Chapter 1
Two Fundamental Laws of Nature

1.1 Types of Work

1.1.1 Mechanical Work

A gas confined to a cylinder absorbs a certain amount of heat, $\delta q$. The process is depicted in Fig. 1.1. According to experimental experience this leads to an expansion of the gas. The expanding gas moves a piston to increase its volume by an amount $\delta V = V_b - V_a$. For simplicity we assume that the motion of the piston is frictionless and that its mass is negligible compared to the mass, $m$, of the weight pushing down on the piston. We do not yet have a clear understanding of what heat is, but we consider it a form of energy which to some extend can be converted into mechanical work, $w$.\(^1\) In our case this is the work needed to lift the mass, $m$, by a height, $\delta s$, against the gravitational force $mg$. From mechanics we know

$$\delta w_{\text{done by gas}} = \int_a^b d\vec{s} \cdot \vec{f}_{\text{gas}} = -\int_a^b d\vec{s} \cdot m\vec{g} = P_{\text{ex}} \int_{V_a}^{V_b} dV = P_{\text{ex}} \delta V.$$

Here $P_{\text{ex}} = mg/A$ is the external pressure exerted on the gas due to the force $mg$ acting on the cross-sectional area, $A$ ($\delta V = A\delta s$).

The process just described leads to a change in the total energy content of the gas, $\delta E$. The gas receives a positive amount of heat, $\delta q$. However, during the expansion it also does work and thereby reduces its total energy content, in the following called

\(^1\) Originally it was thought that heat is a sort of fluid and heat transfer is transfer of this fluid. In addition, it was assumed that the overall amount of this fluid is conserved. Today we understand that heat is a form of dynamical energy due to the disordered motion of microscopic particles and that heat can be changed into other forms of energy. This is what we need to know at this point. The microscopic level will be addressed in Chap. 5.
Fig. 1.1 A gas confined to a cylinder absorbs a certain amount of heat, $\delta q$. The combined result is

$$\delta E = \delta q - P_{ex}\delta V.$$  \hspace{1cm} (1.1)

This is the first law of thermodynamics for this special process. It uses energy conservation to distinguish the different contributions to the total change in internal energy of a system (here the gas) during a thermodynamic process (here absorption of heat plus volume expansion).

We just have introduced two important concepts frequently used in thermodynamics—process and system. The latter requires the ability to define a boundary between “inside” and “outside”. Both, the inside and the outside, may be considered systems individually. Systems usually are distinguished according to their degree of openness. Isolated system means that this system exchanges nothing with its exterior. An open system on the other hand may exchange everything there is to exchange, like heat or matter. A closed system holds back matter but allows heat exchange, e.g. the above gas filled cylinder. Systems are sometimes divided into subsystems. Subsystems, however, are still systems. After having defined or (better) prepared a system we may observe what happens to it or we may actively do something to it. This “what
happens to it” or “doing something” means that the system undergoes a process (of change). A special type of system is the reservoir. A reservoir usually is in thermal contact with our system of interest. Thermal contact means that heat may be transferred between the reservoir and our system of interest. However, the reservoir is so large that there is no measurable change in any of its physical properties due to the exchange.

Now we proceed replacing the above gas by an elastic medium. Those readers who are not sufficiently familiar with the theory of elastic bodies may skip ahead to “Electric work” (p. 7).

**Mechanical Work Involving Elastic Media**

We consider an elastic body composed of volume elements $dV$ depicted in Fig. 1.2.

The total force acting on the elastic body may be calculated according to

$$\int_{V} dV f_\alpha$$  \hspace{1cm}  \(\text{(1.2)}\)

for every component $\alpha (= 1, 2, 3$ or $x, y, z)$. Here $\vec{f}$ is a force density, i.e. force per volume. Assuming that the $f_\alpha$ are purely elastic forces acting between the boundaries of the aforementioned volume elements inside $V$, i.e. excluding for instance gravitational forces or other external fields acting on volume elements inside the elastic body, we may define the internal stress tensor, $\sigma$, via

$$f_\alpha = \sum_{\beta=1}^{3} \frac{\partial \sigma_{\alpha\beta}}{\partial x_\beta} = \frac{\partial \sigma_{\alpha\beta}}{\partial x_\beta}.$$  \hspace{1cm}  \(\text{(1.3)}\)

**Fig. 1.2** Elastic body composed of volume elements $dV$
Here we apply the summation convention, i.e. if the same index appears twice on the same side of an equation then summation over this index is implicitly assumed (unless explicitly stated otherwise). The relation between indices, force components, and the faces of the cubic volume element is depicted in Fig. 1.3. Upper and lower sketches illustrate the shear and the normal contribution to the force component $f_{\alpha}$ acting on the volume element in $\alpha$-direction. Notice that $f_{\alpha}$ can be written as the sum over two shear stress and one normal stress contribution. The latter are stress differences between adjacent faces of the cubic volume element. Note also that the unit of $\sigma_{\alpha\beta}$ is force per area.

We want to calculate the work $\delta w$ done by the $f_{\alpha}$ during attendant small displacements $\delta u_{\alpha}$, i.e.

$$\delta w = \int dV f_{\alpha} \delta u_{\alpha} = \int dV \frac{\partial \sigma_{\alpha\beta}}{\partial x_{\beta}} \delta u_{\alpha}. \quad (1.3)$$

The integral may be rewritten using Green’s theorem in space:

$$\delta w = \oint \sigma_{\alpha\beta} \delta u_{\alpha} dA_{\beta} - \int dV \sigma_{\alpha\beta} \frac{\partial \delta u_{\alpha}}{\partial x_{\beta}}.$$
We neglect the surface contribution and use the symmetry property of the stress tensor to obtain

\[ \delta w = - \int dV \sigma_{\alpha\beta} \frac{\partial \delta u_\alpha}{\partial x_\beta} = - \frac{1}{2} \int dV \sigma_{\alpha\beta} \delta \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right). \]

The quantity \( u_{\alpha\beta} \) is the strain tensor (here for small displacements). The final result is

\[ \delta w = - \int dV \sigma_{\alpha\beta} \delta u_{\alpha\beta}. \tag{1.4} \]

We want to work this out in three simple cases. First we consider a homogeneous dilatation of a cubic volume \( V = L_x L_y L_z \). We also assume that the shear components of the stress tensor vanish, i.e. \( \sigma_{\alpha\beta} = 0 \) for \( \alpha \neq \beta \). In such a system the normal components of the stress tensor should all be the same, i.e. \( \sigma = \sigma_{xx} = \sigma_{yy} = \sigma_{zz} \). We thus have

\[ \sigma_{\alpha\beta} \delta u_{\alpha\beta} = \sigma_{xx} \delta u_{xx} + \sigma_{yy} \delta u_{yy} + \sigma_{zz} \delta u_{zz} = \sigma (\delta u_{xx} + \delta u_{yy} + \delta u_{zz}). \tag{1.5} \]

Homogeneous deformation means

\[ \frac{\partial u_\alpha}{\partial x_\alpha} = \delta \frac{L_\alpha}{L_\alpha}. \tag{1.6} \]

And because \( u_{\alpha\alpha} = \partial u_\alpha / \partial x_\alpha \) (no summation convention here) we obtain

\[ \sigma_{\alpha\beta} \delta u_{\alpha\beta} = \sigma \left( \frac{\delta L_x}{L_x} + \frac{\delta L_y}{L_y} + \frac{\delta L_z}{L_z} \right) = \sigma \frac{\delta V}{V}. \tag{1.7} \]

Integration over the full volume then yields

\[ \int dV (f_\alpha x_\beta - f_\beta x_\alpha) = \int dV \left( \frac{\partial \sigma_{\alpha\gamma}}{\partial x_{\alpha}} x_\beta - \frac{\partial \sigma_{\beta\gamma}}{\partial x_{\alpha}} x_\alpha \right) \]

\[ = \int dV \frac{\partial (\sigma_{\alpha\gamma} x_\beta - \sigma_{\beta\gamma} x_\alpha)}{\partial x_{\gamma}} - \int dV (\sigma_{\alpha\gamma} \delta x_\gamma - \sigma_{\beta\gamma} \delta x_\alpha) \]

\[ = \int (\sigma_{\alpha\gamma} x_\beta - \sigma_{\beta\gamma} x_\alpha) dA_{\gamma} - \int dV (\sigma_{\alpha\beta} - \sigma_{\beta\alpha}). \]

The volume integral must vanish in order for the net torque to be entirely due to forces applied to the surface of the body.
\[ \delta w = -\sigma \delta V, \quad (1.8) \]

i.e. we recover the above gas case with \( P = -\sigma \).

In a second example we consider the homogeneous dilatation of a thin elastic sheet. The sheet’s volume is \( V = Ah = L_x L_y h \), where the thickness, \( h \), is small and constant. Now we have

\[ \sigma_{\alpha \beta} \delta u_{\alpha \beta} = \sigma \left( \frac{\delta L_x}{L_x} + \frac{\delta L_y}{L_y} \right) = \sigma \frac{\delta A}{A} \quad (1.9) \]

and therefore

\[ \delta w = -\sigma h \delta A \equiv -\gamma \delta A. \quad (1.10) \]

The quantity \( \gamma \) is the surface tension.

An obvious third example is the homogeneous dilatation of a thin elastic column \( V = h^2 L_z \). Here \( h^2 \) is the column cross sectional area and \( L_z \) is its length. This time we have

\[ \sigma_{\alpha \beta} \delta u_{\alpha \beta} = \sigma \left( \frac{\delta L_z}{L_z} \right) \quad (1.11) \]

and thus

\[ \delta w = -\sigma A \delta L_z \equiv -T \delta L_z, \quad (1.12) \]

where \( T \) is the tension.

**Example: Expanding Gas.** We consider the special case of the first law expressed in Eq. (1.1). If we include the surface tension contribution to the internal energy of the expanding gas, then the resulting equation is

\[ \delta E = \delta q - P \delta V + \gamma \delta A. \quad (1.13) \]

We remark that the usual context in which one talks about surface tension refers to interfaces. This may be the interface between two liquids or the surface of a liquid film relative to air, e.g. a soap bubble. In the latter case there are actually two surfaces. In such cases we define \( \gamma = f_T / (2l) \), which reflects the presence of two surfaces.

**Example: Fusing Bubbles.** An application of surface tension is depicted in Fig. 1.4. The figure depicts two soap bubbles touching and fusing. We ask whether the small bubble empties its gas content into the large one or vice versa. We may answer this question by considering the work done by one isolated bubble during a small volume change:
Notice that the sign of the surface tension contribution has changed compared to Eq. (1.10). This is because in Eq. (1.10) we compute the work done by the membrane. But here the gas is doing work on the membrane, which changes the sign of this work contribution. The same work, i.e. \( \delta w_{\text{done by gas in bubble}} \), can be written in terms of the pressure, \( P \), inside the bubble,

\[
\delta w_{\text{done by gas in bubble}} = P \delta V.
\]

Combining the two equations and using \( \delta V = 4\pi r^2 \delta r \) and \( \delta A = 8\pi r \delta r \), where \( r \) is the bubble radius, yields

\[
P = P_{ex} + \frac{2\gamma}{r}.
\]

We conclude that the gas inside the smaller bubble has the higher pressure and therefore the smaller bubble empties itself into the larger bubble.

### 1.1.2 Electric Work

We now consider work involving electric and magnetic variables\(^4\),\(^5\) starting with an example.

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\(^4\) Here we use Gaussian units. The conversion to SI-units is tabulated in Appendix C.

\(^5\) Three early but very basic papers in this context are: Guggenheim (1936a, b); Koenig (1937).
Example: Charge Transfer Across a Potential Drop. A charge $\delta q$ in an electric field experiences the force $\vec{F} = \delta q \vec{E}$ (Do not confuse this $\delta q$ with the previously introduced heat change!). Consequently the work done by the charge-field system if the charge moves from point $a$ to point $b$ in space is

$$\delta w_q = \int_a^b d\vec{s} \cdot \vec{F} = -\delta q \int_a^b d\vec{s} \cdot \vec{\nabla} \phi. \quad (1.14)$$

Here $\phi$ is the potential, i.e. $\vec{E} = -\vec{\nabla} \phi$, and thus

$$\delta w_q = -\delta q \phi_{ba}, \quad (1.15)$$

where $\phi_{ba} = \phi(b) - \phi(a)$ is the potential difference between $b$ and $a$. The corresponding internal energy of the charge-field system changes by

$$\delta E_q = -\delta w_q = \delta q \phi_{ba}. \quad (1.16)$$

This equation may be restated for a charge current $I = \delta q / \delta t$, where $\delta t$ is a certain time interval:

$$\delta E_I = I \phi_{ba} \delta t. \quad (1.17)$$

In the presence of the resistance, $R$, the quantity $\delta q_{Joule} = RI^2 \delta t$ is the Joule heat generated by the current (James Prescott Joule, British physicist, *Salford (near Manchester) 24.12.1818, †Sale (County Cheshire) 11.10.1889; made important contributions to our understanding of heat in relation to mechanical work (Joule heat) and internal energy (Joule-Thomson effect)).

Now we consider the following equations appropriate for continuous dielectric media:

$$\vec{\nabla} \times \vec{H} = \frac{1}{c} \frac{\partial}{\partial t} \vec{D} + \frac{4\pi}{c} \vec{j}. \quad (1.18)$$

and

$$\vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial}{\partial t} \vec{B}. \quad (1.19)$$

The second equation simply follows by the usual spatial averaging procedure applied to the corresponding vacuum Maxwell’s equation.\(^6\) Here $\bar{\vec{E}}(\bar{r})$ is the average electric field in a volume element at point $\bar{r}$. This volume element is large compared to atomic dimensions. In the same sense $\bar{\vec{D}}$ is the displacement field given by $\bar{\vec{D}} = \bar{\vec{E}} + 4\pi \bar{\vec{P}}$. $\bar{\vec{P}}$ is the macroscopic polarization, i.e. the local electrical dipole moment per volume. Analogously $\bar{\vec{B}} = \bar{\vec{H}} + 4\pi \bar{\vec{M}}$ is the average magnetic field (magnetic induction).

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\(^6\) James Clerk Maxwell, British physicist, *Edinburgh 13.6.1831, †Cambridge 5.11.1879; particularly known for his unified theory of electromagnetism (Maxwell equations).
and \( \vec{M} \) is the macroscopic magnetization, i.e. the local magnetic dipole moment per volume. The first equation is less obvious and requires a more detailed discussion.

We consider a current density \( \vec{j}_e \) inside a medium due to an extra (“injected”) charge density \( \rho_e \). The two quantities fulfill the continuity equation

\[
\frac{\partial \rho_e}{\partial t} + \nabla \cdot \vec{j}_e = 0.
\]

We also have

\[
\nabla \cdot \vec{D} = 4\pi \rho_e.
\]

Differentiation of this Maxwell equation with respect to time and inserting the result into the previous equation yields

\[
\nabla \cdot \left( \frac{\partial \vec{D}}{\partial t} + 4\pi \vec{j}_e \right) = 0.
\]

The expression in brackets is a vector, which may be expressed as the curl of another vector \( c' \vec{H}' \), i.e.

\[
\nabla \times \vec{H}' = \frac{1}{c'} \frac{\partial \vec{D}}{\partial t} + 4\pi \vec{j}_e.
\]

Comparison of this with Ampere’s law in vacuum suggests indeed \( \vec{H}' = \vec{H} \) and \( c' = c \). We thus arrive at Eq. (1.18). An in-depth discussion can be found in Lifshitz et al. (2004).

We proceed by multiplying Eq. (1.18) with \( c' \vec{E} / (4\pi) \) and Eq. (1.19) with \( -c \vec{H} / (4\pi) \). Adding the two equations yields

\[
\frac{c}{4\pi} \vec{E} \cdot \left( \nabla \times \vec{H} \right) - \frac{c}{4\pi} \vec{H} \cdot \left( \nabla \times \vec{E} \right) = \frac{1}{4\pi} \vec{E} \cdot \frac{\partial \vec{D}}{\partial t} + \frac{1}{4\pi} \vec{H} \cdot \frac{\partial \vec{B}}{\partial t} + \vec{j} \cdot \vec{E}.
\]

With the help of the vector identity \( \nabla \cdot (\vec{a} \times \vec{b}) = \vec{b} \cdot (\nabla \times \vec{a}) - \vec{a} \cdot (\nabla \times \vec{b}) \) this is transformed into

\[
\frac{c}{4\pi} \nabla \cdot \left( \vec{H} \times \vec{E} \right) = \frac{1}{4\pi} \vec{E} \cdot \frac{\partial \vec{D}}{\partial t} + \frac{1}{4\pi} \vec{H} \cdot \frac{\partial \vec{B}}{\partial t} + \vec{j} \cdot \vec{E}.
\]

Now we integrate both sides over the volume \( V \) and use Green’s theorem in space (also called divergence theorem), i.e. \( \int_V dV \nabla \cdot (\vec{H} \times \vec{E}) = \int_A dA \cdot (\vec{H} \times \vec{E}) \), where \( \vec{A} \) is a surface element on the surface of the volume oriented towards the outside of \( V \). If we choose the volume so that the fields vanish on its surface, then \( \int_A dA \cdot (\vec{H} \times \vec{E}) = 0 \) (The configuration of the system is fixed during all of this.). Thus our final result is
Fig. 1.5  A cylindrical volume element whose axis is parallel to \( \vec{j} \)

\[
\int dV \left( \frac{\vec{E} \cdot \vec{D}}{4\pi} + \frac{\vec{H} \cdot \vec{B}}{4\pi} + \vec{j} \cdot \vec{E} \delta t \right) = 0.
\]  

(1.20)

The third term in Eq. (1.20) is the work done by the \( \vec{E} \)-field during the time \( \delta t \). To see this we imagine a cylindrical volume element whose axis is parallel to \( \vec{j} \) depicted in Fig. 1.5. Then \( \delta V = A \delta s \) and \( \delta V \vec{j} = (q/\delta t) \delta \vec{s} \), where \( q \) is the charge passing through the area \( A \) during the time \( \delta t \). Thus \( \delta V \vec{j} \cdot \vec{E} \delta t = q \vec{E} \cdot \delta \vec{s} \), where \( q \vec{E} \) is the force acting on the charge \( q \) doing work (cf. the above example).

We conclude that we may express the work done by the system, \( \delta w = \int dV \vec{j} \cdot \vec{E} \delta t \), by the other two terms in Eq. (1.20) describing the attendant change of the electromagnetic energy content of the system. For a process during which the system exchanges heat and is doing electrical work we now have

\[
\delta E = \delta q + \int dV \left( \frac{\vec{E} \cdot \delta \vec{D}}{4\pi} + \frac{\vec{H} \cdot \delta \vec{B}}{4\pi} \right).
\]

(1.21)

The quantities \( \vec{E}, \vec{D}, \vec{B}, \) and \( \vec{H} \) are more difficult to deal with than fields in vacuum. Nevertheless, for the moment we postpone a more detailed discussion and return to Eq. (1.21) on p. 57.

1.1.3 Chemical Work

As a final example consider an open system—one we can add material to. Generally, work must be done to increase the amount of material in a system. The work done depends on the state of the system. If we add \( \delta n \) moles of material,\(^7\) we write the

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\(^7\) One mole (\( n = 1 \)) is an amount of substance of a system which contains as many elementary units as there are atoms of carbon in 12 g of the pure nuclide carbon-12. The elementary unit may be an atom, molecule, ion, electron, photon, or a specified group of such units.
work done on the system as

$$\delta w_{\text{done on system}} = \mu \delta n.$$  \hfill (1.22)

The quantity $\mu$ is called the chemical potential (per mole added). In a more general situation a system may contain different species. We shall say that these are different components $i$. Now the above equation becomes

$$\delta w_{\text{done on system}} = \sum_{i} \mu_i \delta n_i.$$  \hfill (1.23)

Here $\mu_i$ is the chemical potential of component $i$. Thus for a process involving exchange of heat as well as chemical work we have

$$\delta E = \delta q + \sum_{i} \mu_i \delta n_i.$$  \hfill (1.24)

### 1.1.4 The First Law

The first law is expressing conservation of energy. The specific terms appearing in the first law do depend on the types of work occurring in the process of interest. The following box contains a number of examples.

**Example: Statements of the First Law for Different Processes.**

(i) $\delta E = \delta q - P \delta V + \gamma \delta A + \sum_{i} \mu_i \delta n_i$

This describes a process during which heat is exchanged by the system and its exterior. Mechanical work in the form of volume work and surface work is done in addition. The composition of the system changes as well.

(ii) $\delta E = \delta q - \int dV \vec{j} \cdot \vec{E} \delta t$

Here the process of interest involves heat exchange and electrical work.
(iii) \[ \delta E = \delta q - P \delta V + \int dV \vec{E} \cdot \delta \vec{D} + \vec{H} \cdot \delta \vec{B} \]

This example is for a process during which heat is exchanged and both volume and electrical work is done.

More generally the first law is expressed via

\[ \delta E = \delta q - \delta w. \] \hspace{1cm} (1.25)

However, there is an alternative sign convention used in some of the literature, i.e.

\[ \delta E = \delta q + \delta w. \] \hspace{1cm} (1.26)

The sign preceding \( \delta w \) depends on the meaning of the latter. In Eq. (1.25) \( \delta w \) always is the work done by the system for which we write down the change in the system’s internal energy, \( \delta E \), during a process involving both heat transfer and work. In Eq. (1.26) on the other hand \( \delta w \) is understood as work done on the system. In the following we shall use the sign convention as expressed in Eq. (1.25)!

Another point worth mentioning is the usage of the symbols \( \delta \), \( \Delta \), and \( d \). \( \delta \) denotes a small change (afterwards–before) during a process. \( \Delta \) basically has the same meaning, except that the change is not necessarily small. Even though \( d \) indicates a small change just like \( \delta \), it has an additional meaning—indicating exact differentials. This is something we shall discuss in much detail latter in the text. But for the benefit of those who compare the form of Eq. (1.25) to different texts, we must add a provisional explanation.

In principle every process has a beginning and an end. Beginning and end, as we shall learn, are defined in terms of specific values of certain variables (e.g. values of \( P \) and \( V \)). These two sets of variable values can be connected by different processes or paths in the space in which the variables “live”. If a quantity changes during a process and this change only depends on the two endpoints of the path rather than on the path as a whole, then the quantity possesses an exact differential and vice versa. In the case of mechanical work, for instance, we can imagine pushing a cart from point A to point B. There may be two alternative routes—one involving a lot of friction and a “smooth” one causing less friction. In the former case one may find Eq. (1.25) stated as

\[ dE = \delta q - \delta w. \] \hspace{1cm} (1.27)

This form explicitly distinguishes between the exact differential \( dE \) and the quantities \( \delta q \) and \( \delta w \), which are not exact differentials. In the case of \( \delta w \) this is in accord with our cart-pushing example, because the work does depend on the path we choose. For the two other quantities we shall show their respective property latter in this text (cf. p. 283ff), when we deal with the mathematics of exact differentials.
However, already at this point we remark that the expressions we have derived in our examples for the various types of work will reappear with \( d \) instead of \( \delta \). This is because we focus on what we shall call reversible work. Friction, occurring in the cart-pushing example or possibly in Fig. 1.1 when the gas moves the piston, is neglected as well as other types of loss. The following is an example illustrating what we mean by reversible vs. irreversible work.

**Example: Reversible and Irreversible Work.** In an isotropic elastic body the following equation holds (Landau et al. 1986):

\[
\sigma_{\alpha\beta}^{\alpha \neq \beta} = 2\mu u_{\alpha\beta} = \mu \left( \frac{\partial u_{\alpha}}{\partial x_{\beta}} + \frac{\partial u_{\beta}}{\partial x_{\alpha}} \right),
\]  

(1.28)

On the right is the stress tensor and on the left the product of \( 2\mu \) with the strain tensor (for small strain). The quantity \( \mu \) is the shear modulus (not to be confused with the chemical potential). This equation is related to the two upper sketches in Fig. 1.3. If in the depicted situation (shear force acting on \( \beta \)-face is applied in \( \alpha \)-direction) there is little or ideally no strain in \( \beta \)-direction (this is like shearing a deck of cards), then the above equation may be written as

\[
\sigma_{\mu} \equiv \sigma_{\alpha\beta} = \mu \frac{\partial u_{\alpha}}{\partial x_{\beta}} \equiv \mu u_{\mu}.
\]  

(1.29)

Real shear is accompanied by friction. Experience suggests that friction often can be described by an equation akin to the above:

\[
\sigma_{\eta} = \eta \dot{u}_{\eta}.
\]  

(1.30)

The quantity \( \eta \) is a friction coefficient and \( \dot{u}_{\eta} \) is a strain rate. Figure 1.6, showing a spring and a dashpot, is a pictorial representation of Eqs. (1.29) and (1.30). Figure 1.7 shows three simple combinations (a, b, c) of the two elements depicted in Fig. 1.6. These combinations may be translated into differential equations and serve as simple models for so called viscoelastic behavior (Wrana 2009). Important viscoelastic materials are the tread compounds in automobile tires. In the following we merely focus on sketch (a). Its translation is

\[
\sigma = \sigma_{\mu} + \sigma_{\eta} = \mu u + \eta \dot{u} \quad (u \equiv u_{\mu} = u_{\eta}).
\]  

(1.31)

We assume that the applied stress is \( \sigma = \sigma_o \sin(\omega t + \delta) \), where \( \omega \) is a frequency, \( t \) is time, and \( \delta \) is a phase. The attendant strain is \( u = u_o \sin(\omega t) \) (This is a simple mathematical description of an experimental procedure in what is called
Fig. 1.6  Pictorial representation of Eqs. (1.29) and (1.30)

Fig. 1.7  Three simple combinations (a, b, c) of the two elements

dynamic mechanical analysis.). Inserting this into Eq. (1.31) we find the relations

\[
\begin{align*}
\sigma_0 \cos \delta &= \mu u_o \equiv \mu' u_o & \quad (1.32) \\
\sigma_0 \sin \delta &= \eta \omega u_o \equiv \mu'' u_o. & \quad (1.33)
\end{align*}
\]

The two newly defined quantities \( \mu' \) and \( \mu'' \) are called storage and loss modulus, respectively. Their meaning becomes clear if we compute the work done during one full shear cycle, i.e.

\[
\oint \sigma du = \int_0^{2\pi/\omega} \sigma \dot{u} dt = \pi \mu'' u_o^2.
\quad (1.34)
\]
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Actually this is work per volume, cf. (1.4). However, if we do the same calculation just for the first quarter cycle (form zero to maximum shear strain) the result is

\[
\int_{0}^{\pi/(2\omega)} \sigma \dot{u} dt = \frac{1}{2} \mu' u_0^2 + \frac{1}{4} \pi \mu'' u_0^2.
\] (1.35)

The first term is the reversible part of the work, which does not contribute to the integral in the case of a full cycle. This term is analogous to the elastic energy stored in a stretched/compressed spring. The second term as well as the result in Eq. (1.34) cannot be recovered and is lost, i.e. producing heat. Models like ours only convey a crude understanding of loss or dissipative processes in viscoelastic materials. Considerable effort is spend by the R&D departments of major tire makers to understand and control loss on a molecular basis. In tire materials the moduli themselves strongly depend on the shear amplitude. Understanding and controlling this effect, the Payne effect, is one important ingredient for the improvement of tire materials, e.g. optimizing rolling resistance (Vilgis et al. 2009).

1.2 The Postulates of Kelvin and Clausius

The first law does not address the limitations of heat conversion into work or heat transfer between systems. The following two postulates based on experimental experience do just this. They are the foundation of what is called the second law of thermodynamics.\(^8\)

1.2.1 Postulate of Lord Kelvin (K)

A complete transformation of heat (extracted from a uniform source) into work is impossible.\(^9\)

\(^8\) Here we follow Fermi (1956). Dover (Enrico Fermi, Nobel prize in physics for his contributions to nuclear physics, 1938).

\(^9\) Thomson, Sir (since 1866) William, Lord Kelvin of Largs, (since 1892), British physicist, *Belfast 26.6.1824, †Netherhall (near Largs, North Ayrshire) 17.12.1907; one of the founders of classical thermodynamics; among his achievements are the Kelvin temperature scale, the discovery of the Joule-Thomson effect in 1853 with J. P. Joule and the thermoelectric Thomson effect in 1856, as well as the development of an atomic model with J. J. Thomson in 1898.
1.2.2 Postulate of Clausius (C)

It is impossible to transfer heat from a body at a given temperature to a body at higher temperature as the only result of a transformation.\(^\text{10}\)

**Remark:** At this point we use the “temperature” \(\theta\) to characterize a reservoir as hotter or colder than another. The precise meaning of temperature is discussed in the following section.

These two postulates are equivalent. A way to prove this is by assuming that the first postulate is wrong. This is then shown to contradict the second postulate. Subsequently the same reasoning is applied starting with the second postulate, i.e. the assumption that the second postulate is wrong is shown to contradict the first.

First we assume (K) to be false. Figure 1.8 illustrates what happens. At the top is a reservoir at a temperature \(\theta_1\) surrendering heat \(q\) to a device (circle) which converts this exact amount of heat into work \(w\). A process possible if (K) is false. At the bottom this setup is extended by a friction device (f) converting the work \(w\) into heat \(q\), which is transferred to a second reservoir at \(\theta_2\) (> \(\theta_1\)). Thus the only overall result of the process is the transfer of heat from the colder to the hotter reservoir. We therefore contradict (C).

Now we assume that (C) is false. The upper part of Fig. 1.9 shows heat \(q\) flowing from the colder reservoir to the hotter reservoir—with no other effect. At the bottom this setup is extended. The heat \(q\) is used to do work leaving the upper reservoir unaltered. Clearly, this is in violation of (K). Therefore both postulates are equivalent. They have important consequences, which we explore below.

1.3 Carnot’s Engine and Temperature

Consider a fluid undergoing a cyclic transformation shown in Fig. 1.10. The upper graph shows the cycle in the \(P-V\)-plane, whereas the lower is a sketch illustrating the working principle of a corresponding device. Here the amount of heat \(q_2\) is transferred from a heat reservoir at temperature \(\theta_2\) (\(\theta_2 > \theta_1\)) to the device. During the transfer (path from a to b in the \(P-V\)-diagram) the temperature in the device is \(\theta_2\). This part of the process is an isothermal expansion. Then the device crosses via adiabatic\(^\text{11}\) expansion to a second isotherm at temperature \(\theta_1\), the temperature of a

---

\(^{10}\) Rudolf Julius Emanuel Clausius, German physicist, *Köslin (now Koszalin) 2.1.1822, †Bonn 24.8.1888; one of the developers of the mechanical theory of heat; his achievements encompass the formulation of the second law and the introduction of the “entropy” concept.

\(^{11}\) A transformation of a thermodynamic system is adiabatic if it is reversible and if the system is thermally insulated. Definitions of an adiabatic process taken from the literature:

Pathria (1972): “Hence, for the constancy of \(S\) (Entropy) and \(N\) (number of particles), which defines an adiabatic process, ....”
1.3 Carnot’s Engine and Temperature

**Fig. 1.8** Assumption of postulates: Kelvin

**Fig. 1.9** Assumption of postulates: Clausius
Fermi (1956): “A transformation of a thermodynamic system is said to be adiabatic if it is reversible and if the system is thermally insulated so that no heat can be exchanged between it and its environment during the transformation”

Pauli (1973): “Adiabatic: During the change of state, no addition or removal of heat takes place; ....”

Chandler (1987): “...the change $\Delta S$ is zero for a reversible adiabatic process, and otherwise $\Delta S$ is positive for any natural irreversible adiabatic process.”

Guggenheim (1986): “When a system is surrounded by an insulating boundary the system is said to be thermally insulated and any process taking place in the system is called adiabatic. The name adiabatic appears to be due to Rankine (Maxwell, Theory of Heat, Longmans 1871).”

Kondepudi and Prigogine (1998): “In an adiabatic process the entropy remains constant.”

We note that for some authors “adiabatic” includes “reversibility” and for others, here Pauli, Chandler, and Guggenheim, “reversibility” is a separate requirement, i.e. during an “adiabatic” process no heat change takes place but the process is not necessarily reversible. (see also the discussion of the “adiabatic principle” in Hill (1956).)
second reservoir (path from \( b \) to \( c \) in the \( P-V \)-diagram).\(^{12}\) Now follows an isothermal compression during which the device releases the amount of heat \( q_1 \) into the second reservoir (path from \( c \) to \( d \) in the \( P-V \)-diagram). The final part of the cycle consists of the crossing back via adiabatic compression to the first isotherm (path from \( d \) to \( a \) in the \( P-V \)-diagram). In addition to the heat transfer between reservoirs the device has done the work \( w \). Any device able to perform such a cyclic transformation in both directions is called a Carnot engine.\(^{13,14}\)

According to the first law, \( \delta E = \delta q - \delta w \), applied to the Carnot engine we have \( \Delta E = 0 \) and thus \( w = q_2 - q_1 \). Our Carnot engine has a thermal efficiency, generally defined by

\[
\eta = \frac{\text{work done}}{\text{heat absorbed}} = \frac{w}{q_2},
\]

which is

\[
\eta = 1 - \frac{q_1}{q_2}.
\]

**Remark:** If the arrows in Fig. 1.10 are reversed the result is a heat pump, i.e. a device which uses work to transfer heat from a colder reservoir to a hotter reservoir. The efficiency of such a device is \( 1/\eta \). Here the aim is to use as little work as possible to transfer as much heat as possible.

Now we prove an interesting fact—the Carnot engine is the most efficient device, operating between two temperatures, which can be constructed! This is called Carnot’s theorem. To prove Carnot’s theorem we put the Carnot engine (\( C \)) in series with an arbitrary competing device (\( X \)) as shown in Fig. 1.11.

\(^{12}\) Do you understand why the slopes of the isotherms are less negative than the slopes of the adiabatic curves? You find the answer on p. 40.

\(^{13}\) Nicolas Léonard Sadi Carnot, French physicist, *Paris 1.6.1796, †ibidem 24.8.1832; his calculations of the thermal efficiency for steam engines prepared the grounds for the second law.

\(^{14}\) If you are interested in actual realizations of the Carnot engine and what they are used for visit [http://www.stirlingengine.com](http://www.stirlingengine.com).
First we note that if we operate both devices many cycles we can make their total heat inputs added up over all cycles, \( q_2 \) and \( q'_2 \), equal (i.e., \( q_2 = q'_2 \) with arbitrary precision). After we have realized this we now reverse the Carnot engine (all arrows on C are reversed). Again we operate the two engines for as many cycles as it takes to fulfill \( q_2 = q'_2 \). This means that reservoir 2 is completely unaltered. But what are the consequences of all this?

According to the first law we have

\[
\begin{align*}
th_{\text{total}}^{1\text{law}} &= q_{2,\text{total}} - q_{1,\text{total}} \\
\end{align*}
\]  

(1.38)

where

\[
\begin{align*}
q_{2,\text{total}} &= -q_2 + q'_2 = 0 \\
q_{1,\text{total}} &= -q_1 + q'_1.
\end{align*}
\]

Because the second reservoir is unaltered we must have

\[
w_{\text{total}} \leq 0.
\]  

(1.39)

\( w_{\text{total}} > 0 \) violates Kelvin’s postulate! However, this implies

\[
\begin{align*}
q_{1,\text{total}} &\geq 0 \\
\Rightarrow q'_1 &\geq q_1 \\
\Rightarrow q'_1 q_2 &\geq q_1 q'_2 \\
\Rightarrow \frac{q'_1}{q_2} &\geq \frac{q_1}{q'_2}.
\end{align*}
\]

And therefore

\[
\eta_X = 1 - \frac{q'_1}{q'_2} \leq 1 - \frac{q_1}{q_2} = \eta_{\text{Carnot}}. 
\]  

(1.40)

There is no device more efficient than Carnot’s engine. Question: Do you understand what distinguishes the Carnot engine in this proof from its competitor? It is the reversibility. If the competing device also is fully reversible we can redo the proof with the two engines interchanged. We then find \( \eta_{\text{Carnot}} \leq \eta_X \), and thus \( \eta_{\text{Carnot}} = \eta_X \).

We may immediately conclude the following corollary: All Carnot engines operating between two given temperatures have the same efficiency.

This in turn allows to define a temperature scale using Carnot engines. The idea is illustrated in Fig. 1.12. We imagine a sequence of Carnot engines all producing the same amount of work \( w \). Each machine uses the heat given off by the previous engine as input. According to the first law

\[
w = q_{i+1} - q_i.
\]  

(1.41)
We define the reservoir temperature $\theta_i$ via

$$\theta_i = x q_i,$$  \hspace{1cm} (1.42)

where $x$ is a proportionality constant independent of $i$. Thus the previous equation becomes

$$xw = \theta_{i+1} - \theta_i.$$  \hspace{1cm} (1.43)

We may for instance choose $xw = 1\, K$, i.e. the temperature difference between reservoirs is $1\, K$. We remark that this definition of a temperature scale is independent of the substance used. Furthermore the thermal efficiency of the Carnot engine becomes

$$\eta_{Carnot} = 1 - \frac{\theta_1}{\theta_2}.$$  \hspace{1cm} (1.44)

($\theta_2 > \theta_1$). Notice that the efficiency can be increased by making $\theta_1$ as low and $\theta_2$ as high as possible. Notice also that $\theta_1 = 0$ is not possible, because this violates the second law. $\theta_1$ can be arbitrarily close but not equal to zero. On p. 42 we compute the thermal efficiency for the Carnot cycle in Fig. 1.10 using an ideal gas as working medium. We shall see that for the ideal gas temperature $T \propto \theta$. Thus from here on we use $\theta = T$. 

**Fig. 1.12** Defining temperature scale using Carnot engines

\[\text{Diagram of Carnot engine cycle.} \]
1.4 Entropy

Some of you may have heard about the thermodynamic time arrow. Gases escape from open containers and heat flows from a hot body to its colder environment. Never has spontaneous reversal of such processes been observed. We call these irreversible processes. The world is always heading forward in time. Mathematically this is expressed by Clausius’ theorem.

1.4.1 Theorem of Clausius

In any cyclic transformation throughout which the temperature is defined, the following inequality holds

$$\oint \frac{dq}{T} \leq 0.$$  \hspace{1cm} (1.45)

The integral extends over one cycle of the transformation. The equality holds if the cyclic transformation is reversible.

Proof: We make use of the assembly of Carnot engines and reservoirs shown in Fig. 1.13. The device called system successively visits all reservoirs indicated by the temperatures $T_1$ to $T_n$. After it has visited reservoir $T_n$ it is in the same state as in the beginning.\(^{15}\) According to Eq. (1.42) we may write

---

\(^{15}\) To achieve this not all Carnot engines operate in the same direction.
Thus the total heat surrendered by the reservoir at $T_0$ ($T_0 > T_i$ and $i = 1, 2, ..., n$) in one complete turn around of the system is

$$q_0 = \sum_{i=1}^{n} q_{i,0} = T_0 \sum_{i=1}^{n} \frac{q_i}{T_i}.$$ 

As before, when we compared the thermal efficiency of the Carnot engine to the X-machine (on p. 19), we use the first law, i.e.

$$0 = \Delta E = \sum_{i=1}^{n} q_{i,0} - \sum_{i=1}^{n} q_i - w_{total}.$$ 

Because $w_{total} \leq 0$ if Kelvin’s postulate is correct, we must have $q_0 \leq 0$ and consequently

$$\sum_{i=1}^{n} \frac{q_i}{T_i} \leq 0.$$ 

Taking the limit $n \to \infty$ and $q_i \to dq$ we have

$$\oint \frac{dq}{T} \leq 0.$$ 

If the cycle is reversed, then the signs of all $q_i$ change and we have

$$\sum_{i=1}^{n} \left(- \frac{q_i}{T_i}\right) \leq 0.$$ 

Thus, for a reversible cycle the equal sign holds. This completes our proof.

1.4.2 Consequences of Clausius’ Theorem

(i) Note first that Eq. (1.45) implies that $\int_{A}^{B} \frac{dq}{T}$ is independent of the path joining $A$ and $B$ if the corresponding transformations are reversible. If $I$ and $II$ are two distinct paths joining $A$ and $B$ we have

$$0 = \oint \frac{dq}{T} = \int_{I} \frac{dq}{T} - \int_{II} \frac{dq}{T} \Rightarrow \int_{I} \cdots = \int_{II} \cdots.$$
Next we define the entropy $S$ as follows. Choose an arbitrary fixed state $O$ as reference state. The entropy $S(A)$ of any state $A$ is defined via

$$S(A) \equiv \int_{O}^{A} \frac{dq}{T}. \quad (1.46)$$

The path of integration may be any reversible path joining $O$ and $A$. Thus the value of the entropy depends on the reference state, i.e. it is determined up to an additive constant. The difference in the entropy of two states $A$ and $B$, however, is completely defined:

$$S(B) - S(A) = \int_{A}^{B} \frac{dq}{T}.$$  

Therefore

$$dS = \frac{dq}{T} \quad (1.47)$$

for any infinitesimal reversible transformation.

### 1.4.3 Important Properties of the Entropy

(i) For an irreversible transformation from $A$ to $B$:

$$\int_{A}^{B} \frac{dq}{T} \leq S(B) - S(A). \quad (1.48)$$

Proof: We construct a closed path consisting of the irreversible piece joining $A$ and $B$ and a reversible piece returning to $A$. Thus

$$0 \geq \oint \frac{dq}{T} = \int_{\text{irrev.}} \frac{dq}{T} - \int_{\text{reversible}} \frac{dq}{T},$$

and therefore

$$\int_{\text{irrev.}} \frac{dq}{T} \leq S(B) - S(A). \quad (1.49)$$

(ii) The entropy of a thermally isolated system never decreases.

Proof: Referring to the previous equation thermal isolation means $dq = 0$. It follows that

$$0 \leq S(B) - S(A) \quad \text{or} \quad S(A) \leq S(B). \quad (1.50)$$

This is the manifestation of the thermodynamic arrow of time.

All of the above follows from the two equivalent postulates by Kelvin and Clausius. They constitute the second law of thermodynamics. However, mathematical
formulations of the second law are the Clausius theorem or the last two inequalities above.

(iii) Another important property of the entropy, as we have shown above, is its sole dependence on the state in which the system is in. Like the internal energy the entropy is a state function whereas \( q \) is not (cf. Remark 1 below!). Combining the first law\(^{16}\) with Eq. (1.47) yields

\[
dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{1}{T} \vec{H} \cdot d\vec{m} - \sum_i \frac{\mu_i}{T} dn_i + \ldots, \tag{1.51}
\]

where

\[
\frac{\partial S}{\partial E} \bigg|_{V,\vec{m},n,\ldots} = \frac{1}{T}, \tag{1.52}
\]

\[
\frac{\partial S}{\partial V} \bigg|_{E,\vec{m},n,\ldots} = \frac{1}{P}, \tag{1.53}
\]

\[
\frac{\partial S}{\partial \vec{m}} \bigg|_{E,V,n,\ldots} = -\frac{1}{T} \vec{H}, \tag{1.54}
\]

and

\[
\frac{\partial S}{\partial n_i} \bigg|_{E,V,\vec{m},n_j,\ldots} = -\frac{1}{T} \mu_i. \tag{1.55}
\]

Equation (1.52) may be viewed as a thermodynamic definition of temperature. Note also that here the \( \vec{H} \)-field is assumed to be constant and \( \delta \vec{m} = \int_V dV \delta \vec{M} \). In the analogous electric case \( \vec{H} \cdot d\vec{m} \) is replaced by \( \vec{E} \cdot d\vec{p} \), where \( \delta \vec{p} = \int_V dV \delta \vec{P} \). If the field strengths and the moments are parallel, then we have \( \vec{H} \cdot d\vec{m} = H dm \) and \( \vec{E} \cdot d\vec{p} = Edp \).

Notice the correspondence between the pairs \((H, m), (E, p)\) and \((P, -V)\). In other words, we may convert thermodynamic relations derived for the variables \( P, -V \) via replacement into relations for the variables \( H, m \) and \( E, p \). Even more general is the mapping \((P, -V) \leftrightarrow (\vec{E}, V \vec{D}/(4\pi))\) or \((P, -V) \leftrightarrow (\vec{H}, V \vec{B}/(4\pi))\), where we assume homogeneous fields throughout the (constant) volume \( V \).

Equation (1.51), including modifications thereof according to the types of work involved during the process of interest, is a very important result! For thermodynamics it is what Newton’s equation of motion is in mechanics or the Schrödinger equation in quantum mechanics—except that here there is no time dependence.\(^{17}\)

**Remark 1:** Thus far we have avoided the special mathematics of thermodynamics, e.g. what is a state function, what is its significance, and why is \( q \) not a state functions.

---

\(^{16}\) The type of work to be included of course depends on the problem at hand. The terms in the following equation represent an example.

\(^{17}\) We return to this point in the chapter on non-equilibrium thermodynamics.
function etc. At this point it is advisable to study Appendix A, which introduces the mathematical concepts necessary to develop thermodynamics.

**Remark 2:** The discussion of state functions in Appendix A leads to the conclusion that Eq. (1.51) holds irrespective of whether the differential changes are due to a reversible or irreversible process! \(^{18}\)

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\(^{18}\) We shall clarify the meaning of this in the context of two related equations starting on p. 55.
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