

Chapter 2

Material Equations

In the preceding chapter of this book on *Continuum Physics* we have discussed the notion of material points. They are infinitely small from a macroscopic point of view and infinitely large from a microscopic point of view. Just think of the temperature field $T = T(t, \mathbf{x})$. The material point at location \mathbf{x} at time t is large enough for obeying the rules of infinitely large systems, such as the ideal gas law, for example. On the other hand, it is small enough so that it approaches thermodynamic equilibrium practically immediately. The state of the material point is always an equilibrium, or Gibbs state which is characterized by parameters such as temperature or chemical potentials. Hence $T = T(t, \mathbf{x})$ is defined locally, but may change from location to location and within the course of time.

From a microscopic point of view, a material point is so large that it is rather clear whether a particle is inside or outside of it. Those particles which are partly inside and partly outside form a vanishing minority. Hence, densities are well defined. The same applies to current densities and to volumetric production rates. If something inside a material point increases, it must have been migrated from outside to inside, or it has been produced there. This reasoning is formulated as a balance equation.

We have discussed balance equations for particles of a certain species, for matter and electric charge. If these particles move, they carry their properties with them. These properties, however, may be conveyed as well by interaction. The balance equations for linear momentum and for kinetic, potential, and internal energy are examples. The notion of internal energy, however, alludes to the fact that material points are more than small pieces of mass and charge. Poetically speaking, they have their own life. In particular, they carry energy which is termed internal.

If, moreover, the material point is in thermodynamic equilibrium with its environment, and keeps to be so, it undergoes a reversible process. In the section on entropy we have worked out expressions for the entropy current density and the volumetric entropy production rate. The latter expression, consisting of five terms and should never be negative. This is the essence of the Second law of thermodynamics.

Up to now there is just a continuum. All balance equations must be fulfilled. However, there are far too many fields and too few equations for them. In order to arrive at solutions for a specific problem we have to specify the material at hand.

By specifying particular material equations we describe different fields of applications, such as hydrodynamics, aerodynamics, elastodynamics, heat transport, diffusion, charge transport, thermo-electrical effects, or optics. We refrain from discussing material equation for chemistry¹ because this is a book on the physics of continuous media, not on chemistry.

2.1 Fluid Media

A fluid medium² cannot support shear forces. More precisely, the reversible part of the stress tensor must be such that $dF_i = T'_{ij} dA_j$ is proportional to dA_i . There is no perpendicular component, no shear force. Recall that we denote by $d\mathbf{A}$ an infinitesimal area element and by $d\mathbf{F}$ the force exercised on it.

Therefore, a fluid medium has to be described by the following material equation:

$$T'_{ij} = -\delta_{ij} p, \quad (2.1)$$

where $p = p(t, \mathbf{x})$ is the pressure field. The minus sign is a convention. Normally, pressure is positive, such that the medium on the front of $d\mathbf{A}$ tries to repel the surface element. The medium on the backside exercises the same, but oppositely directed force.

Water and air may serve as prototypes of fluid media. Under ordinary conditions, water is a fluid proper, i.e., a liquid. Air under normal conditions behaves, to a very good approximation, as an ideal gas. “Normal” in this context means “as encountered in nature”.

In the following we will discuss these idealizations in some length, while we just touch how to describe non-ideal gases and not-Newtonian fluids.

The momentum balance equation (1.69) for a fluid reads

$$\varrho(\partial_t v_k + v_i \partial_i v_k) = -\partial_k p + f_k + \partial_i T''_{ik}. \quad (2.2)$$

The left hand side of this equation is simply $\varrho D_t v_k$, i.e., mass times acceleration per unit volume, as felt by a co-moving observer. On the right hand side we find three terms which describe the cause of acceleration: pressure gradient, external forces, and friction.

2.1.1 Incompressible Fluids

Water and many oils are practically incompressible media. Their mass density does only weakly depend on pressure and on temperature. $\varrho(t, \mathbf{x}) = \text{const.}$ is a good approximation within a reasonable pressure and temperature interval.

¹The article on *Reaction and diffusion* is an exception

²As contrasted with a solid medium.

Because of $\partial_i \varrho + \partial_i \varrho v_i = 0$ we conclude

$$\partial_i v_i = 0. \quad (2.3)$$

The velocity field of an incompressible fluid is divergence-free. Solutions of the momentum balance equation (2.2) must additionally fulfill Eq. (2.3).

We mention in passing that a divergence-free field may be represented as the curl of a vector potential, $\mathbf{v} = \nabla \times \mathbf{A}$. One can rewrite the momentum balance equation (2.2) in terms of a vector potential \mathbf{A} . A solution then automatically yields a divergence-free vector field. There is, however, a serious drawback. There are many vector potentials for one and the same velocity field.

2.1.2 Ideal Gas

If the specific volume of a gas is sufficiently large, it behaves as if there were no interactions between its particles, it behaves ideally.

The partial pressure of particles of species a is given by

$$p_a = k_B T n_a, \quad (2.4)$$

where n_a denotes particle density, and T is the absolute temperature. The partial pressures of a mixture of ideal gases add up,

$$p = \sum_a k_B T n_a. \quad (2.5)$$

We define the molar fractions x_a by

$$x_a = \frac{n_a}{n} \text{ where } n = \sum_a n_a. \quad (2.6)$$

n is the total number of particles per unit volume, and x_a is the percentage of particles of species a . Note that $\sum_a x_a = 1$.

The mass density is

$$\varrho = \sum_a m_a n_a, \quad (2.7)$$

where m_a is the mass of a particle of species a . We may write

$$\varrho = \sum_a m_a x_a n = m n \text{ with } m = \sum_a x_a m_a. \quad (2.8)$$

m is the average particle mass with respect to a composition x_1, x_2, \dots . The ideal gas law (2.5) may thus be rewritten as

$$p = \frac{\varrho}{m} k_B T. \quad (2.9)$$

The latter form (2.9) is a substantial simplification if the composition of the ideal gas mixture remains constant. Then, m is a constant, and we may express the pressure field in terms of temperature and mass density. Air within the troposphere³ is an example.

There is still something to be repaired. Boltzmann's constant k_B and the average molecular mass m hint at micro-physics. We multiply both quantities by Avogadro's number N_A . Recall that the amount of N_A particles is a mole⁴ in terms of chemistry. $R = N_A k_B$ is the universal gas constant,⁵ $M = N_A m$ the average molar mass. With this Eq. (2.9) reads

$$p = \frac{\varrho}{M} R T. \quad (2.10)$$

R is the universal gas constant. Pressure p , temperature T and mass density ϱ are fields. For most problems the average molar mass M is a constant as well.⁶

2.1.3 Newtonian Fluid Medium

The dissipative contribution T''_{ik} must be a symmetric tensor which behaves non-standard under time reversal. It describes friction. There is no friction if neighboring material points travel with the same velocity. Hence, the dissipative contribution to the stress tensor will depend on velocity gradients. A Newtonian fluid is characterized by a linear dependency which is a very good approximation for many liquids and gases, such as water and air.

The symmetric velocity gradient G_{ik} may be split into a trace part $\delta_{ik} G_{jj}$ and a traceless rest. Both are linear in velocity gradients, behave as second order rank tensors and transform odd under time reversal. Hence we write

$$T''_{ik} = \eta^b \delta_{ik} G_{jj} + 2\eta^s \left\{ G_{ik} - \frac{1}{3} \delta_{ik} G_{jj} \right\}. \quad (2.11)$$

η^b is the *bulk* (or *volume*) viscosity while η^s denotes the *shear* viscosity. Only the latter comes into play if we investigate incompressible fluids.⁷

³The region which is afflicted by weather phenomena, roughly the first 15 km. It contains 75% of the air mass and more than 98% of water vapor.

⁴One mole of the isotope ^{12}C has a mass of exactly 0.012 kg, by definition.

⁵ $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

⁶0.02897 kg mol⁻¹ for dry air.

⁷Recall $G_{jj} = \partial_j v_j$.

The divergence $\partial_i T''_{ik}$ of (2.11) is

$$\eta^s \Delta v_k + \eta^s \partial_k \partial_j v_j - \frac{2\eta^s}{3} \partial_k \partial_j v_j + \eta^b \partial_k \partial_j v_j. \quad (2.12)$$

Therefore, the momentum balance equation for a Newtonian fluid medium reads

$$\varrho(\partial_t v_k + v_i \partial_i v_k) = -\partial_k p + f_k + \eta^s \Delta v_k + \left\{ \frac{\eta^s}{3} + \eta^b \right\} \partial_k \partial_j v_j. \quad (2.13)$$

We should work out the consequences of the second law of thermodynamics. The volumetric entropy production rate caused by friction is

$$\pi^{\text{fr}} = \frac{1}{T} T''_{ik} G_{ik} = \frac{\eta^b - 2\eta^s/3}{T} (G_{jj})^2 + \frac{2\eta^s}{T} G_{ik} G_{ik}. \quad (2.14)$$

T denotes absolute temperature which is always positive.

If we choose a divergence-free velocity field, $\pi^{\text{fr}} \geq 0$ can only be guaranteed if the shear viscosity vanishes or is positive,

$$\eta^s \geq 0. \quad (2.15)$$

If we insert a velocity field $\mathbf{v} = \gamma \mathbf{x}$, Eq. (2.14) yields $9(\eta^b - 2\eta^s/3)\gamma^2 + 6\eta^s\gamma^2$, divided by T , hence $9\eta^b\gamma^2/T$. The second law of thermodynamics hence demands

$$\eta^b \geq 0. \quad (2.16)$$

2.1.4 Hydrodynamics

To a very good approximation, water is incompressible and behaves as a Newtonian fluid. Thus we have to specialize Eq. (2.13) to $\partial_j v_j = 0$.

The momentum balance equation for an incompressible Newtonian fluid reads

$$\varrho(\partial_t v_k + v_i \partial_i v_k) = -\partial_k p + f_k + \eta \Delta v_k. \quad (2.17)$$

This is the famous Navier-Stokes equation which governs the field of hydrodynamics. ϱ , the mass density is considered to be constant. \mathbf{v} denotes the velocity field, p is the pressure field, \mathbf{f} are external forces per unit volume. $\eta = \eta^s$ is the (shear) viscosity of the fluid. Note that only divergence-free velocity fields are admissible.

The term $\varrho v_i \partial_i v_k$ is quadratic in the velocity field and poses problems for finding analytic or numerical solutions. It should be compared with the friction term $\eta \Delta v_k$. If v is a typical velocity of a problem and ℓ a typical length, then

$$\text{Re} = \frac{\varrho v \ell}{\eta} \quad (2.18)$$

is an estimate of the ratio of inertial to frictional forces. Re is called Reynold's number, it is dimensionless.

A small Reynold number means that friction is dominant, the fluid will flow in smooth layers that glide one over the other. One also speaks of laminar flow. A large Reynold number predicts turbulence. $Re \approx 10^4$ is a very rough guess for the onset of turbulence.

Even if the quadratic-in-velocity term $\varrho v_i \partial_i v_k$ vanishes because of symmetry reasons, the corresponding solution might be unstable if the Reynold number of the problem is too big.

2.1.5 Aerodynamics

The basic material equations for aerodynamics are Newton's expression (2.11) for internal friction and the ideal gas law (2.10) with a constant molar mass M . Even with these simplifications, and only if the mechanical aspect is considered, the problem at hand is already formidable.

The mass density will not be constant, therefore

$$\partial_t \varrho + \partial_i \varrho v_i = 0 \quad (2.19)$$

must hold. Mass density ϱ and the speed v of flow are interlinked.

The momentum balance equation, with the ideal gas law, reads

$$\varrho(\partial_t v_k + v_i \partial_i v_k) = -\frac{R}{M} \partial_k \varrho \frac{\varrho}{T} + f_k + \eta^s \Delta v_k + \left\{ \frac{\eta^s}{3} + \eta^b \right\} \partial_k \partial_j v_j. \quad (2.20)$$

Another field enters the stage, namely temperature T . Often heat conduction in gases may be neglected; then the flow is adiabatic. For a gas of diatomic molecules the following state equation then holds:

$$\frac{T}{T_0} = \left\{ \frac{\varrho}{\varrho_0} \right\}^{2/5}. \quad (2.21)$$

(T_0, ϱ_0) is a reference point.

Altogether we have five fields: mass density ϱ , the three velocity components v_k , and temperature T . Equations (2.19)–(2.21) are likewise five partial differential equations. They are intimately coupled.

Note that the shear viscosity η^s as well as the bulk viscosity η^b will depend on mass density and on temperature, they may become fields. Additional material equations $\eta^s = \eta^s(\varrho, T)$ and $\eta^b = \eta^b(\varrho, T)$ have to be specified, if necessary.

Aerodynamics is a vast field. Just think of airplane or automotive engineering, meteorology and climate models, or such simple things as Bernoulli's law. We have just scratched the surface. Non-ideal gases, non-Newtonian friction, non-adiabatic

flows, chemical reactions such as combustion in a jet engine, and many, many more effects must be taken into account in real-world problems. It is out of the scope of this book to go into details.

A non-ideal gas is characterized by a power series

$$p = \frac{RT}{M} \{ \rho + B_2 \rho^2 + \cdots \}, \quad (2.22)$$

the so called virial expansion. The coefficients B_2 , B_3 and so forth depend on temperature, they can be calculated if the interaction potential between the molecules is known.⁸ It is a fortunate accident that $B_2 = B_2(T)$ for air nearly vanishes at room temperature. Carbon dioxide behaves differently. Similar considerations apply for the osmotic pressure of solvents.

Non-Newtonian friction is, well, non Newtonian. There are many causes for a deviation. The relationship between the dissipative part of the stress tensor and the velocity gradient may be linear, but retarded. This is the case for glasses which behave as elastic solids for short times and as liquids in the long run. Or T''_{ij} depends other than linear on the velocity gradient G_{ij} . A non-laminar air flow may serve as an example.

2.1.6 Summary

A fluid medium, gas or liquid, cannot support static, or reversible shear forces. It is characterized by a pressure field. Very simple, but realistic idealizations are incompressible fluids and ideal gases. We have studied in some detail the concept of a Newtonian fluid medium the internal frictional forces of which are linear functions of the velocity gradients. The dynamics of water, or hydrodynamics, is governed by the Navier-Stokes equation. The Reynold number decides whether the flow is laminar or turbulent. Aerodynamics, the dynamics of air, is even more complicated because temperature comes into the game.

2.2 Solid Media

In contrast with a fluid medium, a solid may support static shear forces. That makes it a solid: it requires strong forces to deform it. Even the elastic part T'_{ik} may have non-diagonal entries. If the solid is relaxed, i.e., if no external forces are exercised, there will be no stress. If, however, the solid medium suffers strain, there will be stress. We shall formulate the idea that, to a first approximation, stress and strain are proportional which is known as Hooke's law. Before we must explain the notion of strain.

⁸By the way, one speaks of *the* ideal gas because $B_1 = 1$ holds true for all kinds of molecules.

2.2.1 Strain

Think of a material point at a certain location \mathbf{x} . These are the coordinates with respect to a Cartesian coordinate system if the medium is relaxed. “Relaxed” means that no forces are present, neither volume forces nor forces upon the boundary of the medium. We speak of the relaxed state of the solid medium.

If, however, such forces act on the medium, if it is deformed, the material points of the continuum will be displaced. The material point, formerly at \mathbf{x} , will now be at $\bar{\mathbf{x}} = \mathbf{x} + \mathbf{u}$. $\mathbf{u} = \mathbf{u}(t, \mathbf{x})$ is the displacement field, it describes the displacement, at time t , of a point which was situated at \mathbf{x} before the displacement, when the medium was relaxed.

Two neighboring points at \mathbf{x} and $\mathbf{x} + d\mathbf{x}$ in the relaxed state will be found at $\bar{\mathbf{x}} = \mathbf{x} + \mathbf{u}(t, \mathbf{x})$ and $\bar{\mathbf{x}} + d\bar{\mathbf{x}} = \mathbf{x} + d\mathbf{x} + \mathbf{u}(t, \mathbf{x} + d\mathbf{x})$ in the stressed state. In the relaxed state, before deformation, their distance was ds where

$$ds^2 = dx_1^2 + dx_2^2 + dx_3^2 = \delta_{ik} dx_i dx_k. \quad (2.23)$$

With

$$d\bar{x}_i = dx_i + dx_j \partial_j u_i(t, \mathbf{x}) \quad (2.24)$$

we arrive at

$$d\bar{s}^2 = \{\delta_{ik} + \partial_i u_k + \partial_k u_i + (\partial_i u_j)(\partial_k u_j)\} dx_i dx_k. \quad (2.25)$$

This is the squared distance of the neighboring points after deformation. It was $ds^2 = \delta_{ik} dx_i dx_k$ in the relaxed state.

We therefore describe the deformation of a solid medium by

$$2S_{ik} = \partial_i u_k + \partial_k u_i + (\partial_i u_j)(\partial_k u_j), \quad (2.26)$$

such that

$$d\bar{s}^2 = ds^2 + 2S_{ik} dx_i dx_k \quad (2.27)$$

holds true. $S_{ik} = S_{ik}(t, \mathbf{x})$ is the strain tensor field.

If the displacement is achieved by a rigid rotation and a translation,

$$\bar{\mathbf{x}} = \mathbf{a} + R\mathbf{x} \text{ or } \mathbf{u} = \mathbf{a} + (R - I)\mathbf{x}, \quad (2.28)$$

where \mathbf{a} is a constant vector and R a constant orthogonal matrix, we work out

$$2S_{ik} = (R - I)_{ik} + (R - I)_{ki} + (R - I)_{ij}(R - I)_{kj} = 0. \quad (2.29)$$

This result is evident when looking at Eq. (2.27). Indeed, the strain tensor field describes deformation. A rigid translation or rotation of a medium does not produce strain.

Note that the displacement gradient $\partial_i u_k$ is dimensionless. For real solids, these gradients are small, and the quadratic contribution $(\partial_i u_j)(\partial_k u_j)$ to Eq. (2.25) may be neglected. Likewise, the square root of Eq. (2.27) may be approximated by

$$d\bar{s} = ds + S_{ik} dx_i dx_k \text{ with } S_{ik} = \frac{\partial_i u_k + \partial_k u_i}{2}. \quad (2.30)$$

ds was the distance between two neighbors in the relaxed state of the medium. $d\bar{s}$ is the distance between the same material points after a deformation which sends \mathbf{x} to $\mathbf{x} + \mathbf{u}(t, \mathbf{x})$. Relation (2.29) is an approximation, it holds true for small displacement gradients, $|\partial_i u_k| \ll 1$. It should not be used if large deformations of rubber-like substances are to be modeled.

The mapping $\mathbf{x} \rightarrow \bar{\mathbf{x}} = \mathbf{x} + \mathbf{u}(t, \mathbf{x})$ changes the volume element dV into

$$d\bar{V} = dV \frac{\partial(\bar{x}_1, \bar{x}_2, \bar{x}_3)}{\partial(x_1, x_2, x_3)}, \quad (2.31)$$

where the quotient denotes the functional determinant. If terms which are quadratic or of higher order in $\partial_i v_k$ are neglected, we obtain the following expression

$$\frac{d\bar{V}}{dV} = 1 + \partial_j u_j. \quad (2.32)$$

This can be written as

$$\frac{d\bar{V} - dV}{dV} = S_{jj}. \quad (2.33)$$

The relative volume change due to deformation is equal to the trace of the strain field.

2.2.2 Hooke's Law

Without stress there is no strain. Hooke's law says that little stress will produce little strain. Put otherwise, strain is proportional to stress.

The most general linear relation reads

$$S_{ij} = \Lambda_{ijkl} T'_{kl}. \quad (2.34)$$

This would mean 84 elasticity constants. However, the strain tensor as well as the stress tensor are symmetric. Moreover, Λ_{ijkl} can be defined as a second derivative of a free energy with respect to T_{ij} and T_{kl} which assures $\Lambda_{ijkl} = \Lambda_{klij}$. This reduces the number of elasticity constants to maximally 21.

This is a horribly large number, and it pertains to mono-crystals of the most complex symmetry only. In practice, matter in its solid state, like steel, concrete, ice and the like are mixtures of micro-crystallites which are oriented randomly and let the material appear isotropic. In the following we concentrate on isotropic solids, but we bear in mind that materials like wood or mono-crystalline LiNbO_3 are not isotropic.

A linear relation between strain and stress for an isotropic material is described by two constants. The stress tensor itself as well as the unit tensor multiplied by the trace of the stress tensor are independent symmetric second rank tensor. Following tradition, we write

$$S_{ik} = \frac{1+\nu}{E} T'_{ik} - \frac{\nu}{E} \delta_{ik} T'_{jj}. \quad (2.35)$$

Note that ν is a dimensionless number. The constant E has the dimension of pressure, or energy density, just as T_{jk} . It is called the elasticity constant, or Young's modulus, and ν is known as Poisson's ratio.

We will work out examples which demonstrate that the elasticity constant E must be positive. We will likewise demonstrate that Poisson's ratio is restricted to values between 0 (very stiff) and 0.5 (rubber, or fluid like):

$$0 \leq \nu \leq \frac{1}{2}. \quad (2.36)$$

This simply says that an elastic medium, if pressed upon, might either not wield or will shrink in volume, but not expand.

Hooke's law for an isotropic elastic medium can also be formulated such that stress appears as a consequence of strain. One has to work out the trace of Eq. (2.34),

$$S_{jj} = \frac{1-2\nu}{E} T'_{jj}, \quad (2.37)$$

and obtains

$$T'_{ik} = \frac{E}{(1+\nu)} \left\{ S_{ik} + \frac{\nu}{1-2\nu} \delta_{ik} S_{jj} \right\}. \quad (2.38)$$

Stress is linearly related with strain by the compliance tensor which can be read off from Eq. (2.38).

2.2.3 Structural Mechanics

The subject of this huge field is the investigation of structures made of solid elastic material. The purpose of such structures like bridges, houses, cars or spanners is that they remain intact when used. Bridges should not collapse under normal load,

houses must be built so that its walls stand up the forces of heavy wind on the roof, a car should be as light as possible but protect its passengers from the effects of collisions in the best possible way, and a spanner should not yield unless excessive torque is applied.

In structural mechanics, static solutions are to be worked out. The momentum balance equation is to be solved for vanishing flow velocity, $\mathbf{v} = 0$. Without flow there will be no friction, i.e., T''_{ik} vanishes. At a first glance, a simple thing:

$$\partial_i T'_{ik} + f_k = 0. \quad (2.39)$$

The external forces f_k per unit volume must be compensated by the gradient of the elastic stress tensor.

However, not every solution of Eq. (2.39) is admissible. The reversible contribution to the stress tensor T'_{ik} must be derived from a strain tensor by Hooke's law (2.38). And: the strain tensor cannot be anything, but must be derived from a displacement field u_i by Eq. (2.30). We refrain here from rewriting the three equations (2.39) into a system of three coupled partial differential equations for the three displacement fields u_1, u_2, u_3 .

A problem is solved if three functions u_k are found which give rise to a strain tensor $S_{ik} = (\partial_i u_k + \partial_k u_i)/2$ and, by Hooke's law, to a stress tensor T'_{ik} which compensates external forces according to Eq. (2.39). And: the solution must match the boundary conditions of the problem at hand.

The next thing should be to investigate the stress tensor field $T'_{ik} = T'_{ik}(\mathbf{x})$. Note that in structural mechanics only *static* solutions are studied, therefore the time argument is absent.

The stress tensor is real and symmetric and can therefore be diagonalized by an orthogonal coordinate transformation, at least locally. T'_{ik} has three eigenvalues $T^1 = T^1(\mathbf{x})$, $T^2 = T^2(\mathbf{x})$, and $T^3 = T^3(\mathbf{x})$. Negative values denote pressure, positive values indicate stress.

Now, for each material there is an upper limit of pressure or stress which it can support. If these limits are exceeded, the material will yield irreversibly, it will break. Concrete, for example, can support a large pressure, but is feeble with respect to stress. Therefore, steel rods are embedded to strengthen its ability to withstand stress.

The main goal of a structural mechanical analysis is to make sure that the structure is safe. This means that nowhere the material's limits of admissible stress or pressure are exceeded. $T^j = T^j(\mathbf{x})$ must always be within the limits of allowed values.

We stop here and do not go into details of the stress-strain relation. As a rule of thumb, the linear relation (Hooke's law) is valid up to a certain point (a thousandth of the elasticity module, or so) where unwanted effects set in, such as permanent deformations.

2.2.4 Elastodynamics

In the preceding section we have discussed an elastic medium at rest. We now allow for oscillating material points. The velocity field $v_i = \dot{u}_i$ is the time derivative of the displacement field. Because we resort to Hooke's law, a linear approximation with respect to \mathbf{u} and therefore \mathbf{v} , we may safely neglect the $\partial_i v_i v_k$ term. We therefore obtain the following three partial differential equations:

$$\rho \ddot{u}_k = \frac{E}{2(1+\nu)} \left\{ \Delta u_k + \frac{1}{1-2\nu} \partial_k \partial_i u_i \right\}. \quad (2.40)$$

This equation which describes the properties of sound in solids does not contain a possible external force. The effect of gravity, for example, is usually negligible. It also refers to an isotropic medium. Moreover, friction has not yet been incorporated. We shall demonstrate in Chap. 4 that there are transversal and longitudinal solution with different propagation constants as well as surface acoustic waves (SAW). Note that E and ν in Eq. (2.40) are adiabatic values which will differ from the values in Eq. (2.38). The former refer to constant entropy (no heat exchange), the latter to constant temperature.

2.2.5 Summary

A solid, or elastic medium can support shear stress even if at rest. If deformed moderately, it will return to its normal state when relaxed. Hooke's law describes the linear relationship between stress and strain. The latter is a tensor field describing the deformation of an elastic medium. We discuss the discipline of structural mechanics, a discipline of physics or engineering science dedicated to the stability of structures made of elastic solid media. From spanners to skyscrapers. We also talk about elastic waves.

2.3 Heat Conduction

Although used widely, the title of this section is not quite correct. It suggests that a physical quantity called heat is transported via conduction. In fact, it is internal energy which is conducted. Recall that energy, in the context of continuum physics, is made up of kinetic energy, potential energy, and a rest which is called internal energy. The first refers to the motion of material points as a whole, the second to its energy in an external gravitational or electric potential. The last contribution to energy takes into account the motion of particles within a resting material point. Also recall that a material point is small on an engineer's point of view but still contains a huge number of particles. There are so many particles that the laws of thermodynamics for infinitely many are applicable.

2.3.1 Fourier's Law

The balance equation for internal energy U reads

$$\varrho D_t u = -\partial_i J_i^u + T_{ik} G_{ik} + J_i^e E_i. \quad (2.41)$$

Here ϱ is the mass density of the medium and u denotes the specific⁹ internal energy. D_t stands for the substantial time derivative, a change in time as observed by a co-moving observer. The conduction contribution to the internal energy current density is denoted as J^u . We call it the heat current density. How it depends on other fields is the subject of this section.

There are at least two mechanisms for the production of internal energy. One is friction, as described by $T_{ik} G_{ik}$. If there is stress (T_{ik}) and a velocity gradient (G_{ik}), then internal energy will be produced. We have discussed this in the section on *fluid media*. Another one is $J_i^e E_i$. If an electric current flows in the presence of an electric field, then internal energy will be produced as well. We shall discuss this effect later in the section on *charge transport*. There are more sources of internal energy production, for instance by radioactivity. Here we concentrate on a relation between the heat current density J^u and other fields which will drive it. Let us assume a situation without electric fields and without concentration gradients first.

Thermodynamic equilibrium is characterized by constant pressure, constant temperature, constant electric potential and constant chemical potentials. Assume that one condition is not met, namely constant temperature. As a consequence, internal energy will flow from warmer into colder regions. A vanishing temperature gradient will cause no flow of internal energy. We postulate that a small temperature gradient will drive a small heat current. So we write, in linear approximation,

$$J_i^u = -\lambda_{ij} \partial_j T. \quad (2.42)$$

This is Fourier's law: the heat current density is a linear function of the local temperature gradient. The coefficients λ_{ij} are constants for small enough temperature differences. If the medium is isotropic, then

$$\lambda_{ij} = \lambda \delta_{ij} \quad (2.43)$$

will hold, with a single heat conduction constant λ . Equation (2.42) then reads

$$J^u = -\lambda \nabla T. \quad (2.44)$$

The heat current density is proportional to the temperature gradient. A positive value of λ guarantees that internal energy flows from warm to colder regions.

⁹Per unit mass.

This is in accordance with the second law of thermodynamics. Recall expression (1.125) for the volumetric entropy production rate by heat conduction:

$$\pi^{\text{hc}} = J_i^u \partial_i \frac{1}{T}. \quad (2.45)$$

We insert Fourier's law (2.41) and find

$$\pi^{\text{hc}} = \frac{1}{T^2} \lambda_{ij} (\partial_i T) (\partial_j T). \quad (2.46)$$

Indeed, the matrix λ_{ij} must be non-negative in order to warrant $\pi^{\text{hc}} \geq 0$. For an isotropic medium this boils down to $\lambda \geq 0$.

2.3.2 More on Heat Conduction

We assume an isotropic medium in order to simplify the discussion. The heat conductivity coefficient λ must not be negative. However, it is not a constant. It depends on composition (i.e., the material under study) and on the local equilibrium parameters such a temperature, pressure, and so forth. The transport of internal energy is a slow process, in general. We need not bother about retardation or non-local effects. Therefore, within a homogeneous material, $\lambda(\mathbf{x}) = \lambda(T(\mathbf{x}))$ is a good approximation in most situations.

Copper is a good heat conductor. Its heat conduction coefficient at $T = 300$ K is $\lambda = 401 \text{ W m}^{-1} \text{ K}^{-1}$. The corresponding values for ice, water and air under normal conditions are 2.18, 0.58 and 0.024, respectively. See the tables of Kaye and Laby [5].

The high thermal conductivity of metals is due to electrons in the conduction band. Isolators, such as ice, transport internal energy via phonon diffusion. In gases, energy transport from one place to another is mediated by collisions of molecules. Liquids are in-between: nearby molecules are correlated just as in crystals, but they behave as dense gases otherwise. Therefore, the metal, crystal, liquid and gas sequence of typical heat transport coefficients is rather plausible.

2.3.3 Heat Equation

Assume a medium at rest, for instance, a solid. Everything shall be in equilibrium except temperature. $T = T(t, \mathbf{x})$ depends on the location \mathbf{x} and will change with time t .

The specific energy u , in this situation, will depend on space and time because it depends on temperature which depends on space and time. Therefore,

$$\varrho \mathbf{D}_t u = \varrho \dot{u} = \varrho \frac{\partial u}{\partial T} \dot{T} \quad (2.47)$$

holds true.

The partial derivative of the specific¹⁰ internal energy with respect to temperature is the specific heat of the material under discussion. It is usually abbreviated by c . With Fourier's law we arrive at

$$\varrho c \dot{T} = \partial_i \lambda \partial_i T + \pi^u. \quad (2.48)$$

Here ϱ is the mass density, c the specific heat, T the temperature, and λ the heat conductivity coefficient. π^u denotes the amount of internal energy produced per unit time and per unit volume. All these quantities are fields depending on time and location. Equation (2.48) is the so-called heat equation.

If there is no internal energy production and if mass density ϱ , specific heat c and the heat conduction coefficient λ may be considered constant, the heat equation simplifies to

$$\dot{T} = \kappa \Delta T, \quad (2.49)$$

with

$$\kappa = \lambda / c \varrho. \quad (2.50)$$

$\Delta = \partial_i \partial_i$ stands for the Laplacian differential operator. Equation (2.49) is applicable only if the temperature differences, for a given problem, are small. κ is called *thermal diffusivity* by many authors.

2.3.4 Summary

Heat conduction is short for the conduction of internal energy. It is caused by a temperature gradient if all other equilibrium parameters are constant. We explain Fourier's law and comment on some subtle points, in particular, why metals, other solids, liquids and gases exhibit wildly different heat conduction coefficients. We also digress on the validity of the so called heat equation.

2.4 Diffusion

We discuss in this section the phenomenon that particles of a given kind flow with another velocity than the center of mass. We recapitulate the appropriate balance equation and let us guide by the entropy production expression to formulate a material equation. This then is rewritten into the well-known diffusion equation.

¹⁰Recall that specific refers to unit mass.

2.4.1 Diffusion Currents

We have denoted by $n^a = n^a(t, \mathbf{x})$ the density of particles of kind a . Note that we cannot enumerate the particles itself because they are indistinguishable. Particles of species a flow with a velocity $\mathbf{v}^a = \mathbf{v}^a(t, \mathbf{x})$. The diffusion currents are

$$\mathbf{J}^a = n^a (\mathbf{v}^a - \mathbf{v}). \quad (2.51)$$

It is the conduction contribution $\mathbf{J}(N^a)$ associated with the number N^a of particles of kind a . The balance equation for N^a may be written in different forms, one is

$$\partial_t n^a + \partial_i n^a v_i + \partial_i J_i^a = \pi^a, \quad (2.52)$$

where the volumetric production rates is given by

$$\pi^a = \sum_r \Gamma^r v^{ra}. \quad (2.53)$$

It describes the appearance or disappearance of particles due to chemical reaction which are labeled by an index r . Γ^r is the number of such reactions per unit time and unit volume. In one reaction v^{ra} particles of kind a are produced or vanish, respectively. See Table 1.1 for an example.

2.4.2 Chemical Potential

If two systems have the same temperature T , they do not exchange energy. Consider likewise two systems the volume of the first may grow or shrink at the expense of the second. If two such systems have the same pressure p , they do not exchange volume. And if the two systems have the same temperature and pressure, but may exchange particles of kind a , they will not do so if their chemical potentials μ^a are equal. T , p and the μ^a are equilibrium parameters.

Just look at the expression

$$\pi^{\text{df}} = - \sum_a J_i^a \partial_i \frac{\mu^a}{T} \quad (2.54)$$

for the volumetric entropy production rate related with diffusion. Like all other contributions it is a sum of products. The first factor is a flux, the second would vanish in an overall equilibrium situation.

We therefore write provisionally

$$\mathbf{J}^a = - \sum_b \Lambda^{ab} \nabla \frac{\mu^b}{T}. \quad (2.55)$$

A non-negative matrix of coefficients Λ^{ab} guarantees that the second law of thermodynamics is respected. By the way, the matrix Λ must also be symmetric because of Onsager's relations. We come back to this issue in the following chapter.

2.4.3 Diffusion Equation

We now specialize to a much simpler situation where only one species of particles is not in overall equilibrium. We refer to it by n , \mathbf{J} and μ : to its density, its diffusion current and its chemical potential. Moreover, the temperature equilibrium is usually attained much faster than the equilibrium with respect to diffusion. Therefore we assume a constant temperature. Equation (2.55) then simplifies to

$$\mathbf{J} = -\frac{\Lambda}{T} \nabla \mu. \quad (2.56)$$

Λ is a positive coefficient.

The chemical potential has a gradient because the particle density is not yet constant, so we write

$$\mathbf{J} = -D \nabla n, \quad (2.57)$$

where the diffusion constant D is defined as

$$D = \frac{\Lambda}{T} \frac{\partial \mu}{\partial n}. \quad (2.58)$$

If there are no chemical reactions, and if the medium in which the diffusing particles are suspended is at rest, we have to solve

$$\partial_t n = \partial_i D \partial_i n, \quad (2.59)$$

the diffusion equation. If the particle density gradients are small, this simplifies even more to

$$\dot{n} = D \Delta n. \quad (2.60)$$

Note the similarity with the heat equation. After all, heat propagation in dense media is nothing else than phonon diffusion. Equation (2.59) is occasionally called *Fick's law*.

2.4.4 Digression on Open Systems

We know that Λ in Eq. (2.58) is positive, and the temperature T as well. In order to show that also the diffusion constant D is positive, we must provide an argument why the particle density n increases with μ , the chemical potential.

Denote by $H = H(\lambda)$ the Hamiltonian¹¹ of the system and by N the particle number operator. The free energy of such an open¹² system is

$$F(T, \lambda, \mu) = -k_B T \ln \text{tr} e^{(\mu N - H)/k_B T}. \quad (2.61)$$

Temperature T and chemical potential μ are Lagrange multipliers.

When looking for the maximum of the entropy functional,

$$S(G) = \max_W S(W) \text{ where } S(W) = -k_B \text{tr} W \ln W, \quad (2.62)$$

the mixed state W is confined by $\text{tr} W = 1$, $\text{tr} WH = U$ and $\text{tr} WN = \bar{N}$. The corresponding three Lagrange multipliers are the free energy F , the temperature T , and the chemical potential μ .

One easily calculates

$$\frac{\partial F}{\partial \mu} = -\langle N \rangle \quad (2.63)$$

and

$$\frac{\partial^2 F}{\partial \mu^2} = -\frac{\langle N^2 \rangle - \langle N \rangle^2}{k_B T}. \quad (2.64)$$

If we refer to unit volume, the above two results show that indeed

$$\frac{\partial n}{\partial \mu} \geq 0 \quad (2.65)$$

holds true because of $\langle N^2 \rangle \geq \langle N \rangle^2$.

2.4.5 Summary

Diffusion currents of particles are driven by gradients of their chemical potentials weighted with the inverse temperature. However, heat conduction is usually much faster than diffusion. So we specialized on diffusion at constant temperature. We derived the diffusion equation and brought forward an argument why the diffusion constant D must be positive. These findings are supported by a more detailed study of *Brownian motion* in Chap. 4. When combined with chemical reactions, diffusion may lead to astonishing solutions, as discussed in the article on *Reactions and Diffusion*.

¹¹ λ stands for the external parameters.

¹²The number of particles within the system is not fixed.

2.5 Charge Transport

In this section we will discuss the various contributions to the electric charge density and the electric charge current density. Ohm's law is formulated for the electrochemical potential.

2.5.1 The Electromagnetic Field in Matter

Let us recall Maxwell's equations for the electromagnetic field \mathbf{E}, \mathbf{B} :

$$\epsilon_0 \nabla \cdot \mathbf{E} = \varrho^e, \quad (2.66)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (2.67)$$

$$\frac{1}{\mu_0} \nabla \times \mathbf{B} = \epsilon_0 \dot{\mathbf{E}} + \mathbf{j}^e, \quad (2.68)$$

$$\nabla \times \mathbf{E} = -\dot{\mathbf{B}}. \quad (2.69)$$

Assume that a continuum is exposed to an electromagnetic field. One effect will be that matter gets polarized: there is a certain density of electric dipole moment which we denote by \mathbf{P} . The negative divergence of this polarization is a contribution to the charge density,

$$-\nabla \cdot \mathbf{P} = \varrho^p. \quad (2.70)$$

We call it the polarization charge density. Likewise, there is a current if the polarization changes with time,

$$\dot{\mathbf{P}} = \mathbf{j}^p. \quad (2.71)$$

Another effect of the electromagnetic field will be magnetization. Denote by \mathbf{M} the density of magnetic moments. Its curl is another contribution to the current density,

$$\nabla \times \mathbf{M} = \mathbf{j}^m. \quad (2.72)$$

In general, the total charge density is made up of two terms,

$$\varrho^e = -\nabla \cdot \mathbf{P} + \varrho^f, \quad (2.73)$$

the current density of three,

$$\mathbf{j}^e = \dot{\mathbf{P}} + \nabla \times \mathbf{M} + \mathbf{j}^f. \quad (2.74)$$

The superscript “f” stands for “free” or “to be freely manipulated”, in contrast to “p” (enforced by polarization) or “m” (enforced by magnetization).

This is a vicious circle: it is the electric field which causes polarization, the latter then contributes to the electric charge density which in turn must be known for working out the electric field. The same applies to the magnetic induction field.

The well known way out is to define auxiliary fields, the dielectric displacement

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (2.75)$$

and the magnetic field strength

$$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}. \quad (2.76)$$

With it Eq. (2.66) may be reformulated as

$$\nabla \cdot \mathbf{D} = \varrho^f, \quad (2.77)$$

while Eq. (2.68) changes into

$$\nabla \times \mathbf{H} = \mathbf{j}^f + \dot{\mathbf{D}}. \quad (2.78)$$

Equations (2.67) and (2.69) remain unchanged.

Now only the density and the current density of free charges show up. The prize to be paid is that we have to cope with two more vector fields. We require additional functional relations between the displacement and the electric fields on the one hand and the magnetic and induction fields on the other. Such relations are material equations because they depend on the material under investigation.

By the way, differentiating Eq. (2.77) with respect to time and working out the divergence of Eq. (2.78) shows that not only charge is a conserved quantity, but also the free charge,

$$\partial_t \varrho^f + \nabla \cdot \mathbf{j}^f = 0. \quad (2.79)$$

We will not discuss magnetization further since magnetism was ignored in the preceding sections. For an isotropic dielectric medium and for quasi-static fields

$$\mathbf{D} = \epsilon \epsilon_0 \mathbf{E} \quad (2.80)$$

is a good approximation. ϵ is the relative dielectric permittivity which can be as large as 80 (for water at 20°C) and even larger.

In Chap. 3 we go beyond this, then also rapidly varying electric fields are dealt with.

2.5.2 Contributions to the Electric Current Density

We have presented two decompositions of the electric current density, one based on Maxwell's equations, the other within the framework of continuum mechanics:

$$\mathbf{j}^e = \dot{\mathbf{P}} + \mathbf{j}^f = (-\nabla \mathbf{P} + \varrho^f) \mathbf{v} + \mathbf{J}^{e'} + \mathbf{J}^{e''}. \quad (2.81)$$

The first sum describes the decomposition into bound and free charges. The second sum has four contributions, two for convection and two for conduction. We interpret these expressions as follows.

- $\varrho^f \mathbf{v}$ is the convection of free charges.
- $\mathbf{J}^{e'} = \dot{\mathbf{P}} + (\mathbf{v} \cdot \nabla) \mathbf{P} = D_t \mathbf{P}$ is the substantial time derivative of the polarization. It describes the reversible (or elastic) charge transport by conduction.
- The remainder $\mathbf{j}^f = \mathbf{J}^{e''}$ is responsible for the irreversible (or inelastic) charge transport by conduction.

The situation simplifies if the medium under discussion is at rest. Then there is no charge transport by convection. Partial and substantial time derivatives coincide, and we may write

$$\mathbf{j}^e = \mathbf{J}^e = \dot{\mathbf{P}} + \mathbf{J}^{e''}. \quad (2.82)$$

2.5.3 Ohm's Law

Let us talk about the normal case that charge is transported by electrons. There are two different causes for electrons to move.

One is the drag of an electric field strength \mathbf{E} which exerts a force $-e\mathbf{E}$ on an electron. We here discuss quasi-static electric fields, therefore the electric field strength can be derived from a potential ϕ^e by $\mathbf{E} = -\nabla \phi^e$.

The second cause is diffusion. If the chemical potential μ^* of free electrons has a gradient, it will make these electrons to move whereby each electron carries the charge $-e$. Therefore, the electrostatic potential must be supplemented by the chemical potential divided by the charge $-e$. We call

$$\psi = \phi^e - \frac{\mu^*}{e} \quad (2.83)$$

the electrochemical potential.

Ohm's law states that the irreversible contribution to the electric conduction current is proportional to the negative gradient of the electrochemical potential:

$$\mathbf{J}_i^{e''} = -\sigma_{ik} \partial_k \psi. \quad (2.84)$$

σ_{ik} is the conductivity tensor. We will prove in Chap. 3 that it is symmetric if i and k are exchanged and if an external quasi-static magnetic field is inverted.

The conductivity tensor σ_{ik} is also positive. This follows from the second law of thermodynamics. We have silently assumed that the medium has constant temperature, therefore the entropy production rate per unit volume is

$$\pi(S) = -\frac{1}{T} J_i^{e''} \partial_i \psi = \frac{1}{T} (\partial_i \psi) \sigma_{ik} (\partial_k \psi). \quad (2.85)$$

If there are no chemical reactions which produce differences in the chemical potential for electrons, and if the medium is isotropic, Ohm's law says

$$\mathbf{j}^e = \sigma \mathbf{E}. \quad (2.86)$$

Note that there were quite a few assumptions which lead to this simple form of Ohm's law.

In older textbooks you may read of an *electromotive force* which pumps electrons. Such pumps may be batteries, photovoltaic cells and voltage differences.

2.5.4 Summary

Charge transport means that charged particles change their location: electrons, holes or ions. A classification in terms of bound and free charges and their corresponding current densities is one subject. Another one is the classification in terms of the general scheme of continuum physics: convection and conduction, the latter reversible or irreversible. We explain how these different points of view are to be reconciled. Electrons, holes or ions move because they are dragged by an electric field, or because they diffuse. The two effects are described by the electrochemical potential. Ohm's law states that the irreversible conduction of electrons is proportional to the negative gradient of the electrochemical potential. The conductivity tensor is symmetric and positive. The subject will be reconsidered in Chap. 3. Also see the article on *Ohms Law and the Hall effect*.

2.6 Thermoelectric Effects

In this section we will discuss cross effects. There is more than one generalized force and there are many corresponding fluxes. The fluxes depend linearly on the generalized forces, but the matrix of kinetic coefficients is neither diagonal nor arbitrary. We postpone a detailed discussion of the underlying Onsager relations to Chap. 3. In order to be specific we discuss a solid electric conductor such that electric charge and internal energy may be transported.

2.6.1 Simultaneous Heat and Charge Transport

We specialize to a solid electrical conductor with non-vanishing electrical and heat conductivities. The possible fluxes are the electric current density \mathbf{J}^e and the heat current density \mathbf{J}^u .

If there were no charge transport, the temperature gradient ∇T would drive the heat current. And vice versa, if there were no temperature gradient and no heat current, the gradient of the electrochemical potential $\nabla\psi$ would drive the electric current. There will be cross effects if both is allowed, charge and heat conduction.

Mobile electrons, which are referred to by an asterisk superscript, will transport both charge and internal energy. On the other hand, diffusion of phonons¹³ causes internal energy transport only. Since each quasi-free electron carries a negative unit charge we may write

$$\mathbf{J}^e = -e\mathbf{J}^*. \quad (2.87)$$

The electrochemical potential is given by

$$\psi = \phi^e - \frac{\mu^*}{e}, \quad (2.88)$$

where ϕ^e is the ordinary electrostatic potential.

2.6.2 Forces and Fluxes

In global thermodynamic equilibrium the potentials are constant and the current densities vanish. ∇T and $\nabla\psi$ are generalized forces X because they transform as forces with respect to time reversal, $X \rightarrow X$. \mathbf{J}^u and \mathbf{J}^e are generalized fluxes Φ because they transform as $\Phi \rightarrow -\Phi$.

One should try to define forces X_a and fluxes Φ_a in such a way that the volumetric entropy production rate reads

$$\pi(S) = \sum_a \Phi_a X_a. \quad (2.89)$$

Since we always discuss only weak deviations from thermodynamic equilibrium, we postulate a linear relationship between fluxes and forces:

$$\Phi_b = \sum_a K_{ba} X_a, \quad (2.90)$$

¹³Quantized lattice vibrations. Phonons are quasi-particles because they cannot live in free space.

where K_{ba} are kinetic coefficients. This simply expresses the fact that no forces produce zero fluxes and that sufficiently small forces cause small fluxes.

A very specialized form of Onsager's theorem says that the kinetic coefficients form a symmetric matrix. We postpone a discussion of this theorem to Chap. 3. There we derive explicit expressions for the kinetic coefficients and show that the symmetry $K_{ab} = K_{ba}$ is a consequence of time reversal invariance.

2.6.3 Kinetic Coefficients for Heat and Charge Transport

The following contributions to the volumetric entropy production rate do not vanish:

$$\pi(S) = \mathbf{J}^u \cdot \nabla \frac{1}{T} - \mathbf{J}^* \cdot \nabla \frac{\mu^*}{T} - \frac{1}{T} \mathbf{J}^e \cdot \mathbf{E}. \quad (2.91)$$

With the entropy conduction current density

$$\mathbf{J}^s = \frac{1}{T} (\mathbf{J}^u - \mu^* \mathbf{J}^*) \quad (2.92)$$

one may rewrite the volumetric entropy production rate as

$$\pi(S) = -\frac{1}{T} (\mathbf{J}^s \cdot \nabla T + \mathbf{J}^e \cdot \nabla \psi). \quad (2.93)$$

This expression has the form Eq. (2.89) up to a common factor which is irrelevant here. We therefore postulate

$$\begin{pmatrix} \mathbf{J}^s \\ \mathbf{J}^e \end{pmatrix} = - \begin{pmatrix} A & B \\ B & C \end{pmatrix} \begin{pmatrix} \nabla T \\ \nabla \psi \end{pmatrix}. \quad (2.94)$$

In accordance with Onsager's symmetry relation the off-diagonal elements are equal. Moreover,

$$A \geq 0, C \geq 0 \text{ and } AC \geq B^2 \quad (2.95)$$

will guarantee that the second law of thermodynamics is respected.

The electric current density is usually written as

$$\mathbf{J}^e = -\sigma(\nabla \psi + \alpha \nabla T). \quad (2.96)$$

We recognize $\sigma = C$, therefore the electric conductivity is always positive. The sign of $\alpha = B/C$ cannot be predicted from first principles. If the temperature is the same everywhere, Eq. (2.96) coincides with Ohm's law (2.84). Moreover, the chemical potential, which depends on temperature and composition, cannot have a

gradient in a homogeneous medium. We may then write $\mathbf{J}^e = \sigma \mathbf{E}$ which is Ohm's law in a narrower sense.

The second relation in Eq. (2.94) can be formulated as

$$\mathbf{J}^u = -\lambda \nabla T + \gamma \mathbf{J}^e. \quad (2.97)$$

Without electric current we obtain Fourier's law $\mathbf{J}^u = -\lambda \nabla T$. The heat conductivity $\lambda = T(A - B^2/C)$ is guaranteed to be positive.

An additional electric current causes additional heat transport. However, the sign of γ cannot be derived from a general rule, just like that of α in Eq. (2.96). The coefficients γ in Eq. (2.97) and α in Eq. (2.96) are related by

$$\gamma = T\alpha - \frac{\mu^*}{e}. \quad (2.98)$$

You will find further details in article on *Thomson, Seebeck and Peltier effect*.

2.6.4 Summary

In general, if there are many driving forces and equally many fluxes, they are related by a matrix K of kinetic coefficients. This matrix is symmetric provided that forces and fluxes are defined in such a way that the volumetric entropy production rate is a sum of flux times force products. As an example of this Onsager relation we study an electric conductor of homogeneous composition. There are two driving forces, namely the electric field strength and the temperature gradient. The corresponding fluxes are the electric and the heat current densities. Besides Ohm's and Fourier's law, there are cross effects.



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