been assumed isotropic so the thermal expansion change rate tensor $\alpha\dot{T}\mathbf{1}$ is proportional to the only (apart from a scalar multiplier) isotropic tensor, $\mathbf{1}$. At this place, it is to be mentioned that, in three space dimensions, $\mathbf{D}$ is a symmetric tensor[74], $\boldsymbol{\varepsilon}_{t_0}$ is also symmetric and, for simple enough solids (like the models treated here) $\boldsymbol{\sigma}$ is symmetric, too, while $\mathbf{L}$ is, in general, not symmetric.[75]

Analogously to (49.5)–(49.8), integrating (58.2) with (58.1) plugged in, we find

$$\boldsymbol{\varepsilon}_{t_0}(t) = \big[\mathbf{D}(t) - \mathbf{D}(t_0)\big] + \alpha\,\big[T(t) - T(t_0)\big]\,\mathbf{1}\,, \tag{58.4}$$

$$\boldsymbol{\varepsilon}_{t_0}(t) = \mathbf{D}(t) - \mathbf{D}(t_0) + \alpha \Delta T_{t_0}(t)\,\mathbf{1} \tag{58.5}$$

with $\Delta T_{t_0}(t) = T(t) - T(t_0)$.

In the uniaxial special case,

$$\dot{D}^{\shortparallel} + \alpha\dot{T} = L^{\shortparallel} = \dot{\varepsilon}^{\shortparallel}_{t_0}\,, \tag{58.6}$$

$$\dot{D}^{\perp} + \alpha\dot{T} = L^{\perp} = \dot{\varepsilon}^{\perp}_{t_0}\,. \tag{58.7}$$

The trace of a tensor can be computed as the sum of diagonal matrix elements in its matrix form taken in any orthonormal basis. Accordingly, in the uniaxial example,

$$\operatorname{tr}\boldsymbol{\sigma} = \sigma^{\shortparallel}\,, \qquad \operatorname{tr}\mathbf{D} = D^{\shortparallel} + 2D^{\perp} \qquad \textit{etc.} \tag{58.8}$$

---

[73] Actually, (58.2) will not need this approximation, and (58.1) will also hold for finite deformations if $\mathbf{L}^{\mathsf{A}} = \mathbf{0}$ and the principal directions of $\mathbf{L}^{\mathsf{S}}$ coincide with those of $\mathbf{D}$.

[74] Beware that, traditionally, the letter $\mathbf{D}$ frequently denotes something else: it is used as a shorthand for $\mathbf{L}^{\mathsf{S}}$. Those traditions have occupied all reasonable letters, not leaving room for introducing further quantities without a clash between notations.

[75] With Cartesian coordinate indices $i, j = 1, 2, 3$, $L_{ij} = \partial_j \mathrm{v}_i$ (velocity gradient) and $\left(\varepsilon_{t_0}\right)_{ij} = \frac{1}{2}\left[\partial_j (u_{t_0})_i + \partial_i (u_{t_0})_j\right]$.

The deviatoric part ($^{\mathrm{dev}}$) and the spherical part ($^{\mathrm{sph}}$) part of a tensor are defined as follows (shown on the example of $\mathbf{D}$):

$$\mathbf{D}^{\mathrm{sph}} = \frac{1}{3}(\operatorname{tr}\mathbf{D})\mathbf{1}\,, \qquad \mathbf{D}^{\mathrm{dev}} = \mathbf{D} - \mathbf{D}^{\mathrm{sph}}\,, \qquad \text{hence, } \textit{e.g.,} \quad \mathbf{1}^{\mathrm{sph}} = \mathbf{1}\,, \quad \mathbf{1}^{\mathrm{dev}} = \mathbf{0}\,. \tag{59.1}$$

It is easy to see that, as consequences of the definition, the trace of the deviatoric part of a tensor is zero, and the trace of the spherical part equals the trace of the original tensor, *e.g.,*

$$\operatorname{tr}\mathbf{D}^{\mathrm{dev}} = 0\,, \qquad \operatorname{tr}\mathbf{D}^{\mathrm{sph}} = \operatorname{tr}\mathbf{D}\,, \quad \text{since} \tag{59.2}$$

$$\operatorname{tr}\mathbf{D}^{\mathrm{sph}} = \operatorname{tr}\left[\frac{1}{3}\,(\operatorname{tr}\mathbf{D})\,\mathbf{1}\right] = \frac{1}{3}\,(\operatorname{tr}\mathbf{D})\,\operatorname{tr}\,[\mathbf{1}] = \frac{1}{3}(\operatorname{tr}\mathbf{D})\cdot 3 = \operatorname{tr}\mathbf{D}\,; \tag{59.3}$$

$$\operatorname{tr}\mathbf{D}^{\mathrm{dev}} = \operatorname{tr}\big(\mathbf{D} - \mathbf{D}^{\mathrm{sph}}\big) = \operatorname{tr}\mathbf{D} - \operatorname{tr}\mathbf{D}^{\mathrm{sph}} \overset{(59.3)}{=} \operatorname{tr}\mathbf{D} - \operatorname{tr}\mathbf{D} = 0\,. \tag{59.4}$$

The decomposition of a tensor to deviatoric and spherical part is unique and can be determined easily by computing the trace of the tensor to be decomposed. This decomposition is distinguished also from the aspect that it is orthogonal[76] in the sense that the product of a deviatoric tensor and a spherical one is traceless,

$$\operatorname{tr}\big(\mathbf{A}^{\mathrm{dev}}\mathbf{B}^{\mathrm{sph}}\big) = 0 \tag{59.5}$$

since

$$\operatorname{tr}\big(\mathbf{A}^{\mathrm{dev}}\mathbf{B}^{\mathrm{sph}}\big) = \operatorname{tr}\Big[\mathbf{A}^{\mathrm{dev}}\frac{1}{3}(\operatorname{tr}\mathbf{B})\mathbf{1}\Big] = \frac{1}{3}(\operatorname{tr}\mathbf{B})\operatorname{tr}\big[\mathbf{A}^{\mathrm{dev}}\mathbf{1}\big] = \frac{1}{3}(\operatorname{tr}\mathbf{B})\operatorname{tr}\big[\mathbf{A}^{\mathrm{dev}}\big] = 0. \tag{59.6}$$

As a consequence,

$$\operatorname{tr}(\mathbf{A}\mathbf{B}) = \operatorname{tr}\big[\big(\mathbf{A}^{\mathrm{dev}} + \mathbf{A}^{\mathrm{sph}}\big)\big(\mathbf{B}^{\mathrm{dev}} + \mathbf{B}^{\mathrm{sph}}\big)\big] \overset{\substack{(59.5)\\ \text{twice}}}{=} \operatorname{tr}\big[\mathbf{A}^{\mathrm{dev}}\mathbf{B}^{\mathrm{dev}}\big] + \operatorname{tr}\big[\mathbf{A}^{\mathrm{sph}}\mathbf{B}^{\mathrm{sph}}\big]\,. \tag{59.7}$$

With the antisymmetric part

$$\mathbf{B}^{\mathsf{A}} = \frac{\mathbf{B} - \mathbf{B}^{\mathsf{T}}}{2} \tag{59.8}$$

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[76] It is actually an orthogonal decomposition with respect to the scalar product $\frac{1}{2}\operatorname{tr}\big(\mathbf{A}^{\mathsf{T}}\mathbf{B}\big)$ of tensors $\mathbf{A}, \mathbf{B}$, where $^{\mathsf{T}}$ denotes the transpose as seen before.

defined analogously to (58.3), further special properties follow from the identities

$$\left(\mathbf{B}^{\mathsf{T}}\right)^{\mathsf{T}} = \mathbf{B}\,, \tag{60.1}$$

$$\operatorname{tr}\mathbf{B}^{\mathsf{T}} = \operatorname{tr}\mathbf{B}\,, \tag{60.2}$$

$$\left(\mathbf{B}^{\mathsf{S}}\right)^{\mathsf{T}} = \mathbf{B}^{\mathsf{S}}\,, \qquad \left(\mathbf{B}^{\mathsf{A}}\right)^{\mathsf{T}} = -\mathbf{B}^{\mathsf{A}}\,, \tag{60.3}$$

$$\left(\mathbf{AB}\right)^{\mathsf{T}} = \mathbf{B}^{\mathsf{T}}\mathbf{A}^{\mathsf{T}}\,, \tag{60.4}$$

$$\operatorname{tr}\left(\mathbf{AB}\right) = \operatorname{tr}\left(\mathbf{BA}\right)\,. \tag{60.5}$$

Namely, the following ones:

$$\operatorname{tr}\mathbf{B}^{\mathsf{S}} = \operatorname{tr}\mathbf{B}\,, \qquad \operatorname{tr}\mathbf{B}^{\mathsf{A}} = 0\,, \tag{60.6}$$

$$\begin{aligned} \operatorname{tr}\left(\mathbf{A}^{\mathsf{S}}\,\mathbf{B}^{\mathsf{A}}\right) &= \operatorname{tr}\left[\mathbf{A}^{\mathsf{S}}\,\frac{1}{2}\left(\mathbf{B}-\mathbf{B}^{\mathsf{T}}\right)\right] = \frac{1}{2}\left[\operatorname{tr}\left(\mathbf{A}^{\mathsf{S}}\,\mathbf{B}\right) - \operatorname{tr}\left(\mathbf{A}^{\mathsf{S}}\,\mathbf{B}^{\mathsf{T}}\right)\right] \\ &= \frac{1}{2}\left[\operatorname{tr}\left(\mathbf{A}^{\mathsf{S}}\,\mathbf{B}\right) - \operatorname{tr}\left(\mathbf{B}^{\mathsf{T}}\mathbf{A}^{\mathsf{S}}\right)\right] = \frac{1}{2}\left[\operatorname{tr}\left(\mathbf{A}^{\mathsf{S}}\,\mathbf{B}\right) - \operatorname{tr}\left(\mathbf{A}^{\mathsf{S}}\,\mathbf{B}\right)\right] = 0\,, \end{aligned} \tag{60.7}$$

$$\operatorname{tr}\left(\mathbf{A}^{\mathsf{S}}\,\mathbf{B}\right) \overset{(60.7)}{=} \operatorname{tr}\left(\mathbf{A}^{\mathsf{S}}\,\mathbf{B}^{\mathsf{S}}\right)\,. \tag{60.8}$$

The deviatoric–spherical decomposition is distinguished not only mathematically but also in the kinematic (motion related) aspects of materials[77], as well as for mechanical and thermodynamical behaviour of isotropic materials whose properties appear particularly simple in this separation.

In the uniaxial example, applying (58.8), we find[78]

$$\left\{\mathbf{D}^{\mathrm{dev}}\right\}_{\mathrm{uniax}} = \begin{pmatrix} \frac{2}{3}(D^{\shortparallel}-D^{\perp}) & 0 & 0 \\ 0 & -\frac{1}{3}(D^{\shortparallel}-D^{\perp}) & 0 \\ 0 & 0 & -\frac{1}{3}(D^{\shortparallel}-D^{\perp}) \end{pmatrix}, \tag{60.9}$$

$$\left\{\mathbf{D}^{\mathrm{sph}}\right\}_{\mathrm{uniax}} = \begin{pmatrix} \frac{1}{3}(D^{\shortparallel}+2D^{\perp}) & 0 & 0 \\ 0 & \frac{1}{3}(D^{\shortparallel}+2D^{\perp}) & 0 \\ 0 & 0 & \frac{1}{3}(D^{\shortparallel}+2D^{\perp}) \end{pmatrix}, \tag{60.10}$$

---

[77] One can show that, due to the logarithmic definition of $\mathbf{D}$ – the 3D generalization of (47.1) –, $\mathbf{D}^{\mathrm{dev}}$ is zero for volume preserving geometric shape changes, describing thus the ‘torsion-like’ part of the extension while $\mathbf{D}^{\mathrm{sph}}$ characterizes the isotropic (direction independent) part of the extension, and measures the volume change with respect to the relaxed volume.

[78] You can check them immediately: is the sum equal to (57.2)? Is $\{\mathbf{D}^{\mathrm{dev}}\}_{\mathrm{uniax}}$ traceless? Is $\{\mathbf{D}^{\mathrm{sph}}\}_{\mathrm{uniax}}$ a multiple of the unit matrix?

and

$$\{\boldsymbol{\sigma}^{\text{dev}}\}_{\text{uniax}} = \begin{pmatrix} \frac{2}{3}\sigma^{\shortparallel} & 0 & 0 \\ 0 & -\frac{1}{3}\sigma^{\shortparallel} & 0 \\ 0 & 0 & -\frac{1}{3}\sigma^{\shortparallel} \end{pmatrix}, \tag{61.1}$$

$$\{\boldsymbol{\sigma}^{\text{sph}}\}_{\text{uniax}} = \begin{pmatrix} \frac{1}{3}\sigma^{\shortparallel} & 0 & 0 \\ 0 & \frac{1}{3}\sigma^{\shortparallel} & 0 \\ 0 & 0 & \frac{1}{3}\sigma^{\shortparallel} \end{pmatrix}. \tag{61.2}$$

In the small-$\mathbf{D}$ regime – which, in an arbitrary Cartesian coordinate system, means $|D_{ij}| \ll 1$ for all components D_{ij} – $\operatorname{tr}\mathbf{D}$ measures the relative volume change with respect to the relaxed volume. This is easy to check for a uniaxial process of a body with a square cuboid (square box) relaxed shape, with relaxed longitudinal length $l^{\shortparallel}_{\text{R}}$ and transversal edges with relaxed length $l^{\perp}_{\text{R}}$. Then, at any time,

$$D^{\shortparallel} \overset{(57.3)}{=} \ln\frac{l^{\shortparallel}}{l^{\shortparallel}_{\text{R}}}, \qquad D^{\perp} \overset{(57.3)}{=} \ln\frac{l^{\perp}}{l^{\perp}_{\text{R}}}, \tag{61.3}$$

while the relative volume change with respect to the relaxed volume is

$$\begin{aligned} \frac{V - V_{\text{R}}}{V_{\text{R}}} &= \frac{V}{V_{\text{R}}} - 1 = \frac{l^{\shortparallel}(l^{\perp})^2}{l^{\shortparallel}_{\text{R}}(l^{\perp}_{\text{R}})^2} - 1 \overset{(61.3)}{=} e^{D^{\shortparallel}}\left(e^{D^{\perp}}\right)^2 - 1 = e^{D^{\shortparallel}}e^{2D^{\perp}} - 1 \\ &= e^{D^{\shortparallel}+2D^{\perp}} - 1 \overset{(58.8)}{=} e^{\operatorname{tr}\mathbf{D}} - 1 \overset{\substack{\text{small}\\\text{def.}}}{\approx} (1 + \operatorname{tr}\mathbf{D}) - 1 = \operatorname{tr}\mathbf{D}. \end{aligned} \tag{61.4}$$

Similarly,

$$\frac{V - V_{t_0}}{V_{t_0}} \overset{\substack{\text{small}\\\text{def.}}}{\approx} \operatorname{tr}\boldsymbol{\varepsilon}_{t_0}. \tag{61.5}$$

Originating from these, the spherical part of a tensor is sometimes called the volumetric part.[79]

3.15 Thermoelasticity of solids – 3D mechanical aspects

As mentioned at the beginning of Sect. 3.14, here, only isotropic materials are treated. Within this context, the 3D version of Hooke's law (47.5) is

$$\boldsymbol{\sigma}^{\text{dev}}_{\text{el}} = E^{\text{dev}}\mathbf{D}^{\text{dev}}, \tag{61.6}$$

$$\boldsymbol{\sigma}^{\text{sph}}_{\text{el}} = E^{\text{sph}}\mathbf{D}^{\text{sph}}, \tag{61.7}$$

---

[79] Actually, $\frac{V}{V_{\text{R}}} = e^{\operatorname{tr}\mathbf{D}}$ holds exactly and in general, not only in the small-deformedness regime and not only in uniaxial processes.

where the conventional notations of the coefficients are

$$E^{\mathrm{dev}} = 2G\,, \qquad E^{\mathrm{sph}} = 3K \tag{62.1}$$

and G is named shear modulus and K called bulk modulus. An equivalent form of (61.6)–(61.7) is

$$\boldsymbol{\sigma}_{\mathrm{el}} = E^{\mathrm{dev}}\,\mathbf{D} + \left(E^{\mathrm{sph}} - E^{\mathrm{dev}}\right)\mathbf{D}^{\mathrm{sph}}\,, \tag{62.2}$$

in which form the coefficients are conventionally denoted as

$$E^{\mathrm{dev}} = 2\mu\,, \qquad E^{\mathrm{sph}} - E^{\mathrm{dev}} = 3\lambda \tag{62.3}$$

and μ, λ are named Lamé coefficients.[80] To see that (62.2) follows from (61.6)–(61.7) take the sum of (61.6) and (61.7); for the reverse direction, take the $^{\mathrm{dev}}$ of (62.2) to obtain (61.6) and take the $^{\mathrm{sph}}$ of (62.2) to obtain (61.7).

In short, therefore, it is enough to write

$$\boldsymbol{\sigma}_{\mathrm{el}} = E^{\mathrm{dev}}\mathbf{D}^{\mathrm{dev}} + E^{\mathrm{sph}}\mathbf{D}^{\mathrm{sph}}\,. \tag{62.4}$$

If – but only if – $\mathbf{D}(t_0) = \mathbf{0}$ then, analogously to (50.1)–(50.2), one can write

$$\mathbf{D}(t) = \boldsymbol{\varepsilon}_{t_0}(t) - \alpha\Delta T_{t_0}(t)\,\mathbf{1}\,, \tag{62.5}$$

$$\boldsymbol{\sigma}_{\mathrm{el}} = E^{\mathrm{dev}}\boldsymbol{\varepsilon}_{t_0}^{\mathrm{dev}} + E^{\mathrm{sph}}\boldsymbol{\varepsilon}_{t_0}^{\mathrm{sph}} - E^{\mathrm{sph}}\alpha\Delta T_{t_0}\mathbf{1}\,, \tag{62.6}$$

expression (62.6) being the full 3D Duhamel–Neumann formula.

In the special case of uniaxial processes, (61.6)–(61.7) get simplified to two one-component equations. (61.7) is nontrivial in the diagonal components, each of which telling

$$\frac{1}{3}\sigma^{\shortparallel} = E^{\mathrm{sph}}\frac{1}{3}\left(D^{\shortparallel} + 2D^{\perp}\right), \qquad \sigma^{\shortparallel} = E^{\mathrm{sph}}\left(D^{\shortparallel} + 2D^{\perp}\right). \tag{62.7}$$

(61.6) is also nontrivial only in the diagonal components; the second and third being identical and actually being proportional to the first – hence, the three each tell

$$\frac{2}{3}\sigma^{\shortparallel} = E^{\mathrm{dev}}\frac{2}{3}\left(D^{\shortparallel} - D^{\perp}\right), \qquad \sigma^{\shortparallel} = E^{\mathrm{dev}}\left(D^{\shortparallel} - D^{\perp}\right). \tag{62.8}$$

---

[80] Yes, $G = \mu$ runs under two notations and two names. Yes, this G is not the Gibbs potential, and this μ is not the chemical potential or specific Gibbs potential.

(62.7)–(62.8) are equivalent to[81]

$$\sigma^{\parallel} = E D^{\parallel}\,, \qquad\qquad E = \frac{3E^{\text{sph}}E^{\text{dev}}}{2E^{\text{sph}} + E^{\text{dev}}}\,, \tag{63.1}$$

$$D^{\perp} = -\nu D^{\parallel}\,, \qquad\qquad \nu = \frac{E^{\text{sph}} - E^{\text{dev}}}{2E^{\text{sph}} + E^{\text{dev}}}\,. \tag{63.2}$$

(63.1) reproduces the 1D Hooke's law (47.5) and explains how Young's modulus E emerges as a combination of the elementary coefficients $E^{\text{dev}}, E^{\text{sph}}$. In parallel, (63.2) defines *Poisson's ratio* ν.

The classical interpretation of Poisson's ratio is

$$-\frac{\varepsilon^{\perp}_{t_0}}{\varepsilon^{\parallel}_{t_0}} \tag{63.3}$$

but, as we have seen, (63.3) equals $-\frac{D^{\perp}}{D^{\parallel}}$ [cf. (63.2)] only when $\mathbf{D}(t_0) = \mathbf{0}$, thermal expansion is negligible, rheology is not present (which is a good assumption for metals but not for rocks or plastics), and, naturally, plastic changes must also be ruled out.

The 3D elastic energy density can be written in various forms:

$$\begin{aligned} \varrho e_{\text{el}}(\mathbf{D}) = \frac{1}{2}\operatorname{tr}\left(\boldsymbol{\sigma}_{\text{el}}\mathbf{D}\right) &\overset{(59.7)}{=} \frac{1}{2}\operatorname{tr}\left(\boldsymbol{\sigma}^{\text{dev}}_{\text{el}}\mathbf{D}^{\text{dev}}\right) + \frac{1}{2}\operatorname{tr}\left(\boldsymbol{\sigma}^{\text{sph}}_{\text{el}}\mathbf{D}^{\text{sph}}\right) \\ &\overset{\substack{(61.6)\\(61.7)}}{=} \frac{E^{\text{dev}}}{2}\operatorname{tr}\left(\mathbf{D}^{\text{dev}}\mathbf{D}^{\text{dev}}\right) + \frac{E^{\text{sph}}}{2}\operatorname{tr}\left(\mathbf{D}^{\text{sph}}\mathbf{D}^{\text{sph}}\right), \end{aligned} \tag{63.4}$$

[cf. (51.6)] with the property

$$\varrho\, \mathrm{d}e_{\text{el}} = \operatorname{tr}\left(\boldsymbol{\sigma}_{\text{el}}\,\mathrm{d}\mathbf{D}\right) = E^{\text{dev}}\operatorname{tr}\left(\mathbf{D}^{\text{dev}}\,\mathrm{d}\mathbf{D}^{\text{dev}}\right) + E^{\text{sph}}\operatorname{tr}\left(\mathbf{D}^{\text{sph}}\,\mathrm{d}\mathbf{D}^{\text{sph}}\right)\,. \tag{63.5}$$

For uniaxial processes, (63.4) reduces to

$$\varrho e_{\text{el}}(\mathbf{D})\big|_{\text{uniax}} = \frac{1}{2}\operatorname{tr}\left(\boldsymbol{\sigma}_{\text{el}}\mathbf{D}\right)\big|_{\text{uniax}} = \frac{1}{2}\operatorname{tr}\begin{pmatrix} \sigma^{\parallel}D^{\parallel} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{2}\sigma^{\parallel}D^{\parallel} \overset{(63.1)}{=} \frac{E}{2}{D^{\parallel}}^2, \tag{63.6}$$

as anticipated in (51.6).

3.16 Thermoelasticity of solids – 3D thermodynamical aspects

The differences between the 3D and 1D treatments of thermoelasticity are mostly technical; there are only a few principal aspects new with respect to what we have seen in Sect. 3.12.

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[81] Check these statements. You won't regret it.

The Hookean formulae (61.6)–(61.7) for $\boldsymbol{\sigma}_{\mathrm{el}}$ remain unmodified in the presence of thermal expansion. The 3D generalizations of (52.1)–(52.2) are

$$\begin{aligned} e(T,\mathbf{D}) &= cT + \frac{\alpha E^{\mathrm{sph}}}{\varrho} T \operatorname{tr}\mathbf{D} + e_{\mathrm{el}}(\mathbf{D}) && (64.1)\\ &\overset{(63.4)}{=} cT + \frac{\alpha E^{\mathrm{sph}}}{\varrho} T \operatorname{tr}\mathbf{D} + \frac{E^{\mathrm{dev}}}{2\varrho} \operatorname{tr}\left(\mathbf{D}^{\mathrm{dev}}\mathbf{D}^{\mathrm{dev}}\right) + \frac{E^{\mathrm{sph}}}{2\varrho} \operatorname{tr}\left(\mathbf{D}^{\mathrm{sph}}\mathbf{D}^{\mathrm{sph}}\right), \\ s(T,\mathbf{D}) &= c \ln \frac{T}{T_{\mathrm{aux}}} + \frac{\alpha E^{\mathrm{sph}}}{\varrho} \operatorname{tr}\mathbf{D}, && (64.2) \end{aligned}$$

in accord with that, for isotropic materials, thermal expansion is isotropic.

(51.8) remains valid with (51.7) and

$$\frac{\text{đ}w}{\mathrm{d}t} \overset{\substack{\text{cf.}\\(51.5)}}{=} \frac{1}{\varrho} \operatorname{tr}\left(\boldsymbol{\sigma}_{\mathrm{el}}\mathbf{L}\right) \overset{(60.8)}{=} \frac{1}{\varrho} \operatorname{tr}\left(\boldsymbol{\sigma}_{\mathrm{el}}\mathbf{L}^{\mathsf{S}}\right) \overset{(58.1)}{=} \frac{1}{\varrho} \operatorname{tr}\left[\boldsymbol{\sigma}_{\mathrm{el}}\left(\dot{\mathbf{D}} + \alpha\dot{T}\mathbf{1}\right)\right], \qquad (64.3)$$

which can be further rewritten with the help of (59.7) when needed.

For adiabatic processes, (53.6) gets generalized to

$$\dot{s}\big|_s = 0, \qquad c\frac{\dot{T}\big|_s}{T} = -\frac{\alpha E^{\mathrm{sph}}}{\varrho} \operatorname{tr}\dot{\mathbf{D}}\Big|_s, \qquad \dot{T}\Big|_s = -\frac{\alpha E^{\mathrm{sph}}}{\varrho c} T \operatorname{tr}\dot{\mathbf{D}}\Big|_s. \qquad (64.4)$$

In the uniaxial case, this reduces to

$$\begin{aligned} \dot{T}\Big|_s &\overset{(60.10)}{=} -\frac{\alpha E^{\mathrm{sph}}}{\varrho c} T \cdot 3 \cdot \frac{1}{3}\left(\dot{D}^{\parallel}\Big|_s + 2\dot{D}^{\perp}\Big|_s\right) \overset{(63.2)}{=} -\frac{\alpha E^{\mathrm{sph}}}{\varrho c} T(1-2\nu)\,\dot{D}^{\parallel}\Big|_s && (64.5)\\ &\overset{(63.2)}{=} -\frac{\alpha E^{\mathrm{sph}}}{\varrho c} T\left(\frac{2E^{\mathrm{sph}} + E^{\mathrm{dev}}}{2E^{\mathrm{sph}} + E^{\mathrm{dev}}} - 2\frac{E^{\mathrm{sph}} - E^{\mathrm{dev}}}{2E^{\mathrm{sph}} + E^{\mathrm{dev}}}\right)\dot{D}^{\parallel}\Big|_s \overset{(63.1)}{=} -\frac{\alpha E}{\varrho c} T\,\dot{D}^{\parallel}\Big|_s, \end{aligned}$$

as seen in (53.6).

4 Temporal thermodynamics

In $\boxed{2}$, we take thermo*dynamics* seriously: processes – functions of time[82] – are *determined* as solutions of ordinary differential equations that describe how systems act on each other.

In $\boxed{2}$, one can already have models that reflect thermodynamical irreversibility, mechanical, electromagnetic and other phenomena (much better) incorporated, while the description remains mathematically simple. Accordingly, $\boxed{2}$ is a good framework for models in/for 'smart' actuators, sensors, cube satellites, implants *etc.*that monitor their own state and their environment by some simple means and run a small, fast, and low-resource program to make decisions about their operation.

4.1 The dynamical equations

Let us take the example of one body and one environment interacting. Here, 'environment' is a body much larger than the other, so much larger that its intensive quantities are not modified by the interaction. Its extensive quantities change in time obeying the conservation laws (38.2)–(38.4):

$$E(t) + E_\mathrm{a}(t) = E_\mathrm{t} = \text{const.}, \qquad \Longrightarrow \qquad \dot{E}_\mathrm{a} = -\dot{E}\,, \tag{65.1}$$

$$V(t) + V_\mathrm{a}(t) = V_\mathrm{t} = \text{const.}, \qquad \Longrightarrow \qquad \dot{V}_\mathrm{a} = -\dot{V}\,, \tag{65.2}$$

with masses considered constant for simplicity ('a' stands for 'ambient' and denotes the quantities of the environment). Correspondingly, the mass variables will not be displayed in the constitutive functions.

The body is described by the constitutive equations

$$p(E,V), \;\; T(E,V) \qquad \text{or} \qquad p(T,V), \;\; E(T,V) \tag{65.3}$$

and the environment by

$$p_\mathrm{a}(E_\mathrm{a},V_\mathrm{a}), \;\; T_\mathrm{a}(E_\mathrm{a},V_\mathrm{a}) \qquad \text{or} \qquad p_\mathrm{a}(T_\mathrm{a},V_\mathrm{a}), \;\; E_\mathrm{a}(T_\mathrm{a},V_\mathrm{a})\,. \tag{65.4}$$

The balance equations for the extensive quantities as differential equations in time, dictating the rate of change of each quantity, with the *interaction functions* $\overset{*}{Q} = \overset{*}{Q}(T,T_\mathrm{a})$ [heating rate, $\overset{*}{Q} = \text{đ}Q/\mathrm{d}t$], $\overset{*}{W} = \overset{*}{W}(p,p_\mathrm{a})$ [working rate, $\overset{*}{W} = \text{đ}W/\mathrm{d}t = -p\overset{*}{V} = -p\,\mathrm{d}V/\mathrm{d}t$], and $\overset{*}{V} = \overset{*}{V}(p,p_\mathrm{a})$ [the interaction function dictating the volume

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[82] Time dependence is thence explicit. Space dependence is not considered in $\boxed{2}$ – more closely, continuous space dependence is not considered while discrete space dependence is allowed: we have discretely many, themselves homogeneous, thermodynamical bodies.

change rate] are chosen as

$$\dot{E} = \overset{*}{Q} + \overset{*}{W}\,, \qquad i.e., \qquad \mathrm{d}E/\mathrm{d}t = \overset{*}{Q}\bigl(T(t), T_\mathrm{a}\bigr) + \overset{*}{W}\bigl(p(t), p_\mathrm{a}\bigr) \tag{66.1}$$

$$\dot{V} = \overset{*}{V}\,, \qquad i.e., \qquad \mathrm{d}V/\mathrm{d}t = \overset{*}{V}\bigl(p(t), p_\mathrm{a}\bigr) \tag{66.2}$$

$$\overset{*}{W} = -p\overset{*}{V}\,, \qquad i.e., \qquad \overset{*}{W}\bigl(p(t), p_\mathrm{a}\bigr) = -p(t)\,\overset{*}{V}\bigl(p(t), p_\mathrm{a}\bigr)\,. \tag{66.3}$$

One of the most frequently used examples for the heating rate interaction function $\overset{*}{Q}(T, T_\mathrm{a})$ is

$$\overset{*}{Q}(T, T_\mathrm{a}) = -\Gamma\,(T - T_\mathrm{a})\,, \tag{66.4}$$

the case of heat transfer via convection, where the positive coefficient Γ is the product of the heat transfer coefficient and of the surface area through which heat transfer occurs.[83] Another engineeringly important example is

$$\overset{*}{Q}(T, T_\mathrm{a}) = -\Gamma_\mathrm{rad}\bigl(T^4 - T_\mathrm{a}^4\bigr)\,, \tag{66.5}$$

describing radiative heat transfer (with another positive coefficient Γ_rad that depends on surface area and other factors). At the general level, we impose the requirement (satisfied by both of these examples)

$$\overset{*}{Q}(T, T_\mathrm{a}) \begin{cases} > 0 & \text{if} \quad T < T_\mathrm{a}\,, \\ = 0 & \text{if} \quad T = T_\mathrm{a}\,, \\ < 0 & \text{if} \quad T > T_\mathrm{a}\,. \end{cases} \tag{66.6}$$

For $\overset{*}{V}$, an example appearing in engineering practice is

$$\overset{*}{V}(p, p_\mathrm{a}) = \Theta\,(p - p_\mathrm{a})\,, \tag{66.7}$$

relevant for hydraulic elements (with some positive coefficient Θ depending on geometric and other characteristics, see more on this under the term 'Hagen–Poiseuille equation'[84]). At the general level, we require[85]

$$\overset{*}{V}(p, p_\mathrm{a}) \begin{cases} > 0 & \text{if} \quad p > p_\mathrm{a}\,, \\ = 0 & \text{if} \quad p = p_\mathrm{a}\,, \\ < 0 & \text{if} \quad p < p_\mathrm{a}\,. \end{cases} \tag{66.8}$$

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[83] The minus sign before the coefficient describes the natural expectation that the heating-type energy increase rate of the body, $\overset{*}{Q}$, is positive if the environment is warmer than the body.

[84] 'Darcy's law', for capillary flows, is also of this form.

[85] Here, we expect expansion ($\mathrm{d}V/\mathrm{d}t > 0$) if the body has larger pressure than that of the environment.

Our system of ordinary differential equations, (66.1)–(66.3) supplemented by the algebraic equations/relationships (65.3)–(65.4), with initial conditions on E and V at some initial time t_0, determines the process uniquely.

As interpretation, (66.1) is the first law of thermodynamics for our system, in other words, the balance of energy. Later, we will see that (66.2) embodies the balance of momentum in this system.[86] Historically, thermodynamics has focused on energy – probably that's why the dynamical point of view is a later development: energy balance in itself is not enough to have a closed set of dynamical equations so progress was possible only having recognized what other dynamical aspects are available (and necessary).

In (37.3), we have seen the Gibbs relation for a body. If the small changes in (37.3) correspond to a small time interval $\mathrm{d}t$ along a process then dividing (37.3) by $\mathrm{d}t$ yields

$$\dot{E} = T\dot{S} - p\dot{V} + \mu\dot{m} \,. \tag{67.1}$$

Bearing in mind that we have constant mass here, comparing (67.1) against (66.1) with (66.3) and (66.2) shows that

$$T\dot{S} = \overset{*}{Q} \,. \tag{67.2}$$

This is the temporal thermodynamical formulation of the customary formula

$$T\,\mathrm{d}S = \text{đ}Q \,, \tag{67.3}$$

which is rewritten now as

$$T\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\text{đ}Q}{\mathrm{d}t} \,, \qquad T\dot{S} = \overset{*}{Q} \,. \tag{67.4}$$

4.2 The second law of thermodynamics in temporal thermodynamics

Let us identify the stationary process(es) of this system. Both because of usual mathematical terminology (see Sect. 4.3) and because of usual thermodynamical terminology, such a solution will be called *equilibrium* here. Now, time independence of V tells us $\overset{*}{V} = 0$ via (66.2), which, by (66.8), imposes $p = p_\mathrm{a}$. Next, $\overset{*}{V} = 0$ also induces $\overset{*}{W} = 0$ [see (66.3)]. As time independence of E says $\dot{E} = 0$, by (66.1) we find $\overset{*}{Q} = 0$, and arrive at $T = T_\mathrm{a}$ due to (66.6). Altogether, we have found that the equilibrium solution must satisfy the equality of the intensive quantities,

$$T = T_\mathrm{a} \,, \qquad p = p_\mathrm{a} \,. \tag{67.5}$$

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[86] And, naturally, when mass is also allowed to change then the balance of mass is also needed.

As the next point to investigate, let us check how total entropy, understood naturally in the sense (38.9), changes along a process allowed for our system. If the small changes in (38.1) correspond to a small time interval $\mathrm{d}t$ along a process then dividing (38.1) by $\mathrm{d}t$ yields

$$\dot{S} = \frac{1}{T}\dot{E} + \frac{p}{T}\dot{V} - \frac{\mu}{T}\dot{m}, \tag{68.1}$$

the last term being zero for us now. Analogously,

$$\dot{S}_\mathrm{a} = \frac{1}{T_\mathrm{a}}\dot{E}_\mathrm{a} + \frac{p_\mathrm{a}}{T_\mathrm{a}}\dot{V}_\mathrm{a} - \frac{\mu_\mathrm{a}}{T_\mathrm{a}}\dot{m}_\mathrm{a} \overset{(65.1)\text{–}(65.2)}{=} -\frac{1}{T_\mathrm{a}}\dot{E} - \frac{p_\mathrm{a}}{T_\mathrm{a}}\dot{V} + \frac{\mu_\mathrm{a}}{T_\mathrm{a}}\dot{m} \tag{68.2}$$

(the last term being zero again). Consequently,

$$\begin{aligned}
\dot{S}_\mathrm{t}\Big|_\mathrm{pr} &= \left(\frac{1}{T} - \frac{1}{T_\mathrm{a}}\right)\dot{E} + \left(\frac{p}{T} - \frac{p_\mathrm{a}}{T_\mathrm{a}}\right)\dot{V} \\
&\overset{(66.1)\text{–}(66.2)}{=} \left(\frac{1}{T} - \frac{1}{T_\mathrm{a}}\right)\left(\overset{*}{Q} + \overset{*}{W}\right) + \left(\frac{p}{T} - \frac{p_\mathrm{a}}{T_\mathrm{a}}\right)\overset{*}{V} \\
&\overset{(66.3)}{=} \left(\frac{1}{T} - \frac{1}{T_\mathrm{a}}\right)\overset{*}{Q} - p\left(\frac{1}{T} - \frac{1}{T_\mathrm{a}}\right)\overset{*}{V} + \left(\frac{p}{T} - \frac{p_\mathrm{a}}{T_\mathrm{a}}\right)\overset{*}{V} \\
&= \left(\frac{1}{T} - \frac{1}{T_\mathrm{a}}\right)\overset{*}{Q} + \left(\frac{p}{T_\mathrm{a}} - \frac{p_\mathrm{a}}{T_\mathrm{a}}\right)\overset{*}{V} = \frac{T_\mathrm{a} - T}{T_\mathrm{a}T}\overset{*}{Q} + \frac{p - p_\mathrm{a}}{T_\mathrm{a}}\overset{*}{V}
\end{aligned} \tag{68.3}$$

which, by virtue of (66.6) and (66.8) (and because of $T, T_\mathrm{a} > 0$) contains two non-negative terms, the first being zero only for $T = T_\mathrm{a}$ and the second only for $p = p_\mathrm{a}$ so, altogether, we have found that

$$\dot{S}_\mathrm{t}\Big|_\mathrm{pr} \begin{cases} = 0 & \text{if } T = T_\mathrm{a} \text{ and } p = p_\mathrm{a}, \\ > 0 & \text{otherwise}. \end{cases} \tag{68.4}$$

In words, total entropy increases along processes, except for in equilibrium.

Next, let us see other important properties of total entropy (considered still as a function of E and V): that it's concave from above, and that it has a strict maximum at equilibrium.

By virtue of (37.5), applied on S_a, and (65.1)–(65.2),

$$\begin{aligned}
S_\mathrm{t}(E, V) &= S + \frac{1}{T_\mathrm{a}}E_\mathrm{a} + \frac{p_\mathrm{a}}{T_\mathrm{a}}V_\mathrm{a} - \frac{\mu_\mathrm{a}}{T_\mathrm{a}}m_\mathrm{a} = S + \frac{1}{T_\mathrm{a}}(E_\mathrm{t} - E) + \frac{p_\mathrm{a}}{T_\mathrm{a}}(V_\mathrm{t} - V) - \frac{\mu_\mathrm{a}}{T_\mathrm{a}}m_\mathrm{a} \\
&= S(E, V) - \frac{1}{T_\mathrm{a}}E - \frac{p_\mathrm{a}}{T_\mathrm{a}}V + \text{const.} = ms\left(\frac{E}{m}, \frac{V}{m}\right) - \frac{1}{T_\mathrm{a}}E - \frac{p_\mathrm{a}}{T_\mathrm{a}}V + \text{const.},
\end{aligned} \tag{68.5}$$

the derivative of which is

$$\mathrm{D}S_{\mathrm{t}}(E,V)=\begin{pmatrix}\frac{\partial S_{\mathrm{t}}}{\partial E}\Big|_V\\[2ex]\frac{\partial S_{\mathrm{t}}}{\partial V}\Big|_E\end{pmatrix}=\begin{pmatrix}m\,\frac{\partial s}{\partial e}\Big|_v\cdot\frac{1}{m}-\frac{1}{T_{\mathrm{a}}}\\[2ex]m\,\frac{\partial s}{\partial v}\Big|_e\cdot\frac{1}{m}-\frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\end{pmatrix}\overset{(28.1)}{=}\begin{pmatrix}\frac{\partial s}{\partial e}\Big|_v-\frac{1}{T_{\mathrm{a}}}\\[2ex]\frac{\partial s}{\partial v}\Big|_e-\frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\end{pmatrix}=\begin{pmatrix}\frac{1}{T}-\frac{1}{T_{\mathrm{a}}}\\[2ex]\frac{p}{T}-\frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\end{pmatrix}, \tag{69.1}$$

in analogy to (38.6), actually. Then, on one side, we see that the first derivative is zero if (and only if) in analogy to (38.7),

$$T=T_{\mathrm{a}}\,,\qquad p=p_{\mathrm{a}}\,. \tag{69.2}$$

which is the condition for equilibrium [see (67.5)]. In parallel, the second derivative is the derivative of

$$\begin{pmatrix}\frac{\partial s}{\partial e}\Big|_v-\frac{1}{T_{\mathrm{a}}}\\[2ex]\frac{\partial s}{\partial v}\Big|_e-\frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\end{pmatrix} \tag{69.3}$$

[as seen in (69.1)], in which the constants $\frac{1}{T_{\mathrm{a}}}$ and $\frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}$ drop out from a subsequent differentiation, while

$$\begin{pmatrix}\frac{\partial}{\partial E}\\[2ex]\frac{\partial}{\partial V}\end{pmatrix}=\begin{pmatrix}\frac{1}{m}\frac{\partial}{\partial e}\\[2ex]\frac{1}{m}\frac{\partial}{\partial v}\end{pmatrix}, \tag{69.4}$$

hence

$$\mathrm{D}^2S_{\mathrm{t}}(E,V)=\tfrac{1}{m}\,\mathrm{D}^2s\,(e,v)\;, \tag{69.5}$$

which has been found to be concave from above (cf. Sect. 3.7 on page 35).

As one consequence, equilibrium is a strict maximum (first derivative is zero, second derivative is strictly negative definite). Moreover, the summary of this section is that, along processes, total entropy increases towards its strict maximum, equilibrium (except for equilibrium itself, which is a stationary process with time independent total entropy). This previous sentence is actually our formulation of the second law of thermodynamics (for the example system 'body plus environment' considered here).

Total entropy of a body and an environment is sometimes called *extropy*. A more frequently appearing related notion is *exergy*, which is extropy multiplied by the temperature of the environment. Up to a constant multiplier, extropy and exergy are the same. Why the latter notion is more popular is that it is of energy dimension[87] so it brings entropy to common ground with the various well-known energy types.

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[87] $\mathbb{M}\frac{\mathbb{L}^2}{\mathbb{T}^2}$, naturally.

Traditionally, power plants have been optimized with respect to thermal efficiency, in other words, with respect to energy efficiency. Recently, optimization with respect to exergy is spreading. This latter approach wants to reduce the amount of irreversibility created during the processes. A generalization of exergy analysis is when various costs are also incorporated in the notion of exergy, making it a powerful tool for business decisions regarding power plants.

4.3 Asymptotic stability and the Lyapunov function

In the previous section, the state of the system was described by two state quantities, E and V, a state ζ was characterized as $\zeta = \begin{pmatrix} E \\ V \end{pmatrix}$, the state space $\mathcal{Z}$ (recall Sect. 3.1) was thus a two-dimensional vector space, a process was parametrized by time, $\zeta(t) = \begin{pmatrix} E(t) \\ V(t) \end{pmatrix}$, and was determined by a set of differential equations,

$$\frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} E \\ V \end{pmatrix} = \begin{pmatrix} \overset{*}{Q} + \overset{*}{W} \\ \overset{*}{V} \end{pmatrix} \tag{70.1}$$

[cf. (66.1)–(66.2)], or, abbreviating the rhs (see Footnote 39 on page 34) of (70.1) by f, [88]

$$\frac{\mathrm{d}\zeta}{\mathrm{d}t} = \mathrm{f}\left(\zeta(t)\right) \tag{70.2}$$

in short.

An ordinary differential equation[89] like (70.2) where the rhs does not depend on t explicitly (but only via the t dependence of ζ, as a composite function) is called *autonomous.* If $\mathrm{f}(\zeta_{\mathrm{e}}) = 0$ at an ζ_{e} then ζ_{e} as a stationary process ($\mathrm{d}\zeta_{\mathrm{e}}/\mathrm{d}t = 0$, $\zeta_{\mathrm{e}} = \text{const.}$) is actually a solution of (70.2) [a rather special solution indeed]. Such a solution is called an *equilibrium* of the autonomous differential equation, as mentioned in the previous section.

An equilibrium ζ_{e} is named *stable* if processes starting from a neighbourhood $\mathcal{B}_1$ of ζ_{e} in $\mathcal{Z}$ (as initial conditions at some t_0) will subsequently stay within some neighbourhood $\mathcal{B}_2$ of ζ_{e} ($\mathcal{B}_2$ is usually larger than $\mathcal{B}_1$). In parallel, an equilibrium ζ_{e} is *attractive* if processes starting from a neighbourhood $\mathcal{B}$ of ζ_{e} in $\mathcal{Z}$ will tend to ζ_{e} [$\zeta(t) \to \zeta_{\mathrm{e}}$] as $t \to \infty$. As a combination, an equilibrium ζ_{e} is *asymptotically stable* if it is stable and attractive.

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[88] For gourmets: f maps from $\mathcal{Z}$ to $\mathcal{Z}/\mathbb{T}$, as can be seen dimensionally from (70.2).

[89] A system of differential equations for scalar unknowns can also be considered as a single differential equation for a vector unknown, a vector formed by those scalars.

Note how important stability and asymptotic stability are for engineering. Stability provides robustness under perturbations/disturbances. Moreover, asymptotic stability ensures that the effect of perturbations/disturbances is not only bounded but will diminish as time passes.

Correspondingly, it is important to determine whether an equilibrium of an autonomous ordinary differential equation is asymptotically stable[90]. For linear differential equations, *i.e.,* when f is a linear map on $\mathcal{Z}$, investigating (asymptotic) stability is usually not very hard – the eigenvalues of the linear map are to be analyzed. On the contrary, for nonlinear cases the task is more difficult. One possibility is linearization of f around ζ_e and provides results in a neighbourhood of ζ_e, which is only partial success. Observe that, in thermodynamics, most situations are expected to be nonlinear – see the example of (66.3): in $\overset{*}{W}$, $\overset{*}{V}$ is some function of p [91] and is multiplied by p.

This is the point where the Lyapunov function technique comes helpful. If a scalar function $\mathcal{L}$ defined on $\mathcal{Z}$ satisfies both of the following two conditions:

- it has a strict maximum at ζ_e,
- its directional derivative in the direction of f, *i.e.,* $\mathrm{D_f}\mathcal{L} \equiv \mathrm{D}\mathcal{L} \cdot \mathrm{f}$, is positive except for at ζ_e [where it is necessarily zero, thanks to $\mathrm{f}(\zeta_\mathrm{e}) = 0\,,$]

then, according to Lyapunov's theorem[92], ζ_e is asymptotically stable.[93]

Let us observe that the second of these conditions is equivalent to that, along processes satisfying (70.2), $\mathcal{L}\left(\zeta(t)\right)$ increases except for at equilibrium: composite function differentiation gives that

$$\frac{\mathrm{d}\mathcal{L}\left(\zeta(t)\right)}{\mathrm{d}t} = \mathrm{D}\mathcal{L} \cdot \frac{\mathrm{d}\zeta}{\mathrm{d}t} \overset{(70.2)}{=} \mathrm{D}\mathcal{L} \cdot \mathrm{f}\left(\zeta(t)\right) = \mathrm{D_f}\mathcal{L}\left(\zeta(t)\right) . \tag{71.1}$$

Accordingly, we can realize that total entropy in Sect. 4.2 is actually a Lyapunov function! In fact, in $\boxed{2}$ in general, thermodynamical consistency criteria guarantee that *total entropy is a Lyapunov function ensuring asymptotic stability of the equilibrium.*

As a final technical remark concerning the Lyapunov technique, the above two conditions can be practically satisfied by showing that

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[90] Stability is more central for mechanics while asymptotic stability is more relevant for thermodynamics, as we will see soon.

[91] Some nontrivial function of p, as it has to satisfy (66.8).

[92] Some mathematical subtleties are not mentioned here.

[93] An analogous theorem exists for stability. Also, in mechanical applications, where $\mathcal{L}$ is usually some energy, minimum and negative directional derivative are required, while here we have a formulation (maximum and positive directional derivative) that is the thermodynamically natural one, as we will see soon. The two conventions can be mapped to one another by a trivial multiplier -1.

- at ζ_e, $\mathcal{L}$ has zero first derivative and negative definite second derivative,
- at ζ_e, $\mathrm{D}\mathcal{L} \cdot \mathrm{f}$ has zero first derivative and positive definite second derivative.

4.4 Volume change rate as an additional state variable

As seen in (66.4)–(66.5), typical heating rate interaction functions satisfy

$$\overset{*}{Q}(T, T_\mathrm{a}) = -\overset{*}{Q}_\mathrm{a}(T_\mathrm{a}, T) \tag{72.1}$$

or, between bodies 1 and 2,

$$\overset{*}{Q}_{12}(T_1, T_2) = -\overset{*}{Q}_{21}(T_2, T_1)\,. \tag{72.2}$$

This is quite natural, actually: heat moves from one body to the other; heat is one type of energy exchange.

It is similarly natural to assume that (66.3) is also symmetric:

$$\overset{*}{W} = -p\overset{*}{V}\,, \qquad \overset{*}{W}_\mathrm{a} = -p_\mathrm{a}\overset{*}{V}_\mathrm{a} \qquad\qquad \big(\text{or } \overset{*}{W}_1 = -p_1\overset{*}{V}_1,\ \ \overset{*}{W}_2 = -p_2\overset{*}{V}_2\big)\,. \tag{72.3}$$

Then we find the ‘inconvenient truth’ that total internal energy is not conserved:

$$\begin{aligned} \dot{E} + \dot{E}_\mathrm{a} &\overset{\substack{\text{along a}\\\text{process}}}{=} \overset{*}{Q} + \overset{*}{W} + \overset{*}{Q}_\mathrm{a} + \overset{*}{W}_\mathrm{a} = \overset{*}{Q} + \overset{*}{Q}_\mathrm{a} + \overset{*}{W} + \overset{*}{W}_\mathrm{a} \\ &= \ \ 0 - p\overset{*}{V} - p_\mathrm{a}\overset{*}{V}_\mathrm{a} \overset{\substack{\text{along a}\\\text{process}}}{=} -p\dot{V} - p_\mathrm{a}\dot{V}_\mathrm{a} \overset{(65.2)}{=} -p\dot{V} + p_\mathrm{a}\dot{V} = (p_\mathrm{a} - p)\dot{V} \not\equiv 0\,. \end{aligned} \tag{72.4}$$

One way to restore total internal energy conservation is if we set

$$\overset{*}{W} = -\frac{p + p_\mathrm{a}}{2}\overset{*}{V}\,, \qquad \overset{*}{W}_\mathrm{a} = -\frac{p + p_\mathrm{a}}{2}\overset{*}{V}_\mathrm{a}\,, \tag{72.5}$$

as it is simple to check, analogously to (72.4). Real-life explanation of such working rates can be if pressure is not so space independent within one body as we have thought: near to the – *e.g.,* membrane-like – boundary (in a ‘boundary layer’) it starts to interpolate between the distant, body-average, pressure p and the other distant, body-average, pressure p_a. Something similar happens to temperature when two solid bodies with different temperatures are touched to one another: there will emerge a contact temperature at the boundary, an intermediate value interpolating between the two distant, body-average, temperatures. Let us not forget that modelling always means introducing a simplifying approximate picture: the prescriptions (72.5) are one valid solution, which, in some cases, can be acceptably realistic.

A second and undoubtedly more frequently close-to-reality solution is when we take the kinetic energy of the piston that separates the two bodies also into account. If the volume of a simple material is $V = Ax$ where x indicates the position of the piston, A the cross-section area of the piston, and m_P its mass, then its kinetic energy is

$$K = \frac{m_\mathrm{P}}{2}\dot{x}^2 = \frac{m_\mathrm{P}}{2}\left(\frac{\dot{V}}{A}\right)^2 = \frac{m_\mathrm{P}}{2A^2}\dot{V}^2 = \frac{\chi_\mathrm{P}}{2}\dot{V}^2 \qquad \text{with} \quad \chi_\mathrm{P} = \frac{m_\mathrm{P}}{A^2}\,. \tag{73.1}$$

In parallel, we take into consideration Newton's mechanical equation of motion for the piston:

$$m_\mathrm{P}\ddot{x} = pA - p_\mathrm{a}A = (p - p_\mathrm{a})A\,, \quad m_\mathrm{P}\ddot{V} = m_\mathrm{P}A\ddot{x} = (p - p_\mathrm{a})A^2\,, \quad \chi_\mathrm{P}\ddot{V} = p - p_\mathrm{a}\,. \tag{73.2}$$

Then we can find that total energy, understood including K as well, is conserved:

$$\begin{aligned}
\dot{E} + \dot{E}_\mathrm{a} + \dot{K} &\overset{\substack{\text{along a}\\ \text{process}}}{=} \overset{*}{Q} + \overset{*}{W} + \overset{*}{Q}_\mathrm{a} + \overset{*}{W}_\mathrm{a} + \chi_\mathrm{P}\dot{V}\ddot{V} \\
&= \overset{*}{Q} + \overset{*}{Q}_\mathrm{a} - p\overset{*}{V} - p_\mathrm{a}\overset{*}{V}_\mathrm{a} + \chi_\mathrm{P}\ddot{V}\dot{V} \\
&\overset{\substack{\text{along a}\\ \text{process}}}{=} 0 - p\overset{*}{V} - p_\mathrm{a}\overset{*}{V}_\mathrm{a} + \overset{(73.2)}{(p - p_\mathrm{a})\dot{V}} \overset{\substack{\text{along a}\\ \text{process}}}{=} -p\dot{V} - p_\mathrm{a}\dot{V}_\mathrm{a} + (p - p_\mathrm{a})\dot{V} \\
&\overset{(65.2)}{=} -p\dot{V} + p_\mathrm{a}\dot{V} + (p - p_\mathrm{a})\dot{V} \equiv 0\,.
\end{aligned} \tag{73.3}$$

We can recognize that $\dot{V}$ has actually emerged to the level of a state variable: some energy contribution (K) depends on it, and how processes are determined has also been modified via it [through (73.2)]. To explicitly display the state variable role of $\dot{V}$, we introduce a standalone notation, B, for it.[94] Accordingly, a state of our system 'body + environment' is described by (E, V, B) (mass transfer still omitted for simplicity), time evolution is described by

$$\dot{E} = \overset{*}{Q} + \overset{*}{W} = \overset{*}{Q} - p\overset{*}{V} = \overset{*}{Q} - pB\,, \tag{73.4}$$

$$\dot{V} = \overset{*}{V} = B\,, \tag{73.5}$$

$$\dot{B} = \overset{*}{B} = \frac{1}{\chi_\mathrm{P}}(p - p_\mathrm{a})\,. \tag{73.6}$$

What happened here is that

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[94] Analogously to how, in mechanics, velocity – originally the time derivative of some other quantity (position) – has historically emerged to the level of an independent state characterizing quantity.

- the interaction functions became B dependent as well,
- the relationship between B and $\dot{V}$ is analogous to how, in mechanics, velocity is related to position, and
- Newton's equation determines the time evolution of B.

Concerning constitutive equations, the only change is that there is an additional energy term,

$$K(B) = \frac{\chi_{\mathrm{P}}}{2} B^2 . \tag{74.1}$$

Now, actually, mechanics has been taken much more seriously and more explicitly:

- in addition to the balance of energy, (73.4), the balance of momentum has also been incorporated – see (73.6) –, though not in full vectorial form but at least to the extent our state variables allow, and
- mechanical energy has also been included.[95]

For determining the equilibrium solution of (73.4)–(73.6), we can start with (73.6), which requires equality of the pressures for constant B. Next, for constant V, (73.5) necessitates $B = 0$. Finally, constant E demands, via (73.4), $\overset{*}{Q} = 0$, which, by (66.6), imposes equality of the temperatures. The equilibrium is thus characterized by the same conditions as for (66.1)–(66.3), supplemented now by $B = 0$. In this sense, B is a *nonequilibrium variable*: it is zero in equilibrium.

Let us now repeat calculation (68.3) for the time evolution equations (73.4)–(73.6)

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[95] You can see here az example how modelling proceeds: we have some knowledge about the relevant laws – here, momentum and energy balance, both its mechanical and heat transfer side, and the constitutive description of the bodies –, we make some simple assumptions – here, we try to survive with only a few scalar state variables that have no space dependence assumed – and realize our general knowledge in the chosen restricted framework.

and with total energy conservation (73.3):

$$\begin{aligned}
\dot{S}_{\mathrm{t}}\Big|_{\mathrm{pr}} &= \dot{S} + \dot{S}_{\mathrm{a}} \overset{(68.1)}{=} \frac{1}{T}\dot{E} + \frac{p}{T}\dot{V} - \frac{\mu}{T}\dot{m} + \frac{1}{T_{\mathrm{a}}}\dot{E}_{\mathrm{a}} + \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\dot{V}_{\mathrm{a}} - \frac{\mu_{\mathrm{a}}}{T_{\mathrm{a}}}\dot{m}_{\mathrm{a}} \\
&\overset{(73.3),\,(65.2)}{=} \left(\frac{1}{T} - \frac{1}{T_{\mathrm{a}}}\right)\dot{E} - \frac{1}{T_{\mathrm{a}}}\dot{K} + \left(\frac{p}{T} - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\right)\dot{V} \\
&\overset{(73.4)\text{–}(73.5)}{=} \left(\frac{1}{T} - \frac{1}{T_{\mathrm{a}}}\right)\overset{*}{Q} - \left(\frac{1}{T} - \frac{1}{T_{\mathrm{a}}}\right)pB - \frac{1}{T_{\mathrm{a}}}\chi_{\mathrm{P}}\overset{(74.1)}{B\dot{B}} + \left(\frac{p}{T} - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\right)B \\
&= \frac{T_{\mathrm{a}} - T}{T_{\mathrm{a}}T}\overset{*}{Q} + \left(\frac{p}{T_{\mathrm{a}}} - \frac{p}{T}\right)B - \overset{(73.6)}{\frac{p - p_{\mathrm{a}}}{T_{\mathrm{a}}}}B + \left(\frac{p}{T} - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\right)B \\
&= \frac{T_{\mathrm{a}} - T}{T_{\mathrm{a}}T}\overset{*}{Q} + \left(\frac{p}{T_{\mathrm{a}}} - \frac{p}{T} - \frac{p}{T_{\mathrm{a}}} + \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}} + \frac{p}{T} - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}\right)B = \frac{T_{\mathrm{a}} - T}{T_{\mathrm{a}}T}\overset{*}{Q}. \qquad (75.1)
\end{aligned}$$

Remarkably, now the mechanical side does not contribute to entropy production. Mechanical interaction can be reversible – here we can see it in thermodynamical language, too.

Total entropy is a Lyapunov function here, too, ensuring asymptotic stability of the equilibrium – to see concavity from above and that its strict maximum at equilibrium, we investigate the first and second derivative of

$$\begin{aligned}
S_{\mathrm{t}}(E, V, B) &= S(E, V) - \frac{1}{T_{\mathrm{a}}}E - \frac{1}{T_{\mathrm{a}}}K - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}V + \text{const.} \\
&= ms\left(\frac{E}{m}, \frac{V}{m}\right) - \frac{1}{T_{\mathrm{a}}}E - \frac{\chi_{\mathrm{P}}}{2T_{\mathrm{a}}}B^2 - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}V + \text{const.} \qquad (75.2)
\end{aligned}$$

[the appropriate generalization of (68.5)]. We find, analogously to (69.1),

$$\mathrm{D}S_{\mathrm{t}}(E, V, B) = \begin{pmatrix} \frac{1}{T} - \frac{1}{T_{\mathrm{a}}} \\ \frac{p}{T} - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}} \\ -\frac{\chi_{\mathrm{P}}}{T_{\mathrm{a}}}B \end{pmatrix}, \qquad (75.3)$$

yielding that equilibrium is characterized by

$$T = T_{\mathrm{a}}, \qquad p = p_{\mathrm{a}}, \qquad B = 0 \qquad (75.4)$$

[(69.2) supplemented with a third condition]. Further, the second derivative is also an extension of (69.5):

$$\mathrm{D}^2 S_{\mathrm{t}}(E, V, B) = \begin{pmatrix} \frac{1}{m}\mathrm{D}^2 s\,(e, v) & 0 \\ 0 & -\frac{\chi_{\mathrm{P}}}{T_{\mathrm{a}}} \end{pmatrix} \qquad (75.5)$$

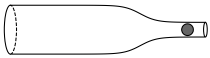
in $(2+1)\times(2+1)$ block matrix notation, which tells that $\mathrm{D}^2 S_{\mathrm{t}}(E,V,B)$ is strictly negative definite – there is one more Sylvester criterion (recall Page 35) fulfilled:

$$\frac{\chi_{\mathrm{P}}}{T_{\mathrm{a}}}\det\left(-\frac{1}{m}\mathrm{D}^2 s\left(e,v\right)\right) > 0\,. \tag{76.1}$$

As a remark, if the expansion is not unidirectional but isotropic, like a helium balloon rising in the air, then χ_{P} turns out to be V dependent. That induces a few additional terms but causes no principal difficulty so here we do not consider that more general scenario.

Briefly mentioning a third possible solution for the paradox raised at the beginning of this Section, the mass of the simple material itself also serves as a source for kinetic energy, with come coefficient χ_{material}. Moreover, the two origins of kinetic energy can be combined so, in general, a coefficient χ may comprise the two contributions.

4.5 Volume change rate as a state variable: an application



As one application of the model described in the previous Section, let us consider an amount of ideal gas in a bottle that lies on a table, separated from the environment by a drop of mercury that is in the bottleneck. This 'plug' is assumed to be able to move frictionlessly in the bottleneck of cross-section area A. χ_{P} is related to the mass of the drop according to (73.1). When the gas reaches equilibrium with the environment, we insulate the bottle well enough so we can suppose $\overset{*}{Q} = 0$ thereafter. Then we knuckle the drop a bit so it starts to make small-amplitude oscillations. Let us calculate the angular frequency of this small oscillation.

Let V_{eq} denote the volume of the gas when it has the same temperature and pressure as that of the environment (T_{a} and p_{a}, respectively). By 'small' oscillations we mean[96] that

$$\Delta V = V - V_{\mathrm{eq}}\,, \tag{76.2}$$

for which we have

$$\dot{\Delta V} = \dot{V}\,, \qquad \ddot{\Delta V} = \ddot{V}\,, \tag{76.3}$$

satisfies

$$\frac{|\Delta V|}{V_{\mathrm{eq}}} \ll 1\,. \tag{76.4}$$

---

[96] Among others – for example, we also hope that the drop does not leave the bottleneck.

The adiabatic condition $\overset{*}{Q} = 0$, via (67.2), (25.5), (16.2), and (34.5), implies the well-known fact that, along adiabatic processes of an ideal gas,

$$pV^\kappa = \text{const.}, \tag{77.1}$$

which we utilize here in the form

$$pV^\kappa = p_\text{a} V_\text{eq}^\kappa . \tag{77.2}$$

Employing the good-to-remember approximation[97]

$$(1+\delta)^a \approx 1 + a\delta \qquad (|\delta| \ll 1) \tag{77.3}$$

for $\delta = \frac{\Delta V}{V_\text{eq}}$, $a = -\kappa$,

$$p \overset{(77.2)}{=} \frac{p_\text{a} V_\text{eq}^\kappa}{V^\kappa} = \frac{p_\text{a} V_\text{eq}^\kappa}{V_\text{eq}^\kappa \left(1 + \frac{\Delta V}{V_\text{eq}}\right)^\kappa} \approx \frac{p_\text{a} V_\text{eq}^\kappa}{V_\text{eq}^\kappa} \left(1 - \kappa \frac{\Delta V}{V_\text{eq}}\right) = p_\text{a} - \frac{p_\text{a}\kappa}{V_\text{eq}} \Delta V . \tag{77.4}$$

Along a process, (73.6) with (73.5) tells us

$$\ddot{V} = \frac{1}{\chi_\text{P}} (p - p_\text{a}) , \tag{77.5}$$

$$\ddot{\Delta V} \approx \frac{1}{\chi_\text{P}} \left(p_\text{a} - \frac{p_\text{a}\kappa}{V_\text{eq}} \Delta V - p_\text{a}\right) = -\frac{p_\text{a} A^2 \kappa}{m_\text{P} V_\text{eq}} \Delta V = -\omega^2 \Delta V \quad \text{with} \quad \omega = \sqrt{\frac{p_\text{a} A^2 \kappa}{m_\text{P} V_\text{eq}}} . \tag{77.6}$$

Now let us recall Page 7: (77.6) has the power to motivate action: by measuring ω and the constants p_a, A, m_P, V_eq, we can determine κ, from

$$\kappa = \omega^2 \frac{m_\text{P} V_\text{eq}}{p_\text{a} A^2} . \tag{77.7}$$

Indeed, this is a historically known method to measure κ.

4.6 Viscosity-type damping in temporal thermodynamics

If we have a new state variable, B, or, its specific version, $b = B/m$, then it can appear in constitutive functions. Let us see what happens if pressure becomes dependent on it. Since b is a nonequilibrium variable (zero for static cases), and has

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[97] It's simply the first-order Taylor expansion.

change-rate meaning ($b = \dot{v}$ along processes allowed by the time evolution equations), let us consider the simplest case when b dependence is a linear contribution to the static situation:[98]

$$p(e, v, b) = p(e, v, 0) - \beta b \equiv p_0(e, v) - \beta b \tag{78.1}$$

[β is not necessarily constant here but can have dependence on e, v, or even b (quasilinear case)]. Everything else is kept unchanged with respect to (73.4)–(74.1) (they just now contain this extended p), and neither $T(e, v)$ nor $s(e, v)$ are not generalized to having b dependence. Then, for repeating calculation (75.1), we have to recognize that (68.1) is still valid for the $b = 0$ situation:[99]

$$\dot{S} = \frac{1}{T}\dot{E} + \frac{p_0}{T}\dot{V} - \frac{\mu}{T}\dot{m}, \tag{78.2}$$

Consequently, the first line of (75.1) is to be written with p_0, or, when written with p substituting $p_0 = p + \beta b$, an additional term $\frac{\beta b}{T}\dot{V}$ is present. That term, rewritable as

$$\frac{\beta b}{T} B = \frac{\beta m}{T} b^2 \tag{78.3}$$

travels through the calculation so, in the result, it remains as an additional term. Hence, we can see that the β related contribution to the system, manifesting itself in the 'mechanical' equation (73.6) that is rewritable as

$$\chi_{\mathrm{P}} \ddot{V} \overset{\substack{\text{along a}\\ \text{process}}}{=} p - p_{\mathrm{a}} = -\beta b + (p_0 - p_{\mathrm{a}}) = -\frac{\beta}{m}\dot{V} + (p_0 - p_{\mathrm{a}}), \tag{78.4}$$

contributes to entropy production and creates irreversibility if $\beta > 0$.

Concerning the physical interpretation of the β related pressure contribution (force contribution), its mechanical role is clear from (78.4): it embodies a damping force proportional to velocity. In other words, this a viscosity-type contribution. Indeed, in $\boxed{4}$, we will see how β can be expressed in terms of the viscosity coefficient. However, β is not necessarily of internal friction origin but a damped motion of a piston can also be modelled via it. Or, as with the case of χ, β may comprise both types of contribution.

Now let us consider 'slow enough' processes, namely, such time dependences when $\chi_{\mathrm{P}}\ddot{V}$ is negligible w.r.t. $-\frac{\beta}{m}\dot{V}$. [As a rule of thumb, a 'slow' limit means that we neglect the highest time derivative (we keep only the lowest time derivative).] Then (78.4) can be rearranged as

$$\dot{V} \approx \frac{m}{\beta}(p_0 - p_{\mathrm{a}}), \tag{78.5}$$

---

[98] It will turn out soon why a $-$ sign before β is natural to introduce in the convention for β.

[99] (68.2) remains untouched.

Comparing this with (66.7) enlights the applicability of the (66.2)-type equation: that describes such ‘slow/overdamped’ situations.

Next, let us take ‘even slower / over-overdamped’ circumstances. Then we neglect the remaining time derivative as well, arriving at

$$p_0 \approxeq p_{\mathrm{a}} \,. \tag{79.1}$$

This is also an enlighting formula: this is the historical ‘quasistatic’, ‘equilibrium’, $\boxed{1}$ picture about processes: the environment enforces its pressure on the body. p_0 can change only if p_{a} changes.

Finally, it is not hard to see that the extra pressure term

$$p_{\mathrm{irr}} = -\beta b \tag{79.2}$$

can be generalized to any

$$p_{\mathrm{irr}}\,(e, v, b) \begin{cases} > 0 & \text{if} \quad b < 0\,, \\ = 0 & \text{if} \quad b = 0\,, \\ < 0 & \text{if} \quad b > 0 \end{cases} \tag{79.3}$$

with the same conclusion: the corresponding entropy production term

$$-\frac{p_{\mathrm{irr}}}{T} m b \tag{79.4}$$

is positive except for the equilibrial value $b = 0$.[100]

4.7 Numerical illustrations for processes in temporal thermodynamics

Both time evolution equations (70.1) and (73.4)–(73.6) are of the form (70.2), and, as mentioned in Page 71, are nonlinear. Therefore, in most cases, we apply some numerical approximate solution.[101]

At the general level, an equation $\frac{\mathrm{d}\zeta}{\mathrm{d}t} = \mathrm{f}\left(\zeta(t)\right)$ [introduced in (70.2)] can most simply be solved in the *explicit Euler scheme*. In this approach, we consider a finite discrete sequence of time values,

$$t^j = j \cdot \Delta t\,, \qquad j = 0, 1, \ldots, J\,, \tag{79.5}$$

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[100] In parallel, the total entropy function (75.2) itself is not modified — only its time dependence along a process – so it remains a Lyapunov function as before.

[101] A few nonlinear problems can be solved exactly analytically, and analytical approximate solutions are also a possible way. Here, we present a simple and generally applicable approach: an explicit finite-difference numerical solution.

by choosing a finite, 'small enough' time step Δt, and wish to know (at least approximate) values of ζ at these instants t^j, $\zeta^j \approx \zeta\bigl(t^j\bigr)$. Approximating the derivative (ratio of differentials) by a ratio of differences,

$$\frac{\mathrm{d}\zeta}{\mathrm{d}t}\bigl(t^j\bigr) \approx \frac{\zeta\bigl(t^{j+1}\bigr) - \zeta\bigl(t^j\bigr)}{t^{j+1} - t^j} \approx \frac{\zeta^{j+1} - \zeta^j}{\Delta t}\,, \tag{80.1}$$

the differential equation is approximated as

$$\frac{\zeta^{j+1} - \zeta^j}{\Delta t} \approx \frac{\mathrm{d}\zeta}{\mathrm{d}t}\bigl(t^j\bigr) = \mathrm{f}\bigl(\zeta\bigl(t^j\bigr)\bigr) \approx \mathrm{f}\left(\zeta^j\right) \equiv \mathrm{f}^j\,, \tag{80.2}$$

$$\zeta^{j+1} \approx \zeta^j + \Delta t \cdot \mathrm{f}^j\,. \tag{80.3}$$

To start the procedure, the initial condition ζ^0 is needed. For simple examples, see Sects. 6.4–6.5.

In temporal thermodynamics, the interaction functions are usually given in terms of intensive quantities while the time evolution equations tell the time evolution of extensive quantities so constitutive functions must also be evaluated in order to obtain the intensives from the extensives.

In the case of the following (66.1)–(66.3) type problem with (66.4) and (66.7),

$$\dot{E} = \overset{*}{Q} + \overset{*}{W} = -\Gamma\,(T - T_{\mathrm{a}}) - p\overset{*}{V}\,, \tag{80.4}$$

$$\dot{V} = \overset{*}{V} = \Theta\,(p - p_{\mathrm{a}})\,, \tag{80.5}$$

$$+ \text{ given } p(E,V),\ T(E,V) \quad [\text{and the consequence } E(T,V)] \tag{80.6}$$

$$+ \text{ initial conditions } T(0),\ V(0) \tag{80.7}$$

(mass being constant and therefore having been omitted from the notations), we can proceed as follows. We calculate the initial values of p and E from (80.6). Then we calculate new V from the discretized version of (80.5) and the old value of p. Then we calculate new E from the discretized version of (80.4) and the old values of T and p. Finally, we calculate new p and T from the new E and V and (80.6). And so on, and so on.

4.8 Non-Newtonian fluids modelled in temporal thermodynamics

Even the general form (79.3) has only a restricted modelling capability. Generalizations of the viscosity-type (also called *Newtonian*) fluid models to ones where the behaviour depends on change rates or on temporal past in some more complex way (so-called *non-Newtonian* fluid models, used to describe toothpaste, shampoo, yoghurt, ketchup, honey, blood *etc.*) should respect the second law of thermodynamics. One way to obtain such models uses the internal variable approach. Here, consider a simplest example of it.

Similarly to that B was found a nonequilibrium state variable (*i.e.,* a one that is zero in equilibrium, hence, a value $B \neq 0$ characterizes how far a state is far from equilibrium), we assume the existence of another nonequilibrium state variable, denoted by ξ.[102]

Now we suppose some irreversibility-related extra term not only in pressure (p_{irr}) but also in specific entropy:

$$s(e,v,\xi) = s(e,v,0) + s_{\mathrm{irr}}(\xi) \equiv s_0(e,v) - \frac{1}{2}\xi^2 \,. \tag{81.1}$$

The special form $-\frac{1}{2}\xi^2$ is chosen based on simplicity – it looks like a Taylor expansion to second order –, it vanishes in equilibrium (where we want $\xi = 0$), and it preserves concavity of total entropy: analogously to (75.2)–(76.1),

$$\begin{aligned} S_{\mathrm{t}}(E,V,B,\xi) &= S_0(E,V) - \frac{m}{2}\xi^2 - \frac{1}{T_{\mathrm{a}}}E - \frac{1}{T_{\mathrm{a}}}K - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}V + \mathrm{const.} \\ &= m s_0\left(\frac{E}{m},\frac{V}{m}\right) - \frac{m}{2}\xi^2 - \frac{1}{T_{\mathrm{a}}}E - \frac{\chi_{\mathrm{P}}}{2T_{\mathrm{a}}}B^2 - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}}V + \mathrm{const.}\,; \end{aligned} \tag{81.2}$$

$$\mathrm{D}S_{\mathrm{t}}(E,V,B,\xi) = \begin{pmatrix} \frac{1}{T} - \frac{1}{T_{\mathrm{a}}} \\ \frac{p}{T} - \frac{p_{\mathrm{a}}}{T_{\mathrm{a}}} \\ -\frac{\chi_{\mathrm{P}}}{T_{\mathrm{a}}}B \\ -m\xi \end{pmatrix}, \qquad \text{equilibrium:} \quad \begin{cases} T = T_{\mathrm{a}}\,, \\ p = p_{\mathrm{a}}\,, \\ B = 0\,, \\ \xi = 0\,; \end{cases} \tag{81.3}$$

$$\mathrm{D}^2 S_{\mathrm{t}}(E,V,B,\xi) = \begin{pmatrix} \frac{1}{m}\mathrm{D}^2 s\,(e,v) & 0 & 0 \\ 0 & -\frac{\chi_{\mathrm{P}}}{T_{\mathrm{a}}} & 0 \\ 0 & 0 & -m \end{pmatrix}; \tag{81.4}$$

the second derivative written in $(2+1+1)\times(2+1+1)$ block matrix notation.

In parallel, w.r.t. (75.1), there are now two additional terms [(in the viscosity-type model – see Sect. 4.6 – there was only one additional term)]:

$$\dot{S}_{\mathrm{t}}\Big|_{\mathrm{pr}} = \frac{T_{\mathrm{a}} - T}{T_{\mathrm{a}}T}\overset{*}{Q} + \frac{m}{T}\left[-p_{\mathrm{irr}}b - T\xi\dot{\xi}\right]. \tag{81.5}$$

---

[102] B itself could also be used for the purposes below but let us explore this more general possibility.

Positive definiteness of the [...] part can, for example, be ensured if

$$p_{\rm irr} = -\beta b\,, \qquad \dot{\xi} = -\beta_\xi \xi \qquad (\beta, \beta_\xi \geq 0) \tag{82.1}$$

but, applying Onsager's idea[103], coupling between the two terms is also possible:

$$p_{\rm irr} = \lambda_{11}\,(-b) + \lambda_{12}\left(-T\dot{\xi}\right), \tag{82.2}$$

$$\xi = \lambda_{21}\,(-b) + \lambda_{22}\left(-T\dot{\xi}\right), \tag{82.3}$$

where the coefficients are not necessarily constants but can be state dependent, most prominently, T dependent. Substituting (82.2)–(82.3) into the [...] part of (81.5) gives

$$-p_{\rm irr}b - T\xi\dot{\xi} = \begin{pmatrix} -b & -T\dot{\xi} \end{pmatrix} \begin{pmatrix} \lambda_{11} & \lambda_{12} \\ \lambda_{21} & \lambda_{22} \end{pmatrix} \begin{pmatrix} -b \\ -T\dot{\xi} \end{pmatrix} \tag{82.4}$$

$$= \begin{pmatrix} -b & -T\dot{\xi} \end{pmatrix} \begin{pmatrix} \lambda_{11} & \frac{\lambda_{12}+\lambda_{21}}{2} \\ \frac{\lambda_{12}+\lambda_{21}}{2} & \lambda_{22} \end{pmatrix} \begin{pmatrix} -b \\ -T\dot{\xi} \end{pmatrix} \tag{82.5}$$

so positive definiteness of this expression (of this entropy production contribution) implies

$$\lambda_{11} \geq 0\,, \quad \lambda_{22} \geq 0\,, \quad \det \begin{pmatrix} \lambda_{11} & \frac{\lambda_{12}+\lambda_{21}}{2} \\ \frac{\lambda_{12}+\lambda_{21}}{2} & \lambda_{22} \end{pmatrix} = \lambda_{11}\lambda_{22} - \left(\tfrac{\lambda_{12}+\lambda_{21}}{2}\right)^2 \geq 0\,. \tag{82.6}$$

If one has knowledge about the physical meaning of the internal variable ξ then the coefficients λ_{ij} can be measured (fitted on measurement data) assuming the validity of (82.2)–(82.3). If not then what we can do is that we eliminate ξ from (82.2)–(82.3), finding one equation for measurable quantities. The result is simple if we assume that T as well as the coefficients λ_{ij} do not change considerably during a process: then we obtain the equation[104]

$$p_{\rm irr} + \tau_{\rm nN}\dot{p}_{\rm irr} = -\hat{E}_{\rm nN}b - \hat{\hat{E}}_{\rm nN}\dot{b} \tag{82.7}$$

with

$$\tau_{\rm nN} = T\lambda_{22} \geq 0\,, \tag{82.8}$$

$$\hat{E}_{\rm nN} = \lambda_{11} \geq 0\,, \tag{82.9}$$

$$\hat{\hat{E}}_{\rm nN} = T(\lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21}) = \lambda_{11}\lambda_{22} - \left(\tfrac{\lambda_{12}+\lambda_{21}}{2}\right)^2 + \left(\tfrac{\lambda_{12}-\lambda_{21}}{2}\right)^2 \geq 0\,, \tag{82.10}$$

---

[103] His Nobel Prize winning idea, which provided theoretical framework for the so-called *cross-effects* including the Seebeck, Peltier, Dufour, Soret, and Darcy effects.

[104] In Sect. 4.9, in the analogous situation for solids, the details of the elimination are given. The notation $_{\rm nN}$ stands for non-Newtonian.

the inequalities following from (82.6). In rheology – the area dealing with rate or past dependent behaviour of materials – (82.7) is called the *Jeffrey model.*

Apparently, viscosity is included as the special case when both τ_{nN} and $\hat{\hat{E}}_{\mathrm{nN}}$ are zero. In parallel, the general situation is sensitive to higher time derivatives so the pressure induced mechanical behaviour has more complicated change rate dependence than for viscosity. For example, $\tau_{\mathrm{nN}} = 0$, $\hat{\hat{E}}_{\mathrm{nN}} > 0$ means acceleration dependent pressure, and $\tau_{\mathrm{nN}} > 0$ makes the picture even trickier. For example, in the 'fast limit' (when changes happen on a time scale that is much smaller than the time scales embodied by the coefficients, τ_{nN} and $\hat{\hat{E}}_{\mathrm{nN}}/\hat{E}_{\mathrm{nN}}$, see more on the fast and slow limits in Sect. 4.9), the highest time derivatives dominate, leading to a seeming/effective viscosity-related coefficient $\hat{\hat{E}}_{\mathrm{nN}}/\tau_{\mathrm{nN}}$, while in the 'slow limit' the lowest time derivatives dominate and $\hat{E}_{\mathrm{nN}}$ appears as the viscosity-related coefficient (and for intermediate-speed processes we see some more-or-less interpolated but more delicate behaviour).

If we generalize the above treatment by allowing nonlinearities here or there then the picture becomes even further trickier.[105]

4.9 Rheology of solids – 1D treatment

Similarly to how an internal variable extension of a simple material model leads to a model (a family of models, in fact) of non-Newtonian behaviour, an elastic solid body model can also be extended to obtain a model family, the Kluitenberg-Verhás family for a rheological model of solids.

For simplicity, let us take the description of solids seen in Sects. 3.11–3.12 with thermal expansion neglected, $\alpha = 0$. On the other side, let us now shift energy rather than entropy. Namely, we assume a 'nonequilibrium' variable η and take

$$e(T, D, \eta) = cT + \frac{E}{2\varrho} D^2 + \frac{1}{2}\eta^2 , \tag{83.1}$$

$$s(T, D, \eta) = c \ln \frac{T}{T_{\mathrm{aux}}} . \tag{83.2}$$

In addition, according to that rheology is most manifest in the mechanics aspect, we suppose stress gets an irreversible contribution,

$$\sigma = \sigma_{\mathrm{el}} + \sigma_{\mathrm{irr}} \overset{(47.5)}{=} ED + \sigma_{\mathrm{irr}} . \tag{83.3}$$

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[105] Even the linear range allows more than one internal variable, which leads to higher time derivatives after elimination. Moreover, in the so-called memory functional approach, distant past dependence can also be incorporated. However, more time derivative coefficients or a whole memory kernel function to fit on experimental data is more error prone so predictive power decreases. Increase complexity only if circumstances enforce you to do it.

Rheology is expected to be an irreversible property of the material, not of a body–environment interaction. Then it is enough to see entropy production within the solid body. Moreover, rheology is expected to produce irreversibility during adiabatic[106] processes, too – it is a form of irreversibility bound to *mechanical work* rather than to *heat*. Then, along any such process,

$$\begin{aligned}
\dot{s}\big|_{\text{process}} &= c\frac{\dot{T}}{T} \overset{(83.1)}{=} \frac{1}{T}\left(e - \frac{E}{2\varrho}D^2 - \frac{1}{2}\eta^2\right)^{\boldsymbol{\cdot}} = \frac{1}{T}\left(\dot{e} - \frac{E}{\varrho}D\dot{D} - \eta\dot{\eta}\right) \\
&= \frac{1}{T}\left(\frac{1}{\varrho}\sigma L - \frac{E}{\varrho}D\dot{D} - \eta\dot{\eta}\right) \overset{(83.3)}{=} \frac{1}{T}\left(\frac{1}{\varrho}EDL + \frac{1}{\varrho}\sigma_{\text{irr}}L - \frac{E}{\varrho}D\dot{D} - \eta\dot{\eta}\right) \\
&\overset{L=\dot{D}}{=} \frac{1}{T}\left(\frac{1}{\varrho}\sigma_{\text{irr}}\dot{D} - \eta\dot{\eta}\right). \qquad (84.1)
\end{aligned}$$

We impose that this should be non-negative, and zero only in equilibrium, and ensure

$$\sigma_{\text{irr}}\dot{D} - \varrho\eta\dot{\eta} \geq 0 \qquad (84.2)$$

via Onsagerian equations, analogously to (82.2)–(82.3):

$$\begin{aligned}
\sigma_{\text{irr}} &= \lambda_{11}\dot{D} + \lambda_{12}\left(-\varrho\dot{\eta}\right), \qquad (84.3) \\
\eta &= \lambda_{21}\dot{D} + \lambda_{22}\left(-\varrho\dot{\eta}\right), \qquad (84.4)
\end{aligned}$$

with actually the same inequality-type restrictions on λ_{ij} as (82.6).

Also similarly to Sect. 4.8, we may have no knowledge about the physical meaning and measurement of η, in which case we eliminate it. If we assume that the material describing coefficients λ_{ij} are constants – at least to a good approximation along a process, *e.g.*, their temperature dependence is not considerable –, then we can proceed as follows. First, we rearrange (84.4) as

$$\eta + \lambda_{22}\varrho\dot{\eta} = \lambda_{21}\dot{D}, \quad \left(1 + \lambda_{22}\varrho\frac{\mathrm{d}}{\mathrm{d}t}\right)\eta = \lambda_{21}\dot{D}, \quad \left(1 + \lambda_{22}\varrho\frac{\mathrm{d}}{\mathrm{d}t}\right)\dot{\eta} \overset{\frac{\mathrm{d}}{\mathrm{d}t}}{=} \lambda_{21}\ddot{D}. \qquad (84.5)$$

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[106] Be careful: here, $T\,\mathrm{d}s \neq \text{đ}q$ any more: irreversible processes inside the material produce additional forms of entropy change.

Next, we apply the found differential operator $1 + \lambda_{22}\varrho\frac{\mathrm{d}}{\mathrm{d}t}$ on (84.3) and obtain

$$\left(1 + \lambda_{22}\varrho\frac{\mathrm{d}}{\mathrm{d}t}\right)\sigma_{\mathrm{irr}} = \left(1 + \lambda_{22}\varrho\frac{\mathrm{d}}{\mathrm{d}t}\right)\lambda_{11}\dot{D} - \lambda_{12}\varrho\left(1 + \lambda_{22}\varrho\frac{\mathrm{d}}{\mathrm{d}t}\right)\dot{\eta}, \tag{85.1}$$

$$\begin{aligned}
\sigma_{\mathrm{irr}} + \underbrace{\lambda_{22}\varrho}_{=:\tau}\dot{\sigma}_{\mathrm{irr}} &= \underbrace{\lambda_{11}}_{=:\hat{I}}\dot{D} + \lambda_{22}\varrho\lambda_{11}\ddot{D} - \lambda_{12}\varrho\cdot\overset{(84.5\,c)}{\lambda_{21}\ddot{D}} \\
&= \hat{I}\dot{D} + \underbrace{\varrho\left(\lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21}\right)}_{=:\hat{\hat{I}}}\ddot{D}
\end{aligned} \tag{85.2}$$

$$\sigma_{\mathrm{irr}} + \tau\dot{\sigma}_{\mathrm{irr}} = \hat{I}\dot{D} + \hat{\hat{I}}\ddot{D}, \tag{85.3}$$

$$\sigma + \tau\dot{\sigma} \overset{(83.3)}{=} ED + \hat{E}\dot{D} + \hat{\hat{E}}\ddot{D} \tag{85.4}$$

with coefficients that inherit the following relationships and inequality properties:

$$\hat{I} = \hat{E} - \tau E \geq 0 \qquad \Longrightarrow \qquad \hat{E} \geq \tau E, \tag{85.5}$$

$$\hat{\hat{I}} = \hat{\hat{E}} - \tau\hat{I} \qquad \Longleftarrow \qquad \hat{\hat{E}} = \hat{\hat{I}} + \tau\hat{I} \geq 0. \tag{85.6}$$

To make a comparison to various well-known rheological models, let us rewrite (85.4), taking the customary supposition $D(t_0) = 0$, using (50.1) with our present assumption of negligible α, and writing simply ε in the place of ε_{t_0}:

$$\sigma + \tau\dot{\sigma} = E\varepsilon + \hat{E}\dot{\varepsilon} + \hat{\hat{E}}\ddot{\varepsilon}. \tag{85.7}$$

When some of the coefficients are zero, we recover the following simpler models, each finding numerous practical applications:

$\sigma = E\varepsilon$	Hooke	(solid)	(85.8)
$\sigma = \hat{E}\dot{\varepsilon}$	Newton	(fluid)	(85.9)
$\sigma = E\varepsilon + \hat{E}\dot{\varepsilon}$	Kelvin–Voigt	(solid)	(85.10)
$\sigma + \tau\dot{\sigma} = E\varepsilon + \hat{E}\dot{\varepsilon}$	Poynting–Thomson–Zener	(solid)	(85.11)
$\sigma + \tau\dot{\sigma} = \hat{E}\dot{\varepsilon}$	Maxwell	(fluid)	(85.12)
$\sigma + \tau\dot{\sigma} = \hat{E}\dot{\varepsilon} + \hat{\hat{E}}\ddot{\varepsilon}$	Jeffrey	(fluid)	(85.13)
$\sigma + \tau\dot{\sigma} = E\varepsilon + \hat{E}\dot{\varepsilon} + \hat{\hat{E}}\ddot{\varepsilon}$	Kluitenberg–Verhás	(solid)	(85.14)

The words in parentheses display whether the given model is applicable for a solid or a fluid (rheological extension of a simple material, like (82.7) in Sect. 4.8, b is related to $\dot{\varepsilon}$). This can be determined as follows: we take the 'slow' limit, by keeping for each quantity only its lowest time derivative. If the result is a Hooke model then the material is a solid; if it's a Newton model then the material is a fluid.

One message of the above models is that, when one measures σ and ε and plots $\sigma(t)$ versus $\varepsilon(t)$, it should not be viewed as the plot of a function $\sigma(\varepsilon)$. If the experiment is repeated at some other speed, the plot can well be quite different, indicating that some above – or more general – model is needed to describe the given material. Rocks, for example, be so 'solid' by our intuition, do typically require some rheological extension beyond the naive Hooke expectation [or any other elastic presupposition $\sigma(\varepsilon)$].[107]

4.10 Rheology of solids – 3D treatment

In the 3D version of the previous section, the additional variable is a symmetric tensor $\boldsymbol{\eta}$ in accord with that we wish to describe additional – irreversible – mechanical stress via it and stress is a symmetric tensor (and elastic deformedness, $\mathbf{D}$, also). (83.1) and (83.3) are generalized to

$$e(T, \mathbf{D}, \boldsymbol{\eta}) = cT + \frac{E^{\mathrm{dev}}}{2\varrho} \operatorname{tr}\left(\mathbf{D}^{\mathrm{dev}} \mathbf{D}^{\mathrm{dev}}\right) + \frac{E^{\mathrm{sph}}}{2\varrho} \operatorname{tr}\left(\mathbf{D}^{\mathrm{sph}} \mathbf{D}^{\mathrm{sph}}\right) + \frac{1}{2} \operatorname{tr}\left(\boldsymbol{\eta}^{\mathrm{dev}} \boldsymbol{\eta}^{\mathrm{dev}}\right) + \frac{1}{2} \operatorname{tr}\left(\boldsymbol{\eta}^{\mathrm{sph}} \boldsymbol{\eta}^{\mathrm{sph}}\right), \tag{86.1}$$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\mathrm{el}} + \boldsymbol{\sigma}_{\mathrm{irr}} \overset{(62.7)}{=} E^{\mathrm{dev}} \mathbf{D}^{\mathrm{dev}} + E^{\mathrm{sph}} \mathbf{D}^{\mathrm{sph}} + \boldsymbol{\sigma}_{\mathrm{irr}}^{\mathrm{dev}} + \boldsymbol{\sigma}_{\mathrm{irr}}^{\mathrm{sph}} \tag{86.2}$$

[cf. (64.1)]. Entropy production proves now to require positive definiteness of

$$\operatorname{tr}\left(\boldsymbol{\sigma}_{\mathrm{irr}} \dot{\mathbf{D}}\right) - \varrho \operatorname{tr}\left(\boldsymbol{\eta}\dot{\boldsymbol{\eta}}\right) = \left[\operatorname{tr}\left(\boldsymbol{\sigma}_{\mathrm{irr}}^{\mathrm{dev}} \dot{\mathbf{D}}^{\mathrm{dev}}\right) - \varrho \operatorname{tr}\left(\boldsymbol{\eta}^{\mathrm{dev}} \dot{\boldsymbol{\eta}}^{\mathrm{dev}}\right)\right] + \left[\operatorname{tr}\left(\boldsymbol{\sigma}_{\mathrm{irr}}^{\mathrm{sph}} \dot{\mathbf{D}}^{\mathrm{sph}}\right) - \varrho \operatorname{tr}\left(\boldsymbol{\eta}^{\mathrm{sph}} \dot{\boldsymbol{\eta}}^{\mathrm{sph}}\right)\right]. \tag{86.3}$$

Deviatoric and spherical tensors are linearly independent so two separate sets of Onsagerian equations emerge:

$$\boldsymbol{\sigma}_{\mathrm{irr}}^{\mathrm{dev}} = \lambda_{11}^{\mathrm{dev}} \dot{\mathbf{D}}^{\mathrm{dev}} + \lambda_{12}^{\mathrm{dev}} \left(-\varrho \dot{\boldsymbol{\eta}}^{\mathrm{dev}}\right), \qquad \boldsymbol{\sigma}_{\mathrm{irr}}^{\mathrm{sph}} = \lambda_{11}^{\mathrm{sph}} \dot{\mathbf{D}}^{\mathrm{sph}} + \lambda_{12}^{\mathrm{sph}} \left(-\varrho \dot{\boldsymbol{\eta}}^{\mathrm{sph}}\right), \tag{86.4}$$

$$\boldsymbol{\eta}^{\mathrm{dev}} = \lambda_{21}^{\mathrm{dev}} \dot{\mathbf{D}}^{\mathrm{dev}} + \lambda_{22}^{\mathrm{dev}} \left(-\varrho \dot{\boldsymbol{\eta}}^{\mathrm{dev}}\right), \qquad \boldsymbol{\eta}^{\mathrm{sph}} = \lambda_{21}^{\mathrm{sph}} \dot{\mathbf{D}}^{\mathrm{sph}} + \lambda_{22}^{\mathrm{sph}} \left(-\varrho \dot{\boldsymbol{\eta}}^{\mathrm{sph}}\right). \tag{86.5}$$

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[107] In parallel, since $\varepsilon \equiv \varepsilon_{t_0}$ is not a state quantity, even elastic models should use some D-like state quantity as variable of constitutive functions.

Consequently, everything said in the 1D case can be repeated, twice: once for the deviatoric part and once for the spherical part. (The two parts are completely independent.) Among others, the elimination leads to

$$\boldsymbol{\sigma}^{\mathrm{dev}} + \tau^{\mathrm{dev}} \dot{\boldsymbol{\sigma}}^{\mathrm{dev}} = E^{\mathrm{dev}} \mathbf{D}^{\mathrm{dev}} + \hat{E}^{\mathrm{dev}} \dot{\mathbf{D}}^{\mathrm{dev}} + \hat{\hat{E}}^{\mathrm{dev}} \ddot{\mathbf{D}}^{\mathrm{dev}} , \tag{87.1}$$

$$\boldsymbol{\sigma}^{\mathrm{sph}} + \tau^{\mathrm{sph}} \dot{\boldsymbol{\sigma}}^{\mathrm{sph}} = E^{\mathrm{sph}} \mathbf{D}^{\mathrm{sph}} + \hat{E}^{\mathrm{sph}} \dot{\mathbf{D}}^{\mathrm{sph}} + \hat{\hat{E}}^{\mathrm{sph}} \ddot{\mathbf{D}}^{\mathrm{sph}} , \tag{87.2}$$

In the special case of uniaxial processes, similarly to how (62.7)–(62.8) are found from (61.6)–(61.7), two one-component equations emerge:

$$\sigma^{\parallel} + \tau^{\mathrm{dev}} \dot{\sigma}^{\parallel} = E^{\mathrm{dev}} \big(D^{\parallel} - D^{\perp} \big) + \hat{E}^{\mathrm{dev}} \Big(\dot{D}^{\parallel} - \dot{D}^{\perp} \Big) + \hat{\hat{E}}^{\mathrm{dev}} \Big(\ddot{D}^{\parallel} - \ddot{D}^{\perp} \Big) , \tag{87.3}$$

$$\sigma^{\parallel} + \tau^{\mathrm{sph}} \dot{\sigma}^{\parallel} = E^{\mathrm{sph}} \big(D^{\parallel} + 2D^{\perp} \big) + \hat{E}^{\mathrm{sph}} \Big(\dot{D}^{\parallel} + 2\dot{D}^{\perp} \Big) + \hat{\hat{E}}^{\mathrm{sph}} \Big(\ddot{D}^{\parallel} + 2\ddot{D}^{\perp} \Big) . \tag{87.4}$$

In many mechanical experiments, transversal strain is not measured, hence, then only $\sigma^{\parallel}(t)$ and $D^{\parallel}(t)$ are available (remember: longitudinal strain provides $D^{\parallel}(t)$ only if $D^{\parallel}(t_0) = 0$). To see what relationship between $\sigma^{\parallel}(t)$ and $D^{\parallel}(t)$ follows from (87.3)–(87.4), we need to eliminate $D^{\perp}(t)$. This can be done, either directly, or via identifying and applying the operators behind, which operators are polynomials of the time derivative operator $\frac{\mathrm{d}}{\mathrm{d}t}$.

First, let us see the direct approach, on the example of the Kelvin – Hooke model, *i.e.,* when one has a Kelvin model in the deviatoric part and a Hooke one in the spherical part:

$$\boldsymbol{\sigma}^{\mathrm{dev}} = E^{\mathrm{dev}} \mathbf{D}^{\mathrm{dev}} + \hat{E}^{\mathrm{dev}} \dot{\mathbf{D}}^{\mathrm{dev}} , \tag{87.5}$$

$$\boldsymbol{\sigma}^{\mathrm{sph}} = E^{\mathrm{sph}} \mathbf{D}^{\mathrm{sph}} , \tag{87.6}$$

which for uniaxial processes gives

$$\sigma^{\parallel} = E^{\mathrm{dev}} \big(D^{\parallel} - D^{\perp} \big) + \hat{E}^{\mathrm{dev}} \Big(\dot{D}^{\parallel} - \dot{D}^{\perp} \Big) , \tag{87.7}$$

$$\sigma^{\parallel} = E^{\mathrm{sph}} \big(D^{\parallel} + 2D^{\perp} \big) \ : \tag{87.8}$$

Expressing $D^{\perp}$ from (87.6), substituting it into (87.5), moving all $\sigma^{\parallel}$ related terms to the lhs, and dividing by the coefficient of $\sigma^{\parallel}$, one obtains

$$\sigma^{\parallel} + \frac{\hat{E}^{\mathrm{dev}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \dot{\sigma}^{\parallel} = \frac{3E^{\mathrm{sph}} E^{\mathrm{dev}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} D^{\parallel} + 3 \frac{E^{\mathrm{sph}} \hat{E}^{\mathrm{dev}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \dot{D}^{\parallel} . \tag{87.9}$$

Therefore, this emergent uniaxial rheology is actually a Poynting–Thomson model. Observe that, on the rhs, the coefficient of $D^{\parallel}$ is Young's modulus [cf. (63.1)], as expected.

At the general level of a Kluitenberg–Verhás – Kluitenberg–Verhás model pair, (87.3)–(87.4), the result is

$$\begin{aligned}
\sigma^{\parallel} &+ \frac{\hat{E}^{\mathrm{dev}} + 2\hat{E}^{\mathrm{sph}} + \tau^{\mathrm{sph}} E^{\mathrm{dev}} + 2\tau^{\mathrm{dev}} E^{\mathrm{sph}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \dot{\sigma}^{\parallel} \\
&+ \frac{\hat{\hat{E}}^{\mathrm{dev}} + 2\hat{\hat{E}}^{\mathrm{sph}} + \tau^{\mathrm{sph}} \hat{E}^{\mathrm{dev}} + 2\tau^{\mathrm{dev}} \hat{E}^{\mathrm{sph}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \ddot{\sigma}^{\parallel} \\
&\qquad + \frac{\tau^{\mathrm{sph}} \hat{\hat{E}}^{\mathrm{dev}} + 2\tau^{\mathrm{dev}} \hat{\hat{E}}^{\mathrm{sph}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \dddot{\sigma}^{\parallel} = \frac{3E^{\mathrm{sph}} E^{\mathrm{dev}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} D^{\parallel} \\
&\qquad\qquad + 3\frac{E^{\mathrm{sph}} \hat{E}^{\mathrm{dev}} + E^{\mathrm{dev}} \hat{E}^{\mathrm{sph}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \dot{D}^{\parallel} \\
&\qquad\qquad + 3\frac{E^{\mathrm{dev}} \hat{\hat{E}}^{\mathrm{sph}} + \hat{E}^{\mathrm{sph}} \hat{E}^{\mathrm{dev}} + E^{\mathrm{sph}} \hat{\hat{E}}^{\mathrm{dev}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \ddot{D}^{\parallel} \\
&\qquad\qquad + 3\frac{\hat{E}^{\mathrm{dev}} \hat{\hat{E}}^{\mathrm{sph}} + \hat{E}^{\mathrm{sph}} \hat{\hat{E}}^{\mathrm{dev}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \dddot{D}^{\parallel} \\
&\qquad\qquad + \frac{3\hat{\hat{E}}^{\mathrm{sph}} \hat{\hat{E}}^{\mathrm{dev}}}{E^{\mathrm{dev}} + 2E^{\mathrm{sph}}} \ddddot{D}^{\parallel} .
\end{aligned} \tag{88.1}$$

This emergent uniaxial rheology contains, therefore, third and fourth time derivative as well, and contains the elementary coefficients in rather intertwined combinations. Now imagine that you wish to fit the rheological coefficients on measurement data, assuming this equation. Measurement data always contain some error/noise, which gets enlarged when time derivatives are defined – by any method – from the measured time series. Furthermore, even if you succeed in obtaining the coefficients in (88.1) [108], you should be able to calculate the elementary coefficients $\tau^{\mathrm{dev}}, E^{\mathrm{dev}}, \hat{E}^{\mathrm{dev}}, \hat{\hat{E}}^{\mathrm{dev}}, \tau^{\mathrm{sph}}, E^{\mathrm{sph}}, \hat{E}^{\mathrm{sph}}, \hat{\hat{E}}^{\mathrm{sph}}$. However, the set of nonlinear equations to solve has multiple solutions, which can be determined only numerically, with errors further amplified.[109]

What to do? Let us measure $D^{\perp}(t)$ as well. Then we are able to the combinations $D^{\parallel} - D^{\perp}$, $D^{\parallel} + 2D^{\perp}$ so the task of determining eight elementary coefficients has been reduced to determining them in two independent groups by fitting on (87.3) and (87.4) separately, where both equations contain directly the elementary coefficients, not nonlinearly derived ones.

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[108] You won't.

[109] The noise can easily lead to equations with complex solutions, rendering the approach useless.

rheological coefficient	fitted value	standard error
$\tau^{\text{dev}}/\text{s}$	0.3600	±0.0659
$E^{\text{dev}}/\text{GPa}$	0.8612	±0.0556
$\hat{E}^{\text{dev}}/(\text{GPa}\cdot\text{s})$	0.4724	±0.0686
$\hat{\hat{E}}^{\text{dev}}/\big(\text{GPa}\cdot\text{s}^2\big)$	0.0029	±0.0010
$\tau^{\text{sph}}/\text{s}$	0.2329	±0.0904
$E^{\text{sph}}/\text{GPa}$	4.5708	±1.0392
$\hat{E}^{\text{sph}}/(\text{GPa}\cdot\text{s})$	1.8566	±0.4401
$\hat{\hat{E}}^{\text{sph}}/\big(\text{GPa}\cdot\text{s}^2\big)$	0.0013	±0.0220

Table 89.1 Fitted rheological coefficients for the data taken on the polyamide-6 sample shown in Sect. 3.12. Results taken from paper `https://doi.org/10.3311/PPci.8628` .

In addition to measuring $\varepsilon_{t_0}^{\perp}$, the best is to measure the temperature of the sample as well, as already emphasized in Sect. 3.12. Then we have additional information regarding reversible and irreversible processes: Joule–Thomson, rheological and plastic each. Thermodynamics helps mechanics to separate these aspects.

4.11 Plasticity of solids

Starting here again with the 1D treatment, the temperature dependence of l_{R} has been seen a reversible type of the change of relaxed length: if we return to an initial temperature, relaxed length returns to its initial value. Plasticity is an another type of change of l_{R}, and that is irreversible. As we see below, it is irreversible not only in the everyday sense that you pull the spring of your ballpoint pen to three times longer and then you cannot push it back to its initial size: it is accompanied by entropy production, too.

If the change rate of relaxed length stems from two sources: temperature change and plastic change,

$$\frac{\mathrm{d}l_{\text{R}}}{\mathrm{d}t} = l_{\text{R}}\alpha\frac{\mathrm{d}T}{\mathrm{d}t} + \left(\overset{*}{l}_{\text{R}}\right)_{\text{plastic}} \tag{89.1}$$

then calculation (49.3) contains an extra term,

$$L = \dot{D} + \alpha\dot{T} + Z\,, \qquad Z = \frac{\left(\overset{*}{l}_{\text{R}}\right)_{\text{plastic}}}{l_{\text{R}}}\,, \tag{89.2}$$

where Z can be named *plastic change rate.* It provides an additive extra contribution in small-deformation strain (49.6), in addition to deformedness change and thermal expansion:

$$\varepsilon_{t_0}(t) = [D(t) - D(t_0)] + \alpha \Delta T_{t_0}(t) + \int_{t_0}^{t} Z(\tilde{t})\,\mathrm{d}\tilde{t} = (\varepsilon_{\mathrm{el}})_{t_0}(t) + (\varepsilon_{\mathrm{th}})_{t_0}(t) + \left(\varepsilon_{\mathrm{pl}}\right)_{t_0}(t). \tag{90.1}$$

Z has to be given – like interaction functions are given – as the function of the state variables as well as change rate type ones like B is for simple materials. Without any attempt to provide a complete treatment of such *flow rules*, for illustration, presented here is just one plausible example for such a flow rule:

$$Z = \begin{cases} \gamma_\sigma \dot{\sigma} & \text{if} \quad |\sigma| \ge \sigma_{\mathrm{yield}} \quad \text{and} \quad \frac{\mathrm{d}}{\mathrm{d}t}|\sigma| \ge 0\,, \\ 0 & \text{otherwise}\,, \end{cases} \tag{90.2}$$

with a positive γ_σ and a positive *yield stress* value σ_{yield}. In words, plastic change rate is proportional to stress change rate, but is nonzero only if (the magnitude of) stress is larger than a certain limit (a 'strength' type characteristic value of the material) and only during loading (when the magnitude of stress increases) – it is zero during unloading[110]. Larger γ_σ means that smaller $\dot{\sigma}$ is needed for a Z; the limit of sending γ_σ to infinity and, correspondingly, $\dot{\sigma}$ to zero is the so-called *ideal plasticity* where the magnitude of stress cannot exceed the yield stress value. For that limiting model of plasticity, not (90.2) but some other formula is needed to predict Z.[111] Fortunately, (90.2) with some ordinary finite γ_σ is typically closer to reality.

If we neglect thermal expansion and start with an initial state with $D(t_0) = 0$ then, during loading above the yield limit, (90.2) tells

$$\dot{\varepsilon}_{t_0} = \dot{D} + Z = \dot{D} + \gamma_\sigma \dot{\sigma} = \dot{D} + \overbrace{\gamma_\sigma E \dot{D}}^{\sigma = ED} = (1 + \gamma_\sigma E)\,\dot{D} = (1 + \gamma_\sigma E)\,\frac{\dot{\sigma}}{E}\,, \tag{90.3}$$

$$\frac{\dot{\sigma}}{\dot{\varepsilon}_{t_0}} = \frac{E}{1 + \gamma_\sigma E}\,, \tag{90.4}$$

that is, the effective Young's modulus has decreased from E to a somewhat lower value. Such a behaviour is observed indeed – see, *e.g.,* Figure 54.1 –, justifying that (90.2) is a realistic (though probably simplistic) model.

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[110] when the level of 'torture' of the material weakens

[111] In the 3D treatment, there is a yield stress (hyper)surface in the space of possible stress tensor values, and the whole story is more involved.

Note that $\frac{\mathrm{d}}{\mathrm{d}t}|\sigma| \geq 0$ can also be formulated as

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(|\sigma|^2\right) \geq 0\,, \qquad \frac{\mathrm{d}}{\mathrm{d}t}\left(\sigma^2\right) \geq 0\,, \qquad \sigma\dot{\sigma} \geq 0\,. \tag{91.1}$$

Without plasticity, solids with elasticity and thermal expansion have been seen reversible in the thermodynamical sense as well, *i.e.,* there has been no entropy production. Here, the extra term $\frac{1}{\varrho}\sigma Z$ in $\overset{*}{w} = \frac{1}{\varrho}\sigma L$ leads to a nonzero entropy production term[112]

$$\frac{1}{\varrho T}\sigma Z\,. \tag{91.2}$$

Thermodynamics requires positive definiteness of this expression. For instance, the above example (90.2) fulfils this [cf. (91.1)]. Observe that 'no plastic change during unloading' is an essential part for this: thermodynamics forbids plastic change during unloading! [113]

Also without showing the details, one finds that the Joule–Thomson temperature change during adiabatic loading seen in Sect. 3.12 is modified to

$$c\,\dot{T}\Big|_s = -\frac{E\alpha}{\varrho}T\,\dot{D}\Big|_s + \frac{1}{\varrho}\sigma Z\,, \tag{91.3}$$

in words: plastic work increases temperature. This has been seen in Figure 54.1, where plasticity originated warming overplayed Joule–Thomson originated cooling.

In the 3D treatment, (89.2) is generalized to

$$\dot{\mathbf{D}} + \alpha\dot{T}\mathbf{1} + \mathbf{Z} = \mathbf{L}^{\mathsf{S}} = \dot{\boldsymbol{\varepsilon}}_{t_0} \tag{91.4}$$

[cf. (58.1)] with the symmetric plastic change rate tensor $\mathbf{Z}$. For metals, $\mathbf{Z}$ may be purely deviatoric ($\mathbf{Z}^{\mathrm{sph}} = \mathbf{0}$) corresponding to volume-preserving plastic change. For materials with different microscopic/mesoscopic structure (with voids and other spatial structures), *e.g.,* for rocks, $\mathbf{Z}^{\mathrm{sph}}$ may also be relevant.

For uniaxial processes, (91.4) is equivalent to the two component equations

$$\dot{\varepsilon}^{\shortparallel}_{t_0} = \dot{D}^{\shortparallel} + \alpha\dot{T} + Z^{\shortparallel}\,, \tag{91.5}$$

$$\dot{\varepsilon}^{\perp}_{t_0} = \dot{D}^{\perp} + \alpha\dot{T} + Z^{\perp} = -\nu\dot{D}^{\shortparallel} + \alpha\dot{T} + Z^{\perp}\,. \tag{91.6}$$

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[112] The calculation can be done basically analogously to (84.1), just here we have no irreversible *stress* contribution nor *energy* contribution but have irreversible *kinematic* contribution.

[113] At least, in the framework presented here. If rheology or other internal processes are also present then an Onsagerian cross-effect can allow plastic change during unloading, at the price of some other irreversible effect.

[cf. (58.6)–(58.7) and (63.2)]. If $\mathbf{Z}^{\mathrm{sph}} = \mathbf{0}$ then $Z^{\perp} = -\frac{1}{2} Z^{\shortparallel}$.

The yield condition in a 3D generalization of the flow rule (90.2) must also be formulated in terms of the stress tensor, *e.g.*, containing scalar invariants of $\boldsymbol{\sigma}$ like $\mathrm{tr}\left[\left(\boldsymbol{\sigma}^{\mathrm{dev}}\right)^2\right]$.

The entropy production formula (91.2) and the change rate of temperature (91.3) are generalized to contain $\mathrm{tr}\,(\boldsymbol{\sigma}\mathbf{Z})$ [and see (64.4)]. For uniaxial processes, $\mathrm{tr}\,(\boldsymbol{\sigma}\mathbf{Z})$ gets simplified to $\sigma^{\shortparallel} Z^{\shortparallel}$ [analogously to (63.6)].

Finally, some summarizing comments are that, if elasticity, thermal expansion, rheology and plasticity are each present then motion of the material is composed of elastic extension, thermal expansion and plastic change, stress is composed of elastic and rheological part. Onsagerian cross-effect between rheology and plasticity can also be present, leading to a 3 × 3 Onsagerian coupling matrix mixing $\mathbf{L}^{\mathsf{S}}$, $\boldsymbol{\eta}$, and $\mathbf{Z}$, leading to rather complicated possible behaviours. Finally, gradual degradation of the structure of the material – caused by any of the above aspects (elasticity, thermal expansion, rheology or plasticity) can also be described via irreversible thermodynamics, for example, with the aid of a scalar irreversible variable (sometimes called *damage*). Damage can be so remarkable that failure can also occur (the sample breaks). Failure[114] may be attributed to loss of thermodynamical asymptotic stability, for example, in the form that concavity of entropy gets violated in some region of the state space. Notably, all these can be modelled in the $\boxed{2}$ framework.

4.12 The Moutier–Serrier–Reitlinger–Chambadal–Novikov–Curzon–Ahlborn engine

The model considered here stands between $\boxed{1}$ and $\boxed{2}$, and was a historically important step for the development concerning $\boxed{2}$. Here, heat is already treated via an interaction function, the related irreversibility is acknowledged, and time is explicitly considered, but time dependence of the process is simplified – constancy during heat absorption and during heat release.

This kind of model was proposed by many independent authors during the history of thermodynamics[115], hence the many names; hereafter, only the abbreviation MSR-CNCA will be used.

We need to start with recalling briefly some properties of the Carnot engine/cycle/model, also fixing some notations. The Carnot engine receives heat Q_+

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[114] And, according to Verhás (see his book listed in Sect. 1.2), plasticity, too.

[115] The – probably incomplete – timeline is: J. Moutier (1872) – L. Serrier (1888) – H. B. Reitlinger (1929) – P. Chambadal (1957) – I. Novikov (1957) – F. L. Curzon & B. Ahlborn (1975). See M. Feidt, *Entropy* **19** (2017) 369, `https://doi.org/10.3390/e19070369`.

at constant temperature T_+ from an environment (reservoir) that also has temperature T_+. Correspondingly, the entropy of the engine increases by $\Delta S_+ = Q_+/T_+$. Then comes an adiabatic subprocess when work is done and the temperature of the engine drops to T_-, the temperature of another environment, to which the engine releases heat, subsequently, the heat-type energy change being $Q_- < 0$. At last, an adiabatic temperature increase happens, back to T_+. The energy loss characterized by Q_- is necessary because it is the corresponding entropy change, $\Delta S_- = Q_-/T_- = -\Delta S_+ < 0$ that brings back entropy, a state quantity, back to its initial value – for a cycle, all state quantities have to return to their original value.

Since the change of internal energy (another state quantity) along a complete cycle is also zero, the total work-type energy change can be expressed with the aid of the first law of thermodynamics:

$$0 = \Delta E = Q_+ + Q_- + W \qquad \Longrightarrow \qquad W = -Q_+ - Q_- . \tag{93.1}$$

Observing

$$\frac{Q_-}{Q_+} = \frac{T_-\Delta S_-}{T_+\Delta S_+} = \frac{T_-}{T_+} \cdot \underbrace{\frac{\Delta S_-}{\Delta S_+}}_{-1} = -\frac{T_-}{T_+}, \tag{93.2}$$

we obtain for the thermal efficiency the following result:

$$\eta = \frac{-W}{Q_+} = \frac{Q_+ + Q_-}{Q_+} = 1 + \frac{Q_-}{Q_+} \overset{(93.2)}{=} 1 - \frac{T_-}{T_+} . \tag{93.3}$$

The MSRCNCA model is the generalization when the engine itself still follows a Carnot cycle with temperatures T_+ and T_- but it receives the heat Q_+ during a specified time interval t_+ from an environment with temperature $T_>$ with the constant heating rate

$$\overset{*}{Q}_+ = -\Gamma_+(T_+ - T_>) , \qquad Q_+ = t_+\overset{*}{Q}_+ > 0 , \tag{93.4}$$

and releasing heat occurs analogously, during a time interval t_-, towards an environment with temperature $T_<$, according to the constant heating rate

$$\overset{*}{Q}_- = -\Gamma_-(T_- - T_<) , \qquad Q_- = t_-\overset{*}{Q}_- < 0 \tag{93.5}$$

(Γ_+, Γ_- being positive constant coefficients). The total time for the cycle is $t_\circ$, and let λ denote the ratio $(t_+ + t_-)/t_\circ$. While thermal efficiency is indeed an informative number, in the current, more realistic, setting, we are able to pose and answer practically more interesting questions as well. Such a question is as follows: with fixed engineering and environmental parameters Γ_+, Γ_-, $T_>$, $T_<$, t_+, t_-, $t_\circ$, at what operating temperatures T_+, T_- will the engine offer highest average useful power?

The average useful power can be expressed and re-expressed as follows:

$$\begin{aligned}
\Pi &= \frac{-W}{t_\circ} = \lambda\frac{-W}{t_+ + t_-} = \lambda\frac{Q_+ + Q_-}{t_+ + t_-} = \lambda\frac{Q_+ + Q_-}{\frac{Q_+}{\Gamma_+(T_> - T_+)} + \frac{Q_-}{\Gamma_-(T_< - T_-)}} = \\
&= \lambda\frac{1 + Q_-/Q_+}{\frac{1}{\Gamma_+(T_> - T_+)} + \frac{Q_-/Q_+}{\Gamma_-(T_< - T_-)}} \overset{(93.2)}{=} \lambda\frac{1 - T_-/T_+}{\frac{1}{\Gamma_+(T_> - T_+)} - \frac{T_-/T_+}{\Gamma_-(T_< - T_-)}} = \\
&= \lambda\Gamma_+(T_> - T_+)\Gamma_-(T_< - T_-)\frac{1 - T_-/T_+}{\Gamma_-(T_< - T_-) - \Gamma_+(T_> - T_+)(T_-/T_+)} = \\
&= \lambda\Gamma_+\Gamma_-\frac{(T_> - T_+)(T_< - T_-)(T_+ - T_-)}{\Gamma_-(T_< - T_-)T_+ - \Gamma_+(T_> - T_+)T_-}\,. \qquad (94.1)
\end{aligned}$$

In order to obtain a maximum, first let us check whether the boundary of the allowed region for the points (T_+, T_-) contains a local maximum. Now, the region in question is determined as $T_< \le T_- \le T_+ \le T_>$. If $T_+ = T_>$ then $Q_+ = 0$ so there is no received heat from which the engine could produce work. Similarly, if $T_- = T_<$ then there is zero released heat, with accompanying zero released entropy ΔS_-, thus with zero gained entropy ΔS_+ and, hence, with zero received heat which again means zero work. Finally, $T_+ = T_-$ means zero thermal efficiency [see (93.3)] and, consequently, zero work [see (93.3) again].

Next, for a maximum within the allowed domain, one has to solve the set of equations

$$\left.\frac{\partial\Pi}{\partial T_+}\right|_{T_-} = 0\,, \qquad \left.\frac{\partial\Pi}{\partial T_-}\right|_{T_+} = 0\,. \qquad (94.2)$$

The calculation is not easy but doable. While the solution $\left(T_+^{\text{opt}}, T_-^{\text{opt}}\right)$ itself is not too illuminating to see, the ratio of the two optimal temperatures, $\frac{T_-^{\text{opt}}}{T_+^{\text{opt}}}$ is remarkable. Namely, one finds that this ratio is independent of all details of the engine and depends only on the environmental temperatures:

$$\frac{T_-^{\text{opt}}}{T_+^{\text{opt}}} = \sqrt{\frac{T_<}{T_>}}\,. \qquad (94.3)$$

It also follows then that

$$\eta_{\text{MSRCNCA}}^{\text{opt}} \overset{(93.3)}{=} 1 - \sqrt{\frac{T_<}{T_>}} \le \left(1 - \sqrt{\frac{T_<}{T_>}}\right)\left(1 + \sqrt{\frac{T_<}{T_>}}\right) = 1 - \frac{T_<}{T_>} = \eta_{\text{Carnot}}^{\text{opt}}\,. \qquad (94.4)$$

The following table compares this optimal RNCNA thermal efficiency to the corresponding Carnot efficiency, and to observed efficiency, in some real-life power plants.

Power plant	$T_<$	$T_>$	η_{Carnot}	$\eta^{\text{opt}}_{\text{MSRCNCA}}$	η_{observed}
West Thurrock (UK) coal-fired power plant	25 °C	565 °C	0.64	0.40	0.36
CANDU (Canada) nuclear power plant	25 °C	300 °C	0.48	0.28	0.30
Larderello (Italy) geothermal power plant	80 °C	250 °C	0.33	0.178	0.16

Table 95.1 Examples taken from `https://en.wikipedia.org/wiki/Endoreversible_thermodynamics` (2017-01-27).

We can observe that, despite the simplifying approximations, the MSRCNCA efficiency provides a surprisingly good estimate to the real-life one, contrary to the Carnot efficiency.

5 Basics of continuum thermodynamics

5.1 Balances

In $\boxed{4}$, equations can be classified into four classes:

- Constitutive relationships,
- Kinematic relationships – the motion of the continuum requires new variables like the velocity field $\mathbf{v}$ and the velocity gradient

$$\mathbf{L} = \mathbf{v} \otimes \overset{\leftarrow}{\nabla} \qquad \text{(in Cartesian components: } L_{ij} = \partial_j \mathrm{v}_i) , \tag{96.1}$$

  which have relationships to already known kinematic ones like $\mathbf{D}$,
- Balances = conservation 'laws' (properties) – for mass, momentum, energy *etc.*
- Interaction functions – among the various degrees of freedom of the material, and with the environment, *e.g.,* volumetric forces (gravity, electromagnetic), heat (*e.g.,* microwave heating), and Onsagerian relationships including cross-effects.

Starting with the integral/global **balance of mass:** mass in a spatial domain $\mathcal{V}$ that is fixed w.r.t. an inertial reference frame is, with customary notations,

$$m_{\mathcal{V}} = \iiint_{\mathcal{V}} \varrho(t, \mathbf{r}) \, \mathrm{d}V , \tag{96.2}$$

which changes in time as material flows out/in through the boundary $\mathcal{A}$ of $\mathcal{V}$:

$$\frac{\mathrm{d}m_{\mathcal{V}}}{\mathrm{d}t} = \iiint_{\mathcal{V}} \frac{\partial \varrho}{\partial t} \, \mathrm{d}V = - \oiint_{\mathcal{A}} \varrho \mathbf{v} \, \mathrm{d}\mathbf{A} \overset{\substack{\text{Gauss'} \\ \text{theorem}}}{=} - \iiint_{\mathcal{V}} \nabla \cdot (\varrho \mathbf{v}) \, \mathrm{d}V , \tag{96.3}$$

from which, at places where the fields $\varrho, \mathbf{v}$ are smooth enough, the differential/local balance of mass follows:[116]

$$\frac{\partial \varrho}{\partial t} = -\nabla \cdot \underbrace{(\varrho \mathbf{v})}_{\substack{\mathbf{i}_m , \\ \text{convective} \\ \text{current}}} = -(\nabla \varrho) \cdot \mathbf{v} - \varrho \nabla \cdot \mathbf{v} . \tag{96.4}$$

The operator combination

$$\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \tag{96.5}$$

---

[116] (96.3) holds for 'any' $\mathcal{V}$ around $\mathbf{r}$ so we divide it by $\iiint_{\mathcal{V}} \mathrm{d}V$ and shrink $\mathcal{V}$ to $\mathbf{r}$.

appears in $\boxed{4}$ frequently, is called material/comoving/substantial/substantive/... time derivative, and tells how a quantity changes in time at a fixed material point while it travels with velocity $\mathbf{v}$. Hereafter, it is denoted simply by an overdot – but do not confuse it with $\frac{\partial}{\partial t}$. A convenient property of the material time derivative is that it fulfils the rules

$$(\mathtt{f}\mathtt{g})^{\dot{}} = \dot{\mathtt{f}}\mathtt{g} + \mathtt{f}\dot{\mathtt{g}}, \qquad \left(\frac{1}{\mathtt{g}}\right)^{\dot{}} = -\frac{\dot{\mathtt{g}}}{\mathtt{g}^2}. \tag{97.1}$$

Accordingly, (96.4) can be re-expressed as

$$\dot{\varrho} = -\varrho \nabla \cdot \mathbf{v}. \tag{97.2}$$

With $v = \frac{1}{\varrho}$, this says

$$-\frac{1}{v^2}\dot{v} = -\frac{1}{v}\nabla \cdot \mathbf{v}, \qquad \frac{\dot{v}}{v} = \varrho\dot{v} = \nabla \cdot \mathbf{v} \overset{(96.1)}{=} \operatorname{tr} \mathbf{L} \overset{(60.6)}{=} \operatorname{tr} \mathbf{L}^{\mathsf{S}}. \tag{97.3}$$

For the balance of momentum, the density of which is $\varrho\mathbf{v}$, one obtains – details omitted here[117] –

$$\varrho\dot{\mathbf{v}} = \nabla \cdot \boldsymbol{\sigma} + \varrho\mathbf{g} \tag{97.4}$$

with the stress tensor $\boldsymbol{\sigma}$ (assumed symmetric) and volumetric field strength vector $\mathbf{g}$ incorporating external gravitational and electromagnetic effects – hereafter, we take $\mathbf{g} = \mathbf{0}$ for simplicity.

In the balance of energy, we have the sum of kinetic energy density and internal energy density,

$$\frac{1}{2}\varrho\mathbf{v}^2 + \varrho e, \tag{97.5}$$

to which the convective current density

$$\left(\frac{1}{2}\varrho\mathbf{v}^2 + \varrho e\right)\mathbf{v} \tag{97.6}$$

is accompanied. There is conductive current density as well: heat current density (loosely called 'heat flux') $\mathbf{j}_E$ describes "heat" (internal energy) loss/gain through $\mathcal{A}$, and the mechanical power $\boldsymbol{\sigma}\mathbf{v}$ of $\boldsymbol{\sigma}$ at $\mathcal{A}$ is another source of energy change. (Volumetric heat sources and potential energy contributions stemming from $\mathbf{g}$ are currently neglected for simplicity). Sparing the somewhat lengthy calculation again[118],

---

[117] Just one comment: (97.2) is also used.

[118] Now both (97.2) and (97.4) are utilized.

the integral balance leads to the following differential one [partially anticipated in (64.3)]:

$$\varrho\dot{e} = -\nabla\cdot\mathbf{j}_E + \operatorname{tr}(\boldsymbol{\sigma}\mathbf{L}) \overset{(60.8)}{=} -\nabla\cdot\mathbf{j}_E + \operatorname{tr}\left(\boldsymbol{\sigma}\mathbf{L}^{\mathsf{S}}\right) . \tag{98.1}$$

Especially, for a continuum at rest w.r.t. the given reference frame, $\mathbf{v} = \mathbf{0}$, involving both $\mathbf{L} = \mathbf{0}$ and that the process is isochoric,

$$\varrho\dot{e} = \varrho\left(\left.\frac{\partial e}{\partial T}\right|_v \dot{T} + \left.\frac{\partial e}{\partial v}\right|_T \underbrace{\dot{v}}_{=0}\right) \overset{(29.4)}{=} \varrho c_v\dot{T} \overset{(98.1)}{=} -\nabla\cdot\mathbf{j}_E . \tag{98.2}$$

Another special case, frequently appearing in practice, is when $\boldsymbol{\sigma}^{\mathrm{dev}} = \mathbf{0}$. Then, instead of $\boldsymbol{\sigma} = \boldsymbol{\sigma}^{\mathrm{sph}}$, pressure $p = -\sigma^{\mathrm{sph}}$ is used customarily, and we find

$$\operatorname{tr}(\boldsymbol{\sigma}\mathbf{L}) = \operatorname{tr}\left(\sigma^{\mathrm{sph}}\mathbf{1}\mathbf{L}\right) \overset{(97.3)}{=} -p\frac{\dot{v}}{v} , \tag{98.3}$$

$$\varrho\dot{e} - \operatorname{tr}(\boldsymbol{\sigma}\mathbf{L}) = \varrho\dot{e} + p\frac{\dot{v}}{v} = \varrho(\dot{e} + p\dot{v}) = \varrho\left(\dot{e} + (pv)^{\cdot} - \dot{p}v\right) \overset{(28.4)}{=} \varrho\left(\dot{h} - \dot{p}v\right) . \tag{98.4}$$

If pressure is constant in time (isobaric process) then this gets further simplified to

$$\varrho\dot{e} - \operatorname{tr}(\boldsymbol{\sigma}\mathbf{L}) = \varrho\dot{h} = \varrho\left(\left.\frac{\partial h}{\partial T}\right|_p \dot{T} + \left.\frac{\partial h}{\partial p}\right|_T \dot{p}\right) = \varrho\left.\frac{\partial h}{\partial T}\right|_p \dot{T} \overset{(29.4)}{=} \varrho c_p\dot{T} \overset{(98.1)}{=} -\nabla\cdot\mathbf{j}_E . \tag{98.5}$$

The balance of entropy reads, analogously,

$$\varrho\dot{s} = -\nabla\cdot\mathbf{j}_S + \pi_S \tag{98.6}$$

with entropy current density $\mathbf{j}_S$, which is usually assumed to be, in analogue with the Gibbs relation (25.7)[119],

$$\mathbf{j}_S = \frac{1}{T}\mathbf{j}_E , \tag{98.7}$$

and entropy production π_S, which, in the spirit of the second law of thermodynamics, should be non-negative.

---

[119] Transferred entropy and internal energy through a given surface.

5.2 Fourier heat conduction

Heat conduction is an irreversible process related to the term $\nabla\cdot\mathbf{j}_E$ in the balance of energy. Now let us consider two special cases, ‘rigid’ and isobaric processes, on the same footing. In light of (26.3), both $\varrho c_v \dot{T}$ in (98.2) and $\varrho c_p \dot{T}$ in (98.5) can be written as

$$\varrho T \left.\frac{\partial s}{\partial T}\right|_{\mathrm{pr}} \dot{T}, \qquad \text{with} \quad |_{\mathrm{pr}} = |_{\mathbf{v}=\mathbf{0}} \quad \text{and} \quad |_{\mathrm{pr}} = |_{p}, \quad \text{respectively.} \tag{99.1}$$

Then, both (98.2) and (98.5) read

$$\varrho c|_{\mathrm{pr}} \dot{T} = -\nabla\cdot\mathbf{j}_E\,. \tag{99.2}$$

We also have

$$\dot{s} = \dot{s}|_{\mathrm{pr}} = \left.\frac{\partial s}{\partial T}\right|_{\mathrm{pr}} \dot{T}, \qquad \varrho\dot{s} = \varrho \left.\frac{\partial s}{\partial T}\right|_{\mathrm{pr}} \dot{T} \overset{(99.1)}{=} \frac{1}{T}\varrho c|_{\mathrm{pr}} \dot{T} \overset{(99.2)}{=} -\frac{1}{T}\nabla\cdot\mathbf{j}_E\,. \tag{99.3}$$

Hence,

$$\begin{aligned} \pi_S \overset{(98.6)}{=} \varrho\dot{s} + \nabla\cdot\mathbf{j}_S &\overset{(99.3)}{=} -\frac{1}{T}\nabla\cdot\mathbf{j}_E + \overset{(98.7)}{\nabla\cdot\left(\frac{1}{T}\mathbf{j}_E\right)} \\ &= -\frac{1}{T}\nabla\cdot\mathbf{j}_E + \nabla\left(\frac{1}{T}\right)\cdot\mathbf{j}_E + \frac{1}{T}\nabla\cdot\mathbf{j}_E = \nabla\left(\frac{1}{T}\right)\cdot\mathbf{j}_E\,. \end{aligned} \tag{99.4}$$

For isotropic materials, the Onsagerian way to ensure $\pi_S \geq 0$ is

$$\mathbf{j}_E = \lambda_{\mathrm{Ons}}\nabla\left(\frac{1}{T}\right), \qquad \lambda_{\mathrm{Ons}} \geq 0\,. \tag{99.5}$$

Here, the scalar multiplier λ_{Ons} may well be temperature dependent. Writing (99.5) further,

$$\mathbf{j}_E = \lambda_{\mathrm{Ons}}\left(-\frac{1}{T^2}\right)\nabla T = -\frac{\lambda_{\mathrm{Ons}}}{T^2}\nabla T = -\lambda_{\mathrm{Fou}}\nabla T\,, \tag{99.6}$$

the latter being the classic form of Fourier’s model for heat conduction.[120] Substituting it back to (99.2), one obtains

$$\begin{aligned} \underline{\varrho c|_{\mathrm{pr}} \dot{T}} &= \nabla\cdot(\lambda_{\mathrm{Fou}}\nabla T) = (\nabla\lambda_{\mathrm{Fou}})\cdot\nabla T + \lambda_{\mathrm{Fou}} \triangle T \\ &= \frac{\mathrm{d}\lambda_{\mathrm{Fou}}}{\mathrm{d}T}\nabla T\cdot\nabla T + \lambda_{\mathrm{Fou}} \triangle T = \underline{\frac{\mathrm{d}\lambda_{\mathrm{Fou}}}{\mathrm{d}T}\left(\nabla T\right)^2 + \lambda_{\mathrm{Fou}} \triangle T}\,, \end{aligned} \tag{99.7}$$

---

[120] The Fourier heat conduction coefficient λ_{Fou} is also frequently denoted by k.

where the first term on the underlined rhs – which term brings in nonlinearity unavoidably – is negligible only if the change of λ_{Fou} is negligible in the range of temperature changes involved.

It is to be mentioned that, if the material is not (so) simple – *e.g.,* it is heterogeneous (like composites, metal foams *etc.*) –, then (among others) (98.7) may need to be generalized, for example, replacing in it the scalar factor $\frac{1}{T}$ with a tensor called Nyíri multiplier, and the Fourier equation (99.7) becomes generalized to the Maxwell–Cattaneo–Vernotte, the Green–Naghdi, the Jeffrey-type, or the Guyer–Krumhansl equation, each bringing some higher time and/or space derivatives of T.

5.3 The Navier–Stokes equation

Now let us discuss a mechanical source of irreversibility. For brevity, now we neglect heat conduction (which can be added later without difficulty; in isotropic materials, vectorial heat conduction cannot have Onsagerian coupling to tensorial mechanics so these two aspects can be summed up without complication).

What follows here is actually the $\boxed{4}$ generalization of the $\boxed{2}$ discussion of viscosity seen in Sect. 4.6. We start with a simple material, and now assume that, in addition to its reversibility related pressure

$$p_0(e,v) = T\,\frac{\partial s}{\partial v}\bigg|_e \tag{100.1}$$

[cf. (28.1)], there is an irreversibility related additional stress term as well:[121]

$$\boldsymbol{\sigma} = -p_0\mathbf{1} + \boldsymbol{\sigma}_{\mathrm{irr}}\,. \tag{100.2}$$

Utilizing for the first term what we have seen in (98.3),

$$\varrho\dot{e} = \operatorname{tr}\left[\left(-p_0\mathbf{1} + \boldsymbol{\sigma}_{\mathrm{irr}}\right)\mathbf{L}\right] = -p_0\frac{\dot{v}}{v} + \operatorname{tr}\left[\boldsymbol{\sigma}_{\mathrm{irr}}\mathbf{L}^{\mathsf{S}}\right]\,. \tag{100.3}$$

Then entropy production is [with $\mathbf{j}_S = \mathbf{0}$, cf. (98.7) and that heat conduction is now omitted]

$$\begin{aligned}\pi_S &\overset{(98.6)}{=} \varrho\dot{s} = \varrho\left(\frac{\partial s}{\partial e}\bigg|_v \dot{e} + \frac{\partial s}{\partial v}\bigg|_e \dot{v}\right) \\ &\overset{(28.1)}{=} \varrho\frac{1}{T}\dot{e} + \varrho\frac{p_0}{T}\dot{v} \overset{(100.3)}{=} \frac{1}{T}\left(-p_0\frac{\dot{v}}{v} + \operatorname{tr}\left[\boldsymbol{\sigma}_{\mathrm{irr}}\mathbf{L}^{\mathsf{S}}\right]\right) + \frac{1}{v}\frac{p_0}{T}\dot{v} = \frac{1}{T}\operatorname{tr}\left[\boldsymbol{\sigma}_{\mathrm{irr}}\mathbf{L}^{\mathsf{S}}\right]\,.\end{aligned} \tag{100.4}$$

---

[121] However, for simplicity, entropy is not extended – that will lead to richer rheology as seen before.

For isotropic materials, non-negativity of this can be guaranteed analogously to 3D rheology of solids seen around (86.3) but, here, there are less terms[122] so the Onsagerian solution is simpler:

$$\boldsymbol{\sigma}_{\mathrm{irr}}^{\mathrm{dev}} = \hat{E}^{\mathrm{dev}}\big(\mathbf{L}^{\mathsf{S}}\big)^{\mathrm{dev}}, \qquad \boldsymbol{\sigma}_{\mathrm{irr}}^{\mathrm{sph}} = \hat{E}^{\mathrm{sph}}\left(\mathbf{L}^{\mathsf{S}}\right)^{\mathrm{sph}}, \qquad \hat{E}^{\mathrm{dev}}, \hat{E}^{\mathrm{sph}} \geq 0\,. \tag{101.1}$$

Put together,

$$\boldsymbol{\sigma}_{\mathrm{irr}} \overset{(59.1)}{=} \hat{E}^{\mathrm{dev}}\Big(\mathbf{L}^{\mathsf{S}} - \big(\mathbf{L}^{\mathsf{S}}\big)^{\mathrm{sph}}\Big) + \hat{E}^{\mathrm{sph}}\left(\mathbf{L}^{\mathsf{S}}\right)^{\mathrm{sph}} = \hat{E}^{\mathrm{dev}}\mathbf{L}^{\mathsf{S}} + \big(\hat{E}^{\mathrm{sph}} - \hat{E}^{\mathrm{dev}}\big)\left(\mathbf{L}^{\mathsf{S}}\right)^{\mathrm{sph}}. \tag{101.2}$$

Substituting this into the differential balance of momentum, (97.4), yields, after steps omitted here,

$$\varrho\dot{\mathbf{v}} = -\nabla p_0 + \varrho\mathbf{g} + \frac{\hat{E}^{\mathrm{dev}}}{2}\,\triangle\mathbf{v} + \frac{2\hat{E}^{\mathrm{sph}} + \hat{E}^{\mathrm{dev}}}{6}\nabla\left(\nabla\cdot\mathbf{v}\right) \tag{101.3}$$

for the simple case of constant $\hat{E}^{\mathrm{dev}}$, $\hat{E}^{\mathrm{sph}}$. Here, $\frac{\hat{E}^{\mathrm{dev}}}{2}$ is the classic viscosity coefficient (denoted usually by η or μ), and $\frac{2\hat{E}^{\mathrm{sph}}+\hat{E}^{\mathrm{dev}}}{6}$ is an independent other coefficient, with various conventional notations but always related to the term 'volume/volumetric viscosity'. In the approximation of an incompressible flow, $\nabla\cdot\mathbf{v} = 0$, the second coefficient becomes irrelevant.

If you recall how considerably viscosity of cooking oil decreases when the frying pan gets warm then you know the limitations of the assumption of constant $\hat{E}^{\mathrm{dev}}$, $\hat{E}^{\mathrm{sph}}$. Deriving the extra terms for nonconstant coefficients is an exercise left to the Reader.

5.4 Merits of the deviatoric–spherical decomposition

Finally, let us observe that the deviatoric–spherical decomposition of tensors has turned out to be useful and insightful from various aspects:

- Hooke's law for isotropic elastic solids is particularly simple [(61.6)–(61.7)];
- Thermal expansion of isotropic solids is present only in the spherical part, see Sect. 3.14;
- Plastic change typically occurs only deviatorically, see Sect. 4.11;

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[122] No $\boldsymbol{\eta}$ related terms.

- Rheology of isotropic solids gets separated to two much simpler submodels, making the otherwise practically intractable situation handleable, see Sect. 4.10;
- Viscosity turns out to be doubled, as seen in this Section, with volumetric viscosity being possibly remarkable for compressible flows.

6 Analytical and numerical computer calculations

Among softwares that are capable to perform analytical as well as numerical mathematical calculations, Maxima[123] is a free and cross-platform one. As all these programs (and as being a pioneering software in its field), Maxima also has its limitations and oddities (maybe more limitations and more oddities than the nonfree ones) but is definitely good enough for basic and medium-level work.[124]

Below follow some Maxima codes, partly to serve as an aid for computer solutions of thermodynamical problems, and partly to provide examples of the syntax of Maxima.

6.1 Ideal gas

Whenever we face at quantities that have dimensions (m, s, kg etc. and combinations), let us try to make them dimensionless using an enough number of nonzero dimensionless constants appearing in the situation. This makes it safe to work with numerical computer calculations, where it is not possible (or, at least, is nontrivial) to treat dimensionful quantities. In case of the ideal gas, we have only one such constant, R, which is not enough for making everything dimensionless. Then, for plotting, we have to choose some arbitrary units (like some SI units), and we have to remind ourselves time and again about this choice.

```
/* Ideal gas */

/* It is safer to claim everything to be positive: */
assume( T > 0, p > 0, s > 0, R > 0, cv > 0, v0 > 0, e0 > 0, _Pa > 0, _m3perkg > 0 );
assume( v > v0, e > e0 );

/* Constitutive functions: */
p_Tv : R*T/v;
e_Tv : cv*T;

/* For checking material stability: */
diff(e_Tv, T);  diff(p_Tv, v);

/* In the natural variables (e, v) of s: */
solve( e_Tv = e, T );
solve( e_Tv = e, T )[1];
T_ev : rhs( solve( e_Tv = e, T )[1] );
p_ev : subst( T_ev, T, p_Tv );  /* valid but not recommended syntax */
p_ev : subst( [T = T_ev], p_Tv );  /* valid and recommended syntax */ 0$

/* Checking the entropic property, in two ways: */
```

---

[123] Install it together with its (probably best) GUI, wxMaxima.

[124] And higher as well: an acquaintance of the author is said to have produced all his results for his PhD in Maxima.

```
diff(1/T_ev, v) - diff(p_ev/T_ev, e);
diff(e_Tv, v) - T*diff(p_Tv, T) + p_Tv;

/* Calculating specific entropy: */
s1_ev : integrate( subst( [v = v0, e = eint], 1/T_ev ), eint, e0, e );

s1_ev_dimgood : cv * log(e/e0);  radcan( s1_ev_dimgood - s1_ev );

s1_ev : s1_ev_dimgood;

s2_ev : integrate( subst( [v = vint], p_ev/T_ev ), vint, v0, v );

s2_ev_dimgood : R * log(v/v0);  radcan( s2_ev_dimgood - s2_ev );
s2_ev : s2_ev_dimgood;
s_ev : s1_ev + s2_ev;  /* s0 is chosen to be zero */ 0$

/* Chemical potential: */
mu_ev : e - T_ev * s_ev + p_ev * v;  mu_Tv : subst( [e = e_Tv], mu_ev );

/* The only constant R cannot make everything dimensionless, therefore:
   Dimensionless pressure:         pd  will have the meaning  p/_Pa
   Dimensionless specific volume:  vd  will have the meaning  v/_m3perkg
   Dimensionless spec. int. en.:   ed  will have the meaning  e/(_Pa*_m3perkg)
   Dimensionless temperature:      Td  will have the meaning  R*T/(_Pa*_m3perkg)  */
pd_Tdvd : subst( [T = _Pa*_m3perkg/R*Td, v = vd*_m3perkg], p_Tv/_Pa );

ed_Tdvd : subst( [T = Td/R*_Pa*_m3perkg, v = vd*_m3perkg], e_Tv/(_Pa*_m3perkg) );

Td_edvd : rhs( solve( ed_Tdvd = ed, Td )[1] );

pd_edvd : subst( [Td = Td_edvd], pd_Tdvd );

aux : [e = _Pa*_m3perkg*ed, e0 = _Pa*_m3perkg*ed0, v = _m3perkg*vd, v0 = _m3perkg*vd0]$
sd_edvd : subst( aux, s_ev/R );  /* otherwise this line is too long. */;

radcan( ( cv/R * log( ed/ed0 ) + log( vd/vd0 ) ) - sd_edvd );
sd_edvd : cv/R * log( ed/ed0 ) + log( vd/vd0 )$

/* Plots: Isothermal lines: */
pd_Td_vd : subst( [Td = 1], pd_Tdvd );
wxplot2d( [pd_Td_vd], [vd, 1, 3] )$  /* ; does the same here. */ 0$

/* (Reversible) adiabatic lines: */
ed_sdvd : rhs( solve( sd_edvd = sd, ed )[1] );

pd_sd_vd : subst( [ed = ed_sdvd, ed0 = 1, vd0 = 1, sd = 1, cv = 3/2*R], pd_edvd );

wxplot2d( [pd_Td_vd, pd_sd_vd], [vd, 1, 3] )$

/* Concavity of specific entropy: */
wxplot3d( subst( [ed0 = 1, vd0 = 1, cv = 3/2*R], sd_edvd ), [ed, 1, 5], [vd, 1, 5] )$
```

```
plot3d( subst( [ed0 = 1, vd0 = 1, cv = 3/2*R], sd_edvd ), [ed, 1, 5], [vd, 1, 5] )$
```

See the comment lines for explanations. The last plotting command uses an external plotting program like Gnuplot[125], depending on configuration settings.

Note the convention for variable names: for example, the function $p(T, v)$ is represented via the expression named `p_Tv`. Always try to store much information in variable names – it is safer than storing them in comments/documentation.

6.2 Plotting discrete points, colour-blind friendly colours

When you obtain numerical results, you may need to plot discrete points (but maybe as connected by the computer so that your result looks continuous). The following code shows examples of the syntax involved.

In parallel, it contains a collection of colour-blind friendly colours. In a group of 25 people, you can expect at least one colour-blind person[126]. For them, pure red, green and blue are the worst.[127] To create figures that are intelligible for colour-blind people, you have various choices (in suggested order):

- using black only, apply various different line widths and types (solid, dashed, dash-dotted etc.), as well as various different symbols (filled and void circle, rectangle, triangle etc.),
- use various shades of grey only,
- choose colour-blind friendly colours (see the RGB codes of such a palette[126] in the example below).

```
/* Plotting discrete points [x1, y1], [x2, y2], ... : we use
   two lists: xl = [x1, x2, ...] and yl = [y1, y2, ...]
   Example: plotting circles using discrete points:
   (also an example for a for-loop and for color-blind-friendly colors)
                                 RGB 0-255      RGB %            CMYK %  Hue o
                               -----------   --------   ---------------  ----- */
cbfyellow    : "\#f0e442"$  /* 240 228  66   95 90 25    10   5  90    0     56 */
cbforange    : "\#e69f00"$  /* 230 159   0   90 60  0     0  50 100    0     41 */
cbfred       : "\#d55e00"$  /* 213  94   0   80 40  0     0  80 100    0     27 */
cbfmagenta   : "\#cc79a7"$  /* 204 121 167   80 60 70    10  70   0    0    326 */
cbflightblue : "\#56b4e9"$  /*  86 180 233   35 70 90    80   0   0    0    202 */
cbfblue      : "\#0072b2"$  /*   0 114 178    0 45 70   100  50   0    0    202 */
cbfgreen     : "\#009e73"$  /*   0 158 115    0 60 50    97   0  75    0    164 */
greyl : ["\#ffffff", "\#eeeeee", "\#dddddd", "\#cccccc", "\#bbbbbb", "\#aaaaaa",
         "\#999999", "\#888888", "\#777777", "\#666666", "\#555555", "\#444444",
         "\#333333", "\#222222", "\#111111", "\#000000"]$
```

---

[125] which may also be provided by the Maxima installer

[126] Kei Ito and Masataka Okabe, August, 2002; `https://jfly.uni-koeln.de/color/` .

[127] (For those interested: the author himself is not colour-blind. He is left-handed.)

```
x1l : makelist()$  y1l : makelist()$  x2l : makelist()$  y2l : makelist()$
x3l : makelist()$  y3l : makelist()$  x4l : makelist()$  y4l : makelist()$
x5l : makelist()$  y5l : makelist()$  x6l : makelist()$  y6l : makelist()$
x7l : makelist()$  y7l : makelist()$  x8l : makelist()$  y8l : makelist()$
R1 : 0.88$  R2 : 2.04$  R3 : 3.2$  R4 : 4.36$
R5 : 5.52$  R6 : 6.68$  R7 : 7.84$  R8 : 9$  N : 50$
for phi : 0 thru 2*%pi step 2*%pi/N do (
  x1l : append( x1l, [ R1*cos(phi) ] ),  y1l : append( y1l, [ R1*sin(phi) ] ),
  x2l : append( x2l, [ R2*cos(phi) ] ),  y2l : append( y2l, [ R2*sin(phi) ] ),
  x3l : append( x3l, [ R3*cos(phi) ] ),  y3l : append( y3l, [ R3*sin(phi) ] ),
  x4l : append( x4l, [ R4*cos(phi) ] ),  y4l : append( y4l, [ R4*sin(phi) ] ),
  x5l : append( x5l, [ R5*cos(phi) ] ),  y5l : append( y5l, [ R5*sin(phi) ] ),
  x6l : append( x6l, [ R6*cos(phi) ] ),  y6l : append( y6l, [ R6*sin(phi) ] ),
  x7l : append( x7l, [ R7*cos(phi) ] ),  y7l : append( y7l, [ R7*sin(phi) ] ),
  x8l : append( x8l, [ R8*cos(phi) ] ),  y8l : append( y8l, [ R8*sin(phi) ] ),
)$
wxplot2d( [ [ discrete, x1l, y1l ], [ discrete, x2l, y2l ],
  [ discrete, x3l, y3l ], [ discrete, x4l, y4l ], [ discrete, x5l, y5l ],
  [ discrete, x6l, y6l ], [ discrete, x7l, y7l ], [ discrete, x8l, y8l ] ],
  [color, cbfyellow, cbforange, cbfred, cbfmagenta,
    cbflightblue, cbfblue, cbfgreen, black],
  [xlabel, "Eight circles"], [ylabel, "In color-blind-friendly colors"],
  [legend, false], [x, -10, 10], [y, -10, 10], [yx_ratio, 1] );
wxplot2d( [ [ discrete, x1l, y1l ], [ discrete, x2l, y2l ],
  [ discrete, x3l, y3l ], [ discrete, x4l, y4l ], [ discrete, x5l, y5l ],
  [ discrete, x6l, y6l ], [ discrete, x7l, y7l ], [ discrete, x8l, y8l ] ],
  [color, greyl[2], greyl[4], greyl[6], greyl[8],
    greyl[10], greyl[12], greyl[14], greyl[16]],
  [xlabel, "Eight circles"], [ylabel, "In shades of grey"], [legend, false],
  [x, -10, 10], [y, -10, 10], [yx_ratio, 1] );
```

The outcomes are:

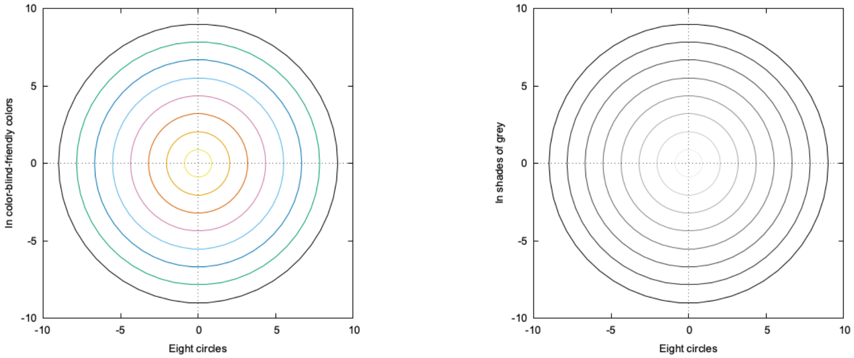

Figure 106.1 Plotting eight circles in colour-blind friendly colours and in shades of grey.

6.3 Interval halving / bisection method

A simple yet efficient algorithm for finding a root of an algebraic equation $f(x) = 0$ in an interval $x_{\text{left}} \leq x \leq x_{\text{right}}$ is realized in the next example. We assume that f is positive at one endpoint and negative at the other one. Then a continuous f has at least one root within the interval.

At each step, the algorithm shrinks the size of the interval to half size by shifting either the left or the right endpoint into the midpoint, depending on whether the value of f at the midpoint is positive or negative – the new interval will still have one endpoint with positive f and another with negative f. We continue until the size of the interval – or, alternatively, the value of f – is small enough for our purposes.

In case we initially know only an x_{left} but are sure a root $x > x_{\text{left}}$ must exist then let us choose a $\Delta x > 0$ and try $x_{\text{left}} + \Delta x$, $x_{\text{left}} + 2\Delta x$, $x_{\text{left}} + 4\Delta x$, $\ldots$, $x_{\text{left}} + 2^n \Delta x$, $\ldots$ as candidates for x_{right}. This is an efficient means of finding an x_{right}.

```
/* Example for interval halving (https://en.wikipedia.org/wiki/Bisection_method): */
/* solving  exp(-x) = x  in the interval  [0, 1]  */

fx : exp(-x) - x$  /* we will seek an x where fx is zero. */
/* First a visual check about the task: */
wxplot2d( [fx], [x, 0, 1], [color, black] );
/* we read off that the root is a bit less than 0.6. How good this guess is: */
subst( x = .6, fx );
wxplot2d( [fx], [x, 0.5, .7], [color, black] );
/* we read off that the root is around 0.56. How good this guess is: */
subst( x = .56, fx );

x_left : 0.$  x_right : 1.$  /* initial endpoints of the interval. */
/* We enforced Maxima to treat them and subsequent numbers as floating-point. */
fx_left : subst( x = x_left, fx )$  fx_right : subst( x = x_right, fx )$
if fx_left > 0 then ( sign_left : 1 ) else ( sign_left : -1 )$
if fx_right > 0 then ( sign_right : 1 ) else ( sign_right : -1 )$
sign_left;  sign_right;  /* we check that the signs are opposite. */
steps : 1$  /* it will register the number of steps performed. */

while abs( fx_right - fx_left ) > 1e-6 do (  /* we will stop only when the function
  is near zero up to 1e-6 = 10^(-6) at the approximate root. */
  x_new : 0.5 * ( x_left + x_right )  /* 0.5 instead of 1/2 to stay floating-point. */,
  fx_new : subst( x = x_new, fx ),
  if fx_new > 0 then ( sign_new : 1 ) else ( sign_new : -1 ),
  if sign_new = sign_left then (
    x_left : x_new, fx_left : fx_new
  ) else (
    x_right : x_new, fx_right : fx_new
  ),
  steps : steps + 1
)$
steps;
```

```
/* Checking whether the found root is around 0.56: */
x_new;  subst( x = x_new, fx );
```

The outcomes are:

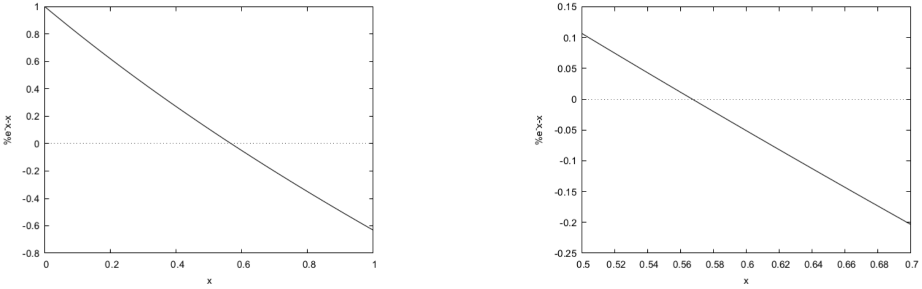

Figure 108.1 Behaviour of $e^{-x} - x$ around its root within the interval $[0, 1]$ (outputs of the plotting commands).

	Approximate root	How near to zero
From the first plot:	0.6	0.051188
From the second plot:	0.56	0.011209
Interval halving (22 steps):	0.567143	5.124564e-7

6.4 Finite difference method – example 1

In the subsequent example, a first order ordinary differential equation is solved numerically, via the simplest finite difference method.

Note that solving differential equations numerically is an art in itself. Here, the analogous advice applies as for choosing a model for a real-life situation: choose a more complicated one only if you have a severe performance reason for it. When switching to a more elaborate numerical scheme, you may gain large performance improvement but you risk losing a lot of time and effort by coding and debugging. (Will you meet the deadline?)

```
/* Example 1 for the finite difference method
   (https://en.wikipedia.org/wiki/Euler_method):
   solving  d f / d t = -k*f(t)  with initial condition  f(0) = f0 > 0 .
   Using units  fu = f0  and  tu = 1/k , we introduce the dimensionless
   quantities  fd = f/fu,  td = t/tu , with which the problem becomes
   d fd / d td = - fd(td),  fd(0) = 1 .
   The Euler scheme is:  fd_new = fd_old + (-fd_old)*Dtd .
   For this problem, we know the exact solution, too,
```

```
   so we will compare the two solutions. */

/* Plotting discrete points [x1, y1], [x2, y2], ... : now we use
   one list of the style  xy_list = [ [x1, y1], [x2, y2], ... ]  */

tdfd_list : makelist()$  tdfd_exact_list : makelist()$
td_final : 4.$  fd_old : 1.$  Dtd : 0.1$
tdfd_list : append( tdfd_list, [ [0, fd_old] ] )$
tdfd_exact_list : append( tdfd_exact_list, [ [0, fd_old] ] )$

for td_old : 0 thru td_final step Dtd do (
  td_new : td_old + Dtd,
  fd_new : fd_old + (-fd_old) * Dtd,
  tdfd_list : append( tdfd_list, [ [td_new, fd_new] ] ),
  fd_old : fd_new,
  tdfd_exact_list : append( tdfd_exact_list, [ [td_new, exp(-td_new)] ] )
)$

wxplot2d( [ [ discrete, tdfd_list ], [ discrete, tdfd_exact_list ] ],
  [color, black, black], [style, [points, 1, 3], lines],
  [x, 0, td_final], [y, -0.1, 1.1], [legend, "numerical", "exact"],
  [xlabel, "t_dimensionless"], [ylabel, "f_dimensionless"] )$
```

The outcome:

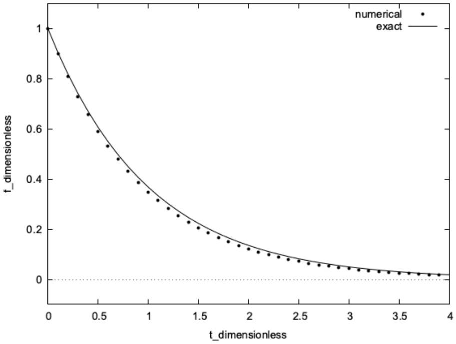

Figure 109.1 The exact solution and the approximate numerical result.

6.5 Finite difference method – example 2

Next, a set of two coupled first-order differential equations is solved with the same method.

```
/* Example 2 for the finite difference method: system of equations:
```

```
   solving  d f / d t = -k*g(t) ,  d g / d t = k*f(t)
   with initial conditions  f(0) = f0 > 0,  g(0) = 0 .
   With units  fu = f0,  tu = 1/k , the dimensionless quantities are
   fd = f/fu,  gd = g/fu,  td = t/tu , with which the problem becomes
   d fd / d td = -gd(td),  d gd / d td = fd(td),  fd(0) = 1,  gd(0) = 0 . */

/* Now, instead of _new, _old, and lists, we use arrays
   (faster but uses more memory).
   Observe that now we only plot every 5th point. */

td : 0.0$  td_final : 8.5$  Dtd : 0.02$  K : 5$
J : ceiling(td_final/Dtd)$
array(fda, flonum, J)$  array(gda, flonum, J)$
fda[0] : 1.0$  tdfd_list : makelist( [ td, fda[0] ] )$
gda[0] : 0.0$  tdgd_list : makelist( [ td, gda[0] ] )$
fdgd_list : makelist( [ fda[0], gda[0] ] )$

for j : 0 thru J-1 do (
  td : td + Dtd,
  fda[j+1] : fda[j] - gda[j] * Dtd,
  gda[j+1] : gda[j] + fda[j] * Dtd,
  if j = K*floor(j/K) then (
    tdfd_list : append( tdfd_list, [ [ td, fda[j+1] ] ] ),
    tdgd_list : append( tdgd_list, [ [ td, gda[j+1] ] ] ),
    fdgd_list : append( fdgd_list, [ [ fda[j+1], gda[j+1] ] ] )
  )
)$
wxplot2d( [ [ discrete, tdfd_list ], [ discrete, tdgd_list ] ],
  [color, cbfblue, cbfgreen], [x, 0, td_final], [y, -1.3, 1.3],
  [legend, "fd", "gd"], [xlabel, "td"], [ylabel, "fd, gd"] )$
wxplot2d( [ discrete, fdgd_list ], [color, cbfred], [yx_ratio, 1],
  [x, -1.3, 1.3], [y, -1.3, 1.3], [xlabel, "fd"],  [ylabel, "gd"] )$
```

The outcomes are:

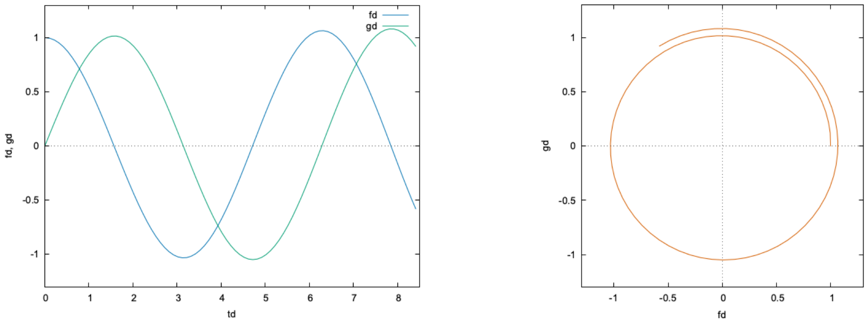

Figure 110.1 Left: $\check{f}(\check{t})$ (bluish line) and $\check{g}(\check{t})$ (greenish line). Right: points $(\check{f}, \check{g})$ parametrized by $\check{t}$.

In the exact solution, the bluish line is a perfect cosine function, the greenish one is a sine, and the reddish curve is a perfect circle. (Think why.)

6.6 How to write midterms and software/other documentations

Add comments to calculational steps and program code parts/lines generously. The train of thought should be found reproducible by your fellow students, your teachers, as well as yourself of five years later. You will be grateful to your five-years-earlier self.

6.7 Problems

Problem 1 During a time interval $0 = t_1 \leq t \leq t_2 = 100\,\mathrm{s}$, pressure of a monoatomic ideal gas changes according to $p(t) = p_1 + at$ with $p_1 = 3\,\mathrm{bar}$, $a = -0.02\,\frac{\mathrm{bar}}{\mathrm{s}}$, while volume changes as $V(t) = V_1 + bt$ with $V_1 = 1\,\mathrm{dm}^3$, $b = 0.01\,\frac{\mathrm{dm}^3}{\mathrm{s}}$. Initially (*i.e.,* at t_1), temperature is $T_1 = 300\,\mathrm{K}$.
A) Determine the minimal temperature value T_{min}, as well as the maximal one T_{max}, during this time interval.
B) Calculate the work ($W_{t_1 \to t_2}$) done on the gas during this time interval, in two ways: once when the process is parametrized by volume, and once when it's parametrized by time. Are the two results the same?
C) Calculate the required heat ($Q_{t_1 \to t_2}$) absorbed by the gas during this time interval.
D) Determine, in two different ways, the time derivative of internal energy as the function of time, $\left(\dot{E}(t)\right)$.
E) In which cell of Table 10.1 did we stay during this problem?

Problem 2 Does the vector field

$$\mathbf{v}\,(x, y, z) = \begin{pmatrix} 4xy \\ 2x^2 + 3z^2 \\ 6yz \end{pmatrix}, \tag{112.1}$$

understood in Cartesian coordinates in a three-dimensional Euclidean vector space, have a potential? If yes, determine it (up to the unavoidable uncertainty of an additive constant).

Problem 3 We have a fixed amount of ideal gas (with constant $c_v = \frac{f}{2}R$).
A) Which are its so-called *polytropic* processes, *i.e.,* those processes along which the specific heat, $c_{\mathrm{process}} = \frac{\mathrm{d}q|_{\mathrm{process}}}{\mathrm{d}T|_{\mathrm{process}}}$, is constant: what relationship should p and v satisfy?
B) Calculate the corresponding polytropic specific heat c_{process}.
C) Determine the work done on the gas along a polytropic process between a state 1 with p_1, V_1 and a state 2 with p_2, V_2.
D) Is it possible to connect any two – randomly chosen – states (p_1, v_1) and (p_2, v_2) in the state space of the material by some appropriate polytropic process? If yes, by which one?

Problem 4 According to an empirical formula for a certain heat convection situation, the heat transfer coefficient α_{conv}, in $\frac{\mathrm{W}}{\mathrm{m^2K}}$, can be expressed in terms of a temperature difference ΔT, in K, and a characteristic length L, in m, as $\alpha_{\mathrm{conv}} = 1.42\left(\frac{\Delta T}{L}\right)^{\frac{1}{4}}$.
A) "Cure" this formula dimensionally, i.e., re-express it in a form that is valid without

requirements about the units of α_{conv}, ΔT, and L.
B) Do the same when the power $\frac{1}{4}$ is replaced by 0.24. (Powers like this are, frequently, results of a fitting on measurement data rather than outcomes of some analytical calculation.)
[Another advantage of such a rewritten form is that, should you change units from SI to units like cal, °F, BTU, ft *etc.*[128], you have to do it only at the coefficient.]
Hint: What the text says is that the formula is to be understood as
$\alpha_{\mathrm{conv}}/\left(\frac{\mathrm{W}}{\mathrm{m^2K}}\right) = 1.42\left(\frac{\Delta T/\mathrm{K}}{L/\mathrm{m}}\right)^{\frac{1}{4}}$. Rearrange this into the user-friendlier form
$\alpha_{\mathrm{conv}} = 1.42\ \text{somecombinationofunits} \cdot \left(\frac{\Delta T}{L}\right)^{\frac{1}{4}}$.

Problem 5 Similarly to the proof in Sect. 3.7, show that $e(s,v)$ is convex from above.

Problem 6 Similarly to calculation (68.3), determine the conclusion analogous to (68.4) when (72.3) is replaced with (72.5).

Problem 7 In view of (31.4) and (16.2), show that total entropy of an ideal gas body plus an environment, (68.5), equals

$$\frac{f}{2}mR\left(\ln\frac{T}{T_{\mathrm{a}}} - \frac{T}{T_{\mathrm{a}}}\right) + mR\left(\ln\frac{v}{v_{\mathrm{a}}} - \frac{v}{v_{\mathrm{a}}}\right) + \text{const.} \tag{113.1}$$

(you are allowed to choose $T_0 = T_{\mathrm{a}}$ and $v_0 = v_{\mathrm{a}}$ where $v_{\mathrm{a}} = RT_{\mathrm{a}}/p_{\mathrm{a}}$ [129]). Check both analytically and numerically (*e.g.*, `plot2d` and `plot3d` in Maxima of $S_{\mathrm{t}}/(mR)$ in the dimensionless temperature and dimensionless specific volume variables $\check{T} = \frac{T}{T_{\mathrm{a}}}$, $\check{v} = \frac{v}{v_{\mathrm{a}}}$, with any reasonable f) that this total entropy is concave from above in both variables T and v, and has a strict global maximum at $(T_{\mathrm{a}}, v_{\mathrm{a}})$.

Problem 8 Convince yourself that the temperature value below which pressure can be negative for a simple material is determined by the solution of the set of equations

$$p(T,v) = 0\,, \qquad \left.\frac{\partial p}{\partial v}\right|_T = 0\,. \tag{113.2}$$

Show that, for the Van der Waals model, this temperature value $T_{p=0}$ is $\frac{1}{4}\frac{a}{bR}$.[130]

---

[128] Wikipedia, 2019-02-19: "A BTU was originally defined as the amount of heat required to raise the temperature of 1 avoirdupois pound of liquid water by 1 degree Fahrenheit at a constant pressure of one atmosphere. There are several different definitions of the BTU that are now known to differ slightly." The same source, on ft: "It varied in length from country to country, from city to city, and sometimes from trade to trade. Its length was usually between 250 mm and 335 mm", and on cal: "Various definitions exist but fall into two broad categories."

[129] Well, v_{a} is not the specific volume of the environment, naturally, but merely such a combination of constants that is convenient here.

[130] Surprisingly, this value is not much lower than $T_{\mathrm{c}} = \frac{8}{27}\frac{a}{bR}$ (see Sect. 3.10): $T_{p=0}/T_{\mathrm{c}} = \frac{1}{4}/\frac{8}{27} = 27/32 \approx 0.84$.

Hint: Express T from one of the equations, substitute it into the other equation, solve for v, and substitute that v into T.

Problem 9 Show statements (56.3).

Problem 10 Verify statement (56.4).

Problem 11 Demonstrate that (72.5) restores energy conservation, and calculate the corresponding entropy production, analogously to (68.3).

Problem 12 Check that result (77.7) is dimensionless, as it should be.

Problem 13 Show that, if we want a dimensionless version of the problem considered in Sect. 4.5 – *e.g.,* for a numerical solution – then we can use the constants T_a, p_a, $m{\cdot}R$, and χ_P to make the problem dimensionless. What length, time, mass, and temperature units can be derived from these constants?

Problem 14 Derive (91.2) and (91.3).