Statistical Mechanics

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Please report typos and other errors to F. Hassler. The translation has been done with the help of Mistral Small 4. In case of ambiguities, it might be helpful to consult the German version.

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Chapter 1

The Laws of Thermodynamics

Thermodynamics is a physical theory that makes statements about systems about which one has only incomplete information and control. It is by no means the case that the theory is incomplete merely because one does not make enough of an effort to understand a system in all its details. On the one hand, quantum mechanics imposes a fundamental limit to knowledge about the system through the randomness of measurement outcomes; on the other hand, even in classical physics the amount of information required for a complete description is so unimaginably large that it is (practically) impossible to know a macroscopic system completely. Consider, for example, one liter (1 dm×1 dm×1 dm) of helium gas at standard conditions.[1] There are roughly 10^{22} particles in it. If we wish to specify the position of each particle to an accuracy of only 1 mm, we already require $10^{22} \cdot 3 \log_2(100) \simeq 20 \times 10^{22}$ bit (about one zettabyte) of information. One can easily imagine how quickly one reaches the limits of information processing for somewhat larger systems.

The foundation of thermodynamics rests on dividing energy into two distinct classes, *heat* (Q) and *work* (W). Work is already familiar from mechanics lectures. In thermodynamics one denotes by work only that part of the energy to which one has explicit access. Indeed, in a concrete experimental setup there are often only a few degrees of freedom that can perform work: in an engine, for example, it is the torque of the crankshaft. Heat then describes the part of the energy that resides in the remaining degrees of freedom. It is now natural that both work (and hence heat) depend on the experimental setup. As a consequence, the thermodynamic concepts of heat, work, temperature, entropy, ... are defined *relative to the experimental setup.* We refer to this as *relatively objective* in order to distance ourselves from the view that statistics and thermodynamics are subjective and therefore cannot do justice to an objective description of nature.

[1] Pressure $p = 1$ atm $\approx 10^5$ Pa, temperature $T = 0\,^\circ$°C.

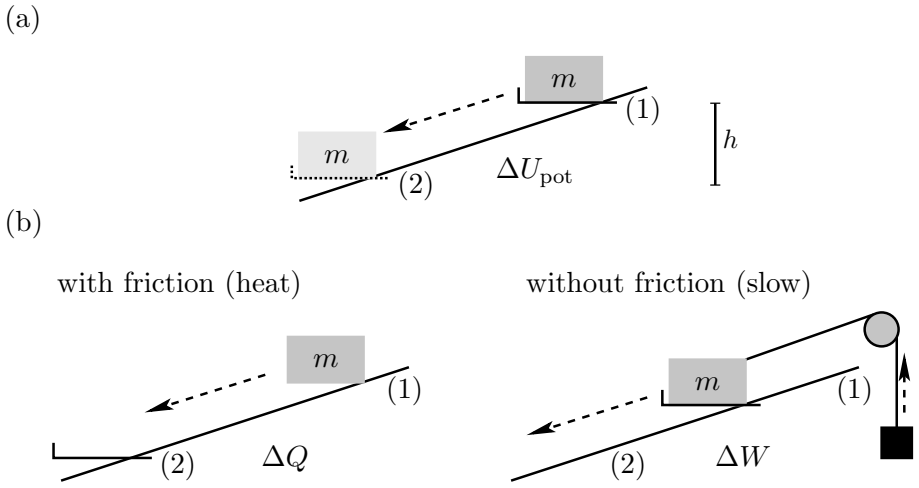


Fig. 1.1: (a) Thermodynamic system consisting of a mass m on an inclined plane in a gravitational field. There are two (equilibrium) states (1) and (2) with an energy difference $\Delta U_{\text{pot}} = U_{\text{pot}}^{(1)} - U_{\text{pot}}^{(2)} = mgh > 0$. The states are set by the slider beneath the mass as an external constraint. In (b) we consider two representative processes that effect the transition (1)→(2). In the left image, the constraint is shifted quickly from (1) to (2). The system is not in equilibrium in the interim because the mass slides down the inclined plane. At the equilibrium point (2) the mass has lost the potential energy ΔU_{pot}, which is entirely converted into heat ΔQ by friction. Alternatively, we can move the system slowly from (1) to (2) without friction, as shown in the right image, by storing the energy in the potential energy (work) of an additional mass. In this case no heat is generated and the energy is entirely converted into work ΔW.

1.1 Introductory Example

We first consider a simple example in which we introduce the basic concepts of work, heat, state, and process of the first law. It is helpful to study this example carefully; when later difficulties arise with the abstract formulation, one can always return to this chapter to concretize the concepts.

In the example, see Figure 1.1, the *thermodynamic system* is given by a mass m in a gravitational field with acceleration g. In mechanics we studied systems without friction. In such systems the energy $E = K + U_{\text{pot}}$ (kinetic energy K and potential energy U_{pot}) is conserved. A point mass starting from rest at point (1) therefore has kinetic energy $K = \Delta U_{\text{pot}} = U_{\text{pot}}^{(1)} - U_{\text{pot}}^{(2)} = mgh$ at point (2). In thermodynamics the conservation of energy is generalized to systems with frictional forces. However, one restricts oneself to *equilibrium states*. In our example, friction $K = 0$ is present at the equilibrium points (1) and (2). These states are characterized by a small number of parameters (the *state variables*), in particular by conserved quantities (energy E, ...) and by constraints (in the example, the slider beneath the mass). In the example

we study *processes* that effect the transition from the equilibrium state (1) to the equilibrium state (2) with the energy difference ΔU_{pot}.

If one shifts the slider from (1) to (2) without attaching a mass, the potential energy is entirely converted into heat via friction, with $\Delta Q = \Delta U_{\text{pot}}$. Alternatively, one can use the dynamics to lift an additional mass (black box in Figure 1.1(b)). If one carries out this process slowly by attaching a suitable counterweight, in the limit no friction arises and $\Delta W = \Delta U_{\text{pot}}$, i.e., all the energy is now stored in the potential energy of the additional mass.[2] In general, of course, not all the energy is converted into work. From energy conservation it follows, however, that $\Delta U_{\text{pot}} = \Delta Q + \Delta W$ for a general process.

From mechanics we know that the total energy U_{pot} of the mass m in equilibrium depends only on the state (the position of the slider). Hence energy is a *state variable*. In the transition from (1) to (2) the energy ΔU_{pot} is released, independent of the process. Work and heat, on the other hand, are *process variables*; that is, they depend on the process. Infinitesimally we write dU (exact differential) for a state variable and δW (inexact differential) for a process variable, thereby expressing that the value of δW depends on the process.

A brief mathematical review of familiar material: a general differential δW with respect to the variables x_j has the form

$$\delta W = \boldsymbol{f}(\boldsymbol{x}) \cdot d\boldsymbol{x} = \sum_j f_j(\boldsymbol{x}) dx_j \,. \tag{1.1}$$

It describes the change in work δW when the variables change by dx_j. In general, however, there is no "potential" $U(\boldsymbol{x})$ such that $\delta W = dU = \sum_j (\partial_{x_j} U) dx_j$. For a potential to exist and for δW to be an exact differential, the integrability condition[3]

$$\frac{\partial f_j}{\partial x_i} = \frac{\partial f_i}{\partial x_j} \tag{1.2}$$

must hold for all i, j. Then for any closed path γ

$$\oint_\gamma \delta W = 0 \tag{1.3}$$

by Stokes's theorem, and one finds a potential

$$U(\boldsymbol{x}) = \int_{\boldsymbol{x}_0}^{\boldsymbol{x}} \delta W \tag{1.4}$$

relative to a fixed initial point $\boldsymbol{x}_0$.

[2] Of course, in this case the additional mass must be chosen so that the forces at the two ends of the rope exactly cancel.

[3] One must also assume that one has a simply connected domain.

The following relations between partial derivatives will be proved in the exercises: consider the variables x, y, z constrained by the condition $f(x, y, z) = 0$. Then (we indicate explicitly with $(\cdot)_z$ which variable, here z, is held fixed during the partial derivative)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \text{and} \qquad \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} . \tag{1.5}$$

If we introduce one more constraint $w(y, z)$, the chain rules

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z , \qquad \left(\frac{\partial x}{\partial z}\right)_w = \left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w . \tag{1.6}$$

hold.

Building on these preliminaries, we will define in the following sections the individual quantities internal energy U, work W, and heat Q as they are used in thermodynamics.

1.2 Internal Energy, Work, Mechanical Equilibrium

Although the formulation of thermodynamics is more general, for the sake of clarity we restrict ourselves in the following to N-particle systems. The energy is given by the Hamiltonian

$$H = K + U_{\text{pot}} = \sum_{j=1}^{N} \frac{\boldsymbol{p}_j^2}{2m} + \sum_{j=1}^{N} U_{\text{ext}}(\boldsymbol{x}_j) + \frac{1}{2} \sum_{i,j=1}^{N} U_{\text{ww}}(|\boldsymbol{x}_i - \boldsymbol{x}_j|) . \tag{1.7}$$

From mechanics we know that a system without an external potential ($U_{\text{ext}} = 0$) has the ten classical conserved quantities—energy ($E = H$), total momentum ($\boldsymbol{P} = \sum_j \boldsymbol{p}_j$), total angular momentum ($\boldsymbol{L} = \sum_j \boldsymbol{x}_j \times \boldsymbol{p}_j$), and the center-of-mass integral ($M\boldsymbol{X} - \boldsymbol{P}t = m\sum_j \boldsymbol{x}_j - \sum_j \boldsymbol{p}_j t$). In thermodynamics one considers a generic system without additional conserved quantities. In particular, one is interested in enclosing the thermodynamic system with U_{ext} in a volume of size V so that in equilibrium there is no macroscopic motion, i.e., no rotational motion ($\boldsymbol{L} = 0$) and no translational motion ($\boldsymbol{P} = 0$). In this case one denotes the energy E in equilibrium as *internal energy* with the symbol U, to indicate that all contributions to the energy arise from internal motions of the system.

The (infinitesimal, quasistatic) work on the system can be written as

$$\delta W = \sum_{\alpha} g_\alpha dZ_\alpha \tag{1.8}$$

with the *work coordinates* Z_α, which are under experimental control, and the *equilibrium quantities* g_α (see below). We adopt the sign convention such that $\delta W > 0$ corresponds to a process in which work is supplied to the system. Thermodynamics

is *relative* to the choice of work coordinates Z_α, which fixes work as a usable form of energy. This is precisely the above-mentioned *relative objectivity*. Once all Z_α are chosen, thermodynamics is uniquely determined.

Example 1: If the coordinates $\boldsymbol{x}_j$ of all particles are fixed, then

$$\delta W = -\sum_{j=1}^{N} \boldsymbol{F}_j \cdot d\boldsymbol{x}_j, \qquad \text{with } \boldsymbol{F}_j = -\partial_{\boldsymbol{x}_j} U_{\text{pot}}\,, \tag{1.9}$$

holds, since any change of the coordinates $\boldsymbol{x}_j$ requires work against the (internal) force $\boldsymbol{F}_j$.

Example 2: (Gas in a container)

For most later applications we use the volume V as the sole work coordinate. To this end we consider a gas confined in a box with

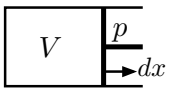
$$U_{\text{ext}}(\boldsymbol{x}) = \begin{cases} 0, & \boldsymbol{x} \in V, \\ \infty, & \text{otherwise.} \end{cases} \tag{1.10}$$

The work done when V is changed is now performed solely against the external potential. We obtain the supplied work

$$\delta W = -p dV \tag{1.11}$$

with the *pressure* p.

That the pressure indeed corresponds to the expression "force per area" is seen by the example of a (frictionless) piston:



If the piston's position is changed by $dx > 0$, the volume increases by $dV = Adx$ with A the cross-sectional area. Thus the gas performs the work $-\delta W = pdV = pAdx$, which by construction corresponds to the force $F = pA$.

Pressure has the SI unit (Pascal) $1\,\text{Pa} = 1\,\text{N/m}^2$. Moreover, the bar with $1\,\text{bar} = 10^5\,\text{Pa}$ is also commonly used. The *standard pressure* (the mean air pressure at sea level) is $1\,\text{atm} = 1.01325\,\text{bar}$.

Since pressure is defined only in equilibrium, the process must be *quasistatic*, i.e. it is carried out so slowly that the system remains in equilibrium at all times. In addition, for the work to equal a change of internal energy, the process must also be *reversible* (i.e. it can be reversed). Concretely this means that the pressure for an infinitesimal compression equals that for an infinitesimal expansion.

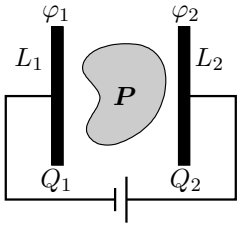
In a realistic piston the externally applied pressure p_K differs from the gas's internal pressure p. Because of static friction between piston and wall one has

$$\begin{aligned} p_K &> p, \quad \text{for compression } (dV < 0), \\ p_K &< p, \quad \text{for expansion } (dV > 0). \end{aligned}$$

Hence a real process is *irreversible*, since the work invested in compression cannot be fully recovered upon subsequent expansion. Thus the real process is not reversible.

With this in mind, in (1.11) the pressure for a quasistatic process refers to the system's internal pressure. Only for a reversible process (without pressure difference) does it also equal the externally applied pressure.

Example 3: (Dielectric in a capacitor)



We consider a polarizable medium with polarization density $\boldsymbol{P}$ inside a capacitor held at fixed applied voltage Φ. For an isotropic medium the (electric) work is given by

$$\delta W = E_0 \, d\mathcal{P} \,, \tag{1.12}$$

with E_0 the field in the capacitor without the medium and the total polarization $\mathcal{P} = \int |\boldsymbol{P}| \, dV$. One sees the nice correspondence $p \leftrightarrow -E_0$, $V \leftrightarrow \mathcal{P}$ with the Example 2.

Proof: The Maxwell equations $\operatorname{curl} \boldsymbol{E} = 0$ and $\operatorname{div} \boldsymbol{D} = \rho$ of electrostatics with $\boldsymbol{D} = \boldsymbol{E} + \boldsymbol{P}$.[4] The electric potential φ determines the electric field via $\boldsymbol{E} = -\boldsymbol{\nabla}\varphi$. The boundary condition $\varphi = \varphi_j$ holds on the conductor L_j.

For a small change of the charge dQ brought from conductor L_1 to conductor L_2 ($dQ_2 = -dQ_1 = dQ$), the work performed by the battery is $\delta W_e = \Phi dQ = (\varphi_2 - \varphi_1)dQ = \varphi_1 dQ_1 + \varphi_2 dQ_2$. The charge or its change is determined by ($\boldsymbol{A}$ is the inner normal)

$$Q_j = -\int_{\partial L_j} \boldsymbol{D} \cdot d\boldsymbol{A}, \quad \text{or} \quad dQ_j = -\int_{\partial L_j} d\boldsymbol{D} \cdot d\boldsymbol{A} \tag{1.13}$$

Hence we obtain

$$\delta W_e = -\sum_{j=1}^{2} \int_{\partial L_j} \varphi_j d\boldsymbol{D} \cdot d\boldsymbol{A} = -\int_G \overbrace{\operatorname{div}(\varphi d\boldsymbol{D})}^{\varphi \, d(\operatorname{div} \boldsymbol{D}) + \boldsymbol{\nabla}\varphi \cdot d\boldsymbol{D}} dV = \int_G \boldsymbol{E} \cdot d\boldsymbol{D} \, dV \tag{1.14}$$

where G is the region outside the conductors.

To obtain the energy contribution of the medium we must still subtract the energy of the system at the same voltage $\Phi_0 = \Phi$ without the dielectric. We find ($d\Phi = d\Phi_0$, $\boldsymbol{D}_0 = \boldsymbol{E}_0$)

$$\begin{aligned} \delta W &= \delta W_e - \delta W_0 = \Phi dQ - \Phi_0 dQ_0 = \Phi_0 (dQ - dQ_0) - Q_0 (d\Phi - d\Phi_0) \\ &= \int_G \boldsymbol{E}_0 \cdot d(\boldsymbol{D} - \boldsymbol{E}_0) \, dV - \int_G \boldsymbol{E}_0 \cdot d(\boldsymbol{E} - \boldsymbol{E}_0) \, dV \\ &= \int_G \boldsymbol{E}_0 \cdot d(\boldsymbol{D} - \boldsymbol{E}) \, dV = \int_G \boldsymbol{E}_0 \cdot d\boldsymbol{P} \, dV. \end{aligned} \tag{1.15}$$

Note that the last expression needs to be integrated only over the medium (as one would expect for the energy contribution of the medium). In the derivation of (1.15) we used that

$$Q_0 d\Phi = -\sum_{j=1}^{2} \int_{\partial L_j} (d\varphi_j) \boldsymbol{E}_0 \cdot d\boldsymbol{A} = -\int_G \overbrace{\operatorname{div}(\boldsymbol{E}_0 d\varphi)}^{(\operatorname{div} \boldsymbol{E}_0) d\varphi + \boldsymbol{E}_0 \cdot d(\nabla\varphi)} dV = \int_G \boldsymbol{E}_0 \cdot d\boldsymbol{E} \, dV \,.$$

[4] We use the SI system with $\varepsilon_0 = \mu_0 = 1$.

In applications it is often the case that, because of the medium's isotropy, $\boldsymbol{P}$ points along $\boldsymbol{E}_0$. For an isotropic medium the (electric) work is given by

$$\delta W = \int E_0 \, dP \, dV = E_0 \, d\mathcal{P} \,, \tag{1.16}$$

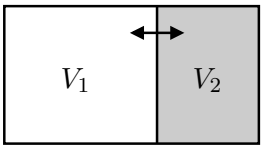
where in the last step we assumed E_0 (the field without the medium) to be constant inside the capacitor.

Example 4: Further common examples of work coordinates are:

g_α	$-p$	σ	E_0	B_0	Φ	μ
dZ_α	dV	dA	$d\mathcal{P}$	$d\mathcal{M}$	dQ	dN

Here σ, A denotes the surface tension, $B_0, \mathcal{M}$ the surface area and N the magnetic field, μ the total magnetization in a coil driven by a constant current source. The last pair is needed for describing particle exchange and chemical processes. Here is the particle number and the chemical potential, which is the work required to add one particle to the system.

For the discussion of *mechanical equilibrium* we restrict ourselves to *additive* work coordinates. As an example we again consider the volume with $V = V_1 + V_2$ for a system composed of two subsystems. On the partition, which acts as a *stop*, there acts the pressure $p_1 - p_2$ (to the right). Hence for a movable partition (removal of the stop) the equilibrium condition becomes



$$p = p_1 = p_2 \,. \tag{1.17}$$

The argument readily generalizes to general additive work coordinates Z_α. *Mechanical equilibrium* is then determined by the condition that the equilibrium variables g_α in the individual subsystems in mechanical contact are equal. In thermodynamics one assumes that equilibrium is reached after waiting a finite time.

For the *stability* of equilibrium it is crucial that for small displacements $dV_1 > 0$ from equilibrium a restoring force arises, i.e.

$$0 \leq \left(\frac{\partial (p_1 - p_2)}{\partial V_1} \right)_V = \frac{dp_1}{dV_1} + \frac{dp_2}{dV_2} \,. \tag{1.18}$$

The principle that a small displacement induces a restoring force is called *Le Chatelier's principle*. In this case it implies that the compressibility $\kappa = -(1/V)(dV/dp)$ must be positive.

Man note that for short-range interactions U_{ww} the internal energy is (approximately) additive as well. We can decompose the internal energy into three parts

$$U = U_1 + U_2 + U_{12}, \tag{1.19}$$

where U_1 denotes the part of the energy H from (1.7) in which the positions $\boldsymbol{x}_j$ lie inside the volume V_1 and vice versa for U_2. Thus for the non-additive "interaction contribution"

$$U_{12} = \sum_{\substack{\boldsymbol{x}_i \in V_1, \\ \boldsymbol{x}_j \in V_2}} U_{\mathrm{ww}}(|\boldsymbol{x}_i - \boldsymbol{x}_j|)\,. \tag{1.20}$$

We now consider the thermodynamic limit $V \to \infty$, where $V_1/V, V_2/V$ remain fixed. If the interaction is confined to the range ξ, only particles in a shell of thickness ξ contribute to U_{12}. The number of terms in (1.20) therefore scales like $(A\xi)\xi^3 \propto V^{2/3}$,[5] while the individual contributions $U_{1,2} \propto V$ grow. In the thermodynamic limit $U_{12} \ll U_1, U_2$ holds and hence the internal energy becomes (approximately) additive with $U = U_1 + U_2$.

In the next chapter we will see that the possibility of *heat exchange* (i.e. energy exchange without moving the wall) leads to *thermal equilibrium*. (Sub-)systems that do not allow heat exchange are called *thermally isolated*.

1.3 First Law of Thermodynamics

After these preliminaries, let us formulate the first law of thermodynamics:

> *Energy principle:*
> In a thermally isolated system ($\Delta U = \Delta W$), the work required for a process (1) $\to$ (2) (between two equilibrium states) is independent of the process itself; but of course it depends on the initial and final states.

Thus the internal energy becomes a state function and the change dU a perfect differential. Furthermore, we define heat for a general (quasistatic) process as the difference $\delta Q = dU - \delta W$. The first law can then be summarized in the compact form (note d versus δ)

$$dU = \delta Q + \delta W \tag{1.21}$$

The first law makes a statement only about states that can be reached by a work process. For example, if one does not allow particle exchange in δW, then work and hence heat for such a process are not defined.

Note: We continue to use the sign convention so that $\delta W, \delta Q > 0$ corresponds to a process in which work or heat is supplied to the system.

Important: Since the internal energy is a state function, one can speak of the value of the internal energy of a state. An analogous statement cannot be made for work or heat. It is not the case that part of the internal energy is work and the rest is heat. The concepts of work and heat are purely process quantities and can be defined only as changes $\delta Q, \delta W$.

[5] For a given particle density n, there are $nA\xi$ particles in the shell, each of which interacts with the particles in a volume ξ^3.

Conclusion 1: (Impossibility of a perpetual-motion machine of the first kind)

Consider a thermally isolated system with $\delta Q = 0$; then $dU = \delta W$ and hence for any *cyclic process* (initial state = final state)

$$\oint \delta W = \oint dU = 0\,. \tag{1.22}$$

Thus it is impossible to extract work in a cyclic process from such a system. As we have seen, in reality the external forces do not even match the internal ones. In the piston example we discussed that one must expend more pressure during compression, and during expansion less pressure is delivered to the outside. For this reason, for a real cyclic process the net work $\oint \delta W = -\oint p_K dV$ is even positive, i.e. one must invest work in order to operate the cycle.

Conclusion 2: The equilibrium variables g_α in (1.8) can be determined by the derivatives

$$g_\alpha = \left(\frac{\partial U}{\partial Z_\alpha}\right)_{\delta Q=0, Z_{\beta\neq\alpha}} \tag{1.23}$$

In particular, for complete mechanical equilibrium

$$\left(\frac{\partial U_1}{\partial Z_{1,\alpha}}\right)_{\delta Q_1=0, Z_{1,\beta\neq\alpha}} = \left(\frac{\partial U_2}{\partial Z_{2,\alpha}}\right)_{\delta Q_2=0, Z_{2,\beta\neq\alpha}}\,. \tag{1.24}$$

The subscript $j = 1, 2$ refers here to two subsystems that are in exchange of Z_α.

Conclusion 3: For two thermally isolated systems ($\delta Q_j = 0$) in *constrained equilibrium*, where the individual volumes V_1, V_2 are held fixed with $V = V_1 + V_2$, one obtains the internal energy

$$U = U_1(V_1) + U_2(V - V_1)\,. \tag{1.25}$$

The equilibrium condition $p_1 = p_2$ corresponds exactly to an extremum of U as a function of V_1 (at $dV = 0$).

The stability condition (1.18) leads to

$$0 \geq \left(\frac{\partial(p_1 - p_2)}{\partial V_1}\right)_{V,\delta Q_j=0} = -\left(\frac{\partial^2 U}{\partial V_1^2}\right)_{V,\delta Q_j=0}\,; \tag{1.26}$$

i.e. a stable equilibrium corresponds to a *minimum of the internal energy* as a function of the constraint V_1.

The argument can be easily generalized. For a system composed of two thermally isolated parts in mechanical contact, $U = U_1 + U_2$, where complete mechanical equilibrium is attained at the minimum of the internal energy. In formulas this means that the Hessian matrix d^2U in a thermally isolated system is positive semidefinite; we write this as $d^2U = (\partial^2 U/\partial Z_\alpha \partial Z_\beta)_{\alpha,\beta} \geq 0$.

Conclusion 4: (Mechanical Maxwell relations)

As seen earlier, δW admits a complete integral on the subspace with $\delta Q = 0$. Hence the integrability conditions (1.2)

$$\left(\frac{\partial g_\alpha}{\partial Z_\beta}\right)_{\delta Q=0, Z_{\beta\neq\alpha}} = \left(\frac{\partial g_\beta}{\partial Z_\alpha}\right)_{\delta Q=0, Z_{\beta\neq\alpha}} . \tag{1.27}$$

hold there. For the case of a gas in which particle exchange is taken into account, with $\delta W = -pdV + \mu dN$, this yields the Maxwell relation

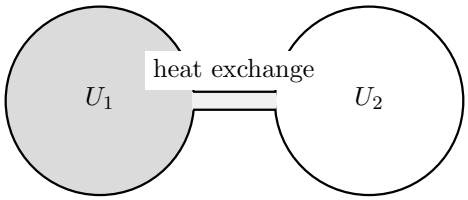
$$-\left(\frac{\partial p}{\partial N}\right)_{V,\delta Q=0} = \left(\frac{\partial \mu}{\partial V}\right)_{N,\delta Q=0} . \tag{1.28}$$

Conclusion 5: The state functions $\boldsymbol{Z} = (U, Z_1, Z_2, \dots)$ uniquely determine an equilibrium state (*thermodynamic state*):

Starting from an arbitrary equilibrium state, one can reach the other equilibrium states by processes. The change in the work coordinates $Z_1, Z_2, \dots$ describes all possible mechanical changes δW. The exchanged heat is fixed by specifying dU via $\delta Q = dU - \delta W$. The first law guarantees that U itself exists and is a state function. Thus every thermodynamic equilibrium state is uniquely determined by specifying $\boldsymbol{Z}$.[6]

In what follows we usually consider processes carried out quasistatically. Such a process can be described by a path in the state space $\boldsymbol{Z}$. Here $\delta W = \sum_\alpha g_\alpha dZ_\alpha$, $\delta Q = dU - \delta W$ correspond to the infinitesimal contributions to work and to heat exchange, respectively.

Consider now once more a thermodynamic system consisting of two parts. In mechanical contact the quantities g_α (for example the pressure, the chemical potential, ...) are equal. For the internal energy $U = U_1 + U_2$ holds. If we now allow *thermal contact* between the parts, this provides the possibility of exchanging energy in the form of heat. The question is then how the total energy U is distributed at equilibrium among the two subsystems.



The *zeroth law of thermodynamics* guarantees that thermal equilibrium is established and that it is also transitive. This means that if 1 is in thermal equilibrium with

[6] Here we implicitly assume that besides energy there is no other conserved quantity in the system. Otherwise the value of the additional conserved quantity must also be given in order to determine the state.

2 and 2 with 3, then 1 is also in equilibrium with 3. The equilibrium quantity associated with the internal energy is called *temperature* ϑ. By thermal contact the temperatures of the subsystems thus equalize. It is natural to choose the sign of the temperature so that U increases when ϑ increases. By symmetry, two systems at the same temperature can exchange heat *reversibly*.

One defines a *heat bath* at temperature ϑ_0 as a system in equilibrium with an internal energy U_0 that is much larger than the systems that are thermally coupled. By thermal coupling another system can thereby also be brought to temperature ϑ_0 through heat exchange. The conventional temperature scale is the degree Celsius (°C). At standard pressure water freezes at 0 °C and boils at 100 °C.

1.4 Ideal Gas, Cyclic Processes

A (monatomic) ideal gas is a N-particle system in volume V without interaction $U_{\text{ww}} = 0$. Hence the internal energy consists only of kinetic energy with $U = K$ (the external potential U_{ext} acts only as a constraint). Physically, dilute noble gases—that is, noble gases at low densities or high temperatures—are in very good approximation ideal gases. We treat ideal gases as a thermodynamic system at fixed particle number so that volume V is the only work coordinate. With the first law a state is uniquely determined by the two state variables (U, V). In particular this implies that there must exist a relation $f(V, p, \vartheta)$ among the three variables V, p, ϑ.

Ideal gases satisfy a number of empirical properties; on *isotherms* (ϑ fixed)

$$\begin{aligned} pV &= \text{const.} && \text{(Boyle-Mariotte)},\\ U &= \text{const.} && \text{(Gay-Lussac)}. \end{aligned}$$

Gay-Lussac determined his law by a free expansion experiment: If one lets an (ideal) gas at temperature T_1 expand from a volume V_1 to a larger volume V_2, the temperature of the gas does not change.

With prior knowledge from mechanics we can show that the two properties are equivalent. To this end it is useful to examine the *virial* $\sum_j \boldsymbol{x}_j \cdot \boldsymbol{p}_j$. Using the Hamiltonian equations of motion we obtain for the time derivative

$$\frac{d}{dt}\sum_j \boldsymbol{x}_j \cdot \boldsymbol{p}_j = \sum_j \boldsymbol{p}_j \cdot \frac{\partial K}{\partial \boldsymbol{p}_j} - \sum_j \boldsymbol{x}_j \cdot \frac{\partial U_{\text{ext}}(\boldsymbol{x}_j)}{\partial \boldsymbol{x}_j} = 2K + \sum_j \boldsymbol{x}_j \cdot \boldsymbol{F}_{\text{ext},j}\,. \tag{1.29}$$

If one averages this equation over the time τ, then on the left side one obtains

$$\overline{\frac{d}{dt}\sum_j \boldsymbol{x}_j \cdot \boldsymbol{p}_j} = \frac{1}{\tau}\int_0^\tau dt\, \frac{d}{dt}\sum_j \boldsymbol{x}_j \cdot \boldsymbol{p}_j = \frac{1}{\tau}\sum_j \boldsymbol{x}_j \cdot \boldsymbol{p}_j\Big|_{t=0}^{\tau} \overset{(\tau\to\infty)}{\to} 0, \tag{1.30}$$

where we have assumed that the system is stable, with $\left|\sum_j \boldsymbol{x}_j \cdot \boldsymbol{p}_j\right| < \infty$. Furthermore,

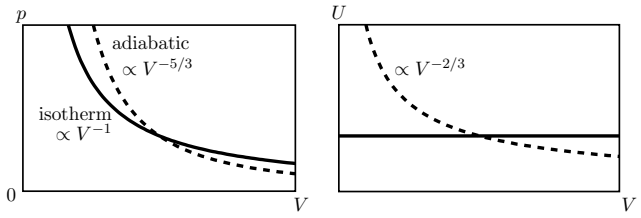


Fig. 1.2: Position and shape of adiabats and isotherms in the p-V and U-V diagram.

in equilibrium (with $\overline{d\boldsymbol{F}_{\rm ext}} = -p\,d\boldsymbol{A}$ on the surface ∂V)

$$-\overline{\sum_j \boldsymbol{x}_j \cdot \boldsymbol{F}_{{\rm ext},j}} = p\int_{\partial V} \boldsymbol{x}\cdot d\boldsymbol{A} = p\int_V \overbrace{\operatorname{div}\boldsymbol{x}}^{=3}\, dV = 3pV\,. \tag{1.31}$$

Hence we obtain the result

$$U \overset{\text{(id. Gas)}}{=} \overline{K} \overset{(1.30)}{=} -\frac{1}{2}\sum_j \overline{\boldsymbol{x}_j\cdot\boldsymbol{F}_{{\rm ext},j}} \overset{(1.31)}{=} \frac{3}{2}pV\,. \tag{1.32}$$

Thus we have shown that Boyle-Mariotte is equivalent to Gay-Lussac. In the general case with $H = K + U_{\rm pot}$ it follows from (1.29) and (1.31) the relation

$$\frac{2}{3}\overline{K} = pV + \frac{1}{3}\sum_j \overline{\boldsymbol{x}_j\cdot\frac{\partial U_{\rm ww}}{\partial \boldsymbol{x}_j}} = pV - \frac{1}{3}\sum_j \overline{\boldsymbol{x}_j\cdot\boldsymbol{F}_{{\rm ww},j}}, \tag{1.33}$$

where the last term corresponds to the virial of the interaction force.

In an isothermal process Gay-Lussac implies that $\delta Q = -\delta W = pdV$. Hence an ideal gas undergoing an isothermal expansion ($V_2 > V_1$) absorbs the heat

$$Q = \int_{(1)}^{(2)} \delta Q = \int_{(1)}^{(2)} pdV = \frac{2}{3}U\int_{(1)}^{(2)}\frac{dV}{V} = \frac{2}{3}U\ln(V_2/V_1) \tag{1.34}$$

Consider next an *adiabatic* process (without heat exchange $\delta Q = 0$) carried out reversibly. One has

$$\frac{3}{2}(V\,dp + p\,dV) = dU \overset{\text{(1.HS)}}{=} \delta W = -p\,dV\,. \tag{1.35}$$

After separation into $dp/p = -\frac{5}{3}(dV/V)$ we obtain the solution

$$pV^{5/3} = \text{const.} \qquad \text{(Adiabatic equation).} \tag{1.36}$$

In Figure 1.2 one sees a comparison of the adiabats with an isotherm for an ideal gas. It is important in what follows that the adiabat is steeper than the isotherm.

As a preliminary to the second law, consider the *Carnot cycle*. A *cyclic process* is a heat engine operating in cycles that converts work into heat or vice versa. In the Carnot process one considers an ideal gas as the *working substance*, which can be

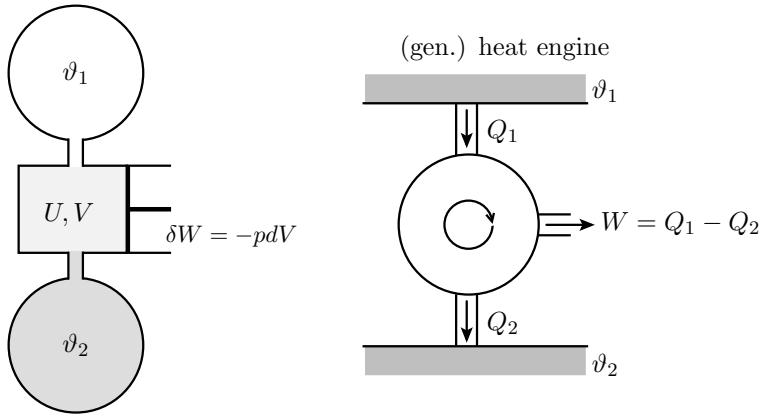
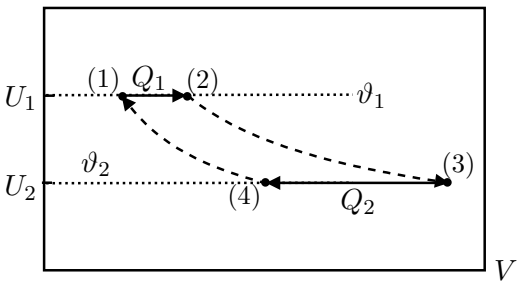


Fig. 1.3: General cyclic process: A heat engine (per cycle) extracts heat Q_1 from the heat bath at the higher temperature and converts it into work W and waste heat Q_2 (into the second heat bath). On the left a schematic setup is drawn. The two heat baths are coupled to the gas U, V via heat conductors. The work is performed by the piston as the work reservoir. On the right the corresponding energy flow diagram is shown. The efficiency η of a heat engine is defined as $\eta =$ work performed/heat supplied $= W/Q_1$.

coupled to two heat baths at temperatures ϑ_1 and $\vartheta_2 < \vartheta_1$ and to a work reservoir, see Figure 1.3.

We now examine the following reversible cyclic process (Carnot process):



Isotherms:
(1)→(2) and (3)→(4)
with $dU = 0, \delta Q = pdV$,
Adiabats:
(2)→(3) and (4)→(1)
with $dU = -pdV, \delta Q = 0$.

Idealized (without additional friction) the cycle is reversible. On the isotherms the ideal gas is coupled to the respective heat bath. With (1.34) we obtain for the heat absorbed (Q_1) and released (Q_2)

$$Q_1 = \frac{2}{3} U_1 \ln(V_2/V_1), \quad \text{or} \quad Q_2 = \frac{2}{3} U_2 \ln(V_3/V_4)\,, \tag{1.37}$$

for the isothermal expansion (1)→(2) and compression (3)→(4), respectively. On the adiabats $V^{2/3}U =$ const. and it follows $V_2/V_1 = V_3/V_4$. The ratio of the heat amounts simplifies to

$$\frac{Q_2}{Q_1} = \frac{U_2}{U_1} = f(\vartheta_1, \vartheta_2) < 1 \tag{1.38}$$

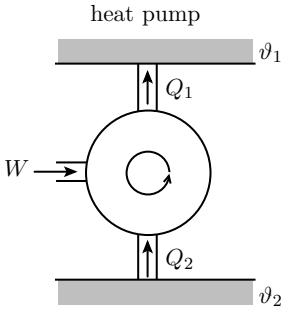
and, by Gay-Lussac, depends only on the function $f(\vartheta_1, \vartheta_2)$ of the temperatures of the two heat baths. As a result one obtains the *Carnot efficiency*

$$\eta_{\rm C} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - f(\vartheta_1, \vartheta_2) > 0\,. \tag{1.39}$$

Since the cycle is reversible, one can also operate it in reverse, from (1)→(4)→(3)→(2)→(1) . In this case the process is a heat pump with efficiency

$$\eta_{\rm WP} = \frac{Q_1}{W} = \frac{1}{\eta_{\rm C}}\,. \tag{1.40}$$

Note that *reversibility* is essential in order to run the process backward.



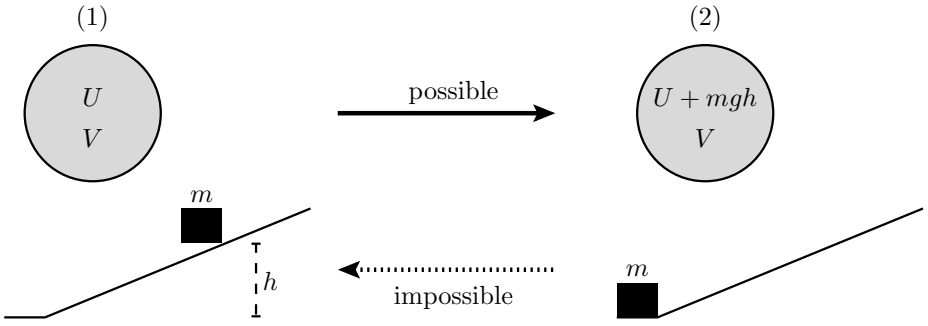
1.5 Second Law of Thermodynamics

The second law of thermodynamics allows us, for systems in thermal contact, to compute the partitioning of the internal energy among the two subsystems. Yet it accomplishes much more. A consequence of the law is the definition of an absolute temperature scale. Furthermore it specifies that irreversible processes can proceed in only one direction. Hence it enables one to distinguish whether a video recording is played forward or backward. The second law with *entropy* as the associated state variable is the core of thermodynamics.

We first consider the second law (postulate) in Kelvin's formulation:

> *(Impossibility of a perpetual-motion machine of the second kind)*
>
> It is impossible to produce work cyclically by merely cooling a single heat bath.

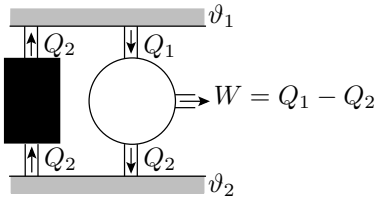
Example: For a heat bath (internal energy U, volume V) and a mass m in a gravitational field



With Kelvin's formulation this exhausts the case of a single heat bath. More interesting is therefore to examine heat engines operating between two heat baths with $\vartheta_2 < \vartheta_1$.

Conclusion 1: (Clausius formulation)

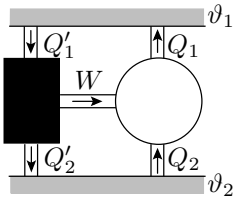
Heat cannot spontaneously flow (without work being performed) in a cyclic process from the cold heat bath to the warm heat bath.



That this formulation is equivalent to Kelvin's formulation is seen by linking the (imaginary) Clausius process (black box) with the Carnot process. One thereby obtains from the Clausius machine a machine that continuously converts the heat $Q_1 - Q_2$ from the heat bath ϑ_1 into work $W = Q_1 - Q_2$, which is forbidden by Kelvin's formulation. (As an exercise one shows the reverse direction.)

Conclusion 2: (Carnot's theorem)

The Carnot efficiency is the maximal efficiency for a cyclic process between two heat baths.



To prove this, one links the (imaginary) machine (black box) with efficiency $\eta > \eta_C$ to the Carnot machine operated as a heat pump ($W/Q_1 = \eta_C, W/Q_1' = \eta$). No work is performed externally, but the heat amount $Q = Q_1 - Q_1' = Q_2 - Q_2' = W(\eta_C^{-1} - \eta^{-1}) > 0$ is transferred from the cold to the warm heat bath.

Conclusion 3: (Universality of reversible cycles)

Since reversible cycles can also be run backward as heat pumps, Carnot's theorem immediately implies that the efficiency of a reversible cycle is always η_C. Otherwise one could run the process in the sketch of Conclusion 2 backward and thereby violate the Clausius formulation. Hence the Carnot efficiency is universal for all reversible cyclic processes with two heat baths. The construction of the Carnot process via the ideal gas in Section 1.4 serves only to show that $\eta_C > 0$, i.e., that a nontrivial reversible cycle exists. With the second law one can show that real gases have the same efficiency when operated reversibly (without additional frictional losses). One therefore denotes all reversible cyclic processes as Carnot processes.

Conclusion 4: (Absolute temperature scale)

For the function $f(\vartheta_1, \vartheta_2) = Q_2/Q_1$ in the Carnot efficiency $\eta_C = 1 - f(\vartheta_1, \vartheta_2)$ for reversible cycles one has (with ϑ_j arbitrary)

$$f(\vartheta_1, \vartheta_2) = \frac{1}{f(\vartheta_2, \vartheta_1)}, \qquad f(\vartheta_1, \vartheta_3) = f(\vartheta_1, \vartheta_2) f(\vartheta_2, \vartheta_3)\,. \tag{1.41}$$

The first relation follows from reversibility. The second relation follows from concatenating the cycle between ϑ_1 and ϑ_2 with one between ϑ_2 and ϑ_3 so that no net heat flows into the heat bath ϑ_2. One thereby effectively has a Carnot

process between the heat bath ϑ_1 and ϑ_3. With $Q_3/Q_1 = (Q_2/Q_1)(Q_3/Q_2)$ the result follows.

By fixing the temperature T_0 of a standard bath 0 one thereby defines the *absolute temperature* (or thermodynamic temperature) $T = T_0 f(\vartheta_0, \vartheta)$ of an arbitrary other heat bath (with the phenomenological temperature ϑ). Hence $T > 0$ and

$$\frac{Q_2}{Q_1} = f(\vartheta_1, \vartheta_2) = \frac{f(\vartheta_0, \vartheta_2)}{f(\vartheta_0, \vartheta_1)} = \frac{T_2}{T_1}\,. \tag{1.42}$$

hold.

The Carnot efficiency takes the simple form

$$\eta_C = 1 - \frac{T_2}{T_1} \tag{1.43}$$

as a function of the absolute temperatures.

Note that the temperature scale thus defined has only one degree of freedom (given by the choice of T_0). In particular the various temperature scales differ only by a multiplicative constant. By this and by the inequality $T > 0$ the *absolute zero* is anchored absolutely (more on this in the third law). Conventionally one fixes the kelvin, as the absolute temperature scale, so that between the freezing and boiling points of water at standard pressure there are exactly 100 kelvin. The conversion formula from the phenomenological to the absolute scale is therefore

$$T[K] = \vartheta[^\circ\mathrm{C}] + 273.15\,. \tag{1.44}$$

From comparing (1.42) with (1.38) one finds $U \propto T$ for the ideal gas. Furthermore U is proportional to the particle number N, so that we obtain the *caloric equation of state*[7]

$$U = \frac{3}{2} N k_B T \tag{1.45}$$

where the Boltzmann constant

$$k_B = 1.38 \times 10^{-23}\,\mathrm{J/K} = 8.62 \times 10^{-5}\,\mathrm{eV/K} \tag{1.46}$$

is experimentally determinable by the choice of the temperature unit. With (1.32) we also obtain the *thermal equation of state*

$$pV = N k_B T\,. \tag{1.47}$$

For macroscopic experiments it is often useful to measure the particle number in units of (Avogadro's constant[8])

$$N_A = 6.022 \times 10^{23}/\mathrm{mol} \tag{1.48}$$

[7]The factor $\frac{3}{2}$ is conventional and ensures that the thermal equation of state (1.47) appears without a factor.

[8]This number is chosen so that a mole gives the ratio of the atomic mass u to one gram.

so that

$$U = \frac{3}{2}nRT, \qquad pV = nRT \tag{1.49}$$

with $n = N/N_A$ the amount of substance (in moles) and the gas constant $R = N_A k_B = 8.31\,\mathrm{J/mol\,K}$.

Conclusion 5: (Clausius' theorem)

For an arbitrary cyclic process

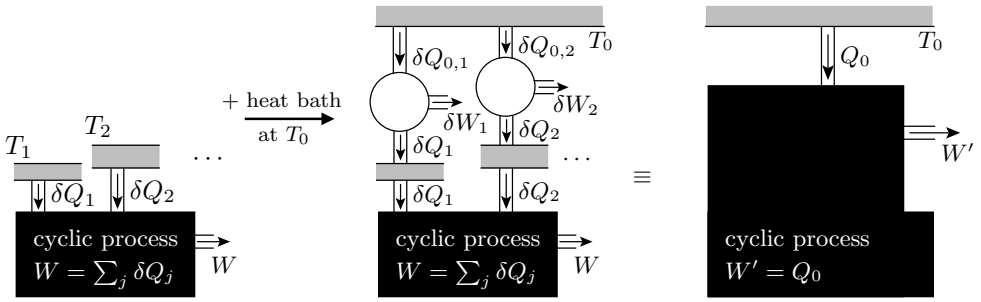
$$\oint \frac{\delta Q}{T} = \sum_j \frac{\delta Q_j}{T_j} \leq 0 \tag{1.50}$$

where T_j denotes the temperature of the heat bath in step j from which the heat amount δQ_j is extracted.

To prove this, we introduce an additional heat bath at temperature $T_0 \geq T_j$ and regard the total system as one thermodynamic system. We then carry out the process stepwise with Carnot machines between T_0 and the respective T_j with $\delta Q_j/\delta Q_{0,j} = T_j/T_0$. At the end of the cycle we have extracted from the heat bath T_0 the heat

$$Q_0 = \sum_j \delta Q_{0,j} = T_0 \sum_j \frac{\delta Q_j}{T_j} \tag{1.51}$$

which, by the first law, has been fully converted into work $W' = Q_0$. This is admissible by the second law only if $Q_0 \leq 0$ (so that in reality work is converted into heat), whence the theorem follows.



Conclusion 6: (Irreversibility)

A reversible cycle can also be run backward; then all heat amounts reverse sign. With Clausius' theorem one then has $-\oint \delta Q/T \leq 0$ and hence (we indicate by subscript "rev" that we restrict to reversible processes)

$$\oint \frac{\delta Q_{\mathrm{rev}}}{T} = 0\,. \tag{1.52}$$

Cyclic processes with $\oint \frac{\delta Q}{T} < 0$ are called *irreversible*, since they cannot be run backward in time. The inequality thus defines a direction of time, the *thermodynamic arrow of time*.

If one therefore restricts to reversible processes (heat exchange without temperature difference, volume change without pressure difference, ...), the integral

$$\int_{(0)}^{(1)} \frac{\delta Q_{\text{rev}}}{T} \tag{1.53}$$

is independent of the process and depends only on the initial and final states. This leads directly to the definition of a new state variable, *entropy*

$$S(\boldsymbol{Z}) = \int_{\boldsymbol{Z}_0}^{\boldsymbol{Z}} \frac{\delta Q_{\text{rev}}}{T} + S_0, \tag{1.54}$$

where the integration runs over an arbitrary reversible process from the fixed state $\boldsymbol{Z}_0$ to $\boldsymbol{Z}$ and S_0 is an integration constant still undetermined. Hence $dS = \delta Q/T$ is an exact differential, so that one can regard the temperature T as an *integrating factor* and restrict to reversible processes. By the second law the entropy is fixed up to the additive constant S_0.

From combining the first and second laws one obtains the *Gibbs fundamental equation*

$$dS = \frac{1}{T} dU - \frac{1}{T} \sum_{\alpha} g_\alpha dZ_\alpha \tag{1.55}$$

The temperature T and the equilibrium variables g_α refer here to properties of the system (i.e., to the state when a constraint is imposed) or to those of the environment, provided the contact is established reversibly. The state function $S(\boldsymbol{Z}) = S(U, Z_1, \dots)$ contains the complete thermodynamics. In particular one obtains the temperature and the equilibrium variables via

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{Z_\alpha}, \qquad \frac{g_\alpha}{T} = -\left(\frac{\partial S}{\partial Z_\alpha}\right)_{U, Z_{\beta \neq \alpha}}. \tag{1.56}$$

For the case that volume is the only work coordinate, one obtains from

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V} \tag{1.57}$$

by rearrangement the caloric equation of state $U(T, V)$ and from

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U} \tag{1.58}$$

the thermal equation of state $p(T, V)$. Moreover one finds the (thermal) Maxwell relation

$$\frac{\partial^2 S}{\partial U \partial V} = \frac{\partial}{\partial V}\left(\frac{1}{T}\right)_U = \frac{\partial}{\partial U}\left(\frac{p}{T}\right)_V. \tag{1.59}$$

Note that for these results it is crucial to express the entropy S as a function of its natural variables (U, V). The function $S(U, V)$ is the first example of a *thermodynamic potential*.

In a thermally isolated system the entropy cannot decrease. One also says that only such processes can occur *spontaneously*. For from Clausius' theorem one has for a process from (1) to (2)

$$S(\boldsymbol{Z}_1) \leq S(\boldsymbol{Z}_2), \qquad \text{(abbreviated as } \Delta S \geq 0 \text{ written)} \tag{1.60}$$

with equality only in the reversible case. To prove this, we complete the (thermally isolated) process to a cycle, carrying out the return from (2) to (1) reversibly (not necessarily adiabatically). We then obtain

$$0 \geq \oint \frac{\delta Q}{T} = \int_{\boldsymbol{Z}_1}^{\boldsymbol{Z}_2} \frac{\overbrace{\delta Q}^{=0}}{T} + \int_{\boldsymbol{Z}_2}^{\boldsymbol{Z}_1} \frac{\delta Q_{\text{rev}}}{T} = S(\boldsymbol{Z}_1) - S(\boldsymbol{Z}_2), \tag{1.61}$$

whence the result follows. Hence an adiabatic process in a thermally isolated system is not equivalent to isentropy ($dS = 0$). Only a reversible adiabatic process is isentropic.

Example 5: (Entropy of the ideal gas)

With these preliminaries we can compute the entropy $S(U, V)$ of the ideal gas. Starting from a reference state (U_0, V_0) with entropy $S_0 = 0$, we reach the state (U, V) by a sequence of an adiabat ($V^{2/3}U = \text{const.}$) and an isotherm (with the temperature T determined by (1.45)). On the adiabat the entropy is conserved and the gas expands to volume $V_1 = (U_0/U)^{3/2}V_0$.

On the isotherm one has (with Eq. (1.34))

$$S = \frac{1}{T}\int_{(U,V_1)}^{(U,V)} \delta Q_{\text{rev}} = Nk_B \ln(V/V_1) = Nk_B\Big[\ln(V/V_0) + \tfrac{3}{2}\ln(U/U_0)\Big]\,. \tag{1.62}$$

Example 6: (Relation between thermal and caloric equations of state)

The second law provides a relation between the thermal $p(V, T)$ and the caloric $U(V, T)$ equations of state. To this end we regard S as a function of (V, T) and obtain

$$\left(\frac{\partial S}{\partial T}\right)_V = \underbrace{\left(\frac{\partial S}{\partial U}\right)_V}_{1/T}\left(\frac{\partial U}{\partial T}\right)_V, \quad \left(\frac{\partial S}{\partial V}\right)_T \overset{(1.6)}{=} \underbrace{\left(\frac{\partial S}{\partial V}\right)_U}_{p/T} + \underbrace{\left(\frac{\partial S}{\partial U}\right)_V}_{1/T}\left(\frac{\partial U}{\partial V}\right)_T,$$

or $T(\partial S/\partial T)_V = (\partial U/\partial T)_V$ and $p = T(\partial S/\partial V)_T - (\partial U/\partial V)_T$. From the first relation one finds $T(\partial^2 S/\partial V \partial T) = (\partial^2 U/\partial V \partial T)$ (by differentiating with respect to V). If one differentiates the second relation with respect to T, one

obtains

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T + \overbrace{T\frac{\partial^2 S}{\partial V \partial T} - \frac{\partial^2 U}{\partial V \partial T}}^{=0} = \frac{p}{T} + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T . \tag{1.63}$$

Hence the thermodynamic relation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{1.64}$$

between the thermal and the caloric equations of state holds, which is equivalent to (1.59).

The thermal equation of state $pV = Nk_BT$ (1.47) together with (1.64) implies that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = 0 . \tag{1.65}$$

Thus in this case the internal energy $U(T)$ is independent of the gas volume V. Note that the internal energy still depends parametrically on the amount of substance N, which in this example we do not treat as a work coordinate.

Example 7: (Relative objectivity of heat/entropy)

To understand the relative objectivity, consider the thermodynamic system from Example 1, in which all particle coordinates are work coordinates. Then $dU_{\text{pot}} = \sum_j (\partial U_{\text{pot}}/\partial \boldsymbol{x}_j) \cdot d\boldsymbol{x}_j = \delta W$. Furthermore $K = 0$, since all particle positions are fixed. Hence $dU = \delta W$. For this system there is therefore no heat ($\delta Q = 0$), since all degrees of freedom are controlled externally. Moreover $S(U, \boldsymbol{x}_1, \dots) = S_0$; the entropy is thus constant (with the third law $S = 0$).

In reality it is of course impossible to control all particle positions. However, the rule holds that with an increasing number of work coordinates the heat amount typically decreases, since in a process between two states more internal energy is converted into work; hence the entropy also becomes smaller. Although entropy is a state variable, it makes no sense to regard "the entropy of a gas" as an absolute quantity. Indeed the entropy depends on the work coordinates and hence on the experimental possibilities (i.e., on the work coordinates). We will deepen this understanding in the chapter on statistical physics.

1.6 Third Law of Thermodynamics

The third law is based on an experimental observation by Nernst, that entropy changes ΔS vanish at low temperatures, i.e. $\Delta S \to 0$ for $T \to 0$. This observation was sharpened by Planck:

(Nernst heat theorem)

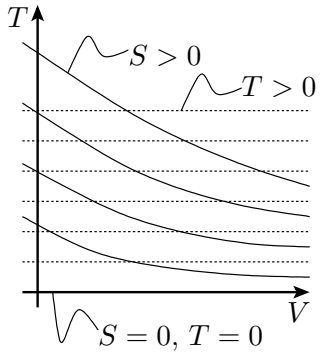
For every system the entropy tends, as $T \to 0$, to a finite value independent of the work coordinates Z_α.

The value is conventionally set to $S_0 = 0$, so that $S \geq 0$ holds. This makes entropies and the other thermodynamic potentials (see the next chapter) comparable between different phases and substances. The third law is therefore important for chemical applications, but it does not have the same status as the other laws. In particular one can imagine (at least theoretically) systems that violate the third law.

Remark: The third law does not hold for the (classical) ideal gas (1.62). One may of course take the opposite view and conclude: Every real gas deviates from ideal behavior for $T \to 0$. Indeed, at low temperatures it is important to take quantum mechanics into account, whereby the third law remains valid.

Conclusion 1: (Unattainability of absolute zero)

We consider a thermodynamic system with $\boldsymbol{Z} = (U, V)$, where V denotes an arbitrary work coordinate. One may describe any process with arbitrary precision by a sequence of isothermal and adiabatic processes. Isotherms of course do not change the temperature. The adiabats are given by $S(\boldsymbol{Z}) = \text{const.}$ and therefore do not intersect. Now the states with $T = 0$ themselves form an adiabat (to $S = 0$). Hence the absolute zero (starting from a state with $T > 0$) can be reached neither along an adiabat nor along an isotherm.



Conclusion 2: (Heat capacity)

The *heat capacities*

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad \text{and} \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{1.66}$$

measure how much heat must be added to the system to raise the temperature by one kelvin. The heat capacities must vanish for $T \to 0$. The reason is that the integrals

$$S(V,T) = \int_0^T dT' \, \frac{C_V(V,T')}{T'} \quad \text{and} \quad S(p,T) = \int_0^T dT' \, \frac{C_p(p,T')}{T'} \,. \tag{1.67}$$

must converge at $T' = 0$ (so that $S_0 = 0$). This requires $C_V, C_p \to 0$ for $T \to 0$.

Chapter 2

Thermodynamic Potentials

In the previous chapter we already found the thermodynamic potential $S(\boldsymbol{Z})$. In principle, the entire thermodynamics can be determined from the properties of the entropy S as a function of the additive quantities $\boldsymbol{Z}$. We summarize the formalism in what follows. However, there are other, equivalent formulations. For example, the internal energy U as a function of S and Z_α is also a thermodynamic potential, and further potentials can be obtained by Legendre transformations. Although all formulations are equivalent, trivial statements in one formulation may be highly nontrivial in another. The art of thermodynamics consists in formulating each question with a thermodynamic potential such that the solution becomes as simple as possible.

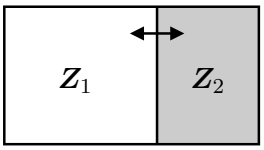
2.1 Entropy

The entropy S as a function of $\boldsymbol{Z} = (U, Z_1, \dots)$ is called a thermodynamic potential, since—as already seen—one can derive the entire thermodynamics, in particular the thermal and caloric equations of state, from it. The entropy thereby satisfies the following important properties:

$$\Delta S \geq 0 \qquad \text{(entropy increases in a thermally isolated system)} \tag{2.1a}$$

$$S(\boldsymbol{Z}_1 + \boldsymbol{Z}_2) \geq S(\boldsymbol{Z}_1) + S(\boldsymbol{Z}_2) \qquad \text{(superadditivity)} \tag{2.1b}$$

$$d^2S \leq 0, dS = 0 \qquad \text{(maximum at equilibrium)} \tag{2.1c}$$



We have already shown property (a) in (1.60). The other properties follow directly: property (b) follows if we consider two subsystems separated by a partition that inhibits exchange. In the initial state $S(\boldsymbol{Z}_1, \boldsymbol{Z}_2) = S(\boldsymbol{Z}_1) + S(\boldsymbol{Z}_2)$ holds, since the inhibited state in the two subsystems can be reached independently, and the heat quantities in (1.54) are additive. After removing the inhibition, the system reaches *complete*

equilibrium, which is determined solely by the total quantities $\boldsymbol{Z}_1 + \boldsymbol{Z}_2$. Since the removal of the partition (ideally) occurs without work or heat exchange, $S(\boldsymbol{Z}_1, \boldsymbol{Z}_2) = S(\boldsymbol{Z}_1) + S(\boldsymbol{Z}_2) \leq S(\boldsymbol{Z}_1 + \boldsymbol{Z}_2)$ holds according to (2.1a).

In thermodynamics, inhibited equilibria represent a class of nonequilibrium states. The *maximum entropy principle*, property (c), states that in an isolated system (with fixed $\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2$) the system is in complete equilibrium precisely when S is maximal, i.e.,

$$\max_{\substack{\boldsymbol{Z}_1, \boldsymbol{Z}_2 \\ (\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2)}} S(\boldsymbol{Z}_1) + S(\boldsymbol{Z}_2) = S(\boldsymbol{Z})\,. \tag{2.2}$$

The inequality $\leq$ follows directly from the superadditivity in (2.1b). The equality $S(\boldsymbol{Z}) = S(\boldsymbol{Z}_1^*) + S(\boldsymbol{Z}_2^*)$ describes that we can achieve complete equilibrium by a specific partitioning of $\boldsymbol{Z}$ into $\boldsymbol{Z}_1^*, \boldsymbol{Z}_2^*$. This is accomplished by reversibly introducing a partition in complete equilibrium, thereby determining $\boldsymbol{Z}_1^*$ and $\boldsymbol{Z}_2^*$.

From the maximum entropy principle (with Eq. (1.55) and $\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2$)

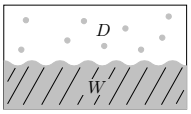
$$\begin{aligned} dS &= \frac{1}{T_1} dU_1 - \frac{1}{T_1} \sum_\alpha g_{1,\alpha} dZ_{1,\alpha} + \frac{1}{T_2} \overbrace{dU_2}^{-dU_1} - \frac{1}{T_2} \sum_\alpha g_{2,\alpha} \overbrace{dZ_{2,\alpha}}^{-dZ_{1,\alpha}} \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \sum_\alpha \left(\frac{1}{T_2} g_{2,\alpha} - \frac{1}{T_1} g_{1,\alpha} \right) dZ_{1,\alpha} = 0 \end{aligned} \tag{2.3}$$

follow the equilibrium conditions

$$\begin{aligned} T_1 &= T_2 && \text{(thermal equilibrium)}, \\ g_{1,\alpha} &= g_{2,\alpha} && \text{(mechanical equilibrium)}. \end{aligned} \tag{2.4}$$

The condition that $d^2 S \leq 0$ (S is a maximum) guarantees that the equilibrium is stable, see (1.18).

Example 1: (Vapor Pressure)



The system of water and water vapor in a closed vessel is in complete equilibrium. The work coordinates are (V, N). The water surface is the partition. The separation is reversible (without surface tension) and hence the entropies are additive, $S_{\text{ges}} = S_W + S_D$. The equilibrium requires that $T \equiv T_W = T_D$, $p \equiv p_W = p_D$ and $\mu \equiv \mu_W = \mu_D$. The quantities p and T are not independent here but are related by the vapor pressure curve $p(T)$, as discussed later.

Example 2: (Heat Transport)

Consider two subsystems that are in mechanical equilibrium but for which $T_1 > T_2$ holds. By removing the inhibition in U_1, U_2, energy exchange in the form of heat is enabled. If we keep the total system thermally isolated,

$dU_1 = -dU_2$ holds. Thus

$$dS = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 = \overbrace{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}^{>0} dU_2 \overset{(2.1a)}{\geq} 0\,. \tag{2.5}$$

With $T_1 > T_2$ it follows $dU_2 \geq 0$, i.e., heat flows from the hotter to the colder part of the system to reach equilibrium.

Example 3: (Incomplete Equilibrium)

One can remove inhibitions sequentially. In particular, consider a *diathermal wall*, which allows heat exchange but inhibits mechanical exchange. In equilibrium one then has $T_1 = T_2$ (but not necessarily $p_1 = p_2$). A movable adiabatic wall, by contrast, leads to mechanical equilibrium, which we already know from Section 1.3 (without $T_1 = T_2$).

Homogeneous Phases: Consider a *homogeneous phase*, for example the water in Example 1. Then we can imagine the system as composed of λ equivalent subsystems in complete equilibrium. By homogeneity, each subsystem is determined by the state variables $\boldsymbol{Z}/\lambda$, so that $\boldsymbol{Z} = (\boldsymbol{Z}/\lambda) + (\boldsymbol{Z}/\lambda) + \cdots$. Hence [1]

$$S(\boldsymbol{Z}) = \underbrace{S(\boldsymbol{Z}/\lambda) + S(\boldsymbol{Z}/\lambda) + \cdots}_{\lambda \text{ times}} = \lambda\, S(\boldsymbol{Z}/\lambda)\,. \tag{2.6}$$

A function $f : \mathbb{R}^n \to \mathbb{R}$ is called homogeneous of degree α if $f(\lambda \boldsymbol{x}) = \lambda^\alpha f(\boldsymbol{x})$. Thus the entropy of a homogeneous system is homogeneous of degree 1, or *extensive*. Extensive quantities are therefore S, U, V, Z_α. The equilibrium quantities such as T, p, μ, being first derivatives of S with respect to $\boldsymbol{Z}$, are then *intensive*, i.e., homogeneous of degree 0.

For homogeneous systems, superadditivity is equivalent to *concavity*

$$S(x\boldsymbol{Z}_1 + (1-x)\boldsymbol{Z}_2) \geq xS(\boldsymbol{Z}_1) + (1-x)S(\boldsymbol{Z}_2), \qquad 0 \leq x \leq 1\,; \tag{2.7}$$

the proof follows directly from the relation $xS(\boldsymbol{Z}_1) + (1-x)S(\boldsymbol{Z}_2) = S(x\boldsymbol{Z}_1) + S((1-x)\boldsymbol{Z}_2)$. Moreover, the Euler homogeneity relation[2] holds

$$S = U\frac{\partial S}{\partial U} + \sum_\alpha Z_\alpha \frac{\partial S}{\partial Z_\alpha} = \frac{1}{T}\Big(U - \sum_\alpha g_\alpha Z_\alpha\Big) = \frac{1}{T}(U + pV - \mu N). \tag{2.8}$$

In the last step we have specialized the general relation to the typical work coordinates (V, N). From (2.8) we obtain for small changes in a homogeneous system

$$dS = \frac{1}{T}\left(dU - \sum_\alpha (g_\alpha dZ_\alpha + Z_\alpha dg_\alpha)\right) - S\frac{dT}{T}\,. \tag{2.9}$$

[1] The entropies are additive because the system is in complete equilibrium.

[2] One derives this directly by differentiating the relation (2.6) with respect to λ and then setting $\lambda = 1$.

Subtracting (1.55) yields the *Gibbs-Duhem relation*

$$0 = SdT + \sum_\alpha Z_\alpha dg_\alpha = SdT - Vdp + Nd\mu\,. \tag{2.10}$$

This relation shows that the intensive variables are not independent.

2.2 Response Functions

The response of a thermodynamic system to changes in external conditions is determined by *response functions*. For the important case with volume V as work coordinate, one defines the following measurable quantities:

$$c_x = \frac{C_x}{N} \qquad \text{(specific heat at } x \in \{V,p\} \text{ constant)} \tag{2.11}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \text{(expansion coefficient)} \tag{2.12}$$

$$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \qquad \text{(tension coefficient)} \tag{2.13}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad \text{(isothermal compressibility)} \tag{2.14}$$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \qquad \text{(adiabatic compressibility)}\,. \tag{2.15}$$

All response functions are intensive and hence (substance-)specific. There are relations among these quantities. For example,

$$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \overset{(1.5)}{=} -\frac{1}{p}\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{p\kappa_T} \tag{2.16}$$

In the exercises we will show that

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T} \quad \text{and} \quad \frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S}, \tag{2.17}$$

so that only three of the six response functions are independent.

Example 4: (ideal gas)

For the ideal gas with $pV = Nk_BT$ and $S(U,V)$ from (1.62) one finds by direct computation

$$c_V = \frac{3}{2}k_B, \quad c_p = \frac{5}{2}k_B, \quad \alpha = \beta = \frac{1}{T}, \quad \kappa_T = \frac{1}{p}, \quad \kappa_S = \frac{3}{5p}\,. \tag{2.18}$$

Example 5: (perfect gas)

For a (thermally) perfect gas the thermal equation of state $pV = Nk_BT$ holds. From (1.64) we know that U and hence c_V can depend only on T. We call a

gas thermally and calorically perfect if c_V is constant. The caloric equation of state is given by

$$U(T) = \int_0^T dT'\, C_V = c_V N T = \frac{c_V}{k_B} pV \tag{2.19}$$

It follows that

$$\delta Q = dU + pdV \overset{(dp=0)}{=} d(U + pV) = N d(c_V T + k_B T)\,. \tag{2.20}$$

Hence for the specific heat at constant pressure

$$c_p = \frac{1}{N}\left(\frac{\partial Q}{\partial T}\right)_p = \frac{\partial(c_V T + k_B T)}{\partial T} = c_V + k_B\,. \tag{2.21}$$

For an adiabatic process (see Eq. (1.35)) one has

$$\frac{c_V}{k_B}(V dp + p dV) = dU = -p dV \tag{2.22}$$

and thus the adiabatic equation

$$pV^\gamma = \text{constant} \tag{2.23}$$

with the *adiabatic exponent*

$$\gamma = \frac{c_p}{c_V} = \frac{c_V + k_B}{c_V} > 1\,. \tag{2.24}$$

The ideal gas with $c_v = \frac{3}{2}k_B$, for example, has an adiabatic exponent of $\gamma = \frac{5}{3}$.

Example 6: (TdS equations)

One has $TdS = dU + pdV = C_V dT + [(\partial U/\partial V)_T + p]dV$. From the relation (1.64) follows the TdS equation

$$\begin{aligned} TdS &= C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \overset{(1.5)}{=} C_V dT - T\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} dV \\ &= C_V dT + \frac{\alpha T}{\kappa_T} dV\,. \end{aligned} \tag{2.25}$$

An analogous calculation with (T, p) as independent variables yields the second TdS equation

$$TdS = C_p dT - \alpha T V dp\,. \tag{2.26}$$

These equations are important because they make the entropy change a measurable quantity.

2.3 Internal Energy

One has $T^{-1} = (\partial S/\partial U)_{Z_\alpha} > 0$ and hence $S(U, Z_\alpha)$ is invertible with the thermodynamic potential (internal energy) $U(S, Z_\alpha)$. One can rearrange the Gibbs fundamental equation (1.55) for dU, with the result

$$dU = TdS + \sum_\alpha g_\alpha dZ_\alpha \,. \tag{2.27}$$

Thus the partial derivatives yield the thermodynamic quantities [cf. Eq. (1.23) and (1.56)]

$$T = \left(\frac{\partial U}{\partial S}\right)_{Z_\alpha}, \qquad g_\alpha = \left(\frac{\partial U}{\partial Z_\alpha}\right)_{S, Z_{\beta\neq\alpha}} . \tag{2.28}$$

The internal energy therefore contains the same information as $S(\boldsymbol{Z})$. Hence U is a thermodynamic potential with the *natural variables* (S, Z_α).

Example 7: (perfect gas)

A perfect gas is characterized by $pV = Nk_BT$ and $(\partial U/\partial V)_T = 0$. The entropy change for a perfect gas is given by $TdS = C_V dT + [(\partial U/\partial V)_T + p]dV = Nc_V dT + pdV$, see Example 6. By integration we obtain the entropy

$$S(T, V) = N \int_0^T dT' \, \frac{c_V(T')}{T'} + Nk_B \ln(V/V_0) \,. \tag{2.29}$$

If the gas is both thermally and calorically perfect, one obtains the compact form (cf. Eq. (1.62))

$$S = N[c_V \ln(T/T_0) + k_B \ln(V/V_0)] = N[c_V \ln(U/U_0) + k_B \ln(V/V_0)] \,. \tag{2.30}$$

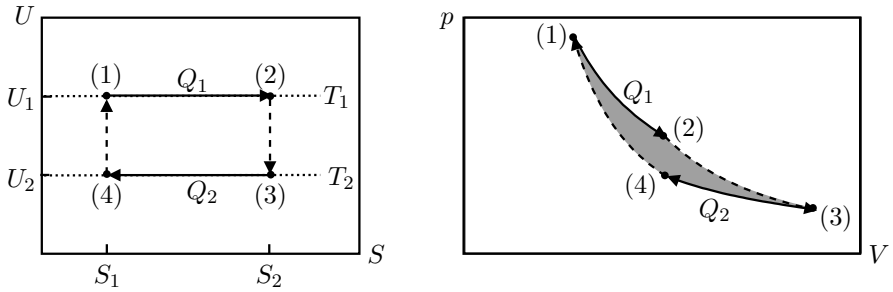
Inverting yields the internal energy (as thermodynamic potential)

$$U(S, V) = U_0 \left(\frac{V_0}{V}\right)^{k_B/c_V} e^{S/Nc_V} = c_V NT \tag{2.31}$$

from which the entire thermodynamics can be determined. The result for the ideal gas is recovered by setting $c_V = \frac{3}{2}k_B$.

Example 8: (Carnot cycle)

With this reformulation we can understand the Carnot process alternatively in the U-S diagram. For a perfect gas the internal energy depends only on temperature. Isotherms (adiabats) therefore become horizontal (vertical) curves.



The work $W = \oint p dV = Q_1 - Q_2$ follows from the first law and equals the area in the p-V diagram. The heat quantities $Q_{1,2} = \Delta S/T_{1,2}$ are fixed by the second law through the entropy difference $\Delta S = S_2 - S_1$ and the respective temperature $T_{1,2}$. One has $Q_1/T_1 = \Delta S = Q_2/T_2$ and hence $W = Q_1 - Q_2 = Q_1(1 - Q_2/Q_1) = \eta_C Q_1$. If one replaces the U-S diagram by a T-S diagram one sees that the Carnot efficiency depends only on the temperature and not on the working substance.

The internal energy as a thermodynamic potential also satisfies relations analogous to (2.1). Consider an arbitrary process (1) $\to$ (2) at S and Z_α fixed (i.e. in particular $\delta W = 0$), then

$$\Delta U \leq 0, \tag{2.32}$$

holds, i.e. the internal energy can only decrease. As proof we complete, as in (1.60), the process by a reversible process to a cyclic process with

$$0 \geq \oint \frac{\delta Q}{T} = \int_{(1)}^{(2)} \frac{\overbrace{\delta Q}^{=dU}}{T} + \overbrace{\int_{(2)}^{(1)} \frac{\delta Q_{\rm rev}}{T}}^{=\Delta S=0} = \int_{(1)}^{(2)} \frac{dU}{T} \overset{3}{\geq} \frac{1}{T_{\rm min}} \Delta U \,. \tag{2.33}$$

An analogous argument as after (2.1) yields from $\Delta U \leq 0$ the subadditivity $U(S_1 + S_2, Z_{1,\alpha} + Z_{2,\alpha}) \leq U(S_1, Z_{1,\alpha}) + U(S_2, Z_{2,\alpha})$ and the *principle of minimal energy*: a system at constant entropy and fixed work coordinates is in complete equilibrium precisely when the internal energy is minimal. Hence for a stable equilibrium $dU = 0$ and $d^2U \geq 0$.

Example 9: (Stability conditions)

For the variables (S, V) the stability condition $d^2U \geq 0$ requires in particular that[4]

$$0 \leq \frac{\partial^2 U}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \quad \text{and} \quad 0 \leq \frac{\partial^2 U}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\kappa_S} \,. \tag{2.34}$$

Thus the conditions

$$c_V > 0 \quad \text{and} \quad \kappa_S > 0 \,, \tag{2.35}$$

[3] Since $0 \geq \int dU/T$ we must estimate T downward in order to make the integral absolutely larger.

[4] Initially the stability conditions only refer to the removal of constraints. However, we can couple any system to a copy of itself (and it should remain stable). Hence it follows that $U(S + dS, V + dV) + U(S - dS, V - dV)$ is a minimum with respect to dS, dV, from which $d^2U \geq 0$ follows.

i.e. with increasing temperature the entropy increases and an increase in volume leads to a decrease in pressure.

The conditions (2.34) are necessary but not sufficient for the Hessian d^2U to be positive semidefinite. The additional condition

$$0 \leq \mathrm{Det}(d^2U) = \frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 \tag{2.36}$$

yields $\kappa_T > 0$, as we will show in Example 13. Together with (2.17) this gives the stability conditions $c_p \geq c_V > 0$ and $\kappa_T \geq \kappa_S > 0$. The second relation we have already encountered in the Carnot process as "adiabats are steeper than isotherms."

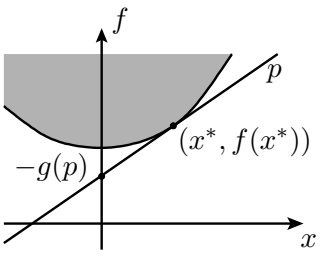
The internal energy is useful when we consider a *isolated* system that is both thermally and mechanically insulated, since then the principle of minimal energy holds. In applications one is, however, often interested in *open systems* that allow heat and/or work exchange. To describe such systems we wish to recall the Legendre transformation once more, which we already know from the mechanics lecture. We will mostly restrict ourselves to the volume V as the sole work coordinate. The results can, however, be easily generalized to magnetization $\mathcal{M}$, ... In particular we will treat the grand potential Ω explicitly, which describes systems with particle exchange. From here on we restrict ourselves to homogeneous systems. Thus we use the notions convex/concave synonymously with sub-/superadditive.

2.4 Legendre Transformation

Starting from a convex function $f\colon \mathbb{R} \to \mathbb{R}$, we define the Legendre-transformed function $g = \mathcal{L}f$ as[5]

$$g(p) = \max_x [xp - f(x)], \tag{2.37}$$

which in turn is convex. The Legendre transformation is an involution, i.e. its own inverse, with $\mathcal{L}(\mathcal{L}f) = f$, so no information is "lost." Geometrically $-g(p)$ corresponds to the intercept of the "shadow" of the function cast by rays of slope p.



Remark: It holds that $-f(x)$ is concave if and only if $f(x)$ is convex. Hence the Legendre transform $g(p, y)$ of a convex function $f(x, y)$ is concave in y while it is convex in p. In thermodynamics one would, however, like $g(p, y)$ also to remain convex in the untransformed variable y. Therefore one usually defines $-g(p, y)$ as

[5] In general one must replace the maximum by a supremum, since the maximum is not always attained.

the Legendre transform of $f(x, y)$ with[6]

$$g(p, y) = -\mathcal{L}f(x, y) = -\max_x[xp - f(x, y)] = \min_x[f(x, y) - xp]\,.$$

For a differentiable function the Legendre transformation can be determined by differentiation. Since at the maximum x^* the derivative vanishes,

$$p = f'(x^*) \tag{2.38}$$

holds, whereby $x = x^*(p)$ is fixed by p. One says that the Legendre transformation switches x from $p = f'(x)$ as independent variable.

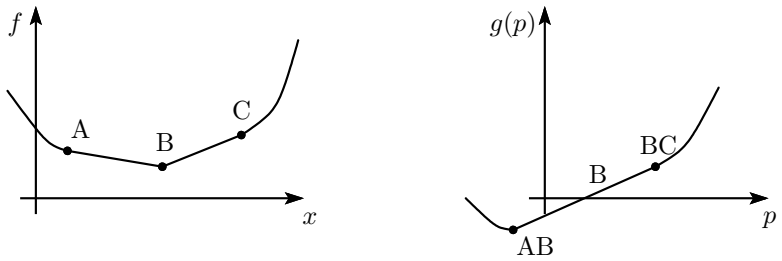
Consider $g(p)$ under small changes; one obtains

$$dg = d(x^*p - f(x^*)) = \overbrace{(p - f'(x^*))}^{0}\, dx^* + x^* dp = x^* dp. \tag{2.39}$$

Hence

$$g'(p) = \frac{dg}{dp}(p) = x^*(p) = x \tag{2.40}$$

and one thereby finds the value x of the original variable by differentiating g with respect to the new variable p. If the function f is not strictly convex but exhibits straight segments, then "straight lines of f" become "kinks of g":



Since $\mathcal{L}$ is an involution, this property also holds in reverse. We will examine this property more closely in the chapter on phase transitions.

2.5 Enthalpy

If one heats a system at constant volume, the entire heat δQ, by the first law, leads to an increase in the internal energy $dU = \delta Q$. In chemical applications the volume is often not held fixed but instead the pressure is kept constant. Then part of the heat is converted into work $\delta W = -pdV$. When one switches, in the expression for the internal energy $U(S, V)$, from V to $p = -(\partial U/\partial V)_S$ as the independent variable, one obtains the *enthalpy*

$$H(S, p) = U + pV \tag{2.41}$$

[6]The function $g(p, y)$ is thus concave in p but convex in y.

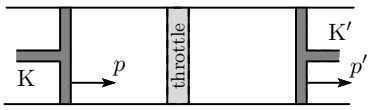


Fig. 2.1: Joule-Thomson process: Pistons K and K′ are moved so that the gas is forced through the wad of cotton. Thereby the pressure p and p' in the respective chambers is maintained. The wad of cotton generates a pressure drop $\Delta p = p' - p > 0$ and the process is irreversible.

i.e., $-H$ is the Legendre transform of U with respect to $-V$. One has

$$dH = \overbrace{dU}^{\delta Q - pdV} + pdV + Vdp = TdS + Vdp\,, \tag{2.42}$$

so that heating a system at constant pressure p leads to an increase in the enthalpy with $dH = \delta Q$. Furthermore, from (2.42) one has

$$T = \left(\frac{\partial H}{\partial S}\right)_p\,, \qquad V = \left(\frac{\partial H}{\partial p}\right)_S\,. \tag{2.43}$$

The enthalpy is convex in S with $H(S_1 + S_2, p) \leq H(S_1, p) + H(S_2, p)$. Its concavity in p is less important, since no constraints can be imposed on intensive quantities. Hence, at equilibrium H is minimal with respect to constraints in S and $\Delta H \leq 0$ for processes at S and p constant.

Example 10: (Chemical reaction heat)

Chemical reactions are typically carried out at fixed pressure. For a reaction the change in enthalpy ΔH per amount of substance is reported. From the foregoing considerations we know that at constant pressure the enthalpy change equals the heat exchanged. Thus

$\Delta H > 0$: endothermic reaction (heat absorbed from the surroundings),
$\Delta H < 0$: exothermic reaction (heat released to the surroundings).

For example, one finds for the reaction $C + O_2 \to CO_2$ under standard conditions $\Delta H = -393.51\,\mathrm{kJ/mol}$. Hence the reaction is exothermic.

Example 11: (Joule-Thomson process[7])

Gay-Lussac's free-expansion experiment showed that for an ideal gas the internal energy depends only on the temperature T. Joule and Thomson refined the experimental setup. The experiment is performed adiabatically with $\delta Q = 0$. The left piston K pushes the gas at constant pressure p through the wad of cotton, which acts as a throttle, see figure 2.1. The right piston K′ recedes at constant pressure $p' < p$. Because of the pressure difference the process is

[7] Thomson is the same person as Kelvin. With his ennoblement in 1866 he changed his name from William Thomson to Lord Kelvin.

irreversible. We consider the steady state that is reached after some time, when the pistons move uniformly. We denote by u, u' the internal energy of the gas per volume on the left and right sides (far from the throttle).

Now consider an (arbitrary) time interval during which the left piston sweeps out volume V and the right piston sweeps out volume V'. Since no heat is exchanged, the first law requires that the work done $\Delta W = pV - p'V'$ equals the change in internal energy $\Delta U = u'V' - uV$. Rearranging gives

$$H = pV + uV = pV' + u'V' = H' \,, \tag{2.44}$$

i.e., the enthalpy is conserved.

We now ask for the change in temperature upon expansion of the gas. In particular, we introduce the Joule-Thomson coefficient

$$\mu_{\rm JT} = \left(\frac{\partial T}{\partial p}\right)_H \tag{2.45}$$

which describes the temperature change for an infinitesimal change in pressure. From (1.5) it follows ($dH = TdS + Vdp$)

$$\mu_{\rm JT} = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} = -\frac{T(\partial S/\partial p)_T + V}{C_P} \,. \tag{2.46}$$

In (2.56) we will show that $(\partial S/\partial p)_T = -(\partial V/\partial T)_p = -\alpha V$ holds. Hence we obtain

$$\mu_{\rm JT} = \frac{V}{C_p}(\alpha T - 1) \,. \tag{2.47}$$

For a perfect gas $\alpha = 1/T$ and therefore $\mu_{\rm JT} = 0$. For real gases at low temperatures $\mu_{\rm JT} > 0$ (the gas cools upon expansion) and at high temperatures $\mu_{\rm JT} < 0$ (the gas heats up). The temperature at which $\mu_{\rm JT} = 0$ is called the *inversion temperature*. For nitrogen (N_2) the inversion temperature, for example, is 607 K. For hydrogen (H_2) it is 202 K.

2.6 Free Energy

Solids are relatively rigid and thus it is natural to describe them at constant volume. However, in solid-state physics it is usually the case that there is heat exchange with a heat bath (at temperature T). The thermodynamic potential that is adapted to such a system is the *free energy* $F(T, V)$, which we in turn write as a Legendre transformation

$$F(T, V) = U - TS, \qquad dF = -SdT - pdV \,, \tag{2.48}$$

where one switches from S to T via $T = (\partial U/\partial S)_V$.

The free energy derives its name from the *principle of maximum work:* for a thermodynamic system in heat exchange with *a* heat bath at temperature T, the (negative)

change in free energy equals the maximum work that can be performed during the process. The proof follows from

$$\Delta S \overset{(1.61)}{\geq} \int_{\boldsymbol{Z}_1}^{\boldsymbol{Z}_2} \frac{\delta Q}{T} = \frac{\Delta Q}{T} \tag{2.49}$$

which, with the first law, can be brought into the form

$$-\Delta W = -\Delta U + \Delta Q \leq -\Delta U + T\Delta S = -\Delta F \tag{2.50}$$

Here $-\Delta W$ is the work done by the system on the outside and the equality holds for a reversible process. As a corollary, for a mechanically isolated system (with $\Delta W = 0$) in contact with a heat bath, the free energy never increases. The free energy is convex in V with $F(T, V_1 + V_2) \leq F(T, V_1) + F(T, V_2)$ and thus F is minimal with respect to constraints on V.

Example 12: (Maxwell relation)

From the interchange of second derivatives we obtain the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial p}{\partial T}\right)_V , \tag{2.51}$$

which we will use in the following example.

Example 13: (Stability)

From the minimum principle we obtain the stability condition

$$0 \leq \frac{\partial^2 F}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{V\kappa_T} \tag{2.52}$$

or $\kappa_T > 0$. This condition is related to the discussion in Example 9. We obtain (U is a function of S and V)

$$\begin{aligned} \frac{\partial^2 F}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_T &\overset{(1.6)}{=} -\overbrace{\left(\frac{\partial p}{\partial V}\right)_S}^{-\partial^2 U/\partial V^2} - \overbrace{\left(\frac{\partial p}{\partial S}\right)_V}^{-\partial^2 U/\partial V \partial S} \overbrace{\left(\frac{\partial S}{\partial V}\right)_T}^{(\partial p/\partial T)_V} \\ &= \frac{\partial^2 U}{\partial V^2} + \frac{\partial^2 U}{\partial S \partial V} \underbrace{\left(\frac{\partial p}{\partial S}\right)_V}_{-\partial^2 U/\partial S \partial V} \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{(\partial^2 U/\partial S^2)^{-1}} = \frac{\mathrm{Det}(d^2 U)}{\partial^2 U/\partial S^2} . \end{aligned} \tag{2.53}$$

Thus the stability condition on F is exactly the condition on the determinant of the Hessian matrix (together with Eq. (2.34)). This corresponds to the fact we have already discussed: all thermodynamic potentials in principle contain the same information. However, 'simple' insights in one formulation are often very complicated in another. Just note the many steps in the derivation of (2.53).

2.7 Gibbs Energy

One may of course also consider systems that are in heat exchange (at fixed temperature T) as well as in work exchange (at fixed pressure p). In this case one defines the *Gibbs energy* or *free enthalpy* (with natural variables T, p)

$$G(T,p) = U - TS + pV = F + pV = H - TS, \qquad dG = -SdT + Vdp \tag{2.54}$$

as a Legendre transformation starting from H (w.r.t. S) or F (w.r.t. V). By coupling to a work reservoir at constant pressure p, the work $-\Delta W = p\Delta V$ is done on the outside. From (2.50) we obtain

$$\Delta G = \Delta F - \Delta W \leq 0\,. \tag{2.55}$$

Thus the Gibbs energy (at fixed temperature T and pressure p) never increases and equilibrium corresponds to a minimum of the Gibbs energy. For homogeneous systems the relation $G = \mu(T,p)N$ from Eq. (2.8) together with (2.54) holds.

Example 14: (Continuation of Example 10)

If one considers only volume work, one cannot introduce constraints on G. Therefore in this example we consider a chemical reaction at constant pressure and temperature, where the particle number acts as a work coordinate. The chemical transformations change the amounts of the individual *species* (and thus lift the constraint on the particle numbers). The minimum principle for the Gibbs energy means that such a reaction can only proceed for $\Delta G = \Delta H - T\Delta S \leq 0$. An endothermic reaction with $\Delta S > 0$ can therefore only proceed spontaneously at temperatures greater than $\Delta H/\Delta S$.

This result also applies to phase transitions. From liquid to gas the enthalpy increases by ΔH (the *latent heat*). However, $\Delta S > 0$, so that the gas phase is stable at high temperatures.

As already seen, Maxwell relations simply follow from the interchange of second derivatives. Each potential leads in this way to its own Maxwell relation, where naturally all Maxwell relations are equivalent. In particular, the relation (1.64) between the thermal and caloric equations of state is an expression of a Maxwell relation. For the Gibbs energy we obtain the Maxwell relation

$$-\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 G}{\partial T \partial p} = \left(\frac{\partial V}{\partial T}\right)_p = V\alpha, \tag{2.56}$$

so that the change in heat as a function of pressure (at constant temperature) is given by $-TV\alpha$. With the third law $(\partial S/\partial p)_T \to 0$ for $T \to 0$. Thus the expansion coefficient vanishes for $T \to 0$. From the Maxwell relation (2.51) for F,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = p\beta\,, \tag{2.57}$$

one equivalently finds that $p\beta$ must also vanish.[8] The relation (2.57) we will encounter

[8] If the pressure remains finite, this also implies that the tension coefficient for $T \to 0$ must vanish.

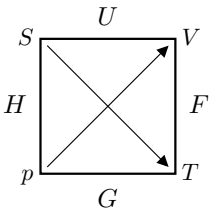


Fig. 2.2: The Guggenheim square shows the four potentials alongside their respective natural variables. The partial derivative of a potential with respect to a variable is diagonal to it. A minus sign arises when one moves against the arrow. Thus $(\partial F/\partial T)_V = -S$ but $(\partial U/\partial S)_V = T$.

again as the Clausius-Clapeyron relation in the context of phase transitions (here $(\partial Q/\partial V)_T = T(\partial S/\partial V)_T$ is the isothermal heat of expansion).

One can remember the four potentials with their respective natural variables using the Guggenheim square in Figure 2.2. From the Guggenheim square one can also obtain the Maxwell relations. To do so, one selects two angles $\llcorner = \lrcorner$ (independent of orientation) from the Guggenheim square that share the long edge. The long edge determines for which potential one finds the Maxwell relation. The angles stand for the partial derivatives

$$\begin{matrix} x \\ y \end{matrix}\!\!\llcorner\!\!\swarrow\!\!\!\!\rule{0.6em}{0.4pt}\, z \equiv \left(\frac{\partial x}{\partial y}\right)_z , \qquad \begin{matrix} x \\ y \end{matrix}\!\!\llcorner\!\!\nearrow\!\!\!\!\rule{0.6em}{0.4pt}\, z \equiv -\left(\frac{\partial x}{\partial y}\right)_z , \tag{2.58}$$

where x, y, z denote the adjacent variables. The minus sign arises depending on the direction of the arrow (into or out of the angle). In particular one obtains (2.56) and (2.57) from

$$\begin{matrix} S \\ p \end{matrix}\!\!\llcorner\!\!\nearrow\!\!\!\!\rule{0.6em}{0.4pt}\, T \;=\; p\!\!\llcorner\!\!\searrow\!\!\!\!\rule{0.6em}{0.4pt}\, \begin{matrix} V \\ T \end{matrix} \qquad \text{and} \qquad p\!\!\lrcorner\!\!\searrow \begin{matrix} V \\ T \end{matrix} \;=\; S\!\!\urcorner\!\!\searrow \begin{matrix} V \\ T \end{matrix} . \tag{2.59}$$

2.8 Particle Exchange and Grand Potential

So far we have only considered volume work. One may of course generalize this procedure to general work coordinates and perform a Legendre transformation with respect to each coordinate, thereby obtaining new thermodynamic potentials. Apart from volume, particle exchange dN is the most important work coordinate in applications. It allows one to describe phase transitions, transport, and also chemical reactions. We start from the free energy $F(T, V, N)$. The free energy is convex in V and N, with $F(T, V_1 + V_2, N_1 + N_2) \leq F(T, V_1, N_1) + F(T, V_2, N_2)$ for arbitrary constraints $V = V_1 + V_2$, $N = N_1 + N_2$. To N belongs the equilibrium quantity μ (the chemical potential). Because of convexity one may go from F to the *grand potential* or *grand canonical potential*

$$\Omega(T, V, \mu) = F - \mu N = U - TS - \mu N, \qquad d\Omega = -SdT - pdV - Nd\mu\,. \tag{2.60}$$

For a homogeneous system Ω is linear in V with $\Omega = -p(T, \mu)V$, so that the convexity condition $\Omega(T, V_1 + V_2, \mu) \leq \Omega(T, V_1, \mu) + \Omega(T, V_2, \mu)$ becomes trivial.

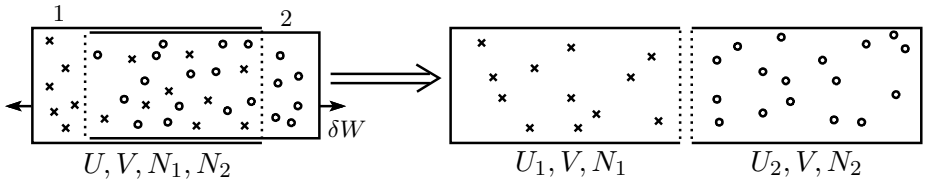


Fig. 2.3: Reversible unmixing: the two species correspond to the crosses (1) and the circles (2). The semipermeable walls are shown as dotted lines. They each allow only one species to pass.

Example 15: (Compressibility relation)

For homogeneous systems there is an alternative expression for the isothermal compressibility that often appears in applications. From the Gibbs-Duhem relation (2.10) we have $Vdp = Nd\mu$ at constant temperature. From this follows for the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\frac{1}{N}\left(\frac{\partial V}{\partial \mu}\right)_{T,N} = -\left(\frac{\partial (V/N)}{\partial \mu}\right)_{T,N}. \tag{2.61}$$

The particle density $n = N/V$ as an intensive quantity, like the pressure, is a function only of T and μ. Thus follows the compressibility relation

$$\kappa_T = -\left(\frac{\partial n^{-1}}{\partial \mu}\right)_T = \frac{1}{n^2}\left(\frac{\partial n}{\partial \mu}\right)_T = \frac{V}{N^2}\left(\frac{\partial N}{\partial \mu}\right)_{T,V} \tag{2.62}$$

For an insulator N (almost) does not depend on the chemical potential μ. From this follows that the electrons in an insulator are incompressible with $\kappa_T \to 0^+$.

2.9 Mixtures of Multiple Species

We consider a thermodynamic system composed of r components (*species*). Initially we do not allow chemical reactions. The work coordinates are $V, N_1, \ldots, N_r$. An equilibrium state is therefore determined by specifying

$$\boldsymbol{Z} = (U, V, N_1, \ldots, N_r) = (U, V, \boldsymbol{N}) \tag{2.63}$$

Thus the entropy is given by $S(U, V, \boldsymbol{N})$ and satisfies

$$TdS = dU + pdV - \sum_{i=1}^{r} \mu_i dN_i = dU + pdV - \boldsymbol{\mu} \cdot d\boldsymbol{N}, \tag{2.64}$$

where μ_i is the chemical potential of the i-th component.

To determine the entropy $S(\boldsymbol{Z})$ we consider the reversible process of unmixing, see Figure 2.3. This requires semipermeable walls that allow heat exchange. Consider the

adiabatic unmixing of two components (the extension to r species is analogous). If we pull the two containers apart (unmix), we must do work $\Delta W(U, V, N_1, N_2)$. At the end of the reversible process each container contains only one of the two components. Thus

$$S(U, V, N_1, N_2) = S_1(U_1, V, N_1) + S_2(U_2, V, N_2) \tag{2.65}$$

with $U + \Delta W = U_1 + U_2$ and $T_1(U_1, V, N_1) = T_2(U_2, V, N_2) = \tilde{T}$ (since S is maximal w.r.t. heat exchange/constraints on U); $\tilde{T}(U, V, N_1, N_2)$ denotes the common temperature in both containers after the adiabatic unmixing.

Ideal mixtures are characterized by $\Delta W = 0$. Then

$$S(U, V, N_1, \ldots, N_r) = \sum_i S_i(U_i, V, N_i), \qquad U = \sum_i U_i, \qquad T_i = \tilde{T}\,. \tag{2.66}$$

One obtains the temperature $\tilde{T}$ after unmixing via

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,\boldsymbol{N}} = \sum_i \underbrace{\left(\frac{\partial S_i}{\partial U_i}\right)_{V,N_i}}_{=T_i^{-1}=\tilde{T}^{-1}} \left(\frac{\partial U_i}{\partial U}\right)_{V,\boldsymbol{N}} = \frac{1}{\tilde{T}} \underbrace{\sum_i \left(\frac{\partial U_i}{\partial U}\right)_{V,\boldsymbol{N}}}_{=1} = \frac{1}{\tilde{T}} \tag{2.67}$$

Ideal adiabatic unmixings are thus carried out isothermally with $T = \tilde{T} = T_i$. The thermodynamics is therefore fully described by that of the pure components. By rearrangement one obtains the internal energy

$$U(S, V, \boldsymbol{N}) = \sum_i U_i(S_i, V, N_i), \qquad S = \sum_i S_i, \qquad T_i = T\,. \tag{2.68}$$

Since the temperature is fixed during ideal unmixing, it is useful to switch to the free energy via

$$F(T, V, \boldsymbol{N}) = U - TS = \sum_i F_i(T, V, N_i)\,. \tag{2.69}$$

Thus follows the *additivity of partial pressures* (Dalton)

$$p(T, V, \boldsymbol{N}) = -\left(\frac{\partial F}{\partial V}\right)_{T,\boldsymbol{N}} = -\sum_i \left(\frac{\partial F_i}{\partial V}\right)_{T,N_i} = \sum_i p_i(T, V, N_i) \tag{2.70}$$

and the fact that the chemical potential

$$\mu_i(T, V, \boldsymbol{N}) = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial F_i}{\partial N_i}\right)_{T,V} = \mu_i^0(T, V, N_i) \tag{2.71}$$

is given by the chemical potential $\mu_i^0(T, p_i)$ of the pure species at the partial pressure p_i.

Note: One calls a mixture with $\Delta W = 0$ an *ideal mixture*, since no interaction effects are taken into account. For such mixtures the free energy F (as a function of the natural variables) is additive, while S, G contain additional terms due to mixing, see Example 16.

Example 16: (Ideal mixture of perfect gases)

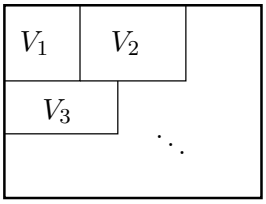
For perfect gases [with $U_i \equiv U_i(T_i, N_i)$ and $p_i V_i = N_i k_B T_i$] we have [with (2.29) and $T_i = T$]

$$S(T, V, \boldsymbol{N}) = \sum_i S_i(T, V, N_i) = \sum_i N_i \left[\int_0^T dT' \, \frac{c_{V,i}}{T'} + k_B \ln(V/V_0) \right] . \quad (2.72)$$

From the additivity of partial pressures follows

$$p = \sum_i \frac{N_i k_B T}{V} = \frac{N k_B T}{V} \qquad \text{with} \qquad N = \sum_i N_i \, . \quad (2.73)$$

We start from the unmixed state, whose entropy is given by $S_0 = \sum_i S_i(T, V_i, N_i)$, where each gas occupies the subvolume $V_i = V N_i/N$, so that $p_i = p$ at $T_i = T$. The lifting of the constraints allows interdiffusion of the gases. In doing so the entropy increases by the *mixing entropy*



$$\begin{aligned} S_{\rm m}(\boldsymbol{N}) = S - S_0 &= \sum_i [S_i(T, V, N_i) - S_i(T, V_i, N_i)] = k_B \sum_i N_i \ln(V/V_i) \\ &= k_B \sum_i N_i \ln(N/N_i) > 0 \, , \end{aligned} \quad (2.74)$$

which depends only on the particle numbers N_i of the different components. Since $S_{\rm m} > 0$, the mixing process is therefore irreversible, i.e., the gases do not unmix spontaneously.

The mixing process is carried out at constant pressure p and constant temperature T. It is therefore convenient to switch to the Gibbs energy

$$\begin{aligned} G(T, p, \boldsymbol{N}) &= U - TS + pV = U - TS_0 + pV - T(S - S_0) \\ &= \sum_i [U_i(T, N_i) - TS_i(T, V_i, N_i) + pV_i] - TS_{\rm m} \\ &= \sum_i G_i(T, p, N_i) - TS_{\rm m} \, . \end{aligned} \quad (2.75)$$

The first term corresponds to the Gibbs energy in the unmixed state. The second term is negative and describes the lowering of the Gibbs energy due to mixing. The derivative with respect to N_i yields the chemical potential

$$\mu_i(T, p, \boldsymbol{N}) = \left(\frac{\partial G_i}{\partial N_i} \right)_T - T \left(\frac{\partial S_{\rm m}}{\partial N_i} \right)_{N_{j \neq i}} = \mu_i^0(T, p) + k_B T \ln(N_i/N) \quad (2.76)$$

of the i-th component in a mixture of perfect gases. Here we used that

$$dS_{\rm m}/k_B = \sum_i \ln(N/N_i) dN_i + \underbrace{\frac{\sum_i N_i}{N} dN - \sum_i dN_i}_{0} \quad (2.77)$$

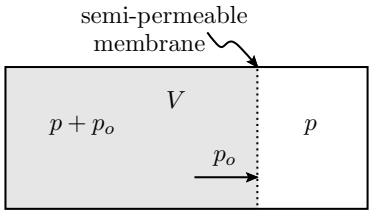


Fig. 2.4: Osmotic pressure illustrated with sugar and water: in the left region there is sugar water, in the right region pure water. The regions are separated by a semipermeable membrane on which the osmotic pressure p_o acts.

Note: If one treats the distinctness of the species as a continuously varying parameter, the mixing entropy vanishes abruptly as soon as the species become identical. One calls this effect the *Gibbs paradox*, although of course nothing paradoxical is involved, since distinctness is not a continuous parameter: either the particles are identical for all possible work processes or they are not.

Example 17: (Solutions)

A solution is a special case of a general mixture, in which the system consists almost entirely of solvent (species 0). The remaining species $\nu = 1, 2, \dots$ are the *solutes*. To describe the solution we introduce the *concentrations* $c_\nu = N_\nu/N \ll 1$ (with $c_0 = N_0/N \approx 1$). From (2.76) we obtain

$$\mu_0(T, p, c_1, \dots) = \mu_0^0(T, p) + k_B T \ln(c_0) \approx \mu_0^0(T, p) - k_B T \sum_\nu c_\nu \tag{2.78}$$

for the chemical potential of the solvent, where we have used the approximation $\ln(c_0) = \ln\bigl(1 - \sum_\nu c_\nu\bigr) \approx -\sum_\nu c_\nu$.

Example 18: (Osmotic pressure)

Osmotic pressure occurs in systems in which the solutes are confined by a semipermeable membrane to a subregion, while the solvent can distribute freely, see Figure 2.4. Since the solvent can move through the membrane, in equilibrium

$$\mu_0(T, p + p_o, \boldsymbol{c}) = \mu_0(T, p, 0) = \mu_0^0(T, p)\,. \tag{2.79}$$

From (2.78) we obtain

$$\mu_0^0(T, p + p_o) - \mu_0^0(T, p) = k_B T \sum_\nu c_\nu \tag{2.80}$$

for a dilute solution. Assuming $p_o \ll p$, we may linearize the left side. We have $(\partial \mu_0^0/\partial p)_T = 1/N_0 (\partial G_0/\partial p)_T = V_0/N_0 \approx V/N$. From this follows for the *osmotic pressure*

$$p_o = \frac{N k_B T}{V} \sum_\nu c_\nu = \frac{k_B T}{V} \sum_\nu N_\nu\,. \tag{2.81}$$

Thus the mnemonic: the solutes exert the same pressure on the membrane as they would as an ideal gas at the same temperature T.

Example 19: (Vapor pressure of a solution)

The vapor pressure $p(T)$ of a substance is defined by the condition that the pressure p_{fl} in the liquid phase equals the pressure p_{g} in the gas phase. Equilibrium requires

$$\mu^0_{\mathrm{fl}}(T,p) = \mu^0_{\mathrm{g}}(T,p)\,, \tag{2.82}$$

see Example 1.

The vapor pressure of a solvent is lowered by the addition of non-volatile solutes by Δp (*Raoult's law*). The reason is that the solutes are present only in the liquid phase, not in the gas phase. Thus the new equilibrium condition

$$\mu_{\mathrm{fl}}(T,p-\Delta p,\boldsymbol{c}) = \mu^0_{\mathrm{g}}(T,p-\Delta p)\,. \tag{2.83}$$

For dilute solutions we obtain from this

$$k_BT\sum_\nu c_\nu \overset{(2.78)}{=} \mu^0_{\mathrm{fl}}(T,p-\Delta p) - \mu_{\mathrm{fl}}(T,p-\Delta p,\boldsymbol{c}) \overset{(2.83)}{=} \mu^0_{\mathrm{fl}}(T,p-\Delta p) - \mu^0_{\mathrm{g}}(T,p-\Delta p).$$

Expanding μ^0 as in the last example in Δp we obtain

$$k_BT\sum_\nu c_\nu = \left(\frac{V_{\mathrm{g}}}{N_{\mathrm{g}}} - \frac{V_{\mathrm{fl}}}{N_{\mathrm{fl}}}\right)\Delta p\,. \tag{2.84}$$

Typically for the specific volume $V_{\mathrm{g}}/N_{\mathrm{g}} \gg V_{\mathrm{fl}}/N_{\mathrm{fl}}$. Using in addition the ideal gas law $V_{\mathrm{g}}/N_{\mathrm{g}} = k_BT/p$, we obtain *Raoult's law*

$$\frac{\Delta p}{p} = \sum_\nu c_\nu \;\geq 0. \tag{2.85}$$

Due to the lowering of the vapor pressure, a solution of salt or sugar in water boils at normal pressure only above 100 °C.

2.10 Chemical Equilibria

In this final section we investigate the possibility that *species* can transform into one another via chemical reactions. In this case of course the particle numbers of the individual species are not conserved. Consider as an example the chemical reaction $\mathrm{C} + \mathrm{O}_2 \rightleftharpoons \mathrm{CO}_2$. Without the reaction the particle numbers N_{C} and N_{O} are conserved. Through the reaction the constraint on the particle number is lifted and a new equilibrium establishes itself, in which N_{C}, N_{O} and N_{CO_2} are determined by thermodynamic considerations.

Consider r species with chemical symbols S_i. The s chemical reactions that can occur are described by the symbolic equations

$$\sum_{i=1}^{r} \nu_i^k \mathrm{S}_i = 0, \qquad k = 1,\ldots,s, \tag{2.86}$$

with the *stoichiometric coefficients* $\nu_i^k \in \mathbb{Z}$. As an example consider the oxyhydrogen reaction $2H_2 + O_2 \rightleftharpoons 2H_2O$ (with $s = 1$). It involves the species H_2, O_2 and H_2O. The stoichiometric equation is given by

$$-2H_2 - O_2 + 2H_2O = 0, \qquad (\text{so that } \nu_{H_2} = -2, \nu_{O_2} = -1, \nu_{H_2O} = 2)\,. \tag{2.87}$$

Chemical transformations can, in a system without particle exchange, change the particle numbers. Here

$$dN_i = \sum_{k=1}^{s} \nu_i^k d\lambda_k \tag{2.88}$$

with arbitrary $d\lambda_1, \ldots, d\lambda_s$. The quantity $d\lambda_k$ indicates how often the reaction k (in the sense of the extent of reaction $\sum_{i=1}^{r} \nu_i^k S_i$) has been carried out; one calls λ_k the *extent of reaction*. With the initial conditions $N_1^0, \ldots, N_r^0$ the particle numbers

$$N_i = N_i^0 + \sum_{k=1}^{s} \nu_i^k \lambda_k \tag{2.89}$$

can thereby be attained by carrying out the s reactions. These particle numbers form a s-dimensional plane on which the chemical equilibrium establishes itself.

Chemical reactions usually proceed at fixed pressure p and fixed temperature T. In this case the chemical equilibrium corresponds to the minimum of the Gibbs energy $G(T, p, \boldsymbol{N})$ as a function of λ_k, see Section 2.7. Thus

$$0 = dG = \sum_{i=1}^{r} \mu_i dN_i \tag{2.90}$$

for all stoichiometrically admissible dN_i from (2.88). This leads to the equilibrium conditions

$$\sum_{i=1}^{r} \nu_i^k \mu_i = 0, \qquad \text{for } k = 1, \ldots, s\,. \tag{2.91}$$

The equilibrium conditions thus correspond exactly to the symbolic equations (2.86), where the chemical symbol is replaced by the corresponding chemical potential of the species.

Mass action law: Consider a single reaction $\sum_{i=1}^{r} \nu_i S_i = 0$ between perfect gases. The chemical potential is then given by (2.76). The equilibrium condition (2.91) thus takes the form

$$0 = \sum_{i=1}^{r} \nu_i \mu_i(T, p, \boldsymbol{N}) = \sum_{i=1}^{r} \nu_i \mu_i^0(T, p) + k_B T \sum_{i=1}^{r} \nu_i \ln(c_i)\,, \tag{2.92}$$

with $\mu_i^0(T, p)$ the chemical potentials of the pure species. After division by $k_B T$ and subsequent exponentiation we obtain the *mass action law*

$$\prod_{i=1}^{r} c_i^{\nu_i} = \exp\left[-\frac{1}{k_B T} \sum_{i=1}^{r} \nu_i \mu_i^0(T, p)\right] \equiv K(T, p)\,. \tag{2.93}$$

The *mass action constant* K depends only on T and p. It determines the equilibrium state $N_1, \ldots, N_r$ on the stoichiometric line $N_i = N_i^0 + \nu_i \lambda$.

Example 20: (Oxyhydrogen reaction)

The mass action constant for the oxyhydrogen reaction at standard conditions ($T = 25°\mathrm{C}$ and $1\,\mathrm{atm}$) is given by $K \approx 10^{83}$. If one notes that there are approximately 10^{50} atoms on Earth and approximately 10^{80} in the visible universe, the equilibrium lies completely on the product side. Conventionally one therefore writes $2\mathrm{H}_2 + \mathrm{O}_2 \to 2\mathrm{H}_2\mathrm{O}$. The reverse reaction (electrolysis) does not proceed spontaneously and requires the input of additional energy.

Example 21: (pH value)

There is another reaction involving water that much more frequently proceeds in reverse. This is the dissociation $\mathrm{H}_2\mathrm{O} \leftrightharpoons \mathrm{H}^+ + \mathrm{OH}^-$ of water into a proton and a hydroxyl molecule. At standard conditions $K \approx 10^{-14}$. From electrical neutrality we also have $c_\mathrm{H} = c_\mathrm{OH}$. From the mass action law it thus follows

$$K = \frac{c_\mathrm{H}\, c_\mathrm{OH}}{\underbrace{c_{\mathrm{H}_2\mathrm{O}}}_{1-2c_\mathrm{H}}} = c_\mathrm{H}^2(1 + O(c_\mathrm{H})), \tag{2.94}$$

that the concentration of protons is $c_\mathrm{H} = 10^{-7}$. One defines the pH value as[9]

$$\mathrm{pH} = -\log_{10} c_\mathrm{H}\,. \tag{2.95}$$

At standard conditions pure water therefore has a pH value of 7.

[9] Chemists use a slightly different definition. The concentrations C are measured in mol/L. At standard conditions $C_{\mathrm{H}_2\mathrm{O}} = 55.5\,\mathrm{mol/L}$. The mass action constant has the more precise value $C_\mathrm{H} C_\mathrm{HO} = 10^{-14}\,\mathrm{mol}^2/\mathrm{L}^2$. Thus one defines $\mathrm{pH} = -\log_{10}(C_\mathrm{H}\,\mathrm{L/mol})$.

Chapter 3

Phase Transitions

3.1 Vaporization

Unlike chemical reactions, phase transitions are processes in which the substances do not change, but rather transform from one *species* to another. Typical species of substances are gaseous (g), liquid (l), and solid (s). As an introductory example, consider the transition from liquid to gaseous (vaporization) or vice versa (condensation). As already seen in Example 2.1, within the transition region part of the system is in the liquid species while another part is already in the gas species. In the following we neglect, as usual, surface effects due to the interface. Since the species are both in thermal and mechanical contact, in equilibrium $p = p_\mathrm{l} = p_\mathrm{g}$ and $T = T_\mathrm{l} = T_\mathrm{g}$ hold. We use the Gibbs energy as the thermodynamic potential and obtain

$$G(T, p, N_\mathrm{g}, N_\mathrm{l}) = G_\mathrm{g}(T, p, N_\mathrm{g}) + G_\mathrm{l}(T, p, N_\mathrm{l}) = N_\mathrm{g}\mu_\mathrm{g}(T, p) + N_\mathrm{l}\mu_\mathrm{l}(T, p)\,. \tag{3.1}$$

The Gibbs energy is additive, since the species are separated without (long-range) interactions. Of course, the particle numbers N_g and N_l in the respective species are constraints that cannot be realized experimentally. Only the total particle number $N = N_\mathrm{g} + N_\mathrm{l}$ remains, and the system reaches an equilibrium state with

$$\mu_\mathrm{g}(T, p) = \mu_\mathrm{l}(T, p)\,. \tag{3.2}$$

Solving this equation for $p(T)$ yields the vapor pressure curve, see Example 2.1.

The functions μ_g and μ_l are not equal, since they describe different species. In a *first-order phase transition* the first derivatives differ. On the vapor pressure curve

$$v_\mathrm{g} = \frac{V_\mathrm{g}}{N_\mathrm{g}} = \left(\frac{\partial \mu_\mathrm{g}}{\partial p}\right)_T > v_\mathrm{l} = \frac{V_\mathrm{l}}{N_\mathrm{l}} = \left(\frac{\partial \mu_\mathrm{l}}{\partial p}\right)_T\,, \tag{3.3}$$

indeed, the *specific volume* $v = V/N$ (volume per particle) in the gas species is larger than in the liquid species. The Gibbs energy $G(T, p, N) = N\mu(T, p)$ of the total system thus has a kink as a function of pressure, see Figure 3.1.

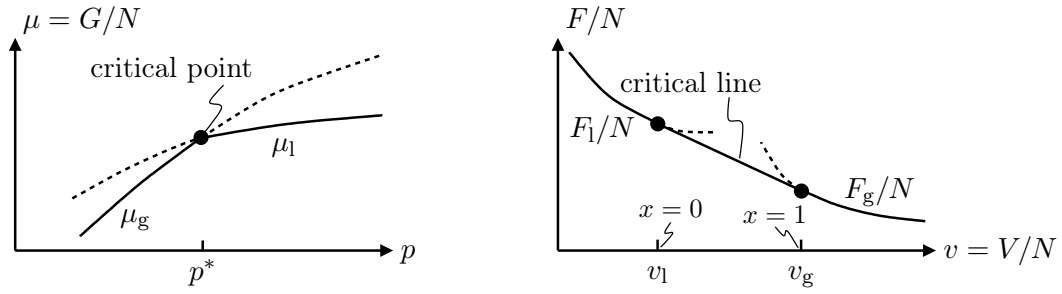


Fig. 3.1: Left: Chemical potential $\mu = G/N$ as a function of pressure p. The chemical potentials μ_{g} and μ_{l} of the respective species intersect at the vapor pressure $p^* = p(T)$. The equilibrium state corresponds to the minimum of the Gibbs energy. The gas species (high specific volume) exists at low pressures. Right: By the Legendre transformation the kink becomes a straight line in the free energy. The free energy F of the total system corresponds to the convex hull of the free energies F_{l}, F_{g}.

The Gibbs energy $G(p, T, N)$ contains all thermodynamic information. However, it is not possible to determine from it the particle numbers N_{g}, N_{l} in the respective species. To do so one must turn to the free energy (per particle)

$$\frac{F}{N} = f(T, v) = \frac{1}{N} \max_p (G(T, p, N) - pV) = \max_p (\mu(T, p) - pv) \tag{3.4}$$

which depends only on T and the specific volume v. The phase transition then corresponds to the critical straight line in Figure 3.1. Starting from a specific volume $v = v_{\mathrm{g}}$ (gas species), by increasing the particle number (or decreasing the volume) more and more particles are transferred into the liquid species. At the value $v = v_{\mathrm{l}}$ the entire system is in the liquid species. The individual points on the critical straight line describe various mixing ratios $0 \leq x \leq 1$ with

$$v = x v_{\mathrm{g}} + (1 - x) v_{\mathrm{l}}\,, \qquad x = \frac{N_{\mathrm{g}}}{N}, \quad 1 - x = \frac{N_{\mathrm{l}}}{N}. \tag{3.5}$$

Denoting by F_{g}, F_{l} the free energies in the respective species, one has

$$\frac{F}{N} = \max_p \big[x\mu_{\mathrm{g}}(T, p) + (1 - x)\mu_{\mathrm{l}}(T, p) - pv\big] \overset{(3.5)}{=} x f_{\mathrm{g}}(T, v_{\mathrm{g}}) + (1 - x) f_{\mathrm{l}}(T, v_{\mathrm{l}}) \tag{3.6}$$

precisely the *convex hull* of the two curves, see Figure 3.1.

Besides the jump in the specific volume (derivative of μ with respect to p) there is naturally also a jump in the specific entropy $s = S/N$ (derivative of μ with respect to $-T$). These derivatives are related via the Gibbs-Duhem relation (2.10) to the vapor pressure curve $p(T)$. Along the vapor pressure curve

$$-s_{\mathrm{g}} dT + v_{\mathrm{g}} dp = d\mu_{\mathrm{g}} = d\mu_{\mathrm{l}} = -s_{\mathrm{l}} dT + v_{\mathrm{l}} dp\,. \tag{3.7}$$

From this follows the *Clausius-Clapeyron relation*

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v} = \frac{s_{\mathrm{g}} - s_{\mathrm{l}}}{v_{\mathrm{g}} - v_{\mathrm{l}}}\,. \tag{3.8}$$

Typically $\Delta s, \Delta v > 0$ and hence the slope of the vapor pressure curve is positive. An anomaly occurs for the ice-water transition: Upon melting the volume decreases ($\Delta v < 0$). Thus the melting curve (phase line between ice and water) is inclined backwards in the p-T diagram.

During the conversion process the *latent heat* per particle

$$\ell = \frac{\Delta H}{N} = \frac{\Delta(TS + N\mu)}{N} = T\Delta s \tag{3.9}$$

must be supplied (with $\Delta\mu = \mu_{\mathrm{g}} - \mu_{\mathrm{l}} = 0$). For the water-water vapor transition at standard pressure, for example, $\ell = 40\,\mathrm{kJ/mol}$ holds.

Example 1: (Vapor Pressure Formula)

We use the following approximation to integrate the Clausius-Clapeyron relation. First, let the latent heat ℓ be temperature independent. Second, assume $\Delta v \approx v_{\mathrm{g}}$ with the ideal gas law with $v_{\mathrm{g}} = k_B T/p$ in the gas species. Under these assumptions the Clausius-Clapeyron relation $dp/dT = \ell/v_g T = \ell p/k_B T^2$ yields the vapor pressure formula

$$p(T) \propto e^{-\ell/k_B T}\,. \tag{3.10}$$

3.2 Gibbs' Phase Rule

Consider more generally r components (substances) distributed among ν species. Denote the respective chemical potentials by $\mu_{i\alpha}$, with $i = 1, \ldots, r$, and $\alpha = 1, \ldots, \nu$. As an intensive quantity $\mu_{i\alpha}$ depends only on p, T and the concentrations $c_{j\alpha} = N_{j\alpha}/N_\alpha$, $N_\alpha = \sum_j N_{j\alpha}$ in the species α. Of these concentrations only $\sum_j c_{j\alpha} = 1$ are independent because of $r - 1$. Altogether there are thus $2 + \nu(r-1)$ independent variables. In equilibrium the conditions

$$\mu_{i\alpha}(T, p, c_{1\alpha}, \ldots, c_{r-1\alpha}) = \mu_{i\beta}(T, p, c_{1\beta}, \ldots, c_{r-1\beta})\,. \tag{3.11}$$

hold. These are exactly $r(\nu - 1)$ in number with i arbitrary and $\alpha \neq \beta$. Hence we obtain as remaining degrees of freedom (*Gibbs' phase rule*)

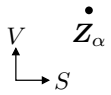
$$f = 2 + \nu(r-1) - r(\nu - 1) = 2 + r - \nu\,. \tag{3.12}$$

The degrees of freedom thus indicate, in a system with r components and ν species, the number of free intensive parameters.

Single-component system: In a system with only one component a pure species ($\nu = 1$) has two degrees of freedom. One must therefore fix both p and T. For the coexistence of two species ($\nu = 2$) only one degree of freedom remains. Hence the coexistence occurs only along a line $p(T)$ in the p-T diagram. We have already encountered this relation in Example 2.1 as the vapor pressure curve. Three species can coexist only at a point (the *triple point*). A coexistence of four species cannot occur in a single-component system.

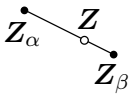
The coexistence of species cannot, as already shown, be described with the Gibbs energy $G(T, p)$. We therefore turn to the internal energy $U(S, V)$. The states are then fully determined by $\boldsymbol{Z} = (S, V)$ (N is held fixed). Depending on the number of coexisting species ν one obtains, for fixed (T, p), the following picture

$\nu = 1$:



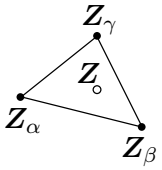
Pure species: the state $\boldsymbol{Z}_\alpha$ is uniquely determined by (T, p).

$\nu = 2$:



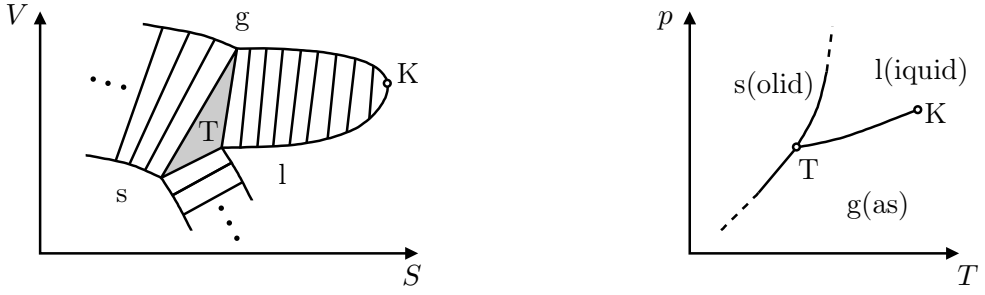
Coexistence of two species α, β: at the phase transition a point (T, p) corresponds to the entire straight line. The endpoints are the pure species. An arbitrary state $\boldsymbol{Z}$ is characterized by the mixing ratio $x_\alpha = N_\alpha/(N_\alpha + N_\beta)$.

$\nu = 3$:



For the coexistence of three species α, β, γ one needs two mixing ratios to specify a general state $\boldsymbol{Z}$. All states form a triangle with the pure species as vertices and the two-species mixtures as edges.

The phase diagram of a single-component system typically has the form:



On the left side the straight lines correspond exactly to the transition curves at fixed (T, p). Depending on the transition they are called melting curve (f-fl), sublimation curve (f-g) and vapor pressure curve (fl-g). At the triple point (T) all three species meet. The triple point thus fixes the temperature T_T and the pressure p_T uniquely. For water (H_2O) one has, for example, $p_\mathrm{T} = 612\,\mathrm{Pa}$ and $T_\mathrm{T} = 273\,\mathrm{K}$. For higher temperatures the transition curves between gaseous and liquid become shorter and vanish entirely at the critical point (K) where $\Delta s = \Delta v = 0$. At the critical point

the first derivatives of $\mu(T,p)$ are continuous and the discontinuity appears only in higher derivatives (*second-order phase transition*). The white region corresponds to the pure species, in which the assignment to (T,p) is unique. The labels "liquid" and "gaseous" have meaning only along the vapor pressure curve. For temperatures above the critical point one can pass from liquid to gaseous without a phase transition.

3.3 van der Waals Gas

Gases behave as ideal gases only at very high temperatures and low pressures. van der Waals, in his dissertation, proposed a phenomenological modification of the ideal gas law $pv = k_B T$ that is able to describe the gas-liquid transition. For this he was awarded the Nobel Prize in 1910. The idea is that, because of strong short-range repulsive forces between atoms, each atom has only the reduced volume $V - b$ available. One calls $b \geq 0$ the *covolume*. The long-range attraction he accounted for by a reduction of the external pressure by a term $-a/v^2$, with $a \geq 0$ the *cohesion pressure parameter*. This effect arises because particles near the wall, unlike those in the bulk, do not experience an isotropic environment and feel a net inward attraction. The strength of this force, acting per particle at the wall, is proportional to the density N/V of the attracting particles. At the same time the number of particles in the wall-near layer (that experience this force) is itself proportional to the density N/V. Since the total pressure loss depends on both factors, the pressure is lowered overall by a term proportional to $(N/V)^2 = 1/v^2$. The equation of state of the van der Waals gas has therefore the form (*van der Waals equation*)

$$\left(p + \frac{a}{v^2}\right)(v - b) = k_B T\,. \tag{3.13}$$

For high temperatures the isotherms in Figure 3.2 are similar to those of the ideal gas. At the critical temperature T_c the isotherm has an inflection point with $(\partial p/\partial V)_T = (\partial^2 p/\partial V^2)_T = 0$. From

$$\left(\frac{\partial p}{\partial v}\right)_T = \frac{2a}{v^3} - \frac{k_B T}{(v-b)^2} = 0, \qquad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2k_B T}{(v-b)^3} - \frac{6a}{v^4} = 0 \tag{3.14}$$

one finds the values

$$v_c = 3b, \qquad k_B T_c = \frac{8}{27}\frac{a}{b} \qquad \text{and} \quad p_c = \frac{1}{27}\frac{a}{b^2}\,, \tag{3.15}$$

at the critical point K. In particular the quantity

$$\frac{p_c v_c}{k_B T_c} = \frac{3}{8} \approx 0.375 \tag{3.16}$$

assumes a universal value, independent of the parameters a, b of the gas. Experimentally one finds a fairly good agreement with slightly reduced values in the range 0.28 to 0.33.

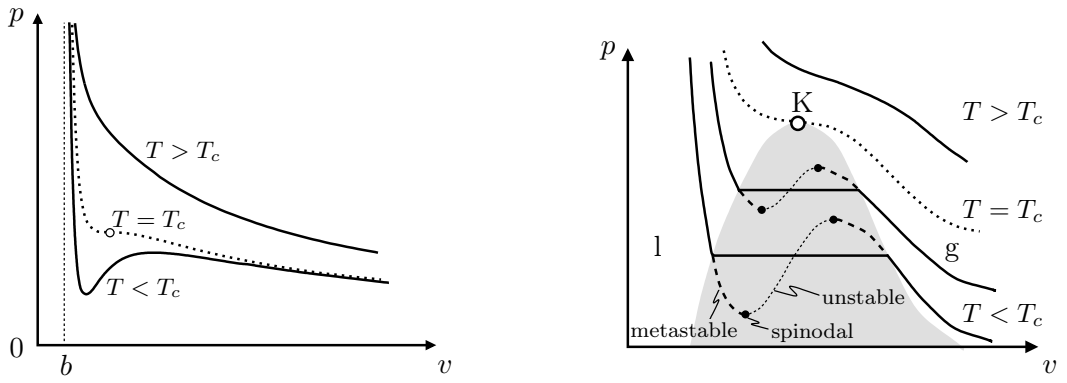
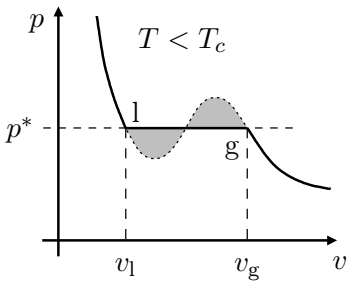


Fig. 3.2: Isotherms of the van der Waals gas (left). The gray region (for $T < T_c$) describes the coexistence of liquid and gas (right). In this region the Maxwell construction ($p = p^*$) replaces the isotherms from (3.13). Besides the equilibrium states the metastable phases (local, but not global minimum of the Gibbs energy) of superheated liquid (boiling delay) and supercooled gas (supersaturation), which end at the spinodals. The region between the spinodals corresponds to unstable states with $\kappa_T < 0$.

For temperatures $T < T_c$ there is, between the spinodals with $(\partial p/\partial v)_T = 0$, an increasing segment that violates the stability condition $(\partial p/\partial v)_T \leq 0$. This is a signal of the phase transition, because then the free energy $F(V,T)$ is not convex. As indicated in Figure 3.1, in this case we replace the free energy by its convex hull. The connecting straight line corresponds to the phase mixture at the phase transition.



We seek the vapor pressure $p^* = p(T)$ that completes the isotherm. It is determined by the equilibrium condition $\mu_{\rm l}(p^*,T) = \mu_{\rm g}(p^*,T)$. From the Gibbs-Duhem relation (2.10) we obtain $(\partial\mu/\partial p)_T = v$ with the solution

$$\mu = \int v\,dp + f(T)\,, \tag{3.17}$$

where $f(T)$ is an undetermined function of the temperature. Along the isotherm one can thus compute the difference of the chemical potential. This yields

$$0 = \mu_{\rm g} - \mu_{\rm l} = \int_{\rm l}^{\rm g} v(p)\,dp\,. \tag{3.18}$$

By partial integration we obtain the *Maxwell construction*

$$0 = \int_{\rm l}^{\rm g} v(p)\,dp = vp\Big|_{\rm l}^{\rm g} - \int_{\rm l}^{\rm g} p\,dv = \int_{\rm l}^{\rm g} (p^* - p)\,dv\,, \tag{3.19}$$

i.e., the gray areas are equal.

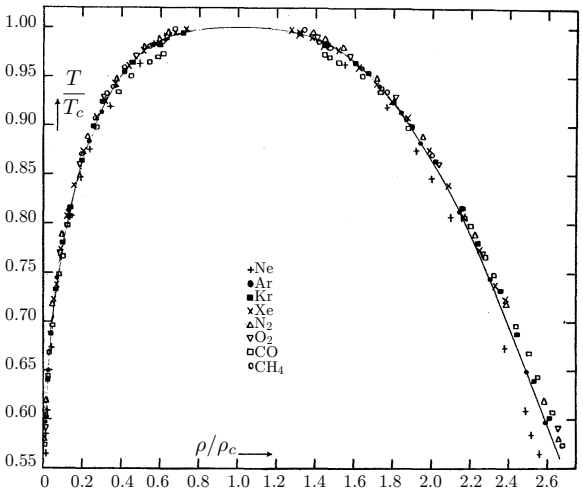


Fig. 3.3: Density $\rho = 1/v$ of the liquid species (ρ_l) and of the gas species (ρ_g) as a function of temperature for various gases. For the reduced variables all data lie on the same curve. From E.A. Guggenheim, '*The Principle of Corresponding States*', J. Chem. Phys. **13**, 253 (1945).

3.4 Universality, Critical Exponents

Passing to dimensionless (reduced) variables $\tilde{T} = T/T_c$, $\tilde{v} = v/v_c$ and $\tilde{p} = p/p_c$ brings the van der Waals equation to the universal form (*law of corresponding states*)

$$\left(\tilde{p} + \frac{3}{\tilde{v}^2}\right)(3\tilde{v} - 1) = 8\tilde{T}\,. \tag{3.20}$$

One therefore expects that all gases show the same behavior when pressure, volume, and temperature are scaled by their values at the critical point. For similar gases this works quite well, see Figure 3.3.

Even better, however, is the universality for the so-called *critical exponents*. To this end we expand $\tilde{p}(\tilde{T}, \tilde{v})$ about $(T, v) = (T_c, v_c)$ or $(\tilde{T}, \tilde{v}) = (1, 1)$. By definition both $\partial\tilde{p}/\partial\tilde{v}$ and $\partial^2\tilde{p}/\partial\tilde{v}^2$ vanish at $T = T_c$. For the remaining coefficients one finds

$$\left(\frac{\partial^3\tilde{p}}{\partial\tilde{v}^3}\right)_c = \left(\frac{3\cdot 4!}{\tilde{v}^5} - \frac{8\cdot 3^3\cdot 3!\,\tilde{T}}{(3\tilde{v}-1)^4}\right)_c = -9, \qquad \left(\frac{\partial\tilde{p}}{\partial\tilde{T}}\right)_c = \left(\frac{8}{3\tilde{v}-1}\right)_c = 4,$$
$$\left(\frac{\partial^2\tilde{p}}{\partial\tilde{T}\partial\tilde{v}}\right)_c = -\left(\frac{8\cdot 3}{(3\tilde{v}-1)^2}\right)_c = -6\,. \tag{3.21}$$

Hence the expansion of $p(T, v)$ about the critical point has the form

$$\tilde{p}(\tilde{T}, \tilde{v}) - 1 = 4(\tilde{T} - 1) - 6(\tilde{T} - 1)(\tilde{v} - 1) - \frac{3}{2}(\tilde{v} - 1)^3 + \cdots\,. \tag{3.22}$$

For $\tilde{T} - 1 \simeq (\tilde{v} - 1)^2$ (compare the second with the third term) the omitted terms are of higher order. We obtain the following critical behavior near the critical point

(a) The isothermal compressibility diverges as one approaches the critical point along an isochore (with $v = v_c$) from high temperatures. One has

$$\kappa_T(T, v_c) = -\frac{1}{v_c}\frac{1}{(\partial p/\partial v)_T} = -\frac{1}{p_c(\partial\tilde{p}/\partial\tilde{v})_T} = \frac{1}{6p_c(\tilde{T}-1)} \propto (T - T_c)^{-\gamma} \tag{3.23}$$

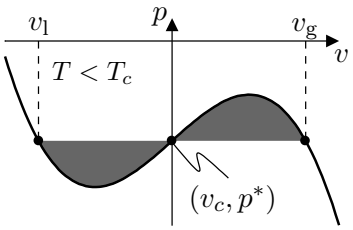
with the critical exponent $\gamma = 1$.

(b) On the critical isotherm ($T = T_c$) the pressure behaves as

$$\tilde{p} - 1 = -\frac{3}{2}(\tilde{v} - 1)^3 \propto (v - v_c)^\delta \tag{3.24}$$

with the critical exponent $\delta = 3$.

(c) Below the critical temperature ($T < T_c$) the expression (3.22) must be supplemented by the Maxwell construction. This is facilitated by the fact that the quantity $\tilde{p} - 1 - 4(\tilde{T} - 1)$ is an odd function of $v - v_c$. The Maxwell construction yields $\tilde{p}^* - 1 = 4(\tilde{T} - 1)$ and hence



$$-6(\tilde{T} - 1)(\tilde{v} - 1) - \frac{3}{2}(\tilde{v} - 1)^3 = 0\,.$$

for the intersection points of the van der Waals equation with the vapor pressure p^*. The solution with $v = v_c$ is unstable. The other two solutions correspond to v_g and v_l. One finds

$$v_{\mathrm{g,l}} = v_c \pm 2v_c\sqrt{1 - T/T_c}\,. \tag{3.25}$$

Hence for the volume change along the vapor pressure curve

$$v_\mathrm{g} - v_\mathrm{l} = 4v_c\sqrt{1 - T/T_c} \propto (T_c - T)^\beta \tag{3.26}$$

with the critical exponent $\beta = \frac{1}{2}$.

Experimentally one finds that the universality of the critical exponents β, γ, δ is very well observable. However, the exponents differ from $\beta \approx 0.3$, $\gamma \approx 1.3$ and $\delta \approx 5.0$. The reason is that close to the critical point our naive theory breaks down, since fluctuations become ever more important. The explanation both of the universality and of the concrete values of the critical exponents via the renormalization group theory is one of the most important achievements of theoretical physics in the second half of the 20th century.

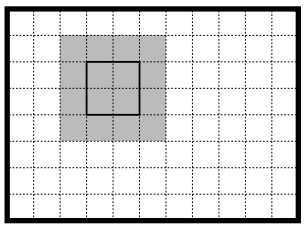
Chapter 4

Statistical Mechanics

The approach of statistical mechanics is to relate the results of thermodynamics to the microscopic laws of physics. While this sacrifices some generality (statistical mechanics in quantum mechanics differs from statistical mechanics in classical physics), it gains predictive power; in particular, the thermodynamic potentials can be computed from the microscopic laws. To derive thermodynamics from the microscopic laws, one must derive the two main laws. The first law is unproblematic, since the concept of (internal) energy already exists microscopically. The crux is therefore to anchor entropy S microscopically. The solution goes back to Boltzmann, who recognized that for every thermodynamic state $\boldsymbol{Z}$ (macrostate) there are many microscopic states. Denoting the number of microscopic states by $\Gamma(\boldsymbol{Z})$, one obtains $S = k_B \ln \Gamma$, as we will see later. One sees clearly that entropy is not a property of the microstate, but is determined only by specifying the macrostate. Linked to this is the statement that entropy depends on the work coordinates and is thus (only) relatively objective. The theory naturally becomes a statistical theory. Thermodynamics is obtained in the *thermodynamic limit* ($U, V, N \to \infty$ with $U/N, V/N$ fixed) of large, homogeneous systems, since fluctuations then vanish.

Example 1: (Relative objectivity of entropy)

We consider a model system, see figure. The microstates are the small boxes. Alice has an experimental setup in which she determines that the state of the system lies in the black-bordered region (consisting of 4 small boxes). She thus determines the entropy $S_A = k_B \ln 4 = 2k_B \ln 2$. Bob has an experimental setup



with only half the resolution. All he can say is that the system lies in the gray region. For him (for his experimental setup), $S_B = k_B \ln 16 = 2S_A$ holds.

4.1 Entropy

Let us start from the definition (Boltzmann)

$$S(\boldsymbol{Z}) = k_B \ln \Gamma(\boldsymbol{Z}) \tag{4.1}$$

The factor k_B merely fixes the temperature scale to the Kelvin scale.[1] Much more important is the fact that S is linked to $\ln\Gamma$. The intuition comes from the fact that $\Gamma(\boldsymbol{Z}_1, \boldsymbol{Z}_2) \approx \Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2)$ for a constrained system with $\boldsymbol{Z}_1 + \boldsymbol{Z}_2 = \boldsymbol{Z}$. By the logarithm, entropy becomes additive as desired. Equation (4.1) shifts the problem of a statistical definition of entropy from S to Γ. Given a measure $\Gamma(\boldsymbol{Z}) \geq 1$ of the microscopic states with[2]

$$\begin{aligned}
&(i): \quad \Gamma_t(\boldsymbol{Z}) = \Gamma(\boldsymbol{Z}) && \text{(stationary with respect to the microscopic dynamics)},\\
&(ii): \quad \Gamma(\boldsymbol{Z}_1, \boldsymbol{Z}_2) = \Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2) && \text{(multiplicative)},\\
&(iii): \quad \ln\Gamma(\boldsymbol{Z}) \propto N && \text{(extensive)},
\end{aligned}$$

the main laws of thermodynamics follow. The condition (i) implies that S is a state function (depends only on the state $\boldsymbol{Z}$ and not on the preparation).

Now consider a system composed of two subsystems with $\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2$. With constraints, the system has entropy

$$S(\boldsymbol{Z}_1, \boldsymbol{Z}_2) = k_B \ln \Gamma(\boldsymbol{Z}_1, \boldsymbol{Z}_2) = k_B \ln[\Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2)] = S(\boldsymbol{Z}_1) + S(\boldsymbol{Z}_2)\,. \tag{4.2}$$

In the equilibrium state $\boldsymbol{Z}$ (without constraints), however, all states must be taken into account in which $\boldsymbol{Z}_1, \boldsymbol{Z}_2$ are arbitrary, subject only to $\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2$. The total number of compatible states is then given by[3]

$$\Gamma(\boldsymbol{Z}) = \sum_{\substack{\boldsymbol{Z}_1, \boldsymbol{Z}_2 \\ (\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2)}} \Gamma(\boldsymbol{Z}_1, \boldsymbol{Z}_2) = \sum_{\substack{\boldsymbol{Z}_1, \boldsymbol{Z}_2 \\ (\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2)}} \Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2) \tag{4.3}$$

Thus one finds the entropy

$$S(\boldsymbol{Z}) = k_B \ln \left(\sum_{\substack{\boldsymbol{Z}_1, \boldsymbol{Z}_2 \\ (\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2)}} \Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2) \right). \tag{4.4}$$

One can estimate the sum from below by a single term ($\ln(x)$ is monotonically increasing) and obtains

$$S(\boldsymbol{Z}) \geq k_B \ln\big[\Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2)\big] = S(\boldsymbol{Z}_1) + S(\boldsymbol{Z}_2) \qquad (S \text{ is superadditive})\,. \tag{4.5}$$

[1] Note that the factor k_B has meaning independent of a 'normalization factor' of Γ, since the latter only shifts the entropy additively.

[2] $\Gamma_t(\boldsymbol{Z})$ denotes the measure of the microscopic states at time t.

[3] Here one uses the property that for disjoint possibilities the total number of states is simply the sum of the respective numbers of states.

From this follows (2.1b) and, by reversing the argument in Section 1.5, also the impossibility of a perpetual motion machine of the second kind (2nd law). For a homogeneous system, entropy is, as shown in Section 2.1, a concave function.

The definition (4.1) fixes entropy only in equilibrium. Nonequilibrium states, however, can be approximated to arbitrary accuracy by constrained equilibrium states. The (maximal) constraint to a single microstate corresponds to $S = 0$. By lifting a constraint, entropy increases due to superadditivity. This explains (2.1a).

From thermodynamics we expect that in complete equilibrium the equality sign in

$$S(\boldsymbol{Z}) \geq S(\boldsymbol{Z}_1^*) + S(\boldsymbol{Z}_2^*)\,. \tag{4.6}$$

holds, with certain state variables $\boldsymbol{Z}_1^*, \boldsymbol{Z}_2^*$ of the two subsystems. In statistical physics this is only approximately satisfied. We denote by $\Gamma(\boldsymbol{Z}_1^*)\Gamma(\boldsymbol{Z}_2^*)$ the largest term in the sum (4.4). In the thermodynamic limit the sum has $\propto N^d$ terms (with d the dimension of the state space $\boldsymbol{Z}$).[4] From (4.4) one then obtains the upper bound

$$S(\boldsymbol{Z}) \leq k_B \ln\Big[O(N^d)\Gamma(\boldsymbol{Z}_1^*)\Gamma(\boldsymbol{Z}_2^*)\Big] = S(\boldsymbol{Z}_1^*) + S(\boldsymbol{Z}_2^*) + O(\ln N)\,. \tag{4.7}$$

With (4.6) this implies

$$S(\boldsymbol{Z}) = S(\boldsymbol{Z}_1^*) + S(\boldsymbol{Z}_2^*) + O(\ln N) \tag{4.8}$$

and from (*iii*) one sees that the term $O(\ln N)$ can be neglected in the thermodynamic limit.

Remark: Without the condition (*iii*) one still obtains a reasonable thermodynamics with (a version of) the second law. However, fluctuations are then not completely suppressed and the subsystems are not determined by a fixed choice of constraint parameters. It is a strength of statistical mechanics that it defines the concepts of heat and entropy even for 'small' systems; more on this later.

From $S(\boldsymbol{Z}) = S(\boldsymbol{Z}_1^*) + S(\boldsymbol{Z}_2^*)$ follows thermal (and mechanical) equilibrium (zeroth law), cf. (2.3) and (2.4). In particular, the equilibrium variables T, g_α are defined as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{Z_\alpha}, \qquad \frac{g_\alpha}{T} = -\left(\frac{\partial S}{\partial Z_\alpha}\right)_{U, Z_{\beta\neq\alpha}}. \tag{4.9}$$

The first law is now obtained from

$$TdS = T\frac{\partial S}{\partial U}dU + T\sum_\alpha \frac{\partial S}{\partial Z_\alpha}dZ_\alpha = dU - \sum_\alpha g_\alpha dZ_\alpha = dU - \delta W\,. \tag{4.10}$$

In statistical physics one identifies heat, as usual, with

$$\delta Q = TdS\,. \tag{4.11}$$

[4] For the energy $U = U_1 + U_2$, for example, $U \propto N$ and $0 \leq U_1, U_2 \leq U$. The sum thus has $U/\Delta \propto N$ terms with energy resolution Δ; analogously for any other state variable Z_α

The third law requires that $\Gamma = 1^+$ for $T \to 0^+$ and holds only in quantum mechanics.

Thus we have reduced the question of how to anchor thermodynamics (statistically) in microscopy to finding a measure Γ of the number of microscopic states with the properties $(i), (ii), (iii)$.

4.2 Quantum mechanics

In the following we restrict ourselves to the work coordinates V, N. With the volume, for example, we can describe work of a gas; the particle number is useful for describing chemical processes or a particle reservoir. The results can of course be directly generalized to other work coordinates (note that then the entropy differs, since the number of microscopic states corresponding to a macrostate naturally changes).

Let us first consider quantum mechanics. A system of N *species* is described by the Schrödinger equation $i\hbar\partial_t \Psi(q,t) = H\Psi(q,t)$ with $q = (\boldsymbol{q}_1, \boldsymbol{q}_2, \dots)$ the $3N$ coordinates of the species. The restriction to the volume V is implemented by a box potential (so that $\Psi(q) = 0$ on the boundary). The energy eigenstates $|n\rangle$ with $H\Psi_n = E_n\Psi_n$ are stationary states in quantum mechanics. Indeed $\Psi_n(t) = \mathcal{U}_t\Psi_n = e^{-iE_nt/\hbar}\Psi_n$ under time evolution, so that the probability that the system is in state $|n\rangle$ does not change.

Now it is important that entropy S only takes into account states that have (internal) energy U. Due to the discreteness of energy levels we cannot demand this exactly. We therefore only require that $U - \Delta \le E_n \le U$. It turns out that for large systems (in the thermodynamic limit) the choice of $\Delta > 0$ is irrelevant. For large systems one may in particular choose $\Delta = U$.

With these preliminaries we define

$$\Gamma(\boldsymbol{Z}) = \Gamma(U,V,N) = \sum_n \delta_\Delta(U - E_n) = \langle \delta_\Delta(U - H)\rangle_{\mathrm{qm}} \tag{4.12}$$

with

$$\langle A\rangle_{\mathrm{qm}} = \sum_n \langle n|A|n\rangle = \mathrm{Tr}(A) \quad \text{and} \quad \delta_\Delta(x) = \begin{cases} 1, & 0 \le x \le \Delta, \\ 0, & \text{otherwise.} \end{cases} \tag{4.13}$$

Thus $\Gamma(\boldsymbol{Z})$ simply corresponds to the number of states compatible with the state variables $\boldsymbol{Z}$. The work coordinates V and N are thereby fixed by constraints on the Hilbert space.

The property (i) follows immediately from the construction with $\mathcal{U}_t = \exp(-iHt/\hbar)$ and

$$\Gamma_t(\boldsymbol{Z}) = \sum_n \langle n|\mathcal{U}_t^\dagger \overbrace{\delta_\Delta(U-H)\mathcal{U}_t}^{\mathcal{U}_t\delta_\Delta(U-H)} |n\rangle = \Gamma_0(\boldsymbol{Z})\,. \tag{4.14}$$

Now to the property (ii): A composite system is described by the Hamiltonian $H = H_1 + H_2$ (energy is approximately additive) on the Hilbert space $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$.

The individual Hilbert spaces implement here the constraints on the work coordinates V and N ($\mathcal{H}_1$ corresponds to the sector with N_1 species in volume V_1). Thus

$$\begin{aligned}\Gamma(\boldsymbol{Z}_1,\boldsymbol{Z}_2) &= \mathrm{Tr}_{\mathcal{H}}[\delta_\Delta(U_1-H_1)\delta_\Delta(U_2-H_2)] = \mathrm{Tr}_{\mathcal{H}_1}\mathrm{Tr}_{\mathcal{H}_2}[\delta_\Delta(U_1-H_1)\delta_\Delta(U_2-H_2)]\\ &= \mathrm{Tr}_{\mathcal{H}_1}\delta_\Delta(U_1-H_1)\ \mathrm{Tr}_{\mathcal{H}_2}\delta_\Delta(U_2-H_2) = \Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2)\,. \end{aligned} \tag{4.15}$$

The definition (4.12) thus provides a microscopic definition of entropy as a state function and hence of all of thermodynamics. The fact (property (*iii*)) that entropy is extensive follows from the exponential growth of the Hilbert space; see also later.

In quantum mechanics there is usually only a single ground state. At low temperatures $T \to 0^+$ (which corresponds to low energies) the system transitions to the ground state, so that $\Gamma \to 1^+$. This explains the third law.

Example 2: (Particle in a box potential)

We consider a particle of mass m with Hamiltonian $H = \boldsymbol{p}^2/2m$ in a box of size $V = L\times L\times L$ as a thermodynamic system. To obtain the number of states (4.12) we need only the spectrum. For completeness, we note that the wave functions (with the boundary condition $\Psi|_{\partial V} = 0$) take the form $\Psi_{\boldsymbol{n}}(\boldsymbol{x}) \propto \sin(\pi n_1 x_1/L)\sin(\pi n_2 x_2/L)\sin(\pi n_3 x_3/L)$ with energy

$$E_{\boldsymbol{n}} = \frac{\pi^2\hbar^2\boldsymbol{n}^2}{2mL^2}, \qquad n_j \in \{1,2,\dots\}\,. \tag{4.16}$$

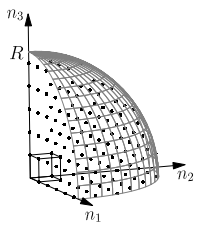
. In applications it is often useful to employ the relation $\delta_\Delta(x) = \Theta(x)-\Theta(x-\Delta)$, with $\Theta(x)$ the step function. It follows that

$$\Gamma(U,V) = \sum_{\boldsymbol{n}}[\Theta(U-E_{\boldsymbol{n}})-\Theta(U-\Delta-E_{\boldsymbol{n}})] = \Sigma(U,V)-\Sigma(U-\Delta,V)\,. \tag{4.17}$$

Thus it remains to evaluate the sum

$$\Sigma(U,V) = \sum_{\boldsymbol{n}}\Theta(U-E_{\boldsymbol{n}}) \overset{\text{(TDL)}}{\to} \int_{E_{\boldsymbol{n}}\le U} d^3n = \frac{1}{8}\Omega_3(\sqrt{2mUL^2/\pi^2\hbar^2}) \tag{4.18}$$

with the volume $\Omega_3(R) = \frac{4\pi}{3}R^3$ of the sphere of radius R. The factor $\frac{1}{8}$ arises because the restriction $n_j \ge 0$ implies that only one octant of the sphere contributes.
In the thermodynamic limit (TDL) boundary conditions are irrelevant. Hence one usually employs *periodic boundary conditions*. Then the wave functions are given by $\Psi_{\boldsymbol{n}}(\boldsymbol{x}) \propto e^{2\pi i\boldsymbol{n}\cdot\boldsymbol{x}/L}$ with energy



$$E_{\boldsymbol{n}} = \frac{4\pi^2\hbar^2\boldsymbol{n}^2}{2mL^2}, \tag{4.19}$$

where now all $\boldsymbol{n} \in \mathbb{Z}^3$ are allowed. In the thermodynamic limit one must therefore compute the volume of the entire sphere, but with only half the radius. Because

$$\frac{V}{(2\pi\hbar)^3}\Omega_3(\sqrt{2mU}) = \Omega_3(\sqrt{2mUL^2/4\pi^2\hbar^2}) = \frac{1}{8}\Omega_3(\sqrt{2mUL^2/\pi^2\hbar^2}) \quad (4.20)$$

both boundary conditions indeed lead to the same result ($h = 2\pi\hbar$ is Planck's constant)

$$\begin{aligned}\Gamma(U,V) &= \frac{V}{h^3}\left[\Omega_3(\sqrt{2mU}) - \Omega_3(\sqrt{2m(U-\Delta)})\right] \\ &= \frac{4\pi}{3}\frac{V}{h^3}(2mU)^{3/2}\underbrace{\left[1-(1-\Delta/U)^{3/2}\right]}_{\approx(3/2)\Delta/U} \\ &\approx 2\pi\frac{V}{h^3}(2mU)^{3/2}\frac{\Delta}{U}\,. \end{aligned} \quad (4.21)$$

In this case the number of states depends on Δ. The reason is that the system with a single particle is very small. From the thermodynamic potential

$$S(U,V) = k_B \ln\Gamma = k_B \ln\left(2\pi\frac{V(2mU)^{3/2}}{h^3}\frac{\Delta}{U}\right) \quad (4.22)$$

one can obtain the entire thermodynamics; in particular the (inverse) temperature

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{2}\frac{k_B}{U} \qquad \text{or} \qquad U = \frac{1}{2}k_B T \quad (4.23)$$

and the pressure

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_U = \frac{k_B}{V} \qquad \text{or} \qquad pV = k_B T\,. \quad (4.24)$$

One sees that in the thermal and caloric equations of state Δ, as expected, drops out. The thermal equation of state is that of a classical ideal gas with a single particle.[5]

4.3 Classical Mechanics

The dynamics in classical mechanics is described by $\dot{q} = \partial_p H, \dot{p} = -\partial_q H$ with the canonical coordinates $(q,p) \in \mathbb{R}^{6N}$. Unlike in quantum mechanics there is no natural way to count the number of states. Nevertheless we seek a measure $\Gamma(\boldsymbol{Z})$ that remains invariant under time evolution. The savior is Liouville's theorem from the mechanics course: the phase-space volume of a subset $\Omega \subset \mathbb{R}^{6N}$ is preserved under time evolution. As a reminder we consider the map ϕ_t (canonical flow) that sends the

[5] For N particles one finds $U = (\frac{3}{2}N - 1)k_B T$. Note that the equipartition theorem, which can be derived in the canonical ensemble, becomes valid for microcanonical systems only in the TDL.

initial condition (q,p) to the solution $(\bar q,\bar p)$ after time t, $(\bar q,\bar p)=(q(t),p(t))=\phi_t(q,p)$. Since the transformation from (q,p) to $(\bar q,\bar p)$ is canonical, we obtain a symplectic Jacobi matrix $J=\partial(\bar q,\bar p)/\partial(q,p)$ with $\mathrm{Det}\,J=1$ (see, for example, Landau-Lifshitz Vol. 1, § 47). From this follows Liouville's theorem

$$\int_{\phi_t(\Omega)} d^{3N}\bar q\, d^{3N}\bar p = \int_\Omega |\,\mathrm{Det}\,J| d^{3N}q\, d^{3N}p = \int_\Omega d^{3N}q\, d^{3N}p\,. \tag{4.25}$$

With these preliminaries we set the "number of states" to ($q_j\in V$ for all j)

$$\Gamma(\boldsymbol{Z})=\Gamma(U,V,N)=\int_V \underbrace{f_N\, d^{3N}q\, d^{3N}p}_{d\Gamma_N}\,\delta_\Delta(U-H)=\langle\delta_\Delta(U-H)\rangle_{\mathrm{kl}}\,. \tag{4.26}$$

and, by Liouville's theorem, $\Gamma(\boldsymbol{Z})$ is stationary (condition (i)). We have introduced the extra factor f_N, which we will determine immediately.

Now consider a partitioned system $S=(\boldsymbol{Z}_1,\boldsymbol{Z}_2)$ with N_1 particles in volume V_1 and N_2 particles in volume V_2.[6] For the spatial integrals we then have (q_1 are the N_1 spatial coordinates in volume V_1 and q_2 the remaining spatial coordinates in volume V_2)

$$\int_S d^{3N}q = \frac{N!}{N_1!\,N_2!}\int_{V_1} d^{3N_1}q_1\int_{V_2} d^{3N_2}q_2 \tag{4.27}$$

the binomial coefficient $N!/N_1!N_2!$ counts the ways to distribute the particles into the two containers. Dividing the equation by $N!$ we obtain

$$\int_S \frac{d^{3N}q}{N!} = \left(\int_{V_1}\frac{d^{3N_1}q_1}{N_1!}\right)\left(\int_{V_2}\frac{d^{3N_2}q_2}{N_2!}\right) \tag{4.28}$$

We recognize that the definition (4.26) is multiplicative if we choose the Gibbs factor

$$f_N=\frac{1}{N!\,h^{3N}},\qquad d\Gamma_N=\frac{d^{3N}q\,d^{3N}p}{h^{3N}N!} \tag{4.29}$$

[7] The extra factor h^{-3N} with h Planck's constant follows from Bohr-Sommerfeld quantization (one state per h of phase space). It is irrelevant in the classical description (changes the entropy only by an additive constant per particle) yet ensures that the quantum entropy goes over to the classical entropy in the classical limit T, see Example 3.

[6] We have $S=\{(q,p)\mid \#\{\boldsymbol{q}_j\in V_1\}=N_1\}$, where it does not matter which N_1 particles reside in volume V_1.

[7] For more information and the connection to the "Gibbs paradox," I recommend the article "*Statistical Mechanics of Classical Systems with Distinguishable Particles*" by R.H. Swendsen, J. Stat. Phys. **107**, 1143 (2002).

With the Gibbs factor we have $\int_S d\Gamma_N = \int_{V_1} d\Gamma_{N_1} \int_{V_2} d\Gamma_{N_2}$ and obtain (cf. (4.15))

$$\begin{aligned}\Gamma(\boldsymbol{Z}_1, \boldsymbol{Z}_2) &= \int_S d\Gamma_N \, \delta_\Delta(U_1 - H_1)\delta_\Delta(U_2 - H_2) \\ &= \int_{V_1} d\Gamma_{N_1} \int_{V_2} d\Gamma_{N_2} \, \delta_\Delta(U_1 - H_1)\delta_\Delta(U_2 - H_2) = \Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2)\,. \end{aligned} \tag{4.30}$$

Hence condition (ii) holds and the entropy is superadditive also in classical statistical mechanics.

Starting from S, lifting the partition in the particle numbers (particle exchange) yields the number of states

$$\begin{aligned}\sum_{N_1+N_2=N} \Gamma(\boldsymbol{Z}_1)\Gamma(\boldsymbol{Z}_2) &= \sum_{N_1+N_2=N} \int_{V_1} d\Gamma_{N_1} \int_{V_2} d\Gamma_{N_2} \, \delta_\Delta(U_1 - H_1)\delta_\Delta(U_2 - H_2) \\ &\overset{8}{=} \int_V d\Gamma_N \, \delta_\Delta(U_1 - H_1)\delta_\Delta(U_2 - H_2) = \Gamma(U_1, V_1, U_2, V_2, N)\,, \end{aligned} \tag{4.31}$$

as desired.

Note: The Gibbs factor appears because the partition fixes only the number N_1, N_2 of particles in each subvolume, without specifying which N particles these are. In a system S' where we know that the N_1-particles with coordinates $q_1 \in \mathbb{R}^{3N_1}$ are in volume V_1 and the N_2-particles with coordinates $q_2 \in \mathbb{R}^{3N_2}$ are in volume V_2, we have directly

$$\int_{S'} d^{3N_1}dq_1 \, d^{3N_2}dq_2 = \int_{V_1} d^{3N_1}dq_1 \int_{V_2} d^{3N_2}dq_2\,, \tag{4.32}$$

without a Gibbs factor. In this description of the system (since we know which particles are in which subvolume) it is no longer possible to lift the restriction on the particle number afterwards.

Example 3: (Classical particle in a box)

We consider the classical version of Example 2. In this case we must determine $\Gamma(U, V)$ from (4.26) ($N = 1$)). It follows that

$$\begin{aligned}\Gamma(U, V) &= \frac{1}{h^3} \overbrace{\int d^3x}^{V} \overbrace{\int d^3p \, \delta_\Delta(U - \boldsymbol{p}^2/2m)}^{\Omega_3(\sqrt{2mU}) - \Omega_3(\sqrt{2m(U-\Delta)})} \\ &= \frac{V}{h^3}\left[\Omega_3(\sqrt{2mU}) - \Omega_3(\sqrt{2m(U-\Delta)})\right]\,. \end{aligned} \tag{4.33}$$

A comparison with (4.21) shows that in this case the quantum result coincides exactly with the classical result (with the factor h^{-3N}).

[8] For this step it is crucial that H_1 depends only on the canonical coordinates of the N_1 particles in volume V_1 and not on which of the total N particles are there. The same holds for H_2.

Example 4: Ideal gas

An ideal gas of N particles of mass m is described by the Hamiltonian

$$H = \sum_{j=1}^{N} \frac{\boldsymbol{p}_j^2}{2m} \,. \tag{4.34}$$

We compute the phase-space volume

$$\Gamma(U,V,N) = \frac{1}{h^{3N}N!} \underbrace{\int d^{3N}x}_{V^N} \int d^{3N}p \, \delta_\Delta(U-H) \,. \tag{4.35}$$

As an auxiliary quantity we introduce the function

$$\Omega_{3N}(R) = \int_{\sum_j \boldsymbol{p}_j^2 \le R^2} d^{3N}p = \text{Vol. of the } 3N\text{-dim. ball of radius } R \tag{4.36}$$

Hence

$$\Gamma(U,V,N) = \frac{V^N}{h^{3N}N!} \Big[\Omega_{3N}(\sqrt{2mU}) - \Omega_{3N}(\sqrt{2m(U-\Delta)}) \Big] \,. \tag{4.37}$$

The volume of the ball is given by

$$\Omega_d(R) = \frac{\pi^{d/2}}{(d/2)!} R^d \,. \tag{4.38}$$

The volume grows so rapidly with R that the bulk of it lies near the surface.[9] We obtain

$$\Omega_d(R) - \Omega_d(R_0) = \frac{\pi^{d/2}}{(d/2)!}(R^d - R_0^d) = \frac{\pi^{d/2}}{(d/2)!} R^d \big[1 - (R_0/R)^d\big] \,. \tag{4.39}$$

Since $R_0 < R$, in the (thermodynamic) limit $d \to \infty$ the first term dominates and the correction becomes arbitrarily small.

Thus

$$\Gamma(U,V,N) \approx \frac{V^N}{h^{3N}N!} \Omega_{3N}(\sqrt{2mU}) = \frac{V^N}{N!} \frac{(2\pi m U/h^2)^{3N/2}}{(3N/2)!} \,. \tag{4.40}$$

In the thermodynamic limit we also use Stirling's formula

$$\ln N! = N(\ln N - 1) + O(\ln N) \tag{4.41}$$

and obtain the entropy of the ideal gas (*Sackur-Tetrode*)

$$S(U,V,N) = k_B \ln \Gamma = N k_B \ln \left[\frac{V}{N} \Big(\frac{4\pi m}{3h^2} \frac{U}{N} \Big)^{3/2} \right] + \frac{5}{2} N k_B \,, \tag{4.42}$$

[9] This is why we chose the asymmetric smearing in (4.13).

valid up to corrections of the form $O(\ln N)$. The argument of the logarithm is intensive with V/N (from $N!$) and U/N (from $(3N/2)!$). The temperature of the ideal gas follows from

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3}{2}\frac{Nk_B}{U} \qquad \text{or} \qquad U = \frac{3}{2}Nk_BT\,. \tag{4.43}$$

For the pressure we find

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{Nk_B}{V} \qquad \text{or} \qquad pV = Nk_BT\,. \tag{4.44}$$

Thus we have derived the thermal and caloric equations of state of the ideal gas microscopically.

4.4 Probability Theory

With Boltzmann's prescription $S = k_B \ln \Gamma$ and the definition $\Gamma = \langle \delta_\Delta(U - H)\rangle$, which holds both in the classical (4.26) and in the quantum case (4.12), we have placed thermodynamics on a microscopic foundation. To gain deeper insight, however, it is useful to view the entire subject from the perspective of probability theory.

We consider a probability space with outcomes $i \in \Omega$. Each outcome occurs with probability p_i. The probabilities satisfy the following properties

$$p_i \geq 0 \qquad \text{and} \qquad \sum_{i\in\Omega} p_i = 1\,. \tag{4.45}$$

One defines the probability that $A \subset \Omega$ occurs as

$$P(A) = \sum_{i\in A} p_i\,. \tag{4.46}$$

Thus the probabilities range from $P(E) = 0$ (impossible event E) to $P(E) = 1$ (sure event). In statistical mechanics it is expedient to interpret probabilities in the *bayesian* sense. We already know this from statements such as: "It will rain tomorrow with 25% probability." Here the probability expresses the degree of belief.

A discrete *random variable* X takes the value x_i on the outcome i. We define the *expectation value* of a function $f(x)$ as

$$\overline{f(X)} = \sum_i p_i f(x_i) = \sum_x P(X = x) f(x)\,. \tag{4.47}$$

If the random variable X is continuous, we introduce the probability density $\rho(x)$ such that

$$P(a \leq X \leq b) = \int_a^b dx\, \rho(x), \qquad \text{d.h.} \qquad \rho(x) = \frac{d}{dx} P(a \leq X \leq x)\,. \tag{4.48}$$

Hence the expectation value is given by

$$\overline{f(X)} = \int dx\, \rho(x) f(x)\,. \tag{4.49}$$

The expectation value is linear with $\overline{\alpha X + \beta Y} = \alpha\overline{X} + \beta\overline{Y}$. Two random variables X, Y are called *independent* if

$$P(X = x, Y = y) = P(X = x)P(Y = y) \tag{4.50}$$

from which one deduces, for example, $\overline{XY} = \overline{X}\,\overline{Y}$.

The expectation value $\overline{X}$ describes the probability distribution $\rho(x)$ by a single number. In applications it is important also to know something about possible deviations from $\overline{X}$. For this one uses the *mean square fluctuation* (variance)

$$(\delta X)^2 = \mathrm{Var}\, X = \overline{(X - \overline{X})^2} = \overline{X^2} - \overline{X}^2\,. \tag{4.51}$$

Thus one knows that the values of X lie with high probability in the range $\overline{X} \pm \delta X$.[10] Probability theory becomes a deterministic theory for $\delta X \to 0$. This exactly corresponds to the thermodynamic limit, in which statistical mechanics reduces to thermodynamics.

The covariance of two random variables is defined as

$$\delta X\, \delta Y = \mathrm{Cov}(X, Y) = \overline{(X - \overline{X})(Y - \overline{Y})} = \overline{XY} - \overline{X}\,\overline{Y}\,. \tag{4.52}$$

One has $\delta X\, \delta Y = 0$ if X and Y are independent.

An important result is the *Law of Large Numbers*: for random variables X_j, $j = 1, \ldots, N$, independently and identically distributed with common mean $\overline{X} = \overline{X_j}$ and variance $(\delta X)^2 = (\delta X_j)^2 < \infty$, one defines the sample mean

$$\mu = \frac{1}{N}\sum_j X_j \qquad \text{with} \quad \overline{\mu} = \overline{X}\,. \tag{4.53}$$

For the variance of the sample mean one obtains

$$(\delta\mu)^2 = \frac{1}{N^2}\sum_{i,j} \overbrace{\delta X_i\, \delta X_j}^{\delta_{ij}(\delta X)^2} = \frac{(\delta X)^2}{N}\,. \tag{4.54}$$

The Law of Large Numbers states

$$\delta\mu = \frac{\delta X}{\sqrt{N}} \sim \frac{1}{\sqrt{N}} \overset{(N\to\infty)}{\to} 0\,. \tag{4.55}$$

[10] For example, the Chebyshev inequality $P(|X - \overline{X}| \geq k) \leq (\delta X)^2/k^2$ holds.

Hence one has shown that the sample mean becomes deterministic for a large sample size N.

In the following we will often use generating functions. For a random variable X one defines the generating function as the expectation value

$$Z(\lambda) = \overline{\exp(\lambda X)} = \sum_i p_i e^{\lambda x_i} \,. \tag{4.56}$$

One has $Z(0) = \sum_i p_i = 1$ and one recovers the expectation value via

$$\overline{X} = \sum_i p_i x_i = \sum_i p_i \frac{d}{d\lambda} e^{\lambda x_i}\Big|_{\lambda=0} = Z'(0) \,. \tag{4.57}$$

More generally one also has $\overline{X^n} = d^n Z(0)/d\lambda^n$ for the *moments* $\overline{X^n}$.

Turning to the *cumulant generating function* $F(\lambda) = \ln Z(\lambda)$ one obtains

$$F(0) = 0, \quad F'(0) = \frac{Z'(0)}{Z(0)} = \overline{X} \,, \quad F''(0) = \frac{Z''(0)}{Z(0)} - \frac{Z'(0)^2}{Z(0)^2} = (\delta X)^2; \tag{4.58}$$

i.e. the first derivative in the Maclaurin series of $F(\lambda)$ is the expectation value and the second is the mean square fluctuation.[11]

Shannon Entropy: We have seen that an event with $P = 1$ certainly occurs while an event with $P = 0$ certainly does not occur. Both events are *deterministic*. If one seeks a measure of uncertainty, one sees that this should vanish for $P = 0$ or $P = 1$ and be maximal for $P = \frac{1}{2}$. As a measure of the uncertainty of a random distribution p_i, $i = 1, \ldots, M$ one defines the *Shannon entropy*[12]

$$S_{\text{Shannon}} = -\sum_{i=1}^{M} p_i \log_2 p_i \geq 0 \,. \tag{4.59}$$

Here the logarithm is conventionally taken base 2, so that S_{Shannon} has the unit "bit." For two events with $p_1 = p$ and $p_2 = q = 1 - p$ one obtains

$$S_{\text{Shannon}} = -p \log_2 p - q \log_2 q \,. \tag{4.60}$$

The function vanishes for $p = 0$ or $p = 1$, is symmetric $p \leftrightarrow q$ and possesses a maximum $S_{\text{Shannon}} = 1\,\text{bit}$ at $p = q = \frac{1}{2}$.

The importance of S_{Shannon} follows from the following result (Shannon): if one takes $N \gg 1$ independent samples from the distribution p_i, then one expects to obtain N_i times the outcome i for a typical sequence with $N_i = p_i N$. The number of typical configurations is given by the multinomial coefficient

$$\Gamma(N_1, \ldots, N_M) = \frac{N!}{N_1! \cdots N_M!} \,. \tag{4.61}$$

[11] More generally one defines the n-th cumulant as $d^n F(0)/d\lambda^n$.

[12] One defines $x \ln x = 0$ for $x = 0$.

With the Stirling formula $N! \sim (N/e)^N$ one obtains for large N the result

$$\Gamma(N_1, \ldots, N_M) \sim \frac{2^{N \log_2 N}}{2^{N_1 \log_2 N_1} \cdots 2^{N_M \log_2 N_M}} = 2^{-\sum_i N_i \log_2(N_i/N)} = 2^{N S_{\text{Shannon}}} . \tag{4.62}$$

For large N one therefore needs $(N S_{\text{Shannon}})$ bits of information to store which of the typical sequences was obtained. We have already met the expression $N S_{\text{Shannon}}$ (up to different units) as the mixing entropy in (2.74).

Furthermore one can show that with overwhelmingly high probability one obtains a typical sequence. A general sequence occurs with probability

$$P(n_1, \ldots, n_M) = \frac{N!}{n_1! \cdots n_M!} p_1^{n_1} \cdots p_M^{n_M} \sim 2^{\sum_i n_i \log_2(N p_i / n_i)} \tag{4.63}$$

Setting $n_i = N_i + dn_i$, with the deviation $dn_i \ll N_i$ from the typical sequence, one obtains

$$n_i \log_2(N p_i / n_i) = -\frac{1}{\ln(2)} \left(dn_i + \frac{dn_i^2}{2N_i} \right) + O(dn_i/N_i)^3 \tag{4.64}$$

and hence ($\sum_i dn_i = 0$, since $\sum_i n_i$ is fixed)

$$P(n_1, \ldots, n_M) \sim 2^{-N \sum_i p_i (dn_i/N_i)^2 / \ln(4)} \tag{4.65}$$

Thus a typical sequence occurs in the limit $N \to \infty$ with probability 1. Shannon's result therefore yields a deterministic statement (sure event) for a stochastic problem in the limit $N \to \infty$. In this sense it is analogous to the transition from statistical physics (with fluctuations) to thermodynamics (without fluctuations) in the thermodynamic limit.

Density Matrix: To describe a quantum mechanical system with incomplete information one usually employs the *density matrix*

$$\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i| , \qquad \langle\psi_i|\psi_j\rangle = \delta_{ij}. \tag{4.66}$$

This describes a mixed state in which the system is described with probability p_i by the (normalized) wave function $|\psi_i\rangle$. In general a density matrix ρ is a linear map $\rho\colon \mathcal{H} \to \mathcal{H}$ with the properties:

- $\rho = \rho^\dagger$ (Hermitian),
- $\rho \geq 0$, i.e. $\langle\psi|\rho|\psi\rangle \geq 0$ for all $|\psi\rangle$ (positive semidefinite),
- $\operatorname{Tr}\rho = 1$ (trace 1).

By Hermiticity the density matrix can be diagonalized in an orthonormal basis $|\psi_i\rangle$ with eigenvalues $p_i \in \mathbb{R}$. One has $p_i \geq 0$ (from point 2) and $\sum_i p_i = 1$ (from point 3). Thus for a general density matrix we have the representation (4.66) where p_i is the

probability of finding the system in state $|\psi_i\rangle$. Pure states are exactly the cases in which ρ is a projector with $\rho^2 = \rho$ (so there exists a i with $p_i = 1$ and $p_{j\neq i} = 0$).

From quantum mechanics we know that the expectation value of a measured quantity X in a pure state $|\psi_i\rangle$ is given by $x_i = \langle\psi_i|X|\psi_i\rangle$. For a general state ρ the corresponding expectation value therefore reads

$$\overline{X} = \sum_i p_i \langle\psi_i|X|\psi_i\rangle = \mathrm{Tr}(\rho X)\,. \tag{4.67}$$

Starting from the state ρ_0 at time $t = 0$ the time evolution of the individual wave functions under the Hamiltonian H is given by the time-dependent Schrödinger equation $\mathcal{U}_t|\psi_i\rangle = e^{-iHt/\hbar}|\psi_i\rangle$. At time t the state is

$$\rho_t = \sum_i p_i \mathcal{U}_t|\psi_i\rangle\langle\psi_i|\mathcal{U}_t^\dagger = e^{-iHt/\hbar}\rho_0 e^{iHt/\hbar}\,. \tag{4.68}$$

The density matrix therefore obeys the *von Neumann equation*

$$\frac{d\rho_t}{dt} = -\frac{i}{\hbar}[H, \rho_t]\,. \tag{4.69}$$

With the density matrix one can write the Shannon entropy in a basis-independent way. One has (von Neumann entropy)

$$S_{\text{von-Neumann}} = -\langle\rho\log_2\rho\rangle = -\,\mathrm{Tr}(\rho\log_2\rho) = -\sum p_i \log_2 p_i = S_{\text{Shannon}}\,. \tag{4.70}$$

For pure states naturally $S_{\text{Shannon}} = 0$. Mixed states lead to $S_{\text{Shannon}} > 0$.

Insert: (Entanglement)

Often an observer ("Alice") in a Hilbert space $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$ has access only to a subspace $\mathcal{H}_A$. Such a case arises, for example, when the system consists of two spin-$\frac{1}{2}$ particles but Alice can manipulate only one spin. The measurements M_A of a state ρ that Alice can perform on her subspace are then described solely by the *reduced density matrix*

$$\rho_A \colon \mathcal{H}_A \to \mathcal{H}_A, \qquad \rho_A = \mathrm{Tr}_B(\rho) \tag{4.71}$$

where Tr_B denotes the trace over the Hilbert space $\mathcal{H}_B$. The expectation value of M_A

$$\langle M_A\rangle = \mathrm{Tr}(\rho M_A) = \underbrace{\mathrm{Tr}_A\,\mathrm{Tr}_B}_{=\mathrm{Tr}_{A\otimes B}}(\rho M_A) = \mathrm{Tr}_A(\rho_A M_A)\,. \tag{4.72}$$

is therefore determined solely by ρ_A. Note that starting from a pure state ρ in general ρ_A is not a pure state.

Consider first the state $|\Psi_1\rangle = |\uparrow\uparrow\rangle$ in the Hilbert space $\mathbb{C}^2 \otimes \mathbb{C}^2$. The corresponding density matrix is given by

$$\rho_1 = |\uparrow\uparrow\rangle\langle\uparrow\uparrow|\,. \tag{4.73}$$

For measurements on Alice's subsystem it suffices to know the reduced density matrix

$$\rho_{1,A} = \mathrm{Tr}_B(\rho_1) = \sum_{m_B=\pm} \big(I_2 \otimes \langle m_B|\big)\,|\uparrow\uparrow\rangle\langle\uparrow\uparrow|\,\big(I_2 \otimes |m_B\rangle\big) = |\uparrow\rangle\langle\uparrow|\,. \tag{4.74}$$

Observe that in this case $\rho_{1,A}$ is again a pure state with $\rho_{1,A}^2 = \rho_{1,A}$.

As a second example consider the state (singlet) $|\Psi_2\rangle = \frac{1}{\sqrt{2}}\big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big)$. The density matrix is then given by

$$\rho_2 = \frac{1}{2}\big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big)\big(\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\big) = \frac{1}{2}\Big(|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + |\downarrow\uparrow\rangle\langle\downarrow\uparrow| - |\uparrow\downarrow\rangle\langle\downarrow\uparrow| - |\downarrow\uparrow\rangle\langle\uparrow\downarrow|\Big)\,. \tag{4.75}$$

In this case the reduced state

$$\rho_{2,A} = \frac{1}{2}\big(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|\big) = \frac{1}{2}\,I_2 \tag{4.76}$$

is not a pure state. The state $\rho_{2,A}$ is in fact the *maximally mixed* state, in which $|\uparrow\rangle$ and $|\downarrow\rangle$ each occur with 50% probability.

The differing behavior of $|\Psi_1\rangle$ and $|\Psi_2\rangle$ is connected with the fact that $|\Psi_1\rangle = |\uparrow\rangle \otimes |\uparrow\rangle$ is a *product state*. One shows in general: let $|\Psi\rangle = |\psi_A\rangle \otimes |\psi_B\rangle$ be a product state with arbitrary $|\psi_A\rangle$ and $|\psi_B\rangle$. Then one finds that the reduced density matrix

$$\rho_A = \mathrm{Tr}_B\big(|\psi_A\rangle \otimes |\psi_B\rangle\langle\psi_A| \otimes \langle\psi_B|\big) = \big(\mathrm{Tr}_B\,|\psi_B\rangle\langle\psi_B|\big)|\psi_A\rangle\langle\psi_A| = |\psi_A\rangle\langle\psi_A| \tag{4.77}$$

corresponds to the pure state $|\psi_A\rangle$. Thus we have the simple criterion for an arbitrary pure state $|\Psi\rangle$ on $\mathcal{H}_A \otimes \mathcal{H}_B$:

$$|\Psi\rangle \text{ can be written as a product state} \quad \Leftrightarrow \quad \rho_A \text{ is a pure state.} \tag{4.78}$$

States that cannot be written as product states are called *entangled* states. In particular we obtain the result that the singlet state $|\Psi_2\rangle$ is an entangled state and hence cannot be written as a product state. In other words, we have shown that there are no unitary operators U_A and U_B such that

$$(U_A \otimes U_B)|\Psi_2\rangle = |\psi_A\rangle \otimes |\psi_B\rangle \tag{4.79}$$

with arbitrary $|\psi_A\rangle$ and $|\psi_B\rangle$.

Notation: For the expectation value of a measured quantity (random variable) X we write

$$\overline{X} = \sum_i p_i x_i\,, \tag{4.80}$$

independent of whether the outcome space is discrete or continuous.

In quantum mechanics the density matrix $\rho\colon \mathcal{H} \to \mathcal{H}$ (Hermitian, positive semidefinite, trace 1) describes the probability distribution on the Hilbert space. A measured quantity X is a linear map $X\colon \mathcal{H} \to \mathcal{H}$, which is likewise Hermitian. For the expectation value one has

$$\overline{X} = \mathrm{Tr}(\rho X) = \langle \rho X \rangle\,. \tag{4.81}$$

Comparison with (4.80) shows that $\langle\cdot\rangle$ plays the role of the sum, ρ the role of p_i and X the role of x_i.

In classical mechanics there is a probability density $\rho(q,p)$ on phase space, and a measured quantity is a function $X(q,p)$. The expectation value reads

$$\overline{X} = \int d\Gamma_N\, \rho(q,p) X(q,p) = \langle \rho X \rangle\,, \tag{4.82}$$

where $d\Gamma_N = d^{3N}q\, d^{3N}p/N!h^{3N}$ denotes the phase-space element of the N-particle system.

Comparison with (4.80) shows that $\langle\cdot\rangle \leftrightarrow \sum_i$, $\rho(q,p) \leftrightarrow p_i$ and $X(q,p) \leftrightarrow x_i$. Hence the classical case follows formally from the quantum mechanical one under the replacement

$$\mathrm{Tr} \mapsto \int d\Gamma_N, \qquad \rho \mapsto \rho(q,p), \qquad X \mapsto X(q,p)\,. \tag{4.83}$$

4.5 Microcanonical Ensemble

We wish to give a statistical interpretation to the Boltzmann formula $S = k_B \ln \Gamma$ with $\Gamma(U) = \langle \delta_\Delta(U-H)\rangle$, which holds in both the classical and the quantum case by the respective definitions of $\langle\cdot\rangle$. The bracket $\langle\cdot\rangle$ gives a weighting of phase space that remains invariant under time evolution. The function $\delta_\Delta(U-H)$ restricts us to the subspace of phase space on which $U = H$ holds (as we have already seen, the concrete value of the uncertainty $\Delta > 0$ is irrelevant). The other constraints are implicit in the formalism (we allow only states of fixed V, N).

The state variables U, V, N thus specify only a macrostate, to which $\Gamma = e^{S/k_B}$ microstates belong. With the limited access/knowledge of the system, we cannot pin down which microstate is realized. The most natural assumption (see the later Gibbs variational principle) is that we assign the same probability to every state. The uniform distribution over the states admitted by the constraints is called the *microcanonical ensemble* (or the *microcanonical collection*) with probability density $\rho_{\mathrm{mk}} = c\,\delta_\Delta(U-H)$. The normalization c is obtained from

$$1 = \langle c\,\delta_\Delta(U-H)\rangle = c\langle\delta_\Delta(U-H)\rangle = c\,\Gamma(U)\,. \tag{4.84}$$

Hence one obtains the probability density (*microcanonical distribution*)

$$\rho_{\mathrm{mk}} = \frac{1}{\Gamma(U)}\delta_\Delta(U-H), \qquad \Gamma(U) = \langle\delta_\Delta(U-H)\rangle, \tag{4.85}$$

where the denominator

$$\Gamma(U) = \begin{cases} \sum_n \delta_\Delta(U-E_n) & \text{(quantum mechanically)}, \\ \int d\Gamma_N\, \delta_\Delta(U-H) & \text{(classically)}, \end{cases} \tag{4.86}$$

is called the *microcanonical partition function.*

To measure the degree of disorder/entropy one computes the Shannon entropy,

$$S_{\mathrm{Gibbs}} = -k_B \sum_i p_i \ln p_i\,, \tag{4.87}$$

which, with the new normalization, is called the Gibbs entropy; one has $S_{\mathrm{Gibbs}} = k_B \ln(2) S_{\mathrm{Shannon}}$.

The microcanonical ensemble has the Gibbs entropy

$$S_{\mathrm{Gibbs}} = -k_B\langle\rho_{\mathrm{mk}} \ln \rho_{\mathrm{mk}}\rangle = k_B \frac{\ln\Gamma(U)}{\Gamma(U)}\langle\delta_\Delta(U-H)\rangle = k_B \ln\Gamma(U) = S, \tag{4.88}$$

which agrees exactly with the Boltzmann definition.

Landauer Principle: The relation $S_{\text{Gibbs}} = k_B \ln(2) S_{\text{Shannon}}$ between thermodynamics and information theory leads to the following conclusion: when one erases a bit on a hard drive, one lowers the Shannon entropy by 1 bit (initially one has $p_0 = p_1 = \frac{1}{2}$, finally $p_0 = 1, p_1 = 0$). In thermodynamic terms this corresponds to a lowering of the entropy by

$$S_{\text{Landauer}} = k_B \ln(2) = 9.57 \times 10^{-24}\,\text{J/K} \tag{4.89}$$

This process cannot occur spontaneously but requires heat exchange. For a heat bath at room temperature $T = 300\,\text{K}$ the heat released is

$$\Delta Q = T S_{\text{Landauer}} \approx 3 \times 10^{-21}\,\text{J} = 3\,\text{zJ} \tag{4.90}$$

Hence erasing a hard drive with $1\,\text{TB} = 8 \times 10^{12}\,\text{Bit}$ bits increases the heat in the room by at least

$$\Delta Q \geq 2 \times 10^{-8}\,\text{J}\,. \tag{4.91}$$

With the statistical description one can extend the second law to systems that are not in the thermodynamic limit and in which fluctuations are not negligible. One has

(Second Law, statistical formulation)

In a closed system it is impossible to lower the entropy *deterministically* (with probability 1) by manipulating only the work coordinates.

It is important to understand (as we have often emphasized) that entropy is a quantity that depends on the available work coordinates. If one controls the position coordinates of all particles, naturally one can reach any state. However in this case there is no heat and the entropy vanishes. For a deeper understanding of the second law I recommend the comic "Max the Demon Vs Entropy of Doom" by Auerbach and Codor.

Statistical mechanics also makes a statement about the probability with which one can achieve a lowering of the entropy $\Delta S < 0$ (from $S \to S' = S + \Delta S$). An entropy decrease corresponds to a reduction of the microcanonical partition function (and hence of the number of states). One starts from $\Gamma = e^{S/k_B}$ states and ends with $\Gamma' = e^{S'/k_B} < \Gamma$. The number of states is (under microscopic time evolution) invariant, both in quantum mechanics (by unitarity) and in classical mechanics (by Liouville's theorem). Hence at most Γ' of Γ states can lead to the entropy decrease. Thus the entropy decreases with probability

$$P(\Delta S < 0) \leq \frac{\Gamma'}{\Gamma} = e^{\Delta S/k_B}\,. \tag{4.92}$$

In the thermodynamic limit one has $\Delta S \propto N$. In this limit the probability vanishes, the entropy never decreases and statistical mechanics reduces to deterministic thermodynamics, cf. (4.65).

For a microscopic change of only 1 bit one has $\Delta S = -S_{\text{Landauer}}$ and we obtain an entropy decrease with probability

$$P(\Delta S = -S_{\text{Landauer}}) \leq e^{-\ln 2} = \frac{1}{2}\,. \tag{4.93}$$

An entropy change on the order of S_{Landauer} is therefore neither forbidden nor especially unlikely in statistical mechanics.

4.6 Canonical Ensemble

We consider a thermodynamic system (with internal energy U_1) in thermal contact with a heat bath ($U_2 \gg U_1$) at temperature T. Since only heat exchange occurs, we restrict ourselves to the state variable U, the work coordinates being held fixed. The total system is closed with $U_{\text{tot}} = U_1 + U_2$. The microcanonical partition function of the total system is given by

$$\Gamma(U_{\text{tot}}) = \Gamma(U_1^*)\Gamma(U_2^*) \tag{4.94}$$

The energies U_1^*, U_2^* at equilibrium are fixed by the condition $\partial S_1(U_1^*)/\partial U_1 = \partial S_2(U_2^*)/\partial U_2 = 1/T$. However we now allow fluctuations and set $U_1 = H$ arbitrary with H the Hamiltonian of the system. Further we are interested only in the system, so we write $U = U_1$ and $S = S_1$.

If the system has energy H, the energy $U_2 = U_{\text{tot}} - H$ remains in the heat bath. The probability of finding the system in a microstate of energy $U = H$ is therefore given by the ratio

$$\rho_{\text{k}}(H) = \frac{\Gamma(U_2)}{\Gamma(U_{\text{tot}})} = \frac{1}{\Gamma(U^*)}\frac{\Gamma(U_2)}{\Gamma(U_2^*)} = e^{-S(U^*)/k_B}\,\frac{e^{S_2(U_{\text{tot}}-H)/k_B}}{e^{S_2(U_{\text{tot}}-U^*)/k_B}}\,. \tag{4.95}$$

of microstates with energy $U_{\text{tot}} - U$ in the heat bath to the total number of microstates with U_{tot} in the closed total system.

Since $H \ll U_{\text{tot}}$, we can expand the exponents in the second factor and obtain

$$S_2(U_{\text{tot}} - H) = S_2(U_{\text{tot}}) - \frac{1}{T}U + O(1/N_{\text{tot}})\,, \tag{4.96}$$

where we have used that $\partial^2 S_2/\partial U^2 = -(T^2 c_V N_{\text{tot}})^{-1} = O(1/N_{\text{tot}})$ with $N_2 \approx N_{\text{tot}}$. Hence one obtains the *canonical distribution*

$$\rho_k(H) = e^{-S(U^*)/k_B + (U^*-H)/k_B T} = e^{(F-H)/k_B T}, \quad F(T) = U^* - TS(U^*)\,. \tag{4.97}$$

We define the *canonical partition function* (the dependence on V is left implicit by assuming that the N particle positions are restricted to the volume V)

$$Z_N(\beta) = \langle e^{-\beta H}\rangle, \qquad \beta = \frac{1}{k_B T}, \tag{4.98}$$

$$= \begin{cases} \sum_n e^{-\beta E_n} & \text{(quantum mechanically)}, \\ \int d\Gamma_N\, e^{-\beta H} & \text{(classically)}, \end{cases} \tag{4.99}$$

with $\rho_\mathrm{k} = e^{-\beta H}/Z_N$. The free energy follows via

$$F(T,V,N) = -k_B T \ln Z_N(\beta)\,. \tag{4.100}$$

The canonical partition function describes a system that is in thermal contact with a heat bath. From a statistical perspective, this also shows that the free energy is the correct potential for describing such a system. In the thermodynamic limit, the microcanonical distribution (isolated system) and the canonical distribution (system in contact with a heat bath) yield the same result. For small systems, however, the fluctuations differ; these can only be calculated using statistical physics. In the canonical distribution, the internal energy U of the system fluctuates. The expectation value is given by

$$U = \overline{H} = \langle \rho_k H\rangle = \frac{1}{Z_N}\langle H e^{-\beta H}\rangle = -\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta} = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{\partial(\beta F)}{\partial \beta}\,. \tag{4.101}$$

The expectation value corresponds exactly to the Gibbs-Helmholtz relation

$$\frac{\partial(\beta F)}{\partial \beta} = F + \beta\frac{\partial F}{\partial \beta} = F - T\frac{\partial F}{\partial T} = F + TS = U \tag{4.102}$$

from thermodynamics. Statistical mechanics extends this result to a system with fluctuations.

For the generating function of the energy, we have

$$Z(\lambda) = \overline{e^{\lambda H}} = \langle \rho_k e^{\lambda H}\rangle = \frac{\langle e^{(\lambda-\beta)H}\rangle}{\langle e^{-\beta H}\rangle} = \frac{Z_N(\beta-\lambda)}{Z_N(\beta)}\,. \tag{4.103}$$

The functions $\ln Z(\lambda)$ and $\ln Z_N(\beta-\lambda)$ thus differ only by an additive constant that is independent of λ. For the calculation of the cumulants, this constant is irrelevant. Moreover, the derivative of $\ln Z_N(\beta-\lambda)$ with respect to λ at $\lambda = 0$ corresponds to a derivative of $\ln Z_N(\beta)$ with respect to $-\beta$ (without subsequently setting $\beta = 0$). For this reason, $\ln Z_N(\beta)$ is also referred to as the cumulant-generating function of the energy with respect to $-\beta$.

With these preliminary considerations, we compute the mean-square fluctuation of the energy

$$\begin{aligned}(\delta H)^2 &= \frac{\partial^2 \ln Z_N(\beta)}{\partial \beta^2} = -\frac{\partial^2(\beta F)}{\partial \beta^2} \overset{(4.102)}{=} -\left(\frac{\partial U}{\partial \beta}\right)_{V,N} = k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{V,N} \\ &= k_B T^2 N c_V\,.\end{aligned} \tag{4.104}$$

as the second derivative of $\ln Z_N(\beta)$ with respect to $-\beta$. Thus, for the relative deviation ($u = U/N$ is the internal energy per particle),

$$\frac{\delta H}{U} = \sqrt{\frac{k_B T^2 c_V}{u^2 N}} \sim \frac{1}{N^{1/2}}\,. \tag{4.105}$$

Note that the derivation of the canonical ensemble only requires that the bath be large ($N_{\text{tot}} \to \infty$). In statistical mechanics, one can study systems with finite N (one may even set $N = 1$). Such systems exhibit fluctuations. Only in the thermodynamic limit do the *relative deviations* vanish and the theory become deterministic.

The relation (4.104) is the first example of a *fluctuation-dissipation relation*. It connects the fluctuations (here of E) with response quantities (here c_V). In computer simulations, it is often easier to determine δE and then compute the specific heat via

$$c_V = \frac{(\delta E)^2}{k_B T^2 N} \tag{4.106}$$

The calculation of the canonical partition function is typically much simpler than that of the microcanonical partition function because it does not restrict to a single energy. Hence, in applications one usually chooses the canonical approach.

Example 5: (Configuration integral)

In classical statistical mechanics of N-particle systems, the Hamiltonian often takes the form $H = \sum_i \boldsymbol{p}_i^2/2m + U_{\text{pot}}(\boldsymbol{x}_1, \dots)$, see (1.7). The integral over the momenta can then be evaluated for an arbitrary potential. One obtains

$$Z_N = \frac{Q}{h^{3N}} \overbrace{\int d^{3N}p\, e^{-\beta \sum_i \boldsymbol{p}_i^2/2m}}^{(2\pi m k_B T)^{3N/2}} = \frac{Q}{\lambda^{3N}} \tag{4.107}$$

with the *configuration integral*

$$Q = \frac{1}{N!} \int d^{3N}x\, e^{-\beta U_{\text{pot}}(x)} \tag{4.108}$$

and the *thermal wavelength*

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}\,. \tag{4.109}$$

For an electron, for instance,

$$\lambda = \frac{74.5\,\text{nm}}{\sqrt{T\,[\text{K}]}}\,. \tag{4.110}$$

Example 6: (Ideal gas)

Returning once more to the ideal gas. In this case, the configuration integral is trivial, with

$$Q = \frac{V^N}{N!}\,. \tag{4.111}$$

For the free energy one then finds

$$F = -k_B T \ln Z_N = -N k_B T \ln\Big(\frac{V}{N\lambda^3}\Big) - N k_B T\,. \tag{4.112}$$

From this, for example, the entropy (4.42) follows by differentiation with respect to $-T$.

Example 7: (Maxwell-Boltzmann distribution)

For a classical ideal gas in an external potential U_{ext}, we obtain the distribution

$$\rho_k = \frac{1}{Z_N} \exp\left[-\beta \sum_i \left(\frac{\boldsymbol{p}_i^2}{2m} + U_{\text{ext}}(\boldsymbol{x}_i) \right)\right] . \tag{4.113}$$

If one is interested only in the position $\boldsymbol{x}$ and momentum $\boldsymbol{p}$ of a single particle, one needs only the marginal distribution (after integrating over the remaining variables). Since the particles are independent (the distribution is a product), the marginal distribution is simply one of the factors. We thus obtain the Maxwell-Boltzmann distribution

$$\rho_{\text{MB}}(\boldsymbol{x}, \boldsymbol{p}) = \frac{1}{Z_1} \exp\left[-\beta \left(\frac{\boldsymbol{p}^2}{2m} + U_{\text{ext}}(\boldsymbol{x}) \right)\right] . \tag{4.114}$$

Example 8: (Equipartition theorem)

Consider a (classical) Hamiltonian system with f degrees of freedom. Let $(x_1, ..., x_{2f}) = (q_1, p_1, \dots, q_f, p_f)$ with q and p the conjugate variables. Then the *equipartition theorem* holds:

$$\begin{aligned} \overline{x_i \frac{\partial H}{\partial x_j}} &= \int \frac{d\Gamma_N}{Z_N} x_i \overbrace{\frac{\partial e^{-\beta H}}{(-\beta)\,\partial x_j}}^{(\partial_{x_j} H) e^{-\beta H}} = \overbrace{\int \frac{d\Gamma_N}{Z_N} \frac{\partial (x_i e^{-\beta H})}{(-\beta)\,\partial x_j}}^{0} - \int \frac{d\Gamma_N}{Z_N} e^{-\beta H} \frac{\partial x_i}{(-\beta)\,\partial x_j} \\ &= k_B T \delta_{ij} , \end{aligned} \tag{4.115}$$

where we have neglected boundary terms under the assumption that the Hamiltonian confines the system to a finite part of phase space.

For the Hamiltonian $H = K + U_{\text{pot}} = \sum_{i=1}^{3N} p_i^2/2m + U_{\text{pot}}(q)$ from Example 5, we can apply the equipartition theorem to the kinetic energy. We obtain

$$k_B T \delta_{ij} = \overline{p_i \frac{\partial H}{\partial p_j}} = \frac{\overline{p_i p_j}}{m} . \tag{4.116}$$

Thus the mean kinetic energy $\overline{p_i^2/2m}$ of each degree of freedom is given by $k_B T/2$. Altogether, therefore,

$$\overline{K} = \frac{3}{2} N k_B T = \frac{1}{2} f k_B T \tag{4.117}$$

with $f = 3N$ the number of degrees of freedom. With the virial theorem (1.32) for the ideal gas, the thermal equation of state

$$N k_B T = pV . \tag{4.118}$$

follows. For an interacting system, (1.33) leads to the thermal equation of state

$$N k_B T = pV + \frac{1}{3} \sum_j \overline{\boldsymbol{x}_j \cdot \frac{\partial U_{\text{ww}}}{\partial \boldsymbol{x}_j}(\boldsymbol{x}_1, \dots)} . \tag{4.119}$$

Thus the ideal gas law is extended by the virial as an additional term. Expanding the virial in powers of the particle density $n = N/V$ yields the so-called virial expansion.

Example 9: (Degrees of freedom)

For a classical, harmonic system with Hamiltonian $H = \sum_{i=1}^{f_p} p_i^2/2m_i + \sum_{i=1}^{f_q} k_i q_i^2/2$, the equipartition theorem implies that each of the $f = f_p + f_q$ degrees of freedom carries a mean energy of $\frac{1}{2}k_B T$ (the proof for the potential part is analogous to the kinetic part in the previous example). The same holds also for the more general kinetic energy $p^2/2m(q)$ where the mass depends on the coordinates $q_1, q_2, \ldots$. It follows that

$$U = \overline{H} = \frac{1}{2} f k_B T \tag{4.120}$$

with f the number of degrees of freedom. Thus, for the specific heat $C_V = N c_V = \frac{1}{2} f k_B$ the system becomes a thermally and calorically perfect gas with adiabatic exponent

$$\gamma = \frac{c_V + k_B}{c_V} = \frac{f + 2N}{f} = 1 + \frac{2N}{f}\,. \tag{4.121}$$

For example, an ideal gas has three kinetic degrees of freedom per particle ($f = f_p = 3N$).

Example 10: (Diatomic molecules)

For (light) diatomic molecules (H_2, N_2, O_2) without interactions, in addition to the three kinetic degrees of freedom (per molecule) there are rotational degrees of freedom. Such a molecule possesses two rotational degrees of freedom whose quadratic kinetic energy is given by $L^2/2I = (p_\theta^2 + p_\phi^2/\sin^2\theta)/2I$, where p_θ, p_ϕ are the momenta conjugate to the angles (θ, ϕ). The angles (θ, ϕ) parametrize the unit vector of the connecting line $\boldsymbol{e} = (\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta)$. Thus the system behaves like a thermally and calorically perfect gas with $f = f_p = (3+2)N = 5N$ degrees of freedom.

Of course, vibrational degrees of freedom also exist. For light molecules, however, these are frozen out at room temperature due to quantum-mechanical effects, as will be discussed later. For heavy molecules (Br_2) or at high temperatures, the vibration along the connecting line can be excited. This vibration contributes two further degrees of freedom per molecule (one each for potential and kinetic energy), so that $f_q = \Delta f_p = N$ and in total $f = f_p + f_q = 6N + N = 7N$ degrees of freedom occur.

Statistical interpretation of heat: In statistical mechanics (canonical ensemble at temperature T), the entropy is given by the Gibbs expression

$$S = -k_B \sum_i p_i \ln p_i, \qquad p_i = e^{-\beta H_i}/Z_N = e^{\beta(F-H_i)} \tag{4.122}$$

Each microstate i is assumed with probability p_i and corresponds to a fixed energy value $E_i = H_i$. The internal energy of thermodynamics is obtained as the expectation value

$$U = \overline{H} = \sum_i p_i H_i \,, \tag{4.123}$$

see (4.101). Thus the entire thermodynamics—including the notions of work and heat—is fixed.

In thermodynamics, heat δQ for a quasistatic process was defined via the first law as $\delta Q = dU - \delta W$, given knowledge of δW. In statistical mechanics, one reverses this logic and defines heat by ($-k_B T \ln p_i = H_i - F$)

$$\delta Q = TdS = -k_B T \sum_i (1 + \ln p_i) dp_i = \sum_i H_i dp_i \,. \tag{4.124}$$

Here we used that $\sum_i dp_i = 0$, because $\sum_i p_i = 1$.

Considering changes in the internal energy, we obtain

$$dU = \sum_i p_i dH_i + \sum_i H_i dp_i = \delta W + \delta Q \,. \tag{4.125}$$

The work $\delta W = \sum_i p_i dH_i$ corresponds here to reversible changes of the internal energy (without altering the probabilities). The heat for the process is given by $\delta Q = \sum_i H_i dp_i$.

Gibbs' variational principle: We motivated the microcanonical distribution by noting that while we possess knowledge of the macrostate, we are completely ignorant of the concrete microstate. One can make this "principle of insufficient reason," originally formulated by Laplace, somewhat more precise. To this end, we seek the probability distribution p_i on the microstates i that maximizes the Gibbs entropy (Gibbs' variational principle). We thus determine the extremum of $S = -k_B \sum_i p_i \ln p_i$ subject to the constraint $\sum_i p_i = 1$. This implies (λ is the Lagrange multiplier)

$$0 = d(S/k_B - \lambda \sum_i p_i) = -\sum_i (\ln p_i + 1 + \lambda) dp_i \,. \tag{4.126}$$

Hence

$$p_i = e^{-1-\lambda} = \text{is constant.}, \tag{4.127}$$

which corresponds exactly to the microcanonical distribution (uniform distribution over the microstates). That the extremum is indeed a maximum follows from the concavity of $-p \ln p$.

In the canonical distribution, we do not fix the internal energy U but allow heat exchange. However, the constraint

$$U = \overline{H} = \sum_i p_i H_i \,. \tag{4.128}$$

holds. To find the extremum of S we therefore need a second Lagrange multiplier β. We obtain

$$0 = d(S/k_B - \lambda \sum_i p_i - \beta \sum_i H_i p_i) = -\sum_i (\ln p_i + 1 + \lambda + \beta H_i) dp_i \,, \tag{4.129}$$

with the result

$$p_i = e^{-1-\lambda-\beta H_i} \propto e^{-\beta H_i}, \tag{4.130}$$

which corresponds exactly to the canonical distribution, with $\beta = 1/k_B T$.

Thus statistical mechanics can be understood more deeply via the "principle of insufficient reason." Since one cannot uniquely determine the microstate from knowledge of the work coordinates alone, one simply assumes that the system is in the state of maximal entropy (given the knowledge about the system). This corresponds exactly to the typical configurations of Shannon. Even though one has no knowledge of the microstate, one can still make statements about measured quantities, since typical sequences for large systems occur with probability 1. In particular, there are quantities whose relative fluctuations vanish in the thermodynamic limit of large systems, so that one can even make deterministic statements.

One can easily extend Gibbs' variational principle by allowing fluctuations in other work coordinates. For example, one can imagine that the system is in contact with a work medium that permits volume changes and fixes the pressure only on average. One sees directly that the additional Lagrange multipliers correspond exactly to the equilibrium quantities g_α. For the work coordinate Z with equilibrium quantity g, one then obtains the probability distribution

$$p_i \propto e^{-\beta(H_i - g Z_i)} \,. \tag{4.131}$$

That this corresponds, in the thermodynamic limit, exactly to a switch from Z to g via a Legendre transformation—and hence that thermodynamics is equivalent—follows from the next section.

4.7 Equivalence of ensembles

We first prove a general result that links the Legendre transformation to the Laplace transformation. Applying this then shows, among other things, that in the thermodynamic limit the microcanonical ensemble yields the same results as the canonical ensemble.

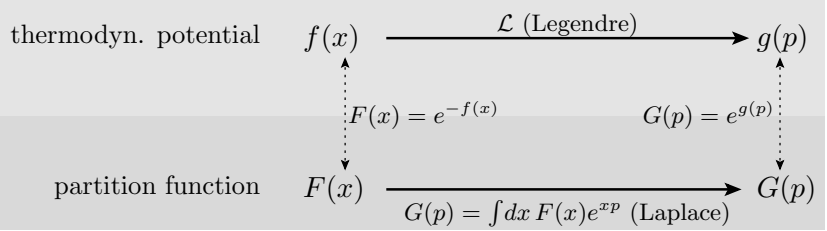


Fig. 4.1: Connection between the Legendre transformation in thermodynamics and the Laplace transformation in statistical mechanics: a switch from x to p as natural variables corresponds to a Laplace transformation on the respective partition functions; up to corrections that vanish in the TDL.

Given an extensive quantity $x \propto N$ for $N \to \infty$, let $f(x)$ be a convex function that is also extensive. Further, define the associated "partition function" $F(x) = e^{-f(x)}$. Then, in the thermodynamic limit $N \to \infty$, a Laplace transformation from $F(x)$ to $G(p)$ corresponds exactly to a Legendre transformation from $f(x)$ to $g(p) = \ln G(p)$ (up to subdominant corrections $O(\ln N)$), see Figure 4.1. In formulas,

$$G(p) = \int dx\, F(x) e^{xp} \quad \Rightarrow \quad g = \mathcal{L}f \text{ with } F(x) = e^{-f(x)}, G(p) = e^{g(p)}\,. \tag{4.132}$$

We now turn to the proof: The function $xp - f(x)$, by the convexity of f, has for each p a well-defined maximum at x^*, see Section 2.4. Thus the integrand $e^{xp-f(x)}$ is dominated by values near this maximum. To second order we obtain

$$xp - f(x) = \overbrace{x^* p - f(x^*)}^{\mathcal{L}f} + \overbrace{(p - f'(x^*))}^{0}(x - x^*) - \frac{1}{2} f''(x^*)(x - x^*)^2\,. \tag{4.133}$$

From extensivity it further follows that $f'' \propto 1/N$. With this approximation (saddle-point approximation), the Laplace transformation can be evaluated explicitly, yielding the result

$$G(p) = e^{\mathcal{L}f} \int dx\, e^{-\frac{1}{2} f''(x^*)(x-x^*)^2} = e^{\mathcal{L}f}\, O(1/f''(x^*)^{1/2}) = e^{\mathcal{L}f}\, O(N^{1/2})\,. \tag{4.134}$$

We obtain

$$g(p) = \ln G(p) = \overbrace{\mathcal{L}f}^{O(N)} + O(\ln N)\,, \tag{4.135}$$

which is what we wished to prove.

Remark: The saddle-point approximation restricts the integral to a region $\delta x = x - x^* \simeq N^{1/2}$. Further, $x^* \propto N$ holds by extensivity. Thus not the fluctuations in x, but only the relative fluctuations become small, see (4.55) and (4.105).

Note: In applications, the integral is often not over all real numbers but only over a subregion. As long as $x^* \pm \delta x$ lies in the integration region, the result continues to

hold. For a similar reason one may replace the integral by a sum over the integers (in the thermodynamic limit many integers lie in the region $x^* \pm \delta x$ and the integrand varies slowly).

Microcanonical and canonical ensembles: There holds the relation

$$\int dU\, \frac{\Gamma(U)}{\Delta} e^{-\beta U} = \int dU\, \frac{\overbrace{\langle \delta_\Delta(U-H) e^{-\beta U}\rangle}^{\approx \delta_\Delta(U-H)e^{-\beta H}}}{\Delta} = \langle e^{-\beta H}\rangle = Z_N(\beta) \tag{4.136}$$

between the canonical and microcanonical partition functions, where we used that $\int dU\, \delta_\Delta(U-H) = \Delta$. Thus the partition functions are linked by a Laplace transformation (the additional factor $1/\Delta$ is unimportant since it only corresponds to a constant shift $\ln \Delta$ of the potentials).

It remains only to choose the functions f, F, g, G and the variables x, p from the theorem (4.132) appropriately in order to show that

$$(-\beta)F(\beta) = \max_U \Big((-\beta)U - \frac{-S(U)}{k_B} \Big) = \max_U \Big(\frac{S(U)}{k_B} - \beta U \Big)\,. \tag{4.137}$$

which (after division by $(-\beta)$) is equivalent to the (standard) result

$$F(\beta) = \min_S \Big(U(S) - \frac{-S}{(-\beta)k_B} \Big) = \min_S \Big(U(S) - TS \Big) \tag{4.138}$$

from (2.48). Thus F and S are linked by a Legendre transformation in the thermodynamic limit, and the two ensembles yield the same results. One says that the ensembles are *equivalent*.

The required connection is provided by $(x \mapsto U, p \mapsto -\beta)$

$$\begin{aligned} f(x) &\mapsto -S(U)/k_B = -\ln \Gamma(U), & F(x) &\mapsto \Gamma(U), \\ g(p) &\mapsto (-\beta)F(\beta) = \ln Z_N(\beta), & G(p) &\mapsto Z_N(\beta)\,, \end{aligned} \tag{4.139}$$

thus proving the equivalence of the ensembles in the thermodynamic limit.

4.8 Grand canonical ensemble

As we saw in the previous section, one can introduce new ensembles by switching from an extensive work coordinate to the corresponding intensive equilibrium quantity. Physically, this corresponds to coupling the system to a reservoir. In applications, particle reservoirs are important, so we carry out the procedure explicitly for this case.

Consider a system coupled both to a heat bath (at temperature T) and to a particle reservoir (with chemical potential μ). Physically, the two reservoirs can naturally

be realized by the same system. We can obtain the *grand canonical distribution* analogously to the derivation of equation (4.95). Equivalently, from Gibbs' variational principle (4.131) (with $g \mapsto \mu, Z \mapsto N$) we obtain the result

$$\rho_{\text{gk}} = \frac{e^{-\beta(H-\mu N)}}{\mathcal{Z}} \,. \tag{4.140}$$

The grand canonical partition function

$$\mathcal{Z}(\beta, z) = \sum_N z^N Z_N(\beta) = \langle e^{-\beta(H-\mu N)} \rangle, \qquad \text{with the } \textit{fugacity } z = e^{\beta\mu} \tag{4.141}$$

is related to the grand potential by

$$\Omega(T, V, \mu) = -k_B T \ln \mathcal{Z}(\beta, z) \,. \tag{4.142}$$

The logarithm of the partition function $\ln \mathcal{Z}(\beta, z)$ is the cumulant-generating function of the energy (with respect to $-\beta$) and of the particle number (with respect to $\ln z$), cf. Eq. (4.103). We obtain[13]

$$U = \overline{H} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \quad \text{and} \quad N = \overline{N} = \frac{\partial \ln \mathcal{Z}}{\partial \ln z} = z \frac{\partial \ln \mathcal{Z}}{\partial z} \tag{4.143}$$

The particle number is fixed only on average in the grand canonical ensemble. For the mean-square fluctuation we find

$$(\delta N)^2 = \frac{\partial^2 \ln \mathcal{Z}}{(\partial \ln z)^2} = \left(\frac{\partial N}{\partial(\beta\mu)} \right)_{\beta,V} = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{\beta,V} \overset{(2.62)}{=} \frac{N^2}{V} \kappa_T k_B T \,. \tag{4.144}$$

In the thermodynamic limit, the relative fluctuations thus vanish with $\delta N/N \propto 1/N^{1/2}$, as is already known from the equivalence of ensembles.

Remark: The grand canonical ensemble requires that one perform the partition sum over systems with arbitrary particle number N. In quantum mechanics this corresponds to taking the trace over the *Fock space*

$$\mathcal{F} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N \,. \tag{4.145}$$

The direct sum runs over the vacuum state $\mathcal{H}_0 = \mathbb{C}$, the one-particle Hilbert space $\mathcal{H}_1 = \mathcal{H}$, the two-particle Hilbert space $\mathcal{H}_2$, ... In nature, not all states in the product space

$$\mathcal{H}_N = \mathcal{H}^{\otimes N} = \underbrace{\mathcal{H} \otimes \cdots \otimes \mathcal{H}}_{N\text{-factors}} \tag{4.146}$$

[13] We denote by N both the random variable and the expectation value. The meaning should be clear from the context.

are realized. Only the symmetric (for bosons) or antisymmetric (for fermions) subspaces with

$$\psi_N(\dots,\boldsymbol{x}_i,\dots,\boldsymbol{x}_j,\dots) = \psi_N(\dots,\boldsymbol{x}_j,\dots,\boldsymbol{x}_i,\dots) \qquad \text{(bosons)}, \tag{4.147}$$

$$\psi_N(\dots,\boldsymbol{x}_i,\dots,\boldsymbol{x}_j,\dots) = -\psi_N(\dots,\boldsymbol{x}_j,\dots,\boldsymbol{x}_i,\dots) \qquad \text{(fermions)}. \tag{4.148}$$

are allowed. A general state in Fock space has the form

$$\Psi = (\psi_0, \psi_1, \psi_2, \dots) \tag{4.149}$$

with the scalar product

$$\langle\Psi|\Phi\rangle = \sum_N \langle\psi_N|\phi_N\rangle_{\mathcal{H}_N}\,. \tag{4.150}$$

Here $|\psi_0|^2$ is the probability that the system is in the vacuum state. The probability density to find N particles at positions $\boldsymbol{x}_1,\dots,\boldsymbol{x}_N$ in the system is accordingly $|\psi_N(\boldsymbol{x}_1,\dots,\boldsymbol{x}_N)|^2$ To compute the grand canonical partition function $\mathcal{Z} = \mathrm{Tr}_{\mathcal{F}}(e^{-\beta(H-\mu N)}) = \sum_N z^N \,\mathrm{Tr}_{\mathcal{H}_N}(e^{-\beta H_N}) = \sum_N z^N Z_N$ one needs the particle-number operator

$$N\Psi = (0, \psi_1, 2\psi_2, \dots) \tag{4.151}$$

and the Hamiltonian on Fock space

$$H\Psi = (0, H_1\psi_1, H_2\psi_2, \dots) \tag{4.152}$$

as functions of the Hamiltonians H_N on the N-particle Hilbert space.

Chapter 5

Quantum Gases

5.1 Rotations of Diatomic Molecules

In Example 4.10 we saw that the rotations of a diatomic molecule classically contribute $H = L^2/2I$ to the specific heat via k_B. The equipartition theorem no longer holds in quantum statistics. The reason is that degrees of freedom can *freeze out*, as we will see in the following.

Quantum mechanically, the Hamiltonian has the spectrum

$$\begin{aligned} &H|l,m\rangle = E_l|l,m\rangle, && |m| \le l,\ l \in \{0,1,\dots\} \\ &E_l = \frac{\hbar^2}{2I} l(l+1)\,. \end{aligned} \tag{5.1}$$

We now compute the partition function[1]

$$Z = Z(\alpha) = \sum_{l,m} e^{-\beta E_{l,m}} = \sum_l (2l+1) e^{-\alpha l(l+1)}, \qquad \alpha = \frac{\hbar^2}{2Ik_BT}\,. \tag{5.2}$$

From this one obtains the specific heat

$$c_V = \frac{\partial U}{\partial T} = -\frac{\partial^2 \ln Z}{\partial T \partial \beta} = k_B \alpha^2 \frac{d^2 \ln Z}{d\alpha^2}\,. \tag{5.3}$$

The dimensionless quantity α distinguishes between high $T \gg T^* = \hbar^2/Ik_B$ ($\alpha \ll 1$) and low temperatures $T \ll T^*$. At low temperatures ($\alpha \gg 1$) only the first terms contribute and one has

$$Z(\alpha) \simeq 1 + 3e^{-2\alpha}, \qquad c_V \simeq 12 k_B \alpha^2 e^{-2\alpha}\,. \tag{5.4}$$

Thus the rotations freeze out exponentially at low temperatures with $c_V \sim e^{-T^*/T}$.

[1] Since we have only one particle there is of course no distinction between canonical and grand canonical.

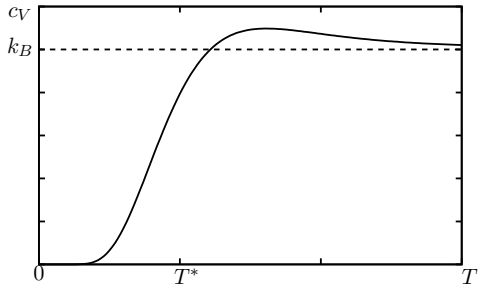


Fig. 5.1: The specific heat of a diatomic molecule as a function of temperature. At low temperatures it is exponentially suppressed and at high temperatures approaches the result k_B from the equipartition theorem. The temperature dependence is anomalous with nonmonotonic behavior.

At high temperatures the sum goes over into a Riemann integral with

$$Z = \int_0^\infty (2l+1) e^{-\alpha l(l+1)}\, dl = -\frac{1}{\alpha} \underbrace{\int_0^\infty \frac{d}{dl} e^{-\alpha l(l+1)}\, dl}_{-1} \,. \tag{5.5}$$

Hence $Z \simeq 1/\alpha$ and $c_V \simeq k_B$, which exactly matches the classical value for two degrees of freedom from the equipartition theorem.

It is interesting that the transition from the value $c_V = k_B$ at high temperatures to the exponential suppression does not proceed monotonically. We can improve the high-temperature result by using the Euler-Maclaurin formula

$$\sum_{l=0}^\infty f(l) \simeq \int_0^\infty dl\, f(l) + \frac{1}{2} f(0) - \frac{1}{12} f'(0) + \frac{1}{720} f'''(0) \tag{5.6}$$

We obtain

$$Z = \frac{1}{\alpha}\Big(1 + \frac{1}{3}\alpha + \frac{1}{15}\alpha^2 + \cdots\Big), \qquad c_V = k_B\Big(1 + \frac{1}{45}\alpha^2 + \cdots\Big)\,. \tag{5.7}$$

Thus there is an *anomaly* of the specific heat: it first increases before being suppressed.

5.2 Phonon Gas

Consider a solid with N atoms. The atoms of mass M are arranged at equilibrium positions $\boldsymbol{r}_i$ $(i = 1, \ldots, N)$ in a cubic crystal lattice. For small deviations $\boldsymbol{u}_i = (u_{i,\alpha})_{\alpha=1,2,3}$ from the equilibrium positions one may expand the energy to quadratic order. One obtains the Hamiltonian

$$H = \sum_i \frac{\boldsymbol{p}_i^2}{2M} + \frac{1}{2} M \sum_{\substack{i,j \\ \alpha,\beta}} D_{\alpha\beta}(\boldsymbol{r}_i - \boldsymbol{r}_j) u_{i,\alpha} u_{j,\beta} \tag{5.8}$$

with $\boldsymbol{p}_i = M\dot{\boldsymbol{u}}_i$ the canonical momentum conjugate to $\boldsymbol{u}_i$. The *dynamical matrix* D is symmetric $D_{\alpha\beta}(\boldsymbol{r}) = D_{\beta\alpha}(-\boldsymbol{r})$, positive semidefinite, and depends, because of translational symmetry, only on $\boldsymbol{r}_i - \boldsymbol{r}_j$.

Important are the eigenmodes and eigenfrequencies, which diagonalize the problem. To this end we determine the $3N$-solution $\boldsymbol{u}_i^{(\nu)}$ of the eigenvalue equation

$$\sum_{j,\alpha} D_{\alpha\beta}(\boldsymbol{r}_i - \boldsymbol{r}_j) u_{j,\beta}^{(\nu)} = \omega_\nu^2 \, u_{i,\alpha}^{(\nu)} \,, \qquad \nu = 1, 2, \cdots, 3N \,. \tag{5.9}$$

with eigenfrequencies ω_ν. The eigenmodes are related to the original degrees of freedom by an orthogonal principal-axis transformation. With respect to the eigenmodes the Hamiltonian separates. We set $\boldsymbol{u}_i = \sum_\nu q_\nu \boldsymbol{u}_i^{(\nu)}$ and obtain[2]

$$H = \sum_{\nu=1}^{3N} H_\nu = \sum_{\nu=1}^{3N} \left(\frac{p_\nu^2}{2M} + \frac{1}{2} M \omega_\nu^2 q_\nu^2 \right) \tag{5.10}$$

with $p_\nu = M \dot{q}_\nu$.

Each term H_ν is a harmonic oscillator with the spectrum

$$E_{n_\nu} = \hbar\omega_\nu \left(n_\nu + \frac{1}{2} \right) , \qquad n_\nu = 0, 1, 2, \ldots \,. \tag{5.11}$$

The total spectrum is therefore given by

$$E_{n_1, \cdots, n_{3N}} = \sum_\nu E_{n_\nu} = \sum_\nu \hbar\omega_\nu \left(n_\nu + \frac{1}{2} \right) \,. \tag{5.12}$$

To obtain the thermodynamics at temperature T we compute the canonical partition function

$$\begin{aligned} Z &= \sum_{n_1, \cdots, n_{3N}} e^{-\beta E_{n_1, \cdots, n_{3N}}} = \left(\sum_{n_1} e^{-\beta E_{n_1}} \right) \cdots \left(\sum_{n_{3N}} e^{-\beta E_{n_{3N}}} \right) \\ &= \prod_\nu Z_\nu, \qquad\qquad Z_\nu = \sum_{n_\nu=0}^{\infty} e^{-\beta E_{n_\nu}} \,. \end{aligned} \tag{5.13}$$

Note that the factorization of the partition function into the contributions of the individual eigenmodes is a general property of a system composed of noninteracting subsystems. As a consequence the (free) energy becomes a sum over the subsystems.

We only need to compute the partition function Z_ν of a single eigenmode (harmonic oscillator), with the result

$$Z_\nu = \sum_{n_\nu=0}^{\infty} e^{-\beta\hbar\omega_\nu (n_\nu + \frac{1}{2})} = e^{-\beta\hbar\omega_\nu/2} \frac{1}{1 - e^{-\beta\hbar\omega_\nu}} = \left[2 \sinh \left(\frac{\hbar\omega_\nu}{2 k_B T} \right) \right]^{-1} \,. \tag{5.14}$$

[2] Because of the orthogonality of the transformation one has $\sum_i \boldsymbol{u}_i^{(\nu)} \cdot \boldsymbol{u}_i^{(\nu')} = \delta_{\nu\nu'}$.

The internal energy is therefore given by

$$U = -\frac{\partial \ln Z}{\partial \beta} = \sum_\nu \frac{\partial}{\partial \beta} \ln\left[2\sinh(\beta\hbar\omega_\nu/2)\right] = \sum_\nu \frac{1}{2}\hbar\omega_\nu \coth\left(\frac{\hbar\omega_\nu}{2k_BT}\right)$$
$$= \sum_\nu \hbar\omega_\nu \left(\overline{n_\nu} + \frac{1}{2}\right) \tag{5.15}$$

with the mean occupation number (*Bose-Einstein distribution*)

$$\overline{n_\nu} = \frac{1}{e^{\hbar\omega_\nu/k_BT} - 1}\,. \tag{5.16}$$

At high temperatures $k_BT \gg \hbar\omega_\nu$ the occupation number goes over into

$$\overline{n_\nu} = \frac{k_BT}{\hbar\omega_\nu}\,. \tag{5.17}$$

In this limit we obtain the heat capacity (*Dulong-Petit law*)

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} k_BT \sum_{\nu=1}^{3N} = 3Nk_B\,. \tag{5.18}$$

Thus at high temperatures we recover the result from the equipartition theorem.

At low temperatures some of the degrees of freedom freeze out. To compute the heat capacity we need the eigenfrequencies ω_ν. Because of translational invariance the eigenvalue problem is already diagonal in Fourier space, so that only the diagonalization of the 3×3-matrix

$$\tilde{D}_{\alpha\beta}(\boldsymbol{k}) = \sum_i e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_i} D_{\alpha\beta}(\boldsymbol{r}_i) \tag{5.19}$$

remains. The system then has three polarizations and the eigenfrequencies are given by $\omega_\lambda(\boldsymbol{k})$, $\lambda = 1, 2, 3$.

An important property of the system is that the energy does not change under a homogeneous displacement $\boldsymbol{u}_i = \boldsymbol{d}$ of the crystal. From this it follows

$$0 = \sum_i D(\boldsymbol{r}_i) = \tilde{D}(\boldsymbol{k} = 0) \tag{5.20}$$

and hence the Goldstone theorem $\omega_\lambda(\boldsymbol{k} \to 0) \to 0$. The excitations are therefore (linear) sound modes

$$\omega_\lambda(\boldsymbol{k}) = \begin{cases} s_\parallel|\boldsymbol{k}|, & \text{longitudinal mode with } \boldsymbol{u} \parallel \boldsymbol{k}, \\ s_\perp|\boldsymbol{k}|, & \text{transverse mode with } \boldsymbol{u} \perp \boldsymbol{k}, \end{cases} \tag{5.21}$$

where the sound velocities $s_\perp$ of the two transverse modes are equal by symmetry.[3] The linear dispersion relations are of course valid only for small $\boldsymbol{k}$.

We consider the system in a box of volume $V = L^3$. The quantization of the $\boldsymbol{k}$ modes is $\boldsymbol{k} = (2\pi/L)\boldsymbol{n}$, as in Example 4.2 (with periodic boundary conditions). We obtain the internal energy

$$U = V \int \overbrace{\frac{d^3k}{(2\pi)^3}}^{k^2\,dk/2\pi^2} \sum_\lambda \hbar\omega_\lambda(\boldsymbol{k}) \left(\overline{n_{\boldsymbol{k},\lambda}} + \frac{1}{2}\right) = V \int \frac{dk}{2\pi^2} k^2 \sum_\lambda \hbar\omega_\lambda(\boldsymbol{k}) \overline{n_{\boldsymbol{k},\lambda}} + U_0\,, \quad (5.22)$$

where U_0 is the zero-point energy. We determine the excitation energy relative to U_0 by changing variables from $k = |\boldsymbol{k}|$ to ω. We obtain[4]

$$U = V \int_0^\infty \frac{d\omega}{2\pi^2} \frac{3\hbar\omega^3}{s^3} \frac{1}{e^{\hbar\omega/k_BT} - 1} = \frac{3}{2\pi^2} \frac{V k_B^4 T^4}{\hbar^3 s^3} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^2}{10} \frac{V k_B^4 T^4}{\hbar^3 s^3}, \quad (5.23)$$

with s the "mean" sound velocity defined by

$$\frac{1}{s^3} = \frac{1}{3} \sum_\lambda \frac{1}{s_\lambda^3} = \frac{2}{3s_\perp^3} + \frac{1}{3s_\parallel^3}\,. \quad (5.24)$$

The heat capacity of the phonon gas (at low temperatures) is therefore given by

$$C_V = \frac{\partial U}{\partial T} = \frac{2\pi^2}{5} k_B V \left(\frac{k_BT}{\hbar s}\right)^3\,. \quad (5.25)$$

The linearization of the spectrum in (5.21) is of course valid only for small energies and hence low temperatures. In fact it turns out that (5.25) lies above the classical Dulong-Petit value at high temperatures. The problem is that in the integral (5.23) there occur frequencies for which the linearization is no longer valid. Debye therefore proposed to replace the upper limit of the integral by the *Debye frequency*

$$\omega_D = \left(\frac{6\pi^2 s^3 N}{V}\right)^{1/3} \quad (5.26)$$

chosen so that for $T \gg \hbar\omega_D/k_B$, as desired, the Dulong-Petit law holds.[5] The Debye energy $\hbar\omega_D$ plays in the phonon gas a role analogous to the Fermi energy ε_F in the theory of the Fermi gas, in that it separates the high-temperature (classical) regime from the low-temperature (quantum) regime.

[3] The dynamical matrix has the general Taylor expansion $D_{\alpha\beta}(\boldsymbol{k}) = \lambda \boldsymbol{k}^2 \delta_{\alpha\beta} + \mu k_\alpha k_\beta + O(k^3)$ with the Lamé constants λ, μ. The Goldstone theorem ensures that the linear term vanishes. The linear term is forbidden by semidefiniteness ($D \geq 0$). The quadratic term can be parametrized by the two (Lamé) constants μ, λ with $\lambda \geq 0$ and $\lambda + \mu \geq 0$ because of $D \geq 0$. The sound velocities are then given by $s_\parallel = \sqrt{\lambda + \mu}$ and $s_\perp = \sqrt{\lambda}$.

[4] We use the result $\int_0^\infty dx\, x^3/(e^x - 1) = \pi^4/15$.

[5] One obtains the result with $\int_0^{\hbar\omega_D/k_BT} dx\, x^3/(e^x - 1) \simeq \int_0^{\hbar\omega_D/k_BT} x^2 \simeq \frac{1}{3}(\hbar\omega_D/k_BT)^3$ for $k_BT \gg \hbar\omega_D$.

5.3 Blackbody Radiation

The theory of blackbody radiation, also called cavity radiation, has many similarities with the phonon gas from the previous section. The system consists of a cavity (vacuum) surrounded by walls at temperature T. By absorption and emission of photons the walls thermalize with the photon gas in the cavity. The photons correspond to the quantized modes of the wave equation, which one obtains from the Maxwell equations in vacuum. Each eigenfrequency ω_ν corresponds to a harmonic oscillator that in equilibrium has the mean occupation $\overline{n_\nu} = 1/(\exp(\hbar\omega_\nu/k_BT) - 1)$.

There are essential differences between the phonon gas and the photon gas. On the one hand the speed of the photons is always the speed of light c, on the other hand, because of $\boldsymbol{\nabla} \cdot \boldsymbol{E} = 0$, there are only the two transverse modes. Thus in this case for the mean velocity (from Eq. (5.24)) we have

$$\frac{1}{s^3} = \frac{2}{3c^3}, \qquad \text{and hence} \qquad s = \left(\frac{3}{2}\right)^{1/3} c\,. \tag{5.27}$$

The spectrum is linear without a cutoff frequency ω_D. From (5.27) and (5.23) one obtains the *Stefan-Boltzmann law*

$$U = \frac{\pi^2}{15}\frac{Vk_B^4T^4}{\hbar^3c^3} = aVT^4, \qquad a = \frac{\pi^2}{15}\frac{k_B^4}{\hbar^3c^3}\,. \tag{5.28}$$

The energy density $u = U/V$ in the cavity thus grows with the fourth power of the temperature.

The internal energy $U(V,T)$ as a function of volume and temperature is not a thermodynamic potential and therefore does not contain the complete information about the thermodynamics. In particular we still need the thermal equation of state $p(T)$. Note that, because of the lack of particle-number conservation, the pressure p can depend only on the single intensive variable T. From the general expression (1.64) we know that

$$\left(\frac{\partial U}{\partial V}\right)_T = aT^4 = T\frac{dp}{dT} - p \tag{5.29}$$

with the solution[6]

$$p(T) = \frac{a}{3}T^4 = \frac{u}{3}\,. \tag{5.30}$$

The relation $pV = U/3$, which the phonon gas satisfies, is the (ultra)relativistic generalization of (1.32).

From the relation $u(T) = \int d\omega\, \tilde{u}(\omega, T)$ in (5.23) one further obtains the *spectral energy density*

$$\tilde{u}(\omega, T) = \frac{\omega^2}{\pi^2c^3}\frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}\,. \tag{5.31}$$

[6]The linear term $\propto T$ must vanish because of (2.57).

The maximum of this function occurs at the frequency (*Wien's displacement law*)

$$\omega_0(T) = x_0 \frac{k_B T}{\hbar}\,, \tag{5.32}$$

where $x_0 \simeq 2.82$ denotes the position of the maximum of the function $x^3/(e^x - 1)$.

The theoretical description of blackbody radiation goes back to Max Planck. From the experimentally known results for a and $\omega_0(T)$ he determined the constants $\hbar$ and k_B. With the knowledge of the value of the universal gas constant R he also obtained the then most accurate value of the Avogadro constant $N_A = R/k_B$.

5.4 Ideal Quantum Gases

We have now seen in several examples how quantum theory modifies the results of classical statistical mechanics by freezing out high-frequency degrees of freedom at low temperatures. A completely different mechanism leads to deviations from the ideal gas laws due to quantum mechanics at low temperatures. In this case the concept of indistinguishable particles with bosonic or fermionic *exchange statistics* leads to deviations from classical behavior. Although all ideal gases are described by the same Hamiltonian $H_N = \sum_{i=1}^{N} \boldsymbol{p}_i^2/2m$ with only kinetic energy, the properties of bosonic gases at low temperatures are fundamentally different from those of fermionic gases.

The single-particle eigenfunctions $H_1 = \boldsymbol{p}^2/2m$ are given by plane waves (we again consider periodic boundary conditions)

$$\psi_{\boldsymbol{k},\sigma}(\boldsymbol{r}, m_s) \propto \delta_{\sigma m_s} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \qquad \boldsymbol{k} = \frac{2\pi}{L}\boldsymbol{n}, \quad \sigma \in \{-s, -s+1, \ldots, s\} \tag{5.33}$$

with the spin s and the momentum $\hbar\boldsymbol{k}$ of the particle. The single-particle energies are then given by

$$\varepsilon_{\boldsymbol{k},\sigma} = \frac{\hbar^2 \boldsymbol{k}^2}{2m}, \qquad \text{with} \quad H_1 \psi_{\boldsymbol{k},\sigma}(\boldsymbol{r}, m_s) = \varepsilon_{\boldsymbol{k},\sigma} \psi_{\boldsymbol{k},\sigma}(\boldsymbol{r}, m_s). \tag{5.34}$$

Since there is no interaction in the problem, one may take the many-particle wavefunctions (initially without statistics) as product wavefunctions

$$\psi_N(x_1, \ldots, x_N) \propto \psi_{\alpha_1}(x_1) \cdots \psi_{\alpha_N}(x_N) \tag{5.35}$$

with $\alpha = (\boldsymbol{k}, \sigma)$ and $x = (\boldsymbol{r}, m_s)$. This wavefunction has the eigenenergy $E_N = \sum_i \varepsilon_{\alpha_i}$.

In the following it is useful to introduce the *occupation-number basis*. Because of the indistinguishability of the particles, the state is uniquely determined by specifying how many particles $n_\alpha \in \{0, 1, \ldots\}$ occupy each single-particle state ψ_α. Thus we obtain the eigenstate ($\{n_\alpha\} = \{n_{\alpha_1}, n_{\alpha_2}, \ldots\}$)

$$\psi_{\{n_\alpha\}}(x_1, \ldots, x_N) \propto \mathcal{P}_\pm \Big[\underbrace{\psi_{\alpha_1}(x_1) \cdots \psi_{\alpha_1}(x_{n_{\alpha_1}})}_{n_{\alpha_1} \text{ times}} \underbrace{\psi_{\alpha_2}(\cdot) \cdots \psi_{\alpha_2}(\cdot)}_{n_{\alpha_2} \text{ times}} \cdots \Big] \tag{5.36}$$

with energy

$$E = \sum_\alpha n_\alpha \varepsilon_\alpha \qquad \text{and particle number} \qquad N = \sum_\alpha n_\alpha \,, \tag{5.37}$$

where $\mathcal{P}_+$ projects onto the bosonic and $\mathcal{P}_-$ onto the fermionic subspace. For fermionic states the *Pauli principle* holds, which restricts the occupation numbers to the values 0 or 1. In fact one has

$$\mathcal{P}_-\Big[\varphi_\alpha(x_1)\varphi_\alpha(x_2)\Big] \propto \varphi_\alpha(x_1)\varphi_\alpha(x_2) - \varphi_\alpha(x_2)\varphi_\alpha(x_1) = 0 \,, \tag{5.38}$$

so that no states with $n_\alpha \geq 2$ exist.

Since the results of all ensembles agree in the thermodynamic limit, it is simplest to describe the system in the grand canonical ensemble. The grand canonical distribution depends only on the combination $H - \mu N$. The eigenstates (5.36) with

$$n_\alpha = \begin{cases} 0, 1, 2, 3, \ldots & \text{(Bosons)}, \\ 0, 1 & \text{(Fermions)}, \end{cases} \tag{5.39}$$

are complete in the Fock space and satisfy the eigenvalue equation

$$(H - \mu N)\psi_{\{n_\alpha\}} = (E - \mu N)\psi_{\{n_\alpha\}} = \sum_\alpha (\varepsilon_\alpha - \mu) n_\alpha \psi_{\{n_\alpha\}} \,. \tag{5.40}$$

We obtain the grand canonical partition function

$$\begin{aligned} \mathcal{Z} &= \sum_{\{n_\alpha\}} \exp\Big(-\sum_\alpha \beta(\varepsilon_\alpha - \mu) n_\alpha\Big) = \sum_{\{n_\alpha\}} \prod_\alpha e^{\beta(\mu-\varepsilon_\alpha)n_\alpha} = \prod_\alpha \sum_n e^{\beta(\mu-\varepsilon_\alpha)n} \\ &= \prod_\alpha \mathcal{Z}_\alpha = \prod_\alpha \begin{cases} \Big(1 - e^{\beta(\mu-\varepsilon_\alpha)}\Big)^{-1} & \text{(Bosons)}, \\ 1 + e^{\beta(\mu-\varepsilon_\alpha)} & \text{(Fermions)}. \end{cases} \end{aligned} \tag{5.41}$$

Note that in the bosonic case we need $\mu < \min_\alpha \varepsilon_\alpha$ for the partition function to converge. Since the subsystems for different α are independent, the partition function is a product of the individual contributions.

The logarithm turns the product into a sum with the result

$$\ln \mathcal{Z} = \sum_\alpha \begin{cases} -\ln\Big(1 - e^{\beta(\mu-\varepsilon_\alpha)}\Big) & \text{(Bosons)}, \\ \ln\Big(1 + e^{\beta(\mu-\varepsilon_\alpha)}\Big) & \text{(Fermions)}. \end{cases} \tag{5.42}$$

For the mean occupation number $\overline{n_\alpha}$ one finds from this

$$\overline{n_\alpha} = -\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \varepsilon_\alpha}\right)_{\mu,\beta,\varepsilon_{\beta\neq\alpha}} = \begin{cases} \dfrac{1}{e^{\beta(\varepsilon_\alpha-\mu)} - 1} & \text{(Bosons)}, \\ \dfrac{1}{e^{\beta(\varepsilon_\alpha-\mu)} + 1} & \text{(Fermions)}, \end{cases} \tag{5.43}$$

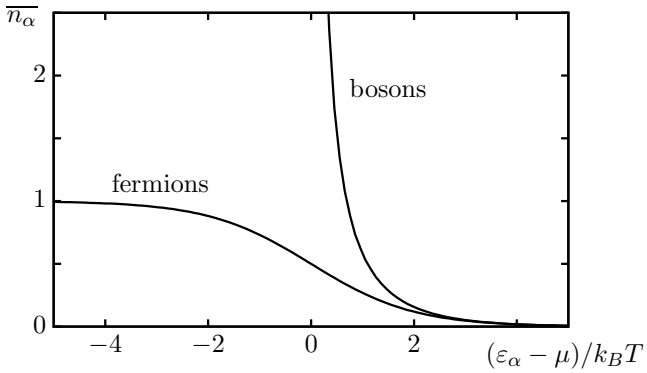


Fig. 5.2: Bose-Einstein and Fermi-Dirac distributions

see Figure 5.2. The distribution of the bosons is called the *Bose-Einstein distribution*. We have already seen this in the examples of the phonon gas and the photon gas with $\mu = 0$ (without particle-number conservation). The distribution of the fermions is called the *Fermi-Dirac distribution*.

From the mean occupation number one can, for an ideal quantum gas, obtain the various thermodynamic quantities. The mean particle number, for example, is given by

$$N = \sum_\alpha \overline{n_\alpha}\,. \tag{5.44}$$

The internal energy follows from

$$U = \overline{\sum_\alpha \varepsilon_\alpha n_\alpha} = \sum_\alpha \varepsilon_\alpha \overline{n_\alpha}\,. \tag{5.45}$$

From the relation $\Omega = -k_B T \ln \mathcal{Z} = -pV$ one can finally determine the pressure

$$\frac{pV}{k_B T} = \ln \mathcal{Z} = \sum_\alpha \begin{cases} \ln(1 + \overline{n_\alpha}) & \text{(Bosons)}\,, \\ -\ln(1 - \overline{n_\alpha}) & \text{(Fermions)} \end{cases} \tag{5.46}$$

The entropy follows from (2.8) with the result

$$S = \frac{1}{T}(U + pV - \mu N) = k_B \ln \mathcal{Z} + k_B \sum_\alpha \beta(\varepsilon_\alpha - \mu)\overline{n_\alpha}\,. \tag{5.47}$$

With

$$e^{\beta(\varepsilon_\alpha - \mu)} = \begin{cases} (1 + \overline{n_\alpha})/\overline{n_\alpha} & \text{(Bosons)}\,, \\ (1 - \overline{n_\alpha})/\overline{n_\alpha} & \text{(Fermions)}\,, \end{cases} \tag{5.48}$$

one can express the factor $\beta(\varepsilon_\alpha - \mu)$ in terms of the occupation numbers. One thereby obtains the expression

$$S = -k_B \sum_\alpha \begin{cases} \overline{n_\alpha} \ln \overline{n_\alpha} - (1 + \overline{n_\alpha}) \ln(1 + \overline{n_\alpha}) & \text{(Bosons)}\,, \\ \overline{n_\alpha} \ln \overline{n_\alpha} + (1 - \overline{n_\alpha}) \ln(1 - \overline{n_\alpha}) & \text{(Fermions)}\,, \end{cases} \tag{5.49}$$

which depends only on the mean occupation numbers. The fermionic result can be interpreted with (4.87) as follows: the state α is occupied with probability $p_\alpha = \overline{n_\alpha}$ and unoccupied with probability $1 - p_\alpha$. The interpretation of the bosonic result is as follows: Consider the state α with energy ε_α. Then the system has with probability

$$p_{n_\alpha} = \frac{1}{\mathcal{Z}_\alpha} e^{-\beta n_\alpha(\varepsilon_\alpha - \mu)} \overset{(5.48)}{=} \frac{1}{1+\overline{n_\alpha}} \left(\frac{\overline{n_\alpha}}{1+\overline{n_\alpha}} \right)^{n_\alpha} \tag{5.50}$$

the occupation number n_α with $\mathcal{Z}_\alpha$ from (5.41) and the mean occupation number $\overline{n_\alpha} = [e^{\beta(\varepsilon_\alpha - \mu)} - 1]^{-1}$. The occupation number is therefore geometrically distributed and the Gibbs entropy of the state is given by

$$S_\alpha = -k_B \sum_{n_\alpha} p_{n_\alpha} \ln p_{n_\alpha} = -k_B \overline{n_\alpha} \ln \overline{n_\alpha} + k_B (1+\overline{n_\alpha}) \ln(1+\overline{n_\alpha}) \,. \tag{5.51}$$

Ideal Quantum Gas: For the ideal gas one has $\varepsilon_\alpha = \varepsilon_{\boldsymbol{k}} = \hbar^2 \boldsymbol{k}^2 / 2m$. In the thermodynamic limit $\sum_{\boldsymbol{k}} \to (L/2\pi)^3 \int d^3k$ and $\Omega = -k_B T \ln \mathcal{Z} = -pV$. From the general expression (5.42) we obtain the result ($z = e^{\beta\mu}$, with $+$ for fermions and $-$ for bosons)

$$\frac{p}{k_B T} = \pm \frac{1}{V} \sum_{\boldsymbol{k},\sigma} \ln(1 \pm z e^{-\beta \varepsilon_{\boldsymbol{k}}}) = \pm \frac{g_s}{(2\pi)^3} \int d^3k \, \ln(1 \pm z e^{-\beta \varepsilon_{\boldsymbol{k}}}) \tag{5.52}$$

with the spin degeneracy $g_s = 2s+1$. We now use the substitution ($\lambda = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength from Eq. (4.109))

$$x^2 = \beta \varepsilon_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2 m k_B T} = \frac{\lambda^2 k^2}{4\pi}, \qquad d^3k = 4\pi k^2 dk = \frac{(4\pi)^{5/2}}{\lambda^3} x^2 \, dx \tag{5.53}$$

and obtain

$$\frac{p}{k_B T} = \frac{g_s}{\lambda^3} f^{\pm}_{5/2}(z) \qquad \text{with} \qquad f^{\pm}_{5/2}(z) = \pm \frac{4}{\sqrt{\pi}} \int_0^\infty dx \, x^2 \ln(1 \pm z e^{-x^2}) \,. \tag{5.54}$$

With $\ln(1-z) = -\sum_{n=1}^\infty z^n/n$, ($|z| < 1$) and

$$\frac{4}{\sqrt{\pi}} \int_0^\infty dx \, x^2 e^{-n x^2} = \frac{1}{n^{3/2}} \tag{5.55}$$

one obtains the power-series expansion

$$f^{\pm}_{5/2}(z) = \mp f_{5/2}(\mp z) \qquad \text{with} \qquad f_{5/2}(z) = \sum_{l=1}^\infty \frac{z^l}{l^{5/2}} \,. \tag{5.56}$$

We further define

$$f^{\pm}_{3/2}(z) = \mp f_{3/2}(\mp z) \qquad \text{with} \qquad f_{3/2}(z) = \sum_{l=1}^\infty \frac{z^l}{l^{3/2}} = z \frac{d}{dz} f_{5/2} = \frac{d}{d \ln z} f_{5/2} \,, \tag{5.57}$$

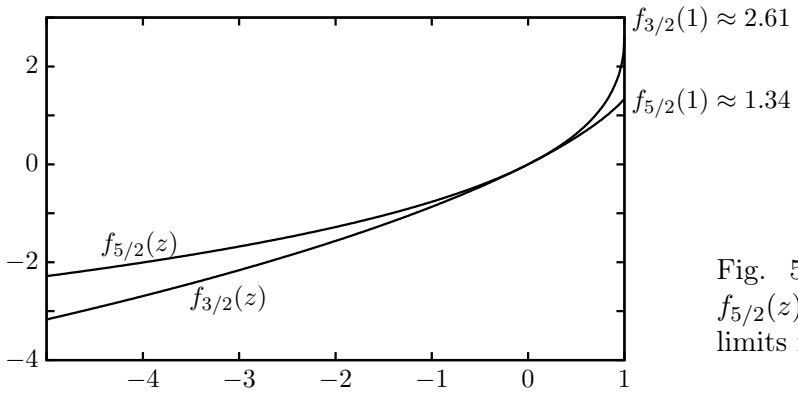


Fig. 5.3: The functions $f_{5/2}(z)$ and $f_{3/2}(z)$ with the limits for $z \to 1^-$.

see Figure 5.3.

Equation (5.54) is analogous to the thermal equation of state of the (classical) ideal gas. However, the fugacity z is related to the (mean) particle number N by $N = (\partial \ln \mathcal{Z}/\partial \ln z)_{T,V}$. Thus for the ideal quantum gases the relations

$$\frac{p}{k_B T} = \frac{g_s}{\lambda^3} f^{\pm}_{5/2}(z), \tag{5.58}$$

$$\frac{N}{V} = \frac{g_s}{\lambda^3} f^{\pm}_{3/2}(z) \qquad \left(= \partial(p/k_B T)/\partial \ln z \right), \tag{5.59}$$

hold, which determine the thermodynamics.

The internal energy is given by

$$U = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right)_{V,z} . \tag{5.60}$$

At fixed z one has $\beta p \propto \lambda^{-3} \propto \beta^{-3/2}$. With $\ln \mathcal{Z} = pV/k_B T$ one obtains from this

$$\frac{U}{V} = -\left(\frac{\partial(\beta p)}{\partial \beta} \right)_z = \frac{3}{2} p \,. \tag{5.61}$$

Thus the result

$$U = \frac{3}{2} pV \tag{5.62}$$

from the virial theorem (1.32) remains valid also in quantum mechanics. All effects due to exchange symmetry are therefore contained in the (thermal) equation of state

$$\frac{pV}{N k_B T} = \frac{f^{\pm}_{5/2}(z)}{f^{\pm}_{3/2}(z)} , \tag{5.63}$$

or, in other words, in the deviation of the right-hand side from the classical value 1. Using (5.59), to express z in terms of the particle density, we obtain the result shown in Figure 5.4

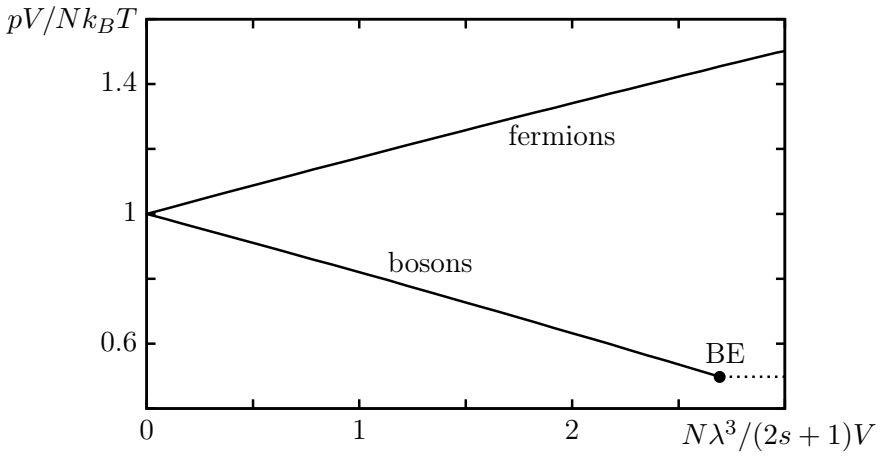


Fig. 5.4: Deviation of the thermal equation of state pV/Nk_BT from the classical result 1 as a function of $N\lambda^3/V$, the number of particles in the volume λ^3.

Classical limit: The classical limit is reached for

$$\frac{V}{N} \gg \lambda^3 \,, \tag{5.64}$$

that is, when the typical interparticle distance is larger than the thermal wavelength λ. Here λ denotes the de Broglie wavelength of a particle of energy k_BT. The classical limit corresponds therefore to low densities or high temperatures. From (5.59) one has $|z| \ll 1$ and we may restrict ourselves to the terms with $l = 1$ in the expansion of $f^{\pm}_{\alpha}(z)$. One then has

$$\frac{f^{\pm}_{5/2}(z)}{f^{\pm}_{3/2}(z)} = 1 + O(z) \tag{5.65}$$

and we obtain the relations $pV = Nk_BT$ and $U = \frac{3}{2}Nk_BT$ of the classical ideal gas.

The next order in z (up to $l = 2$) yields $f^{\pm}_{5/2}(z)/f^{\pm}_{3/2}(z) = 1 \pm (2^{-3/2} - 2^{-5/2})z = 1 \pm z/2^{5/2}$ and hence the first exchange effects. From (5.59) one obtains

$$\frac{1}{g_s}\frac{\lambda^3 N}{V} = z + O(z^2) \,. \tag{5.66}$$

and hence

$$pV = Nk_BT\left(1 \pm \frac{1}{g_s}\frac{\lambda^3 N}{2^{5/2}V} + O(z^2)\right) \,. \tag{5.67}$$

The Fermi gas has (at fixed $T, N/V$) a higher pressure (Pauli principle) and the Bose gas a lower pressure than the classical gas.

5.5 The Degenerate Fermi Gas

Under a degenerate gas one understands the case $\lambda^3 \gg V/N$, in which exchange effects dominate due to quantum mechanics. This corresponds to the limiting case of high densities or low temperatures. Let us first consider the case $T = 0$. Then the Fermi-Dirac distribution has the form

$$\overline{n_{\boldsymbol{k},\sigma}} = \Theta(\varepsilon_F - \varepsilon_{\boldsymbol{k},\sigma}) = \begin{cases} 1, & \varepsilon_{\boldsymbol{k},\sigma} \leq \varepsilon_F, \\ 0, & \varepsilon_{\boldsymbol{k},\sigma} > \varepsilon_F, \end{cases} \tag{5.68}$$

with the Fermi energy ε_F, the chemical potential μ at $T = 0$. The Fermi energy is related to the particle density N/V by the relation

$$\frac{N}{V} = \frac{1}{V}\sum_{\boldsymbol{k},\sigma} \overline{n_{\boldsymbol{k},\sigma}} = g_s \int \frac{d^3k}{(2\pi)^3} \overbrace{\Theta(\varepsilon_F - \hbar^2k^2/2m)}^{\text{sphere of radius } k_F = \sqrt{2m\varepsilon_F}/\hbar} = \frac{g_s}{(2\pi)^3}\frac{4\pi k_F^3}{3} \tag{5.69}$$

that is

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 N}{g_s V}\right)^{2/3} . \tag{5.70}$$

The ground-state energy $E_0 = U(T = 0)$ is given by

$$\begin{aligned} E_0 &= \sum_{\boldsymbol{k},\sigma} \varepsilon_{\boldsymbol{k},\sigma}\overline{n_{\boldsymbol{k},\sigma}} = g_s V \int \frac{d^3k}{(2\pi)^3}\frac{\hbar^2k^2}{2m}\Theta(\varepsilon_F - \hbar^2k^2/2m) \\ &= \frac{3}{5}N\varepsilon_F \end{aligned} \tag{5.71}$$

The *zero-point pressure* (pressure in the ground state) has the value

$$p_0 = -\left(\frac{\partial E_0}{\partial V}\right)_N = -\frac{3}{5}N\left(\frac{\partial \varepsilon_F}{\partial V}\right)_N = \frac{2}{5}\frac{N}{V}\varepsilon_F . \tag{5.72}$$

Electrons in a metal have the density $N/V \simeq 10^{22}\,\mathrm{cm}^{-3}$. Thus $\varepsilon_F/k_B \simeq 10^4\,\mathrm{K}$. Hence metals are also at room temperature in good approximation degenerate. The electrons thereby exert a zero-point pressure of $p_0 \simeq 10^4\,\mathrm{atm}$. As a function of V at fixed particle number N the zero-point pressure is given by $p_0 \propto V^{-5/3}$.

Sommerfeld expansion: To obtain results at finite temperatures, we need the expansion of $f^+_{5/2}(z)$ for $z \to \infty$. The asymptotic expansion (*Sommerfeld expansion*)

$$f^+_{5/2}(z) = \frac{8}{15\sqrt{\pi}}\left(\ln^{5/2} z + \frac{5\pi^2}{8}\ln^{1/2} z + O(\ln^{-3/2} z)\right) . \tag{5.73}$$

also implies

$$f^+_{3/2}(z) = \frac{d}{d\ln z} f^+_{5/2}(z) = \frac{4}{3\sqrt{\pi}}\left(\ln^{3/2} z + \frac{\pi^2}{8}\ln^{-1/2} z + O(\ln^{-5/2} z)\right) . \tag{5.74}$$

Inserting the Sommerfeld expansion into (5.59) yields the relation

$$\ln^{3/2} z + \frac{\pi^2}{8} \ln^{-1/2} z \simeq \frac{3\sqrt{\pi}\lambda^3 N}{4 g_s V} = (\varepsilon_F / k_B T)^{3/2} , \tag{5.75}$$

in other words

$$\ln z \times \left(1 + \frac{\pi^2}{8 \ln^2 z}\right)^{2/3} \simeq \frac{\epsilon_F}{k_B T} . \tag{5.76}$$

We solve this equation iteratively for $\ln z$ and obtain the result

$$\mu = k_B T \ln z = \varepsilon_F \left(1 - \frac{\pi^2}{12} (k_B T/\varepsilon_F)^2 + O(k_B T/\varepsilon_F)^4\right) . \tag{5.77}$$

At fixed particle density this gives, as expected, $\mu \to \varepsilon_F$ for $T \to 0^+$.

Furthermore, from (5.63) we find

$$\begin{aligned} \frac{pV}{N k_B T} = \frac{f^+_{5/2}(z)}{f^+_{3/2}(z)} &= \frac{2}{5}\Big(\ln z + \overbrace{\frac{\pi^2}{2}}^{5\pi^2/8 - \pi^2/8} \frac{1}{\ln z} + O(\ln^{-2} z)\Big) \\ &= \frac{2}{5} \frac{\varepsilon_F}{k_B T}\Big(1 + \underbrace{\frac{5\pi^2}{12}}_{\pi^2/2 - \pi^2/12} (k_B T/\varepsilon_F)^2 + O(k_B T/\varepsilon_F)^4\Big) . \end{aligned} \tag{5.78}$$

The pressure

$$p = p_0 \left(1 + \frac{5\pi^2}{12} (k_B T/\varepsilon_F)^2\right) \tag{5.79}$$

(at fixed particle density) is therefore higher at finite temperature than the zero-point pressure.

We further obtain the specific heat

$$c_V = \frac{1}{N} \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3V}{2N} \left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{\pi^2}{2} \frac{k_B T}{\varepsilon_F} k_B , \tag{5.80}$$

which, at low temperatures, grows linearly in T. In particular $c_V \to 0$ holds for $T \to 0$, as required by the third law.

5.6 The Degenerate Bose Gas

As we have already seen, for bosonic exchange statistics the pressure is lowered compared with the classical gas. However, the functions $f^-_{3/2}(z)$ and $f^-_{5/2}(z)$ attain a maximum value of $\zeta(\frac{3}{2}) = \sum_{l=1}^{\infty} l^{-3/2} \approx 2.61$ and $\zeta(\frac{5}{2}) = \sum_{l=1}^{\infty} l^{-5/2} \approx 1.34$ at the *critical point* with $z = 1$ or $\mu = 0$, respectively, see Figure 5.3. Indeed the curve ends at point BE in Figure 5.4 with

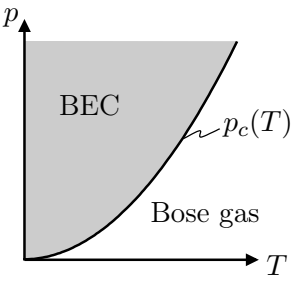
$$\left(\frac{\lambda^3 n}{g_s}\right)_c = f^-_{3/2}(1) \approx 2.61 \quad \text{and} \quad \left(\frac{p}{n k_B T}\right)_c = \frac{f^-_{5/2}(1)}{f^-_{3/2}(1)} \approx 0.514 \tag{5.81}$$

Thus at the critical point of the three intensive quantities $T, p, n = N/V$ only one is independent.[7] At fixed temperature this yields a critical particle density

$$n_c(T) = \frac{1}{v_c(T)} = \frac{2.61\, g_s}{\lambda^3} \propto T^{3/2} \tag{5.82}$$

and a critical pressure

$$p_c(T) = 0.514\, n_c k_B T \propto T^{5/2}\,. \tag{5.83}$$



The relations (5.58) and (5.59) for the Bose gas are therefore valid only for $p \le p_c$ and hence $n \le n_c$. At pressure p_c a phase transition occurs, the so-called *Bose-Einstein condensation*.

Superfluid ^{4}He: At a fixed pressure p one finds from the condition $p = p_c(T_c)$ that Bose-Einstein condensation takes place at the *lambda temperature*

$$T_c = \frac{1}{k_B}\left(\frac{h^3 p}{1.34\, g_s (2\pi m)^{3/2}}\right)^{2/5} \tag{5.84}$$

The lambda temperature is therefore highest for light atoms. Consider the example of ^{4}He. It consists of two protons and two neutrons and is therefore overall a boson with spin $s = 0$ (an even number of bound fermions has bosonic statistics). Its mass is $m = 4\,\mathrm{u} = 6.6 \times 10^{-27}\,\mathrm{kg}$. At a typical pressure of $p = 1\,\mathrm{atm}$ one therefore expects a Bose-Einstein condensation at

$$T_c \approx 1.7\,\mathrm{K}, \qquad (\text{with } n_c \approx 8.5\,\mathrm{nm}^{-3})\,. \tag{5.85}$$

This value corresponds roughly to the observed phase transition to a superfluid at $T_c = 2.177\,\mathrm{K}$. Comparing this behavior with ^{3}He (two protons, one neutron, $s = \frac{1}{2}$), one finds that at these temperatures He remains liquid. The reason is that ^{3}He is a Fermi gas and therefore does not undergo Bose-Einstein condensation. Only at a much lower temperature $\simeq 2\,\mathrm{mK}$ does ^{3}He also become a superfluid. In this case the physical mechanism is based on pairing (to form bosons from ^{3}He) followed by condensation of the pairs.

The Bose gas (bg) has the maximum particle density $n_c(T)$. Hence it can accommodate at most $N_{\mathrm{bg}} = n_c V$ particles in the volume V. One therefore asks what happens to $N > n_c V$. To keep the particle number fixed we must switch to the free energy. We have (for $N > N_{\mathrm{bg}}$, so that $\mu = 0$)

$$F(T, V, N) = \min_\mu(\Omega + \mu N) = V \min_\mu(\mu n - p) \overset{(\mu=0)}{=} -p_c(T) V\,. \tag{5.86}$$

Because $\mu = 0$ the free energy does not depend on N, of course.

[7] This corresponds to the Gibbs phase rule with 2 phases and 1 component.

One may alternatively write the free energy as

$$\frac{F}{N} = x f_{\rm bg} + (1-x) f_{\rm BEK}, \qquad x = \frac{v}{v_c} = \frac{N_{\rm bg}}{N} = \left(\frac{T}{T_c}\right)^{3/2} \tag{5.87}$$

with

$$f_{\rm bg}(T, v_c) = -p_c v_c \overset{(5.83)}{=} -0.514\, k_B T \qquad \text{and} \qquad f_{\rm BEK}(T, 0) = 0 \tag{5.88}$$

In the language of Chapter 3 (cf. Figure 3.1) this corresponds to a coexistence of the ideal Bose gas (bg) (with specific volume v_c) with the Bose-Einstein condensate (BEC) (with specific volume $v_{\rm BEK} = 0$). The unphysical property of vanishing specific volume of the BEC (corresponding to infinite density) is due to the fact that we have neglected interactions. The BEC is therefore an idealized system with $s_{\rm BEK} = u_{\rm BEK} = v_{\rm BEK} = 0$.

We have seen that the equation (5.59) accounts only for those particles $N_{\rm bg} = n_c V < N$ that form the ideal Bose gas. The question therefore arises where in the derivation the other particles have been "lost." Mathematically, below the BEC the second equality sign in (5.52) is no longer correct. The reason is that the single-particle ground state with energy $\varepsilon = 0$ and momentum $\hbar \boldsymbol{k} = 0$ is *macroscopically occupied* with

$$\overline{n_0} = N_{\rm BEK} = N - N_{\rm bg} = (1-x)N = \left(1 - \frac{v}{v_c}\right) N\,. \tag{5.89}$$

The macroscopic occupation means that $\overline{n_0}$ is an extensive quantity, while the occupation of all other states follows the Bose-Einstein distribution and is therefore intensive. For this reason one must treat the term at $\boldsymbol{k} = 0$ separately in (5.52). One obtains the relation

$$\begin{aligned} \frac{p}{k_B T} &= -\frac{g_s}{V} \ln(1-z) - \frac{g_s}{(2\pi)^3} \int d^3k\, \ln(1 - z e^{-\beta \varepsilon_{\boldsymbol{k},\sigma}}) \\ &= -\frac{g_s}{V} \ln(1-z) + \frac{g_s}{\lambda^3} f^-_{5/2}(z)\,. \end{aligned} \tag{5.90}$$

Usually in the thermodynamic limit $V \to \infty$ the contribution of the BEC vanishes. However, since $f_{5/2}(z)$ is bounded from above, for $n > n_c$ in the limit $\mu \to 0^-$ ($z \to 1^-$) the contribution of the first term becomes as important as that of the remaining states.[8]

To interpret the lambda temperature as a phase transition more precisely, we compute from the free energy $F = -p_c V$ in (5.86) the entropy (with $p_c \propto T^{5/2}$ for $T < T_c$)

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = V \frac{\partial p_c}{\partial T} = \frac{5}{2} \frac{V p_c}{T} \propto T^{3/2}\,. \tag{5.91}$$

Thus for the ideal Bose gas the third law is satisfied. Rewriting the entropy as $S = s_{\rm bg} N_{\rm bg}$, we see that the entropy is carried only by the particles in the Bose gas

[8] See also Chapter 12 in the book by K. Huang

with $s_{\mathrm{bg}} = 0.514\,\frac{5}{2}k_B$. The entropy difference between the two phases in the phase mixture is therefore given by $\Delta s = s_{\mathrm{bg}}$. Hence the system has the latent heat

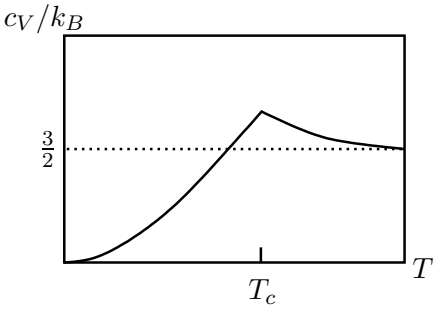
$$\ell = T\Delta s = 0.514\,\frac{5}{2}k_B T\,. \tag{5.92}$$

Moreover, there is a jump $\Delta v = v_c$ in the specific volume. The Clausius-Clapeyron relation (3.8), which can be verified directly, connects the ratio of these jumps with the derivative $\partial p_c/\partial T$ of the "vapor-pressure curve" (5.83).

The specific heat below the lambda temperature is given by

$$c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V = \frac{15}{4}\frac{vp_c}{T} \overset{(5.83)}{=} \frac{15}{4} \times 0.514 k_B \frac{v}{v_c} = 1.93\,k_B \left(\frac{T}{T_c}\right)^{3/2}. \tag{5.93}$$

The specific heat therefore increases at low temperatures like $T^{3/2}$. At the lambda temperature the specific heat has the value $1.93\,k_B$, which is larger than the value $\frac{3}{2}k_B$ at high temperatures. Overall, the specific heat exhibits a maximum (an anomaly) at the lambda temperature. At this point the heat capacity shows a kink (its first derivative with respect to temperature is discontinuous). This characteristic shape is also called a λ jump, since the temperature dependence of the heat capacity near the transition temperature resembles the Greek letter λ.



Chapter 6

Magnetism

Magnetic systems provide a testing ground for the results of statistical physics. On the one hand, the systems are sufficiently simple to obtain theoretical results (in part even exact ones), while on the other hand there exist experimental methods—such as neutron scattering—with which magnetic properties of materials can be determined very precisely. A further advantage is that in most materials the typical energy scale of magnetism lies in the conveniently accessible range of 100-1000 K and that the magnetic degrees of freedom are relatively strongly decoupled from other degrees of freedom, so that they can be understood separately.

Within classical physics, magnetism cannot be explained. In fact, the *Bohr-van Leeuwen theorem* states that there is no classical magnetism. Quantum mechanics leads to charged particles producing a diamagnetic response to applied magnetic fields due to their orbital degrees of freedom. In addition, there is an intrinsic angular momentum, the spin, which generates a magnetic dipole and thus gives rise to a paramagnetic response. In quantum mechanics there are many different magnetic phases (para-, ferro-, antiferro-, spin-glass magnetism, ...) with the most diverse phase transitions between them. In this chapter we can only explain some basic principles. For more information, consult advanced literature, for example the book by Chaikin and Lubensky.

6.1 Generalities

In magnetic systems the work coordinate is the magnetization $\mathcal{M}$ along the magnetic field with the corresponding equilibrium quantity B_0, see Example 1.4. In what follows we consider the spin of N particles, keeping N fixed. The (quasistatic) work is then given by

$$\delta W = B_0 \, d\mathcal{M} \,. \tag{6.1}$$

Compared to the fluids and gases we studied in Chapter 1, the relation $(V, -p) \leftrightarrow (\mathcal{M}, B_0)$ holds. By this analogy we label the relevant thermodynamic potentials—the

internal energy $U(S,\mathcal{M})$, the free energy $F(T,\mathcal{M})$, and the Gibbs energy $G(T,B_0)$—with

$$F = U - TS \qquad \text{and} \qquad G = U - TS - B_0\mathcal{M}\,. \tag{6.2}$$

They satisfy the fundamental equations

$$dF = -SdT + B_0\,d\mathcal{M} \qquad \text{and} \qquad dG = -SdT - \mathcal{M}\,dB_0\,. \tag{6.3}$$

The magnetic analogue of compressibility is the magnetic *susceptibility*[1]

$$\chi_x = \left(\frac{\partial\mathcal{M}}{\partial B_0}\right)_x, \qquad \text{isotherm (for } x=T\text{) and adiabatically (for } x=S)\,. \tag{6.4}$$

Equation (2.17) now takes the form

$$C_{B_0} - C_{\mathcal{M}} = \frac{T}{\chi_T}\left(\frac{\partial\mathcal{M}}{\partial T}\right)^2_{B_0} \tag{6.5}$$

with the heat capacity C_x at fixed $x = B_0, \mathcal{M}$. For *paramagnetic* substances $\chi_T > 0$ holds and hence $C_{B_0} \geq C_{\mathcal{M}}$. For *diamagnetic* substances with $\chi_T < 0$ one finds instead $C_{B_0} \leq C_{\mathcal{M}}$.

Example 1: (Stability conditions)

The minimum principle applied to the potentials $U(S,\mathcal{M})$, $H(S,B_0)$ leads in particular to

$$\frac{T}{C_{\mathcal{M}}} = \frac{\partial^2 U}{\partial S^2} \geq 0, \quad \frac{T}{C_{B_0}} = \frac{\partial^2 H}{\partial S^2} \geq 0.$$

Thus the specific heats satisfy the stability conditions $C_{\mathcal{M}}$, $C_{B_0} > 0$. [2]

Example 2: (Adiabatic demagnetization)

When a body is magnetized adiabatically, its temperature changes. This follows from the relation

$$\left(\frac{\partial T}{\partial B_0}\right)_S = -\left(\frac{\partial\mathcal{M}}{\partial S}\right)_{B_0} = -\left(\frac{\partial\mathcal{M}}{\partial T}\right)_{B_0}\left(\frac{\partial T}{\partial S}\right)_{B_0} = -\frac{T}{C_{B_0}}\left(\frac{\partial\mathcal{M}}{\partial T}\right)_{B_0}. \tag{6.6}$$

In the first equality we used the Maxwell relation

$$\left(\frac{\partial T}{\partial B_0}\right)_S = \frac{\partial^2 H}{\partial S\partial B_0} = -\left(\frac{\partial\mathcal{M}}{\partial S}\right)_{B_0} \tag{6.7}$$

[1] Unlike compressibility, we define χ as an extensive response quantity.

[2] The stability conditions for χ_S, χ_T follow from the second derivatives of $U^{\rm em}(S,\mathcal{M})$, $F^{\rm em}(T,\mathcal{M})$ with respect to $\mathcal{M}$. Here one must, however, take into account that $B_0 d\mathcal{M}$ is only the magnetostatic energy of the magnetic substance, to which one must add the field energy term $Vd(\frac{1}{2}B_0^2) = VB_0\,dB_0$. Hence $dF^{\rm em} = dF + VB_0\,dB_0 = -SdT + B_0(VdB_0 + d\mathcal{M}) = -SdT + B_0\big(V/\chi_T + 1\big)d\mathcal{M}$. The stability condition $\partial^2 F^{\rm em}/\partial\mathcal{M}^2 \geq 0$ reads $\chi_T \geq -V$. Analogously one obtains for $U^{\rm em}$ the condition $\chi_S \geq -V$.

for the enthalpy $H(S, B_0)$ with $dH = TdS - \mathcal{M}\, dB_0$. If $(\partial\mathcal{M}/\partial T)_{B_0}$ does not vanish, the temperature of the body changes when the external magnetic field B_0 is varied. This is the so-called *magnetocaloric effect*. At room temperature it is small, but at low temperatures it can become substantial. For paramagnetic materials the Curie law $\mathcal{M} \propto T^{-1}$ applies (see below). Hence $\partial\mathcal{M}/\partial T \propto -T^{-2} < 0$ and we obtain $(\partial T/\partial B_0)_S > 0$. In adiabatic *demagnetization* ($dB_0 < 0$) the temperature of the body is thereby lowered.

6.2 Ideal Paramagnetism

A simple model of magnetism considers only the potential (Zeeman) energy $H_B = -\sum_{i=1}^{N} \boldsymbol{m}_i \cdot \boldsymbol{B}_0$ of N magnetic moments $\boldsymbol{m}_i$ in an external field $\boldsymbol{B}_0$. We further assume that the magnetic moments of magnitude $\mu = |\boldsymbol{m}_i|$ can take only two orientations, with $\boldsymbol{m}_i \cdot \boldsymbol{B}_0 = m_i B_0 = s_i \mu B_0$ and $s_i = \pm 1$ (*Ising spin*): either they align with the field ($s_i = +1$) or they point in the opposite direction ($s_i = -1$). Altogether there are 2^N possible configurations. The partition function (at fixed B_0) is then[3]

$$\begin{aligned} Z_B &= \sum_{s_1,\ldots,s_N} e^{-\beta H_B} = \sum_{s_1,\ldots,s_N} e^{\beta\mu B_0 \sum_i s_i} = \Big(\sum_{s_1} e^{\beta\mu B_0 s_1}\Big) \cdots \Big(\sum_{s_N} e^{\beta\mu B_0 s_N}\Big) \\ &= \Big(\sum_{s} e^{\beta\mu B_0 s}\Big)^N = 2^N \cosh^N(\beta\mu B_0)\,. \end{aligned} \tag{6.8}$$

From the partition function one obtains the Gibbs energy

$$G(T, B_0) = -k_B T \ln Z_B = -N k_B T \ln[2\cosh(\mu B_0/k_B T)]\,, \tag{6.9}$$

the magnetization

$$\mathcal{M} = \overline{\sum_i m_i} = -\left(\frac{\partial G}{\partial B_0}\right)_T = N\mu \tanh(\mu B_0/k_B T) \tag{6.10}$$

and the entropy

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{B_0} = N k_B \ln 2 + N k_B \ln\cosh(\mu B_0/k_B T) - \frac{B_0}{T}\mathcal{M} \\ &= -N k_B (p_+ \ln p_+ + p_- \ln p_-)\,. \end{aligned} \tag{6.11}$$

Here $p_\pm = \left(1 + e^{\mp 2\mu B_0/k_B T}\right)^{-1}$ is the probability that a magnetic moment takes the value $s_i = \pm 1$. For the ideal paramagnet the average energy[4]

$$\overline{H_B} = -B_0 \mathcal{M} = -N\mu B_0 \tanh(\mu B_0/k_B T) \tag{6.12}$$

[3] Compared to a gas, Z_B corresponds to the isothermal-isobaric partition function. The term H_B corresponds to the Laplace transform of $\mathcal{M}$ to B_0, see (4.131).

[4] The energy $\overline{H_B} = -B_0\mathcal{M} = -\sum_{i=1}^{N} \boldsymbol{m}_i \cdot \boldsymbol{B}_0$ does not contribute to the "internal energy" in this formalism, but corresponds "only" to the Legendre transform of $\mathcal{M}$ with respect to B_0. Hence $U = 0$ and $\overline{H_B} = G + TS = -B_0\mathcal{M} = \partial(\beta G)/\partial\beta$. The reason is that for the present noninteracting system the energy is proportional to the magnetization. Thus $S(U, \mathcal{M})$ and $U(S, \mathcal{M})$ are not well defined.

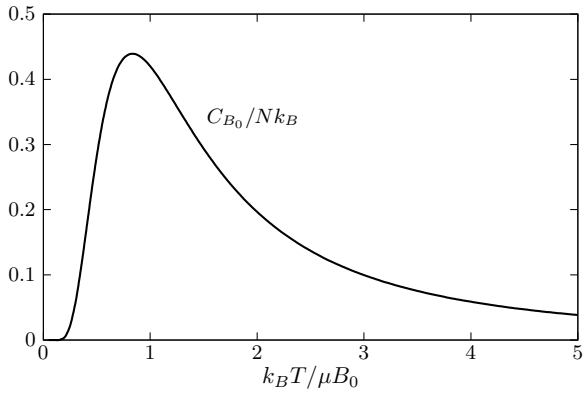


Fig. 6.1: The heat capacity of an ideal paramagnet shows the Schottky anomaly. Its value is small at both high and low temperatures. It has a maximum $C^*_{B_0} \approx 0.44Nk_B$ at $k_BT \approx 0.83\mu B_0$.

is proportional to the magnetization.

In the high-temperature limit ($k_BT \gg \mu B_0$) one finds from (6.10) the *Curie law*

$$\mathcal{M} = \frac{N\mu^2 B_0}{k_B T} \,. \tag{6.13}$$

At low temperatures with $k_BT \ll \mu B_0$ the magnetization

$$\mathcal{M} = N\mu(1 - 2e^{-2\mu B_0/k_BT}) \tag{6.14}$$

saturates at the maximal value $N\mu$ up to exponential corrections.

For a finite magnetic field B_0 both the heat capacity[5]

$$C_{B_0} = T\left(\frac{\partial S}{\partial T}\right)_{B_0} = \frac{N\mu^2 B_0^2}{k_B T^2 \cosh^2(\mu B_0/k_BT)} \tag{6.15}$$

and the susceptibility

$$\chi_T = \left(\frac{\partial \mathcal{M}}{\partial B_0}\right)_T = \frac{N\mu^2}{k_BT\cosh^2(\mu B_0/k_BT)} = \frac{TC_{B_0}}{B_0^2} \tag{6.16}$$

exhibit a maximum at $\mu B_0 \sim k_BT$ before the degrees of freedom freeze out (exponentially) at low temperatures, see Figure 6.1. At low temperatures we find the behavior $C_{B_0} \propto T^{-2}e^{-2\mu B_0/k_BT}$ and $\chi_T \propto T^{-1}e^{-2\mu B_0/k_BT}$. In the high-temperature regime, by contrast, cosh $\to 1$, so that $C_{B_0} \propto T^{-2}$ and $\chi_T \propto T^{-1}$.

For $B_0 = 0$ the Curie law

$$\chi_T = \frac{N\mu^2}{k_BT} \tag{6.17}$$

holds at all temperatures.

[5]Since at fixed magnetization the average energy is fixed, one obtains the degenerate result $C_{\mathcal{M}} = 0$.

6.3 Ising Model

The ideal paramagnet neglects interactions between the magnetic moments and therefore cannot describe phase transitions. Adding an interaction energy of the form

$$H = -\frac{1}{2}\sum_{i,j} J_{ij} s_i s_j - h\sum_i s_i, \qquad h = \mu B_0, \tag{6.18}$$

yields the *Ising model*. The factor $\frac{1}{2}$ ensures that each spin pair is counted only once. The coupling constants $J_{ij} = J_{ji}$ have the units of "energy" and describe the interaction of spin i with spin j. Note that because of $s_i^2 = 1$, equation (6.18) represents the most general interaction for Ising spins. The interaction can describe ferromagnetism ($J_{ij} > 0$), antiferromagnetism ($J_{ij} < 0$), and spin glasses (J_{ij} randomly). Usually the origin of the interaction J is the *exchange interaction*, i.e., the combination of electrostatic Coulomb interaction with the Pauli principle. Typical energy scales are $|J|/k_B \simeq$ 100-1000 K.

We restrict ourselves to the case of a d-dimensional cubic lattice with

$$J_{ij} = \begin{cases} J, & i \text{ and } j \text{ are nearest neighbors} \\ 0, & \text{otherwise.} \end{cases} \tag{6.19}$$

For L moments in each dimension the system has a total of $N = L^d$ spins. The Gibbs energy is obtained from the partition function

$$Z_B = \sum_{s_1,\ldots,s_N} e^{-\beta H} = e^{-\beta G}\,. \tag{6.20}$$

In general this partition function is not analytically solvable. A useful approximation is the *molecular-field approximation*. One replaces the interaction term $s_i s_j$ by the interaction of s_i with the (position-independent) average spin $m = \overline{s}$ (molecular field). We write

$$s_i = m + (s_i - m) = m + \delta_i\,. \tag{6.21}$$

The energy is then given by ($\langle i,j\rangle$ summed over the nearest neighbors)

$$\begin{aligned} H &= -J\sum_{\langle i,j\rangle} s_i s_j - h\sum_i s_i = -J\sum_{\langle i,j\rangle}(m+\delta_i)(m+\delta_j) - h\sum_i s_i \\ &= -J\sum_{\langle i,j\rangle}\Big[m^2 + m(s_i - m) + m(s_j - m) + \delta_i\delta_j\Big] - h\sum_i s_i \\ &= -J\sum_i\Big(zms_i - \tfrac{1}{2}zm^2\Big) - h\sum_i s_i - J\sum_{\langle i,j\rangle}\delta_i\delta_j\,. \end{aligned} \tag{6.22}$$

The parameter $z = 2d$ denotes the number of nearest neighbors. Apart from the last term the spins are independent. We therefore wish to neglect the last term. To do so

we require that the correlations are small with

$$\frac{\delta s_i\,\delta s_j}{m^2} = \frac{\overline{\delta_i \delta_j}}{m^2} \ll 1 \tag{6.23}$$

Since molecular-field theory neglects correlations, it breaks down in particular near a phase transition, see also below.

Without the last term, the energy takes the form

$$H_{\mathrm{MF}} = -h_{\mathrm{eff}} \sum_i s_i + \frac{z}{2} N J m^2 \,. \tag{6.24}$$

This is the energy of an ideal paramagnet in the effective field $h_{\mathrm{eff}} = h + zJm$. An analogous calculation as in the previous chapter leads to, cf. (6.9),

$$G(T,h,m) = \frac{z}{2} N J m^2 - N k_B T \ln[2\cosh(\beta h_{\mathrm{eff}})] \,. \tag{6.25}$$

In equilibrium, the Gibbs energy is minimal with respect to the inhibition m. Thus

$$0 = \frac{\partial G}{\partial m} = zNJm - zNJ \tanh(\beta h_{\mathrm{eff}}) \,. \tag{6.26}$$

This equation corresponds to the *self-consistency equation*

$$m = \overline{s_i} = \frac{\sum_{s_i=\pm 1} s_i e^{\beta h_{\mathrm{eff}} s_i}}{\sum_{s_i=\pm 1} e^{\beta h_{\mathrm{eff}} s_i}} = \tanh(\beta h_{\mathrm{eff}}) = \tanh\Big[\beta(h+zJm)\Big] = -\frac{1}{N}\frac{\partial G}{\partial h} \tag{6.27}$$

for the average spin. The equation is a nonlinear equation for m. The solution $m^* = m^*(T,h)$, which minimizes the potential $G(T,h) = G(T,h,m^*)$ from (6.25) yields the thermodynamics.

In particular, one is interested in the susceptibility

$$\chi_T = -\mu^2 \frac{\partial^2 G(T,h)}{\partial h^2} \overset{(6.27)}{=} N\mu^2 \frac{\partial m^*}{\partial h} \tag{6.28}$$

With the self-consistency equation $m^* = \tanh(\beta h_{\mathrm{eff}})$ we obtain

$$\frac{\chi_T}{N\mu^2} = \overbrace{\frac{\partial \tanh(\beta h_{\mathrm{eff}})}{\partial h_{\mathrm{eff}}}}^{\beta[1-\tanh^2(\beta h_{\mathrm{eff}})]} \frac{\partial h_{\mathrm{eff}}}{\partial h} = \beta(1-m^{*2})\left(1 + zJ\frac{\partial m^*}{\partial h}\right) = \beta(1-m^{*2})\left(1 + \frac{zJ\chi_T}{N\mu^2}\right)$$

and hence the susceptibility

$$\chi_T = \frac{N\mu^2}{k_B T/(1-m^{*2}) - zJ} \tag{6.29}$$

as a function of the average spin $m^* = \overline{s_i}$.

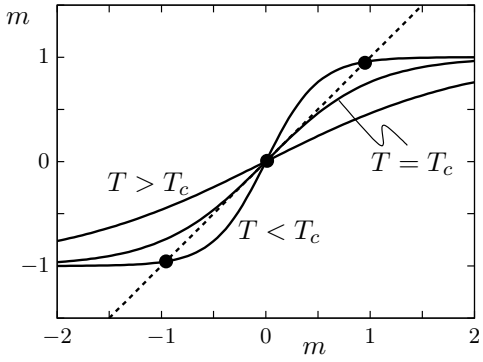


Fig. 6.2: Graphical solution of the self-consistency equation for $h = 0$: The intersection between the dashed line ($m = m$) and the curve $\tanh(T_c m/T)$ gives the solutions. In the ferromagnetic phase ($T < T_c$) there are 3 solutions whereas in the paramagnetic phase ($T > T_c$) there is only 1 solution.

6.4 Magnetic Phase Transition

The disordered phase at high temperatures (above the critical point T_c, see later) is called the *paramagnetic* phase. In the paramagnetic phase, the approximation $\tanh x \approx x$ can be used in the self-consistency equation. This yields the solution

$$m^* = \frac{h}{k_B T - zJ} \tag{6.30}$$

In particular, $m^* = 0$ holds for $B_0 = h = 0$. The Curie law is modified in this case to the *Curie-Weiss law*

$$\chi_T = \frac{N\mu^2}{k_B(T - T_c)}, \qquad (\text{for } T > T_c,\ h = 0) \tag{6.31}$$

The susceptibility diverges at the critical temperature (we consider in the following the ferromagnetic case with $J > 0$)

$$T_c = \frac{zJ}{k_B}\,. \tag{6.32}$$

The divergence indicates that the paramagnetic solution at $m^* = 0$ for $T \leq T_c$ becomes unstable.

We investigate this instability using the self-consistency equation. For $h = 0$ we seek a solution of

$$m = \tanh(\beta z J m) = \tanh(T_c m/T)\,. \tag{6.33}$$

The value $m = 0$ is always a solution. As can be seen from the graph in Figure 6.2, for $T < T_c$ there exist additional solutions $\pm m(T, 0)$. These solutions are degenerate and minimize G. One calls $\mathcal{M} = N\mu\, m(T, 0)$ the *spontaneous magnetization*, since it occurs without an appropriate external field. Thus the system is in an *ferromagnetic* phase for $T < T_c$.

Near the critical point the magnetization is small and one can use the expansion $\tanh(x) \approx x - x^3/3$. For low temperatures the magnetization saturates $m^* \to 1^-$, so

that one can use $\tanh x \approx 1 - 2e^{-2x}$. This yields the approximation

$$m^*(T,0) \begin{cases} = 0, & T \geq T_c\,, \\ \approx \sqrt{3(1-T/T_c)}, & T \lesssim T_c\,, \\ \approx 1 - 2e^{-2T_c/T}, & T \ll T_c \end{cases} \tag{6.34}$$

for the magnetization. The magnetization has a nonanalytic behavior at $T = T_c$, which signals the phase transition. For a finite magnetic field the self-consistency equation takes the form

$$m = \tanh\Big[(k_B T_c m + h)/k_B T\Big]\,. \tag{6.35}$$

For $h > 0$ the degeneracy $\pm m$ is lifted and there is only one solution with $m^* > 0$, which minimizes the Gibbs energy. We investigate the case $T = T_c$. With the expansion of $\tanh x$ we obtain

$$m^*(T_c,h) \approx \begin{cases} (3h/k_B T_c)^{1/3}, & h \ll k_B T_c\,, \\ 1 - 2e^{-2h/k_B T_c}, & h \gg k_B T_c\,. \end{cases} \tag{6.36}$$

The remaining thermodynamic quantities can be expressed in terms of the solution $m^*(T,h)$.

The susceptibility is given by (6.29). For $h = 0$ it diverges at the phase transition with

$$\chi_T \begin{cases} = \frac{N\mu^2}{k_B(T-T_c)}, & T > T_c\,, \\ \approx \frac{N\mu^2}{2k_B(T_c-T)}, & T \lesssim T_c\,. \end{cases} \tag{6.37}$$

Starting from the Gibbs energy (6.25)

$$G(T, h=0) = \frac{1}{2} N k_B T_c m^{*2} - N k_B T \ln\big[2\cosh(T_c m^*/T)\big] \tag{6.38}$$

we obtain the entropy $S(T, h=0)$ by differentiation with respect to T. Here one needs to use only the explicit T dependence, since G is a minimum with respect to m^*. We obtain

$$\begin{aligned} S(T,h=0) &= -\left(\frac{\partial G}{\partial T}\right)_h = N k_B \ln\big[2\cosh(T_c m^*/T)\big] - \frac{N k_B T_c m^*}{T} \overbrace{\tanh(T_c m^*/T)}^{m^*} \\ &= N k_B \ln\big[2\cosh(T_c m^*/T)\big] - \frac{N k_B T_c m^{*2}}{T}\,. \end{aligned} \tag{6.39}$$

At low temperatures $\cosh(x) \approx \frac{1}{2} e^x$. Thus the system satisfies the third law with

$$S(T \ll T_c, h=0) \approx N k_B T_c \frac{m^*(1-m^*)}{T} \overset{(6.34)}{\approx} \frac{2 N k_B T_c e^{-2T_c/T}}{T} \tag{6.40}$$

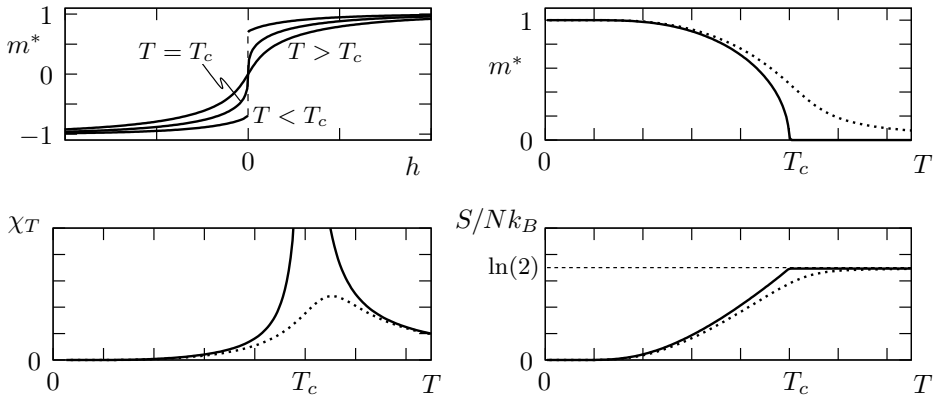


Fig. 6.3: Results of the molecular-field approximation for the ferromagnetic Ising model for the magnetization $\mathcal{M} = N\mu m^*$, the isothermal susceptibility χ_T, and the entropy S. The solid lines are results for an external magnetic field $B_0 = \mu h$. The dashed curves apply for $h > 0$. The system has a critical point at $(T, B_0) = (T_c, 0)$. The singularities are softened by a finite magnetic field.

and the degrees of freedom freeze out at low temperatures. For temperatures $T \lesssim T_c$ we can expand the entropy for small m^* with the result

$$S = Nk_B \ln(2) + Nk_B \underbrace{\frac{T_c(T_c - 2T)}{2T^2}}_{\approx -1/2} m^{*2} + O(m^{*4}) \,. \tag{6.41}$$

For $T > T_c$ we have $m^* = 0$ and obtain $S(T > T_c, h = 0) = Nk_B \ln(2)$ from N disordered Ising spins. Altogether

$$S(T, h = 0) \begin{cases} = Nk_B \ln(2), & T > T_c, \\ \approx Nk_B \ln(2) - \frac{3}{2} Nk_B (1 - T/T_c), & T \lesssim T_c, \\ \approx 2Nk_B T_c e^{-2T_c/T}/T, & T \ll T_c \,. \end{cases} \tag{6.42}$$

The entropy thus has a nonanalytic behavior at $T = T_c$, which signals the phase transition, see Figure 6.3. Correspondingly, the heat capacity

$$C_{B_0}(T, h = 0) = T \left(\frac{\partial S}{\partial T} \right)_h \begin{cases} = 0, & T > T_c, \\ \approx \frac{3}{2} Nk_B, & T \lesssim T_c, \\ \approx 4Nk_B T_c^2 e^{-2T_c/T}/T^2, & T \ll T_c \,. \end{cases} \tag{6.43}$$

has a jump of height $\frac{3}{2} Nk_B$ at the phase transition.

In the vicinity of the critical point $(T, h) = (T_c, 0)$ the behavior of the system is described by critical exponents. These are

$$C_{B_0, h=0} \propto |T - T_c|^{-\alpha}, \qquad m^*_{h=0, T<T_c} \propto (T_c - T)^{\beta},$$
$$\chi_{T, h=0} \propto |T - T_c|^{-\gamma}, \qquad m^*_{T=T_c} \propto h^{1/\delta} \,.$$

The results from (6.43), (6.34), (6.37) and (6.36) yield the values $\alpha = 0$, $\beta = \frac{1}{2}$, $\gamma = 1$, $\delta = 3$. These are the same values that we already found for the van der Waals gas. The critical exponents do not depend on the system in the molecular-field approximation. In particular, the dimension d of the system only affects T_c but not the nature of the phase transition. It turns out, however, that the molecular-field approximation is valid only for $d \geq 4$, since the condition (6.23) is not applicable near the phase transition for lower dimensions. In particular, there is no phase transition for $d = 1$. In the other dimensions one finds:

d	α	β	γ	δ	
2	0	1/8	7/4	15	(Onsager solution)
3	0.110	0.326	1.24	4.79	(Monte Carlo simulation)
≥ 4	0	1/2	1	3	(molecular-field approximation)

These exponents are called the Ising exponents. The liquid-gas phase transition belongs to the same *universality class* and thus has the same exponents. There are, however, also other universality classes with different exponents. If one considers instead of Ising spins, for example, classical unit vectors $\boldsymbol{e} \in \mathbb{R}^2$ in the plane, then one is in the XY universality class. Unit vectors in 3D space are called the Heisenberg universality class, see also the book by Chaikin and Lubensky.

It turns out that of the four critical exponents only two are independent. In general the inequalities

$$\begin{aligned} &\alpha' + 2\beta + \gamma' \geq 2 && \text{(Rushbrooke)}, \\ &\alpha' + \beta(\delta + 1) \geq 2 && \text{(Griffiths)}, \\ &\gamma' \geq \beta(\delta - 1) && \text{(Widom)}, \end{aligned} \tag{6.44}$$

hold, where α', γ' denotes the exponents when approaching the critical point from the low-temperature phase.[6] Only two of the three inequalities are independent, since (R) = (G) + (W) holds.

The inequalities follow from thermodynamic considerations. For example, the Rushbrooke inequality follows from the relation

$$C_{B_0}(T, h = 0) \overset{(6.5)}{=} \frac{T}{\chi_T} \left(\frac{\partial \mathcal{M}}{\partial T} \right)^2_{B_0} + \overbrace{C_{\mathcal{M}}}^{\geq 0} \geq \frac{N^2 \mu^2 T}{\chi_T} \left(\frac{\partial m^*}{\partial T} \right)^2_{h=0} . \tag{6.45}$$

For $T \lesssim T_c$ we have $C_{B_0} \propto (T_c - T)^{-\alpha'}$, $\chi_T \propto (T_c - T)^{-\gamma'}$, $m^*_{h=0} \propto (T_c - T)^{\beta}$. From (6.45) we obtain (for $T \to T_c^-$)

$$(T_c - T)^{-\alpha' - \gamma' - 2(\beta - 1)} \geq \text{const.} \tag{6.46}$$

Thus the Rushbrooke inequality holds in the form $0 \geq -\alpha' - \gamma' - 2(\beta - 1)$.

[6] No such distinction exists for β and δ.

The *scaling hypothesis* $G(\lambda^a t, \lambda^b h) = \lambda G(t,h)$ with $t = T/T_c - 1$, which follows from the renormalization-group theory, reduces all critical exponents to a and b. For example, for the magnetization $\mathcal{M} \propto m^*$ one obtains the scaling behavior

$$\lambda m^*(t,h) \propto -\lambda \left(\frac{\partial G}{\partial h}\right)_t = -\left(\frac{\partial G(\lambda^a t, \lambda^b h)}{\partial h}\right)_t \propto \lambda^b m^*(\lambda^a t, \lambda^b h)\,. \tag{6.47}$$

Setting here $h = 0$ and $\lambda = (-t)^{-1/a}$ (for $t < 0$) yields

$$m^*(t,0) \propto (-t)^{(1-b)/a} m^*(-1,0)\,. \tag{6.48}$$

Thus $\beta = (1-b)/a$. Furthermore, the choice $t = 0$ and $\lambda = h^{-1/b}$ gives the relation $1/\delta = 1/b - 1$. Extending these considerations to the second derivatives, one obtains the relations

$$\alpha = \alpha' = 2 - \frac{1}{a}, \qquad \beta = \frac{1-b}{a}, \qquad \gamma = \gamma' = \frac{2b-1}{a}, \qquad \delta = \frac{b}{1-b}\,. \tag{6.49}$$

Thus all critical exponents are reduced to a and b. In particular, the scaling hypothesis requires that $\alpha = \alpha'$, $\gamma = \gamma'$ and that the inequalities in (6.44) become equalities. The exponents a, b are not measurable. Mostly one therefore treats β, γ as "free" critical exponents. Solving the equations in (6.44) for α, δ leads then to the relation

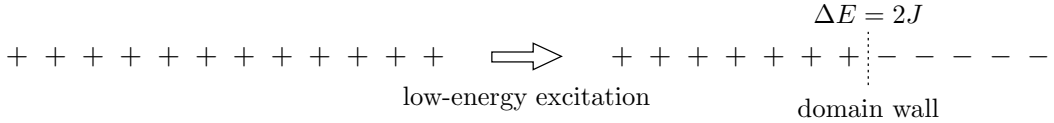
$$\alpha = 2(1-\beta) - \gamma \qquad \text{and} \qquad \delta = 1 + \frac{\gamma}{\beta}\,. \tag{6.50}$$

One easily verifies that the critical exponents of the Ising model satisfy these relations.

6.5 Peierls Argument

We have seen that the results of the molecular-field approximation are especially wrong in low dimensions. The reason is that in low dimensions the coordination number $z = 2d$ is small, so that the fluctuations (6.23) are important and not negligible. Thus one needs an alternative approach to understand low dimensions. We treat the Peierls argument, which in particular shows that the Ising model in one dimension has no phase transition.

1D: We wish to show that in one dimension there is no spontaneous magnetization for $T > 0$. Hence at finite temperatures there exists only the paramagnetic phase without a phase transition. The ground state at $T = h = 0$ is the configuration $s_i = +1$ for all i; or $s_i = -1$, but the argument remains unchanged in this case. This spontaneous magnetization also persists for small $T > 0$ if typical configurations from the canonical ensemble remain predominantly aligned. It vanishes, however, if large domains of reversed spins become probable.



Consider now the probability of a configuration with a domain wall. The energy difference is $\Delta E = 2J > 0$. Thus, the probability of a *particular* domain wall is suppressed by the Boltzmann factor $e^{-\beta\Delta E}$. However, there are $\Gamma = N - 1$ positions for the domain wall. The probability for an *arbitrary* domain boundary is therefore (p_0 is the probability of the ground state)

$$p_{\text{Wand}} = p_0(N-1)e^{-\beta\Delta E} = p_0 e^{-\beta\Delta F} \tag{6.51}$$

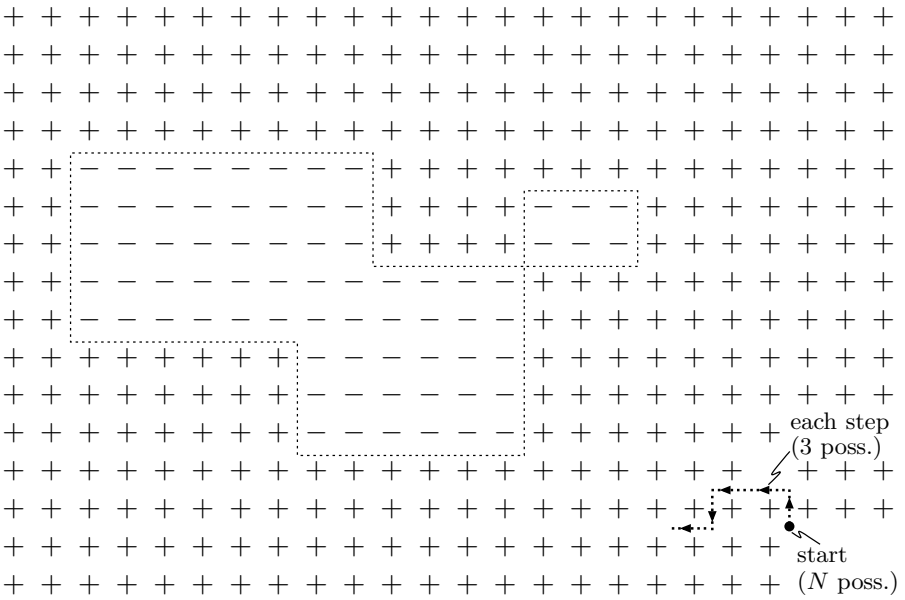
with the difference in the free energy

$$\Delta F = \Delta E - k_B T \ln(N-1) = 2J - k_B T \ln(N-1)\,. \tag{6.52}$$

The second term corresponds to the entropy difference $-T\Delta S$ due to $\Delta S = k_B \ln(N-1)$ the $N-1$ possibilities for the domain wall. In the thermodynamic limit $N \to \infty$, the entropic term dominates.

Thus $p_{\text{Wand}} \gg p_0$, and the spontaneous magnetization of the ground state is destroyed at any finite temperature.

2D: Also in two dimensions we consider a domain of $-$ which is embedded in the ground state $+$. The energy difference to the ground state is $\Delta E = 2JL$ with L the length of the domain wall. The number Γ of domains with a perimeter L is $\Gamma \lesssim 4N3^{L-1}$. This inequality follows from the following consideration: One can draw a domain wall by starting at an arbitrary plaquette (N possibilities) and then moving in an arbitrary direction (4 possibilities). At every further step one then has at most 3 possibilities (since one may no longer take the same path back).



Thus there is the entropy difference

$$\Delta S = k_B \ln\Gamma \lesssim k_B L \ln(3) + O(\ln L)\,. \tag{6.53}$$

between the ground state and a state with a (large) domain wall with $L^2 \propto N$. Hence we obtain the difference in the free energy

$$\Delta F \gtrsim L\big[2J - \ln(3) k_B T\big] \,. \tag{6.54}$$

For temperatures with $k_B T \leq 2J/\ln(3) \approx 1.8J$ is $\Delta F \geq 0$ and domain walls are suppressed. Thus the spontaneous magnetization of the ground state persists even at finite temperatures. The Peierls argument is quite good in its simplicity, since the exact transition point is at $k_B T_c = 2J/\ln(1+\sqrt{2}) \approx 2.27\, J$.

Chapter 7

Nonequilibrium and Transport

Up to now we have studied systems in equilibrium without considering how equilibrium is reached in the first place. In this final chapter we provide a brief outlook on systems that are not in equilibrium. Here we restrict ourselves to systems that are only slightly driven out of equilibrium. In particular, we assume that there are fast processes that bring a system into *local equilibrium*. Such an equilibrium is described by local equilibrium quantities $T(\boldsymbol{r},t), p(\boldsymbol{r},t), \mu(\boldsymbol{r},t), \ldots$. In complete equilibrium, of course, T, p, μ are constants. The attainment of complete equilibrium is accomplished by the *hydrodynamic* modes.

7.1 Thermal Conduction

We begin with thermal conduction in a homogeneous system. Away from equilibrium, the state variables become position dependent. The system can then be described by local equilibrium quantities and local state variables, such as the internal energy density $u(\boldsymbol{r},t)$, the entropy density $s(\boldsymbol{r},t)$, ...

Energy conservation leads to the continuity equation

$$\frac{\partial u}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}^q = 0\,, \tag{7.1}$$

with u the energy density ($[u]$ = energy/volume) and $\boldsymbol{j}^q$ the heat current density ($[j^q]$ = power/area). Here $\boldsymbol{j}^q \cdot \boldsymbol{n}\, dA$ is the heat flow through the area dA with normal vector $\boldsymbol{n}$. A position dependence of the temperature $T(\boldsymbol{r},t)$ gives rise to a heat current density $\boldsymbol{j}^q$. For small temperature gradients the *Fourier law*

$$\boldsymbol{j}^q = -\kappa \boldsymbol{\nabla} T \tag{7.2}$$

holds, with thermal conductivity κ. The thermal conductivity κ must be positive so that heat flows from the hotter to the colder place.

To obtain a closed system of equations, we still need to use the thermodynamic relation

$$du = nc_V dT \tag{7.3}$$

with $n = N/V$ the particle density and c_V the specific heat per particle. We have thereby assumed that we describe heat conduction in a solid so that we can neglect thermal expansion effects (n remains fixed, so that $dn = dv = 0$). Inserting the relations (7.2) and (7.3) into the continuity equation, we obtain the *heat equation* ($\kappa = \text{const.}$)

$$\frac{\partial T}{\partial t} = D\,\Delta T \tag{7.4}$$

with the (thermal) diffusion constant

$$D = \frac{\kappa}{nc_V}\,. \tag{7.5}$$

Starting from a temperature distribution $T_0(\boldsymbol{r}) \leq T_{\max}$ at time $t = 0$, the solution of the heat equation at time $t > 0$ is given by

$$T(\boldsymbol{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \int d^3r' e^{-|\boldsymbol{r}-\boldsymbol{r}'|^2/4Dt}\, T_0(\boldsymbol{r}')\,. \tag{7.6}$$

Thus, for the gradient we have the estimate

$$\begin{aligned} |\boldsymbol{\nabla} T(\boldsymbol{r}, t)| &= \frac{1}{(4\pi Dt)^{3/2}(2Dt)} \left| \int d^3r'\, (\boldsymbol{r}' - \boldsymbol{r}) e^{-|\boldsymbol{r}-\boldsymbol{r}'|^2/4Dt}\, T_0(\boldsymbol{r}') \right| \\ &\leq \frac{T_{\max}}{(4\pi Dt)^{3/2}(2Dt)} \underbrace{\int d^3x\, x\, e^{-x^2/4Dt}}_{=4\pi \int_0^\infty dx\, x^3 e^{-x^2/4Dt} = 32\pi D^2 t^2} = \frac{2T_{\max}}{\sqrt{\pi Dt}}\,. \end{aligned} \tag{7.7}$$

Diffusion therefore causes the temperature gradient to decrease and, in the limit $t \to \infty$, to vanish. Hence the heat equation describes the thermalization of the system. For a system of size L, heat conduction requires the typical time $\tau_{\text{diff}} = L^2/D$ to equilibrate a typical gradient $T_{\max}/L$.

Remark: The heat equation holds only in the hydrodynamic regime for lengths $L \gg \ell$ with ℓ the *mean free path* and times $\gg \tau$ with $\tau = v\ell$ the *collision time* (v is the typical particle velocity). For shorter times and lengths a microscopic description, such as the Boltzmann equation, must be used. A system that is strongly out of equilibrium first thermalizes on the length scale ℓ and time scale τ into local equilibrium. Thereafter follows the "slow" heat conduction on the time scale τ_{diff}, which is referred to as hydrodynamic transport.

7.2 Entropy Flow

Heat transport is an irreversible process. Hence it is accompanied by an entropy change. With the definition $du = Tds$ (no expansion $dv = 0$) we find from the

continuity equation (7.1) the relation

$$\frac{\partial s}{\partial t} = -\frac{1}{T}\boldsymbol{\nabla}\cdot\boldsymbol{j}^q = -\boldsymbol{\nabla}\cdot\frac{\boldsymbol{j}^q}{T} - \frac{1}{T^2}\boldsymbol{j}^q\cdot\boldsymbol{\nabla}T\,. \tag{7.8}$$

The term $\boldsymbol{j}^s = \boldsymbol{j}^q/T$ is the entropy current density/entropy flow. Entropy is not conserved. Hence entropy does not satisfy a source-free continuity equation; instead we have

$$\frac{\partial s}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}^s = \dot{\mathsf{s}} \tag{7.9}$$

with the *entropy production rate* (per volume)

$$\dot{\mathsf{s}} = -\frac{\boldsymbol{j}^q\cdot\boldsymbol{\nabla}T}{T^2} \overset{(7.2)}{=} \kappa\frac{(\boldsymbol{\nabla}T)^2}{T^2} \geq 0\,. \tag{7.10}$$

Note that local entropy production is always positive, in accordance with the second law. In equilibrium $\boldsymbol{\nabla}T = 0$ and hence no new entropy is produced. The entropy flow then leads to $s = \text{const.}$. As a result the total entropy $S = Vs$ is extensive in equilibrium.

7.3 Onsager Reciprocity Relations

We now generalize these considerations. To this end we examine a small subsystem (much larger than ℓ but also much smaller than the system size L). This is described by the state variables $\tilde{\alpha}_i = \alpha_{0,i} + \alpha_i$, $i = 1, 2, \ldots, f$ (for example U, N, $\ldots$). In equilibrium these take the values $\alpha_{0,i}$ with entropy S_0. Now consider a fluctuation α_i with the entropy change

$$\Delta S = S - S_0 = \frac{1}{2}\sum_{i,j}(d^2S)_{ij}\alpha_i\alpha_j, \tag{7.11}$$

where $d^2S \leq 0$. The probability density to find the system in a state with deviations α_i is given by[1]

$$\rho(\boldsymbol{\alpha}) = \rho(\alpha_1, \ldots, \alpha_f) = \rho(0, \ldots, 0)e^{\Delta S/k_B}\,. \tag{7.12}$$

In the following it is helpful to introduce the *thermodynamically conjugate quantities*

$$\gamma_i = \frac{\partial S}{\partial \alpha_i} = \sum_j (d^2S)_{ij}\alpha_j \tag{7.13}$$

In equilibrium S is maximal and hence $\gamma_j = 0$. One also calls γ_i the *thermodynamic forces*. This yields the correlations

$$\begin{aligned}\overline{\alpha_i\gamma_j} &= \int d^f\alpha\,\alpha_i\gamma_j\rho(\boldsymbol{\alpha}) = k_B\int d^f\alpha\,\alpha_i\frac{\partial\rho(\boldsymbol{\alpha})}{\partial\alpha_j} = -k_B\int d^f\alpha\,\rho(\boldsymbol{\alpha})\frac{\partial\alpha_i}{\partial\alpha_j}\\ &= -k_B\delta_{ij}\,.\end{aligned} \tag{7.14}$$

[1] For short time scales (naturally still longer than the collision time) one may view the system locally as a closed system. Only later are the constraints lifted by the hydrodynamic modes.

Often it is easiest to determine the conjugate quantities via the property: The entropy production is given by

$$\dot{S} = \sum_i \frac{\partial S}{\partial \alpha_i} \frac{d\alpha_i}{dt} = \sum_i \gamma_i \frac{d\alpha_i}{dt} \tag{7.15}$$

where $d\alpha_i/dt$ is the current density conjugate to the force γ_i.

Example 1: We determine the quantity conjugate to $\alpha = U$ for heat transport from Chapter 7.1. To this end we consider two systems in thermal contact. The heat current is given by $I^q = \dot{U}_2 = -\dot{U}_1$. The entropies S_i of the two systems change according to $dS_i = dU_i/T_i$ (no expansion). The entropy production then follows as, cf. (2.5),

$$\dot{S} = \dot{S}_1 + \dot{S}_2 = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) I^q = \Delta\left(\frac{1}{T}\right) I^q \,. \tag{7.16}$$

Thus the thermodynamic force is $\gamma = \Delta(1/T) = 1/T_2 - 1/T_1$.

With the heat current $I^q = \frac{1}{2}(\dot{U}_2 - \dot{U}_1)$ there is an accompanying entropy current $I^s = \frac{1}{2}(\dot{S}_2 - \dot{S}_1)$. Hence one obtains the discrete version $\dot{S}_1 + I^s = \frac{1}{2}\dot{S}$ of the entropy balance equation (7.9), which means that in this analogy half of the total entropy production is attributed to system 1. Correspondingly for the second system $\dot{S}_2 - I_s = \frac{1}{2}\dot{S}$, so that also here the second half of the entropy production is accounted for.

Example 2: In applications one often uses a local version of the last example. Here the energy density u plays the role of the local state variable. The entropy density can change according to (7.9) both by an entropy flow (heat current without temperature difference) and by entropy production $\dot{\mathsf{s}}$. The local version of the entropy production (7.16) is

$$\dot{\mathsf{s}} \overset{(7.10)}{=} -\frac{\boldsymbol{j}^q \cdot \boldsymbol{\nabla} T}{T^2} = \left(\boldsymbol{\nabla}\frac{1}{T}\right) \cdot \boldsymbol{j}^q \,. \tag{7.17}$$

Entropy production occurs because of a heat current from a hot to a cold temperature. Comparing with (7.15) shows that $\gamma_i = \partial_i(1/T)$ are the conjugate forces to the current densities $d\alpha_i/dt = j_i^q$.

In equilibrium $\alpha_i = \gamma_j = 0$. If the deviations from equilibrium are small, the quantities α_i satisfy linear equations of motion

$$\frac{d\alpha_i(t)}{dt} = \sum_j L_{ij}\gamma_j(t) = \sum_{j,k} L_{ij}\,(d^2S)_{jk}\,\alpha_k(t) \tag{7.18}$$

with the Onsager transport coefficients L_{ij}.

The Onsager reciprocity relations follow from *microscopic reversibility*. We first consider a time-reversal-invariant system ($\boldsymbol{B}_0 = 0$) in equilibrium and assume that all α_i are invariant under time reversal. Then for microscopic fluctuations ($\tau > 0$)

$$\overline{\alpha_i(t)\alpha_j(t+\tau)} \overset{(\tau\mapsto-\tau)}{=} \overline{\alpha_i(t)\alpha_j(t-\tau)} \overset{(t\mapsto t+\tau)}{=} \overline{\alpha_j(t)\alpha_i(t+\tau)} \tag{7.19}$$

Differentiating this relation with respect to τ using (7.18) leads to

$$\sum_k L_{jk}\,\overline{\alpha_i(t)\gamma_k(t+\tau)} = \sum_k L_{ik}\,\overline{\alpha_j(t)\gamma_k(t+\tau)}\,. \tag{7.20}$$

In the limit $\tau \to 0^+$ we obtain with (7.14) the reciprocity relation

$$L_{ji} = L_{ij}\,. \tag{7.21}$$

One can generalize this relation with an analogous proof: let ϵ_i be the parity of the state variable α_i under time reversal, i.e.

$$\epsilon_i = \begin{cases} 1, & \text{if } \alpha_i(t) = \alpha_i(-t), \\ -1, & \text{if } \alpha_i(t) = -\alpha_i(-t). \end{cases} \tag{7.22}$$

Then the *Onsager reciprocity relation*

$$L_{ij}(\boldsymbol{B}_0) = \epsilon_i\epsilon_j L_{ji}(-\boldsymbol{B}_0)\,. \tag{7.23}$$

holds. Note that α_i and γ_i have the same parity, whereas the current $d\alpha_i/dt$ has opposite parity. Hence the (macroscopic) equations of motion (7.18) break time-reversal invariance and (in general) lead to irreversible dynamics.

Example 3: (Electrical reciprocity)

Electrical transport is described by the *Ohm's law*

$$j_i = \sum_{j=1}^{3} \sigma_{ij}\,E_j\,. \tag{7.24}$$

The conductivity tensor σ_{ij} then relates the electric field strength $\boldsymbol{E}$ to the electric current density $\boldsymbol{j}$. The current produces the electric power density

$$\dot{u} = \boldsymbol{E}\cdot\boldsymbol{j} = \sum_{i,j} \sigma_{ik}E_iE_k \geq 0\,. \tag{7.25}$$

At the (fixed) temperature T this leads to entropy production (per volume)

$$\dot{\mathsf{s}} = \frac{\dot{u}}{T} = \frac{1}{T}\boldsymbol{E}\cdot\boldsymbol{j}\,. \tag{7.26}$$

Hence $\gamma_i = E_i/T$ is the thermodynamic force conjugate to the electric current density $d\alpha_i/dt = j_i$.

Comparing (7.24) with (7.18) shows that the Onsager *transport coefficients* are given by

$$L_{ij} = T\sigma_{ij}\,. \tag{7.27}$$

For electrical transport the reciprocity relation

$$\sigma_{ij}(\boldsymbol{B}_0) = \sigma_{ji}(-\boldsymbol{B}_0)\,. \tag{7.28}$$

For an isotropic material $\sigma_{ij} = \delta_{ij}\sigma$. Consequently σ must be an even function of the magnetic field $\boldsymbol{B}_0$.

The conductivity σ_{yx} is measured in an experiment where one applies the voltage along the x-direction and measures the current in the y-direction. Without an applied magnetic field ($\boldsymbol{B}_0 = 0$) reciprocity requires that the result be the same if one interchanges the voltage and current leads (and thus measures σ_{xy}).

Example 4: (Dissipative and reactive transport coefficients)

The entropy production takes the form, cf. (7.15),

$$\dot{\mathsf{s}} = \sum_i \gamma_i \frac{d\alpha_i}{dt} = \sum_{i,j} L_{ij}(\boldsymbol{B}_0)\gamma_i\gamma_j = \sum_{i,j} \tilde{L}_{ij}(\boldsymbol{B}_0)\gamma_i\gamma_j \tag{7.29}$$

with the symmetric matrix

$$\tilde{L}_{ij}(\boldsymbol{B}_0) = \frac{1}{2}\big[L_{ij}(\boldsymbol{B}_0) + L_{ji}(\boldsymbol{B}_0)\big] = \frac{1}{2}\big[L_{ij}(\boldsymbol{B}_0) + \epsilon_i\epsilon_j L_{ij}(-\boldsymbol{B}_0)\big]\,. \tag{7.30}$$

For the entropy production (as required by the second law) to be always non-negative, the matrix $\tilde{L}_{ij}$ must be positive semi-definite. One calls $\tilde{L}$ the *dissipative* part of the transport coefficients. If the degrees of freedom i and j have the same parity ($\epsilon_i\epsilon_j = 1$), then $\tilde{L}_{ij}$ is an even function of the magnetic field $\boldsymbol{B}_0$. In the opposite case $\tilde{L}_{ij}$ is an odd function. The remaining part

$$\hat{L}_{ij} = \frac{1}{2}\big[L_{ij}(\boldsymbol{B}_0) - L_{ji}(\boldsymbol{B}_0)\big] = \frac{1}{2}\big[L_{ij}(\boldsymbol{B}_0) - \epsilon_i\epsilon_j L_{ij}(-\boldsymbol{B}_0)\big] \tag{7.31}$$

with $L_{ij} = \tilde{L}_{ij} + \hat{L}_{ij}$ is called the *reactive* transport coefficients, which exhibit the opposite parity as a function of the magnetic field $\boldsymbol{B}_0$.

Example 5: (Electrical transport in 2D)

Electrical transport in 2D is described by the conductivity tensor (B_0 is the magnetic field strength perpendicular to the plane)

$$\sigma = \begin{pmatrix} \sigma_{xx}(B_0) & \sigma_{xy}(B_0) \\ \sigma_{yx}(B_0) & \sigma_{yy}(B_0) \end{pmatrix}\,. \tag{7.32}$$

For an isotropic material $\sigma_{xx} = \sigma_{yy}$ and $\sigma_{xy} = -\sigma_{yx}$, since only the two (real) matrices $I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and $J = i\sigma_2 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$ remain invariant under general rotations $R = e^{\phi J}$ in the plane with $R(\alpha I + \beta J)R^T = \alpha I + \beta J$.

From the results of the previous example the *longitudinal* conductivity $\sigma_{xx}(B_0) = \sigma_{yy}(B_0)$ is even in B_0 and leads to dissipation. The *transverse* conductivity $\sigma_{xy}(B_0) = -\sigma_{yx}(B_0)$ (odd in B_0) is purely reactive. For small magnetic field strengths σ_{xy} becomes proportional to B_0 (*Hall effect*). In the perfect Hall effect $\sigma_{xx} = \sigma_{yy} = 0$ (no dissipation). Thus this effect can be described in a closed system with a Hamiltonian. Quantizing the problem leads to Landau levels and to $\sigma_{xy} = \nu e^2/h$ with $\nu \in \mathbb{Z}$ (*quantum Hall effect*).

7.4 Thermoelectric effects

We apply the results of the previous chapter to thermoelectric processes. We consider a system of charged particles with charge q. Unlike in Chapter 7.1 we now allow for particle transport in addition to energy transport. The change in particle number gives rise to the work

$$\delta W = \delta W_{\text{chem.}} + \delta W_{\text{eletr.}} = \mu dN + \Phi dQ = (\mu + q\,\Phi) dN = \mu_e dN \tag{7.33}$$

with the electrochemical potential $\mu_e = \mu + q\,\Phi$. For charged particles the electrochemical potential plays the role of the chemical potential. In particular $\mu_e(\boldsymbol{r}) = \text{const.}$ in equilibrium.

Remark: In a metal the chemical potential μ is normally fixed by the positive background charge to ε_F and cannot be changed appreciably. For this reason in a metal we may replace the electrochemical force $\boldsymbol{\nabla}\mu_e = -q\boldsymbol{\mathcal{E}}$ by the electric force $q\boldsymbol{\nabla}\Phi = -q\boldsymbol{E}$.

The change in entropy is described by $Tds = du - \mu_e dn$ (we again neglect thermal expansion effects). This leads to the relation

$$T\frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \mu_e \frac{\partial n}{\partial t}\,. \tag{7.34}$$

The change in particle density is given by the continuity equation

$$\frac{\partial n}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}^n = 0 \tag{7.35}$$

with the particle current density $\boldsymbol{j}^n$. For the energy one has analogously

$$\frac{\partial u}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}^e = 0 \tag{7.36}$$

with the energy current density $\boldsymbol{j}^e$. Compared to equation (7.1) not all of the energy current is a heat current because of the electrochemical work. Rather one has

$$\boldsymbol{j}^q = T\boldsymbol{j}^s = \boldsymbol{j}^e - \mu_e \boldsymbol{j}^n \tag{7.37}$$

owing to the fundamental relation $Tds = du - \mu_e dn$. To clarify the heat current $\boldsymbol{j}^q$ consider particle exchange in which each particle carries energy $\varepsilon = \mu_e$. In this case $\boldsymbol{j}^e = \mu_e \boldsymbol{j}^n$ and the process proceeds reversibly without heat exchange. A finite heat current therefore corresponds to the exchange of "hot" ($\varepsilon > \mu_e$) or "cold" ($\varepsilon < \mu_e$) particles.

We use the two continuity equations in (7.34) and obtain

$$\frac{\partial s}{\partial t} = -\frac{1}{T}\boldsymbol{\nabla}\cdot\boldsymbol{j}^e + \mu_e \boldsymbol{\nabla}\cdot\boldsymbol{j}^n \overset{(7.37)}{=} -\boldsymbol{\nabla}\cdot\boldsymbol{j}^s + \boldsymbol{j}^e\cdot\boldsymbol{\nabla}\frac{1}{T} - \boldsymbol{j}^n\cdot\boldsymbol{\nabla}\frac{\mu_e}{T} \tag{7.38}$$

A comparison with (7.9) shows that the last two terms are the entropy production rate $\dot{\mathsf{s}}$. Hence

$$\dot{\mathsf{s}} = \boldsymbol{j}^e \cdot \boldsymbol{\nabla}\frac{1}{T} - \boldsymbol{j}^n \cdot \boldsymbol{\nabla}\frac{\mu_e}{T} = \left(\boldsymbol{\nabla}\frac{1}{T}\right) \cdot \boldsymbol{j}^q - \frac{1}{T}(\boldsymbol{\nabla}\mu_e) \cdot \boldsymbol{j}^n \,. \tag{7.39}$$

As already shown, the first term describes entropy production from heat flow from a higher to a lower temperature. The second term is the Joule heating $\boldsymbol{\mathcal{E}} \cdot \boldsymbol{j}$, where $\boldsymbol{j} = q\boldsymbol{j}^n$ denotes the electric current density. It arises because electrochemical work is converted into heat.

Comparing (7.39) with (7.15) shows that $\boldsymbol{\nabla}(1/T)$ and $-(\boldsymbol{\nabla}\mu_e)/T$ are the thermodynamic forces conjugate to the currents $\boldsymbol{j}^q$ and $\boldsymbol{j}^n$.[2] The reciprocity relations (for $\boldsymbol{B}_0 = 0$) read

$$\begin{aligned} \boldsymbol{j}^n &= -L_{11}\frac{1}{T}\boldsymbol{\nabla}\mu_e + L_{12}\boldsymbol{\nabla}\frac{1}{T} = -\frac{L_{11}}{T}\boldsymbol{\nabla}\mu_e - \frac{L_{12}}{T^2}\boldsymbol{\nabla}T \,, \\ \boldsymbol{j}^q &= -L_{12}\frac{1}{T}\boldsymbol{\nabla}\mu_e + L_{22}\boldsymbol{\nabla}\frac{1}{T} = -\frac{L_{12}}{T}\boldsymbol{\nabla}\mu_e - \frac{L_{22}}{T^2}\boldsymbol{\nabla}T \,. \end{aligned} \tag{7.40}$$

We now relate the three transport quantities L_{11}, L_{12}, L_{22} to already familiar quantities. For heat and charge transport one has the standard form

$$\boldsymbol{j}^q = -\kappa\,\boldsymbol{\nabla}T + \Pi\,\boldsymbol{j} \,, \qquad\qquad \boldsymbol{\mathcal{E}} = \frac{1}{\sigma}\,\boldsymbol{j} + \epsilon\,\boldsymbol{\nabla}T \,, \tag{7.41}$$

with the Peltier coefficient Π and the thermopower ϵ (Seebeck coefficient). The reason for this notation is that experimentally the electric current $\boldsymbol{j} = q\,\boldsymbol{j}^n$ and the temperature gradient $\boldsymbol{\nabla}T$ are most easily held fixed. Comparing (7.40) and (7.41) yields relations between the coefficients. For example, in the case $\boldsymbol{\nabla}T = 0$ one obtains

$$\sigma = \frac{q^2 L_{11}}{T} \qquad \text{and} \qquad \sigma\Pi = \frac{qL_{12}}{T} \,. \tag{7.42}$$

Likewise for $\boldsymbol{\nabla}\mu_e = -q\boldsymbol{\mathcal{E}} = 0$ we find the relations

$$\sigma\epsilon = \frac{qL_{12}}{T^2} \qquad \text{and} \qquad \kappa + \sigma\epsilon\Pi = \frac{L_{22}}{T^2} \,. \tag{7.43}$$

Comparing the two expressions for L_{12} gives the reciprocity relation

$$\Pi = \epsilon\,T \tag{7.44}$$

between the Peltier coefficient and the thermopower.

We illustrate equations (7.41) with a few examples.

[2] Alternatively one could treat $\boldsymbol{j}^e$ and $\boldsymbol{j}^n$ as the independent currents. In that case the forces would be $\boldsymbol{\nabla}(1/T)$ and $-\boldsymbol{\nabla}(\mu_e/T)$.

Example 6: (Electrical conduction)

For a system without a temperature gradient $\boldsymbol{\nabla} T = 0$ Ohm's law

$$\boldsymbol{j} = \sigma \boldsymbol{\mathcal{E}} \,, \tag{7.45}$$

holds, where $\boldsymbol{\mathcal{E}} = \boldsymbol{E} - (1/q)\boldsymbol{\nabla}\mu$ accounts for the full electrochemical force. Note that even without a temperature gradient heat is transported according to

$$\boldsymbol{j}^q = \Pi \, \boldsymbol{j} = \Pi \, \sigma \boldsymbol{\mathcal{E}} \,. \tag{7.46}$$

Example 7: (Thermal conduction)

Thermal conduction from Chapter 7.1 is recovered when no electric current/particle current flows, $\boldsymbol{j} = 0$. One then obtains Fourier's law

$$\boldsymbol{j}^q = -\kappa \boldsymbol{\nabla} T \,. \tag{7.47}$$

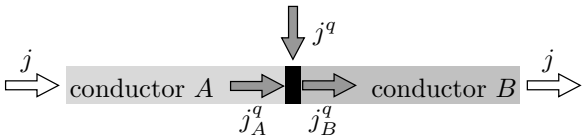
Note that in this case the electrochemical force does not vanish but instead

$$\boldsymbol{\mathcal{E}} = \epsilon \boldsymbol{\nabla} T \tag{7.48}$$

holds. For this reason the coefficient ϵ is called the *thermopower*.

Example 8: (Peltier effect)

We consider two different metals (A and B) at a uniform temperature T. We drive an electric current j through the contact.

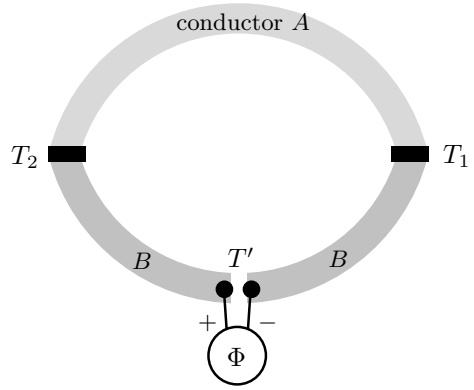


The heat current is then given by (7.46). At the junction there is a discontinuity of magnitude

$$j^q = j^q_B - j^q_A = (\Pi_B - \Pi_A) j \,. \tag{7.49}$$

In the steady state this heat must be supplied to the junction if the current j flows from conductor A to conductor B. Reversing the current direction also reverses the sign of j^q. For one current direction the junction cools, for the opposite it heats.

Example 9: (Seebeck effect)



The Seebeck effect is closely related to the Peltier effect. Here one considers an (electrically) open circuit with $\boldsymbol{j} = 0$. Two metals are joined by two contacts at different temperatures T_1, T_2. The resulting voltage Φ can then be measured with a voltmeter at temperature T'.

In the open circuit (7.48) applies. The electromotive force is given by

$$\Phi = -\oint \boldsymbol{\mathcal{E}} \cdot d\boldsymbol{s} = -\oint \epsilon \boldsymbol{\nabla} T \cdot d\boldsymbol{s} = \oint T \boldsymbol{\nabla} \epsilon \cdot d\boldsymbol{s} \,. \tag{7.50}$$

In the last form the integral receives a contribution only at the contacts.[3] Hence

$$\Phi = T_1(\epsilon_A - \epsilon_B) + T_2(\epsilon_B - \epsilon_A) = (\epsilon_B - \epsilon_A)(T_2 - T_1) \,. \tag{7.51}$$

Example 10: (Thomson effect)

We consider a material with a steady current distribution $\nabla \cdot \boldsymbol{j} = 0$ subject to a temperature gradient. The local energy generation is given by

$$\frac{\partial u}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{j}^e \overset{(7.37)}{=} -\boldsymbol{\nabla} \cdot \boldsymbol{j}^q - \boldsymbol{\nabla} \cdot \left(\frac{\mu_e}{q} \boldsymbol{j} \right) = -\boldsymbol{\nabla} \cdot \boldsymbol{j}^q + \boldsymbol{\mathcal{E}} \cdot \boldsymbol{j} - \frac{\mu_e}{q} \underbrace{\boldsymbol{\nabla} \cdot \boldsymbol{j}}_{=0, \text{ since steady}}$$

Inserting the relations (7.41) yields the result

$$\frac{\partial u}{\partial t} = \boldsymbol{\nabla} \cdot (\kappa \boldsymbol{\nabla} T) + \frac{1}{\sigma} \boldsymbol{j}^2 + \underbrace{\left(\epsilon - \frac{d\Pi}{dT} \right)}_{-T d\epsilon / dT} \boldsymbol{\nabla} T \cdot \boldsymbol{j} \,, \tag{7.52}$$

where we have used that Π depends only on T.

The first term describes heating from sources in the heat current $-\kappa \boldsymbol{\nabla} T$ driven by the temperature gradient. The second term is the (electric) Joule heating $\boldsymbol{E} \cdot \boldsymbol{j}$. The last term is the *Thomson heat*

$$\dot{q}_{\text{Th}} = -\tau \boldsymbol{\nabla} T \cdot \boldsymbol{j}, \qquad \text{Thomson coefficient } \tau = T \frac{d\epsilon}{dT} \,. \tag{7.53}$$

[3] We assume that the temperature dependence of ϵ within a material is much smaller than the difference between the materials.

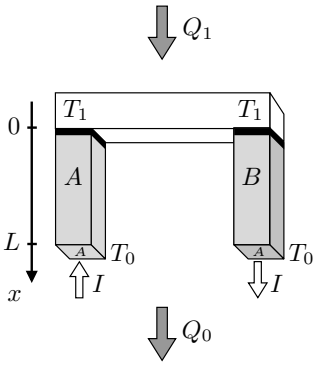


Fig. 7.1: Setup of a Peltier element. It consists of three conductors. Two columns made of the conductor materials A and B are connected by a crossbar. The lower ends of the columns at $x = L$ are at room temperature T_0. A current I is driven clockwise through the system. We denote the Peltier coefficients of the two junctions by Π_A, Π_B. By the experimental arrangement (with $\Pi_B > \Pi_A$) the crossbar is cooled to the temperature $T_1 < T_0$.

The Thomson coefficient measures how much heat is absorbed or released per temperature change in an electrical conductor when a current flows through a temperature gradient.

Remark: The Thomson coefficient τ is important because it can be measured directly for a material. The Peltier coefficient Π and the thermopower ϵ can only be determined relative to another material. A typical choice for the reference material is platinum.

Peltier Element: To conclude, we consider a Peltier element as a typical example of a nonequilibrium problem. Such elements are used as portable cooling devices. The system consists of two conductors A and B with Peltier coefficients $\Pi_B > \Pi_A$, which are coupled by two junctions to a conductor that is to be cooled, see Figure 7.1. The system is driven by an electric current I. The conductors have cross-sectional area A with the electric current densities $j_B = -j_A = I/A$ along the x axis. We consider the steady state that is established after some time. We simplify the problem by assuming that the material constants κ, σ and $\epsilon = \Pi/T$ are temperature independent.

The electric problem is solved by specifying the current density. The thermal problem is governed by the equation (7.52) and (7.41). In the steady state, because of (7.52), in conductor A

$$0 = \boldsymbol{\nabla} \cdot (\kappa_A \boldsymbol{\nabla} T_A) + \frac{1}{\sigma_A} \boldsymbol{j}^2 = \kappa_A T_A''(x) + \frac{I^2}{\sigma_A A^2} \,. \tag{7.54}$$

The temperature distribution with the boundary conditions $T_A(L) = T_0$ and $T(0) = T_1$ is given by

$$T_A(x) = T_1 + \frac{(T_0 - T_1)x}{L} + \frac{I^2}{2A^2 \sigma_A \kappa_A} x(L - x) \,. \tag{7.55}$$

In conductor B the same relation holds with $\sigma_A, \kappa_A \mapsto \sigma_B, \kappa_B$.

The waste heat power $\dot{Q}_0$ into the heat bath T_0 is given by $A\big[j_A^q(L) + j_B^q(L)\big]$. From

(7.41) we obtain

$$\begin{aligned}\dot{Q}_0 &= -A\kappa_A T_A'(L) + A\epsilon_A T_0 j_A - A\kappa_B T_B'(L) + A\epsilon_B T_0 j_B \\ &= \epsilon T_0 I + \frac{1}{2}RI^2 - K\Delta T \end{aligned} \tag{7.56}$$

with

$$\epsilon = \epsilon_B - \epsilon_A, \qquad R = \frac{L(\sigma_A^{-1} + \sigma_B^{-1})}{A}, \qquad K = \frac{A(\kappa_A + \kappa_B)}{L}, \qquad \Delta T = T_0 - T_1\,.$$

Analogously one obtains the cooling power

$$\dot{Q}_1 = A\big[j_A^q(0) + j_B^q(0)\big] = \epsilon T_1 I - \frac{1}{2}RI^2 - K\Delta T \tag{7.57}$$

With the first law of thermodynamics

$$\dot{W} = \dot{Q}_0 - \dot{Q}_1 = RI^2 + \epsilon I\Delta T\,. \tag{7.58}$$

This power must be supplied by the voltage source driving the current I. The electric power is $\dot{W} = IV$. Hence we find that the voltage

$$V = RI + \epsilon\Delta T \tag{7.59}$$

is dropped across the system. The first term is the voltage drop across the resistance. The second term corresponds to the additional voltage drop due to the Seebeck effect.

The efficiency of the cooling element is given by

$$\begin{aligned}\eta = \frac{\dot{Q}_1}{\dot{W}} &= \frac{\epsilon T_1 I - \frac{1}{2}RI^2 - K\Delta T}{RI^2 + \epsilon I\Delta T} = \frac{KR + \overline{T}\epsilon^2}{\epsilon(RI + \epsilon\Delta T)} - \frac{K}{\epsilon I} - \frac{1}{2} \\ &= \frac{1}{T_0/T_1 - 1} - \frac{RI^2\overline{T} + K(\Delta T)^2}{(RI^2 + \epsilon I\Delta T)\Delta T}\end{aligned} \tag{7.60}$$

with the average temperature $\overline{T} = \frac{1}{2}(T_0 + T_1)$. The efficiency as a function of the current has a maximum. Solving the condition $\partial\eta/\partial I = 0$ for I yields

$$I^* = \frac{\epsilon\Delta T}{R(\sqrt{1 + Z\overline{T}} - 1)} \tag{7.61}$$

with the figure of merit

$$Z = \frac{\epsilon^2}{RK}\,. \tag{7.62}$$

At the optimal current I^* the system reaches the maximum efficiency

$$\eta^* = \frac{1}{T_0/T_1 - 1}\left(1 - \frac{T_0/T_1 + 1}{\sqrt{1 + Z\overline{T}} + 1}\right)\,. \tag{7.63}$$

The first term is the optimal result of a Carnot machine. The second term is negative and thus the Peltier element operates at a lower efficiency. For a large efficiency the dimensionless figure of merit $Z\overline{T}$ should be as large as possible. To this end it is necessary to have materials with small resistance and small thermal conductivity.

In metals the figure of merit is bounded by the Wiedemann-Franz law

$$RK = \frac{\pi^2}{3}\frac{k_B^2}{e^2}T \tag{7.64}$$

In realistic situations K is even larger than the electronic contribution of the Wiedemann-Franz law due to the phonon contribution. Altogether we have the estimate

$$Z\overline{T} \lesssim \frac{3e^2\epsilon^2}{\pi^2 k_B^2} \approx 4 \times 10^{-5} \left(\epsilon\,[\mu\mathrm{V/K}]\right)^2 . \tag{7.65}$$

Typical metals have a thermopower ϵ on the order of a few μV/K. Thus metals are unsuitable as Peltier elements.

In semiconductor heterostructures the Wiedemann-Franz law does not hold. Although there is no thermodynamic bound on $Z\overline{T}$, all known materials have values $\lesssim 3$. Finding systems with $Z\overline{T} \gg 1$ is an active field of research. This is technologically important in particular because one can operate a Peltier element in reverse (as a heat engine) and thereby generate electric power from a temperature difference. The idea is to use such elements in electric circuits for heat recovery. However, the efficiency η^* depends only very weakly (via the square root) on the figure of merit.

For a cooling element the minimal temperature $T_1 = T_{\min}$ that can be reached is given by the point where $\eta^* = 0$. We obtain

$$T_{\min} = \frac{T_0}{\sqrt{1+Z\overline{T}}}, \qquad \text{or equivalently} \qquad T_{\min} = \frac{\sqrt{1+2ZT_0}-1}{Z} . \tag{7.66}$$

The current required to reach this minimal temperature is

$$I_{\max} \overset{(7.61)}{=} \frac{\epsilon\Delta T}{R(T_0/T_{\min}-1)} = \frac{\epsilon\, T_{\min}}{R} . \tag{7.67}$$

This current is delivered at a voltage

$$V_{\max} = RI_{\max} + \epsilon(T_0 - T_{\min}) = \epsilon\, T_0 \tag{7.68}$$

Rather than maximizing the efficiency, for practical applications it is often more useful, at given temperatures T_0, T_1, to achieve a maximum cooling power $\dot{Q}_1$. The expression (7.57) is optimized at the current

$$I_{\mathrm{KL}} = \frac{\epsilon\, T_1}{R} \tag{7.69}$$

One sees that this expression coincides with $T_1 = T_{\min}$ with (7.67). Thus at the minimal temperature maximum cooling power and maximum efficiency coincide. However, at this point $\eta^* = 0$ so that the cooling power vanishes.

In general, at a given temperature T_1 the maximum cooling power

$$\begin{aligned}\dot{Q}_{\max} = \dot{Q}_1\big|_{I=I_{\mathrm{KL}}} &= \frac{\epsilon^2 T_1^2}{2R} - K\Delta T = K\left(\frac{ZT_1^2}{2} - \Delta T\right) \\ &= \frac{\epsilon^2}{2R}(T_1^2 - T_{\min}^2) + K(T_1 - T_{\min}) \end{aligned} \tag{7.70}$$

can be achieved. It turns out that the cooling power is proportional to the thermal conductivity K and vanishes as the difference between the temperature of the cooling element and the minimal temperature $T_{\min}$ decreases.

Notation

dU	exact differential
δW	general differential
$(\partial U/\partial T)_V$	derivative dU/dT at constant V
W, Q	work, heat
S	entropy
V, U, N	volume, internal energy, particle number (extensive quantities)
p, T, μ	pressure, temperature, chemical potential (intensive quantities)
H, F, G, Ω	enthalpy, free energy, Gibbs energy, grand potential
Z_α, g_α	general work coordinate, general equilibrium quantity
d^2U	Hessian matrix
$\boldsymbol{Z}$	all (ext.) quantities $(U, Z_1, Z_2, \dots)$ that determine a state
$Z_N, \mathcal{Z}$	canonical, grand canonical partition function
$\Gamma(\boldsymbol{Z})$	number of microstates compatible with a macrostate $\boldsymbol{Z}$
$\overline{X}$	expectation value of X
$(\delta X)^2$	fluctuation square/variance of X
$v = V/N$	specific volume
$n = v^{-1}$	particle density
λ	thermal wavelength
$c_i = N_i/N$	concentrations of species i