Statistical Mechanics

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Chapter 1

The Laws of Thermodynamics

Thermodynamics is a physical theory that makes statements about systems for which we have incomplete information and control. It is not the case that the theory is incomplete simply because we do not make enough effort to understand a system in all its details. On the one hand, quantum mechanics imposes a fundamental limit on knowledge about the system due to the randomness of measurement results, and 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 fully know a macroscopic system. For example, consider a liter ($1\,\mathrm{dm}\times 1\,\mathrm{dm}\times 1\,\mathrm{dm}$) of helium gas at standard conditions.[1] There are approximately 10^{22} particles in that volume. If we want to specify the position of each particle with an accuracy of just $1\,\mathrm{mm}$, we would already need about $10^{22}\times 3\log_2(100)\simeq 20\times 10^{22}$ bits (approximately one zetabyte) of information. One can easily imagine how quickly we reach the limits of information processing with slightly larger systems.

The foundation of thermodynamics is based on dividing energy into two different classes, *heat* (Q) and *work* (W). Work has been known since the mechanics lecture. In thermodynamics, work refers only to the part of energy to which we have explicit access. In fact, in a specific experimental setup, there are often only a few degrees of freedom that can perform work: for example, in an engine, it is the torque of the crankshaft. Heat describes the part of energy that is contained in the remaining degrees of freedom. It is natural that work (and therefore heat) depends on the experimental setup. Thus, the thermodynamic terms heat, work, temperature, entropy, ... are relative to the experimental setup. We refer to this as *relatively objective* to distinguish ourselves from the position that statistics and thermodynamics are subjective and therefore not suitable for an objective description of nature.

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[1] Pressure $p = 1\,\mathrm{bar} = 10^5\,\mathrm{Pa}$, temperature $T = 300\,\mathrm{K}$.

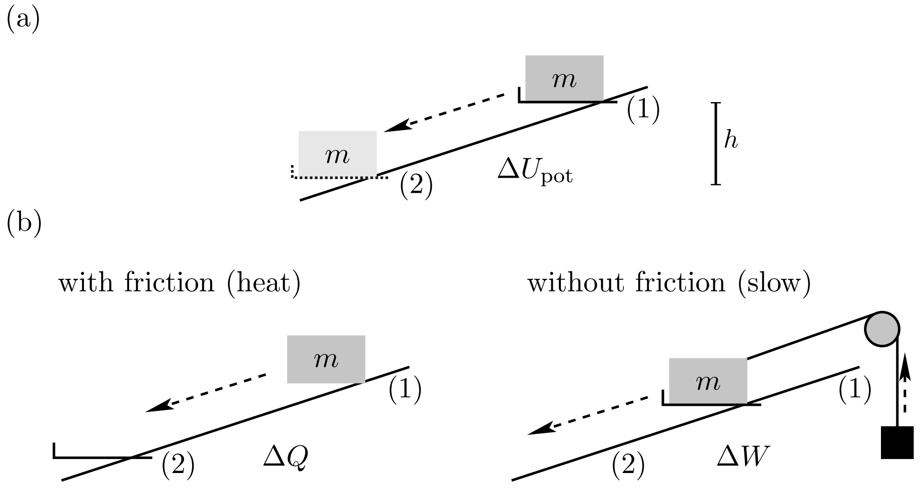

Fig. 1.1: (a) Thermodynamic system consisting of a mass m on an inclined plane in a gravitational field. There are two (equilibrium) states (1) and (2) with an energy difference $\Delta U_{\text{pot}} = U_{\text{pot}}^{(1)} - U_{\text{pot}}^{(2)} = mgh > 0$. The states are set by the slider under the mass as an external constraint. In (b) we consider two representative processes that undergo the transition (1)→(2). In the left image, the constraint is quickly moved from (1) to (2). The system is temporarily out of equilibrium as the mass slides down the inclined plane. At the equilibrium point (2), the mass has lost the potential energy ΔU_{pot}, which has been completely converted into heat ΔQ through friction. Alternatively, we can move the system slowly from (1) to (2) without friction, by investing the energy in the potential energy (work) of an additional mass as shown in the right image. In this case, no heat is generated and the energy is completely converted into work ΔW.

1.1 Introductory Example

We will 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. In case of later difficulties with the abstract formulation, one can also refer back to this chapter to concretize the concepts.

In the example, see Fig. 1.1, the *thermodynamic system* is given by a mass m in a gravitational field with acceleration g. In mechanics, we have studied systems without friction. In this case, the energy $E = K + U_{\text{pot}}$ (kinetic energy K and potential energy U_{pot}) remains constant. A mass point starting at rest at point (1) will have 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, this is limited to *equilibrium states.* In our example, due to friction, $K = 0$ at equilibrium at (1) and (2). These states are characterized by a small number of parameters (the *state variables*), especially by conservation quantities (energy E, ...) and by constraints (in the example, the sliders below the mass). In the example, we study *processes* that lead the transition from equilibrium state (1) to equilibrium state (2) with the energy difference ΔU_{pot}.

If the slider is moved from (1) to (2) without attaching a mass, the potential energy is completely converted into heat through friction with $\Delta Q = \Delta U_{\text{pot}}$. Alternatively, one can use dynamics to lift an additional mass (black box in Fig. 1.1(b)). By carrying out this process slowly, by attaching a suitable counterweight, there is no friction in the limit and $\Delta W = \Delta U_{\text{pot}}$, i.e. all the energy is now in the potential energy of the additional mass.[2] In general, not all the energy is converted into work. However, conservation of energy implies 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 sliders). Thus, energy is a *state quantity*. When transitioning from (1) to (2), the energy ΔU_{pot} is released independently of the process. On the other hand, work and heat are *process quantities*, meaning they depend on the process. Infinitesimally, we write dU (complete differential) for a state quantity and δW (general differential) for a process quantity, to express that the value of δW depends on the process.

A small mathematical review of the known: 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, there is no 'potential' $U(\boldsymbol{x})$ such that $\delta W = dU = \sum_j (\partial_{x_j} U) dx_j$. For there to be a potential and δW to be a complete differential, the integrability condition must be satisfied[3]

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

for all i, j. Then, for any closed path γ, we have

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

according to Stokes' theorem, and we find a potential

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

with respect to any initial point $\boldsymbol{x}_0$.

We will prove the following relationships between differential quotients in the exercises: Consider the variables x, y, z which are linked by the condition $f(x, y, z) = 0$. Then,

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

[3] It must also be noted that we have a simply-connected domain.

the following holds (we explicitly indicate with $(\cdot)_z$ which variable is held constant in 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 an additional condition $w(y, z)$, the chain rules hold:

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

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

1.2 Internal Energy, Work, Mechanical Equilibrium

Although the formulation of thermodynamics is more general, we will focus on N-particle systems for the sake of clarity. The energy is given by the Hamiltonian function

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

From mechanics, we know that a system without external potential ($U_{\text{ext}} = 0$) exhibits the 10 classical conservation 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 ($M\boldsymbol{X} - \boldsymbol{P}t = m \sum_j \boldsymbol{x}_j - \sum_j \boldsymbol{p}_j t$). Thermodynamics considers a generic system without additional conservation quantities. In particular, the interest lies in enclosing the thermodynamic system with U_{ext} in a volume of size V in such a way that at equilibrium, there is no macroscopic motion, i.e. no rotational motion ($\boldsymbol{L} = 0$) and no translational motion ($\boldsymbol{P} = 0$). In this case, the energy E at equilibrium is referred to as the *internal energy* with the symbol U, to indicate that all contributions to the energy result from internal motions of the system.

The (infinitesimal) work can be written as

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

with the *working coordinates* Z_α, which are under experimental control, and the *equilibrium quantities* g_α (see below). We use the sign convention so that $\delta W > 0$ corresponds to a process where work is supplied to the system. Thermodynamics is relative to the choice of working coordinates Z_α, which determine work as a usable form of energy. This is precisely the relative objectivity mentioned above. Once all Z_α are chosen, thermodynamics is uniquely determined.

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

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

as work is done against the (internal) force $\boldsymbol{F}_j$ when the coordinates $\boldsymbol{x}_j$ are changed.

Example 2: (Gas in a Container)

For most applications later on, we use the volume V as the only working coordinate. We consider a gas enclosed in a box with

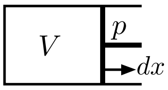
$$U_{\text{ext}}(\boldsymbol{x}) = \begin{cases} 0, & \boldsymbol{x} \in V, \\ \infty, & \text{otherwise.} \end{cases} \tag{1.10}$$

The work done when changing V is now only against the external potential. We obtain the supplied work

$$\delta W = -pdV \tag{1.11}$$

with the *pressure* p.

To see that the pressure really corresponds to the expression 'force per area,' consider the example of a (frictionless) piston:



If the position of the piston is changed by $dx > 0$, the volume increases by $dV = Adx$ with A being the cross-sectional area. Therefore, the gas performs work $-\delta W = pdV = pAdx$, where $F = pA$ corresponds to the force as desired.

The pressure has SI units (Pascal) $1\,\text{Pa} = 1\,\text{N/m}^2$. Furthermore, the Bar is also often used with $1\,\text{bar} = 10^5\,\text{Pa}$. The *standard pressure* (the average air pressure at sea level) is $1\,\text{atm} = 1.01325\,\text{bar}$.

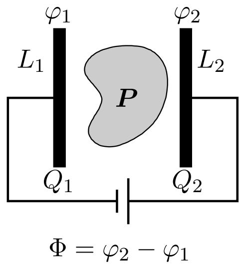
Since pressure is only defined in equilibrium, the process must proceed *quasi-statically*, meaning it is carried out so slowly that the system always remains in equilibrium. In order for the work of a change in internal energy to correspond, the process must also be *reversible*, meaning it can be reversed. This concretely means that the pressure for an infinitesimal compression is equal to that for an infinitesimal expansion.

In a realistic piston, the externally applied pressure p_K is not equal to the internal gas pressure p. Due to static friction between the piston and the wall, we have

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

Therefore, a real process is *irreversible*, as the work put into the system during compression cannot be fully recovered during a subsequent expansion. This makes the real process irreversible.

Example 3: (Dielectric in a Capacitor)



We consider a polarizable medium with polarization density $\boldsymbol{P}$ in a capacitor at a 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 being the field strength in the capacitor without the medium and the total polarization $\mathcal{P} = \int |\boldsymbol{P}|\, dV$. One can see the correspondence $p \leftrightarrow -E_0$, $V \leftrightarrow \mathcal{P}$ with the example 2.

Proof: The Maxwell equations $\mathrm{rot}\,\boldsymbol{E} = 0$ and $\mathrm{div}\,\boldsymbol{D} = \rho$ of electrostatics hold, 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 is $\varphi = \varphi_j$ on the conductor L_j.

During a small change in charge dQ brought from conductor L_1 to conductor L_2 ($dQ_2 = -dQ_1 = dQ$), the work done 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)

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

Thus, we obtain

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

where G is the region outside the conductors.

To obtain the energy contribution of the medium, we still need to subtract the energy of the system at the same voltage $\Phi_0 = \Phi$ without the dielectric. We obtain ($d\Phi = d\Phi_0$)

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

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

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

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[4] We use a unit system with $\varepsilon_0 = \mu_0 = 1$.

In applications, it is often the case that due to the isotropy of the medium, $\boldsymbol{P}$ is aligned with $\boldsymbol{E}_0$. For an isotropic medium, the (electrical) work is given by

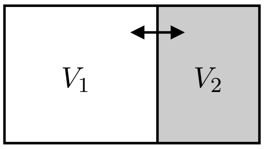
$$\delta W = \int E_0 \, dP \, dV = E_0 \, d\mathcal{P} \,, \tag{1.16}$$

where in the last step we assumed that E_0 (the field without the medium) is constant in the capacitance.

Example 4: Further examples of work coordinates that are often encountered are:

$$\begin{array}{c|cccccc} g_\alpha & -p & \sigma & E_0 & B_0 & \Phi & \mu \\ \hline dZ_\alpha & dV & dA & d\mathcal{P} & d\mathcal{M} & dQ & dN \end{array} .$$

Here, σ, A denote surface tension, surface area, and $B_0, \mathcal{M}$ the magnetic field, the total magnetization in a coil operated with a constant current source. The last pair is needed for describing particle exchange and chemical processes. Here, N is the number of particles and μ is the chemical potential, which corresponds to the work that must be done to add a particle to the system.



For the discussion of *mechanical equilibrium*, we want to focus on *additive* work coordinates. As an example, we consider the volume with $V = V_1 + V_2$ for a system consisting of two subsystems. The partition wall, which acts as an *inhibition*, experiences a pressure $p_1 - p_2$ (to the right). This leads to the equilibrium condition

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

This argument can be easily generalized to general additive work coordinates Z_α. The *mechanical equilibrium* is determined by the equilibrium quantities g_α being equal in the individual subsystems in mechanical contact.

For the *stability* of the equilibrium, it is crucial that at small deviations $dV_1 > 0$ from equilibrium, a restoring force is established, i.e.

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

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

Note that for short-range interaction U_{ww}, the internal energy is also (approximately) additive. We can decompose the internal energy into three parts

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

where U_1 includes the part of the energy H from (1.7) where the positions $\boldsymbol{x}_j$ are in 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 limited to a range ξ, only particles in a shell of thickness ξ contribute to U_{12}. The number of terms in (1.20) therefore scales as $(A\xi)\xi^3 \propto V^{2/3}$,[5] while the individual contributions $U_{1,2} \propto V$ increase. In the thermodynamic limit, $U_{12} \ll U_1, U_2$, and thus the internal energy is (approximately) additive with $U = U_1 + U_2$.

1.3 First Law of Thermodynamics

After these preliminary considerations, we want to formulate the first law of thermodynamics:

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

Thus, the internal energy becomes a state variable and the change dU becomes a complete differential. Furthermore, we define heat for a general 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 only makes a statement about states that can be reached by a work process. For example, if no particle exchange is allowed in δW, the work and thus the 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 variable, one can talk about how large the internal energy of a state is. A similar statement cannot be made about work and heat. It is not the case that part of the internal energy is work and the rest is heat. The terms work and heat are purely process quantities and can only be defined as changes $\delta Q, \delta W$.

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[5] Given particle density n, there are $nA\xi$ particles in the shell, each interacting with particles in a volume ξ^3.

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

Let us consider a thermally isolated system with $\delta Q = 0$, then we have $dU = \delta W$ and thus for any arbitrary *cycle process* (initial state = final state)

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

Therefore, it is not possible to extract work from a system in a cycle process. As we have seen, in reality, the external forces do not exactly correspond to the internal forces. In the piston example, we discussed that more pressure must be applied during compression, and less pressure is exerted outward during expansion. For this reason, for a real cycle process, the total work $\oint \delta W = -\oint p_K dV$ is actually positive, meaning that work must be invested to operate the cycle process.

Consequence 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, we have

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

The index $j = 1, 2$ refers to two subsystems exchanging Z_α.

Consequence 3: For two thermally isolated systems ($\delta Q_j = 0$) in *constrained equilibrium*, where the individual volumes V_1, V_2 are kept fixed with $V = V_1 + V_2$, we obtain 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 value of U as a function of V_1 (at $dV = 0$).

The stability condition (1.18) leads to

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

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

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

Consequence 4: (mechanical Maxwell relations)

As seen before, δW has a complete integral on the subspace with $\delta Q = 0$. Therefore, the integrability conditions (1.2) hold there

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

For the case of a gas considering particle exchange, with $\delta W = -pdV + \mu dN$, the Maxwell relation holds

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

Consequence 5: The state variables $\boldsymbol{Z} = (U, Z_1, Z_2, \dots)$ uniquely determine an equilibrium state.

Starting from any equilibrium state, one can reach the other equilibrium states through processes. The change in the work variables $Z_1, Z_2, \dots$ describes all possible mechanical changes δW. The amount of heat exchanged is determined by specifying dU through $\delta Q = dU - \delta W$. The first law guarantees that U itself exists and is a state quantity. Thus, every thermodynamic equilibrium state is uniquely determined by specifying $\boldsymbol{Z}$.

Let us consider again a thermodynamic system consisting of two parts. In mechanical contact, the quantities g_α (such as pressure, chemical potential, …) are equal. For the internal energy, $U = U_1 + U_2$. If we now allow *thermal contact* between the parts, this allows for the exchange of energy in the form of heat. The question now is how the total energy U is distributed among the two subsystems in equilibrium.

The *zeroth law of thermodynamics* guarantees that a thermal equilibrium is established and that it is also transitive. This means that if 1 is in thermal equilibrium with 2 and 2 is in thermal equilibrium with 3, then 1 is also in equilibrium with 3. The equilibrium quantity associated with internal energy is called *temperature* ϑ. Through thermal contact, the temperatures of the subsystems equalize. It is natural to choose the sign of the temperature so that U increases when ϑ increases. Due to 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 be brought to the temperature ϑ_0 through heat exchange. The conventional temperature scale is degrees Celsius (°C). At normal pressure, water freezes at 0 °C and boils at 100 °C.

1.4 Ideal Gas, Cycles

An (monoatomic) ideal gas is an N-particle system in volume V without interactions $U_{\mathrm{ww}} = 0$. Therefore, the internal energy consists only of kinetic energy with $U = K$ (the external potential U_{ext} only acts as a hindrance). Physically, thin noble gases, i.e., noble gases at low densities or high temperatures, are very well approximated as ideal gases. We consider ideal gases as a thermodynamic system with a fixed number of particles, so that the volume V is the only working coordinate. With the first law, a state is uniquely determined by the two state variables (U, V). In particular, this implies that there must be a relationship $f(V, p, \vartheta)$ between the three variables V, p, ϑ. Ideal gases satisfy a series of empirical properties, in particular, 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 through an overflow experiment: if an (ideal) gas with temperature T_1 expands from a volume V_1 to a larger volume V_2, the temperature of the gas does not change.

With the prior knowledge from mechanics, we can show that the two properties are equivalent. For this purpose, it is useful to look at the *virial* $\sum_j \boldsymbol{x}_j \cdot \boldsymbol{p}_j$. Using the Hamiltonian equations of motion, we obtain for the temporal change

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

When averaging this equation over time τ, the left side becomes

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

where we have assumed that the system is stable, with $\left|\sum_j \boldsymbol{x}_j \cdot \boldsymbol{p}_j\right| < \infty$. Furthermore, in equilibrium (with $\overline{d\boldsymbol{F}_{\mathrm{ext}}} = -p\,d\boldsymbol{A}$ on the surface ∂V)

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

This leads to the result

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

Thus, we have shown that Boyle's Law is equivalent to Gay-Lussac's Law. In the general case with $H = K + U_{\mathrm{pot}}$, the relationship

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

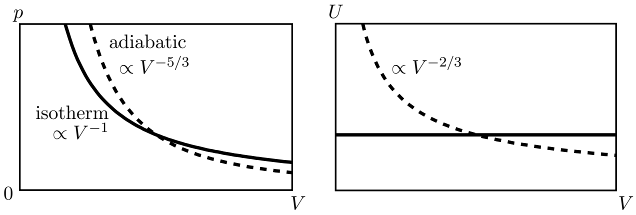


Fig. 1.2: Position and shape of adiabats and isotherms in the p-V and U-V diagrams.

where the last term corresponds to the virial of the interaction force, follows from (1.29) and (1.31).

In an isothermal process, according to Gay-Lussac, $\delta Q = -\delta W = pdV$. Therefore, in an ideal gas during an isothermal expansion ($V_2 > V_1$), the heat

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

is absorbed. Now, let's consider an *adiabatic* process (without heat exchange $\delta Q = 0$) that is carried out reversibly. It holds that

$$\frac{3}{2}(Vdp + pdV) = dU \overset{\text{(1st law)}}{=} \delta W = -pdV\,. \tag{1.35}$$

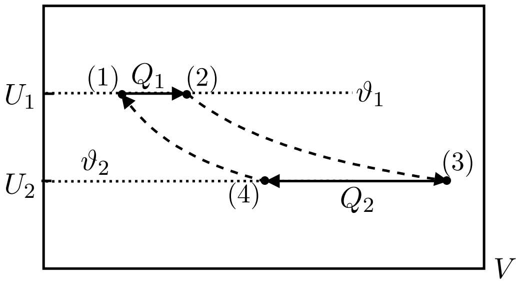
After separation in $(dp/p) = -\frac{5}{3}(dV/V)$, we obtain the solution

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

In Fig. 1.2, a comparison of adiabats with an isotherm for an ideal gas can be seen. It is important to note that the adiabat is steeper than the isotherm.

As a preliminary consideration for the second law, let's look at the *Carnot cycle*. A *cycle process* is a cyclically operating (heat) engine that converts work into heat or vice versa. In the Carnot process, an ideal gas is considered as a *heat engine*, which can be connected to two heat baths with temperatures ϑ_1 and $\vartheta_2 < \vartheta_1$, and to a working medium, as shown in Fig. 1.3.

We now examine the following reversible cycle 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 circular process is reversible. On the isotherms, the ideal gas is coupled to the respective heat bath. Using (1.34), we

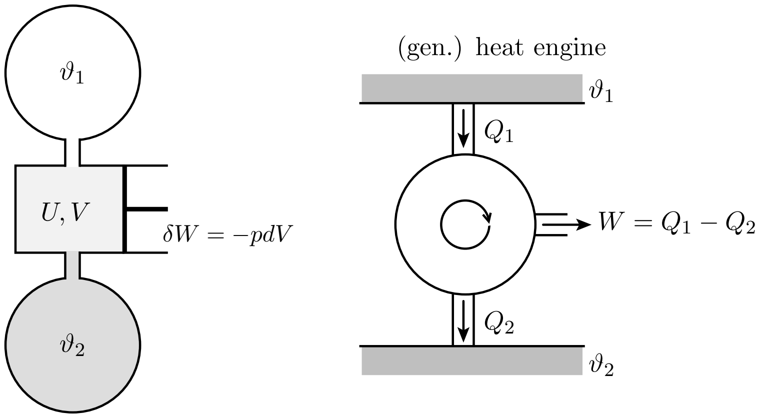


Fig. 1.3: General cycle process: A power machine extracts heat Q_1 from the heat bath at the higher temperature and converts it into work W and waste heat Q_2 (into the second heat bath). On the left, an experimental setup is shown. The two heat baths are coupled to the gas U, V with heat conductors. The work is done by the piston as the working medium. On the right, the corresponding energy flow diagram is shown. The efficiency η of a power machine is defined as η = work done/heat expended = W/Q_1.

obtain for the heat input (Q_1) and heat output (Q_2)

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

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

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

and is only a function $f(\vartheta_1, \vartheta_2)$ of the temperatures of the two heat baths due to Gay-Lussac. As a result, the *Carnot efficiency* is obtained

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

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

$$\eta_\mathrm{WP} = \frac{Q_1}{W} = \frac{1}{\eta_C}\,. \tag{1.40}$$

Note that the condition *reversible* is essential in order to be able to operate the process in reverse.

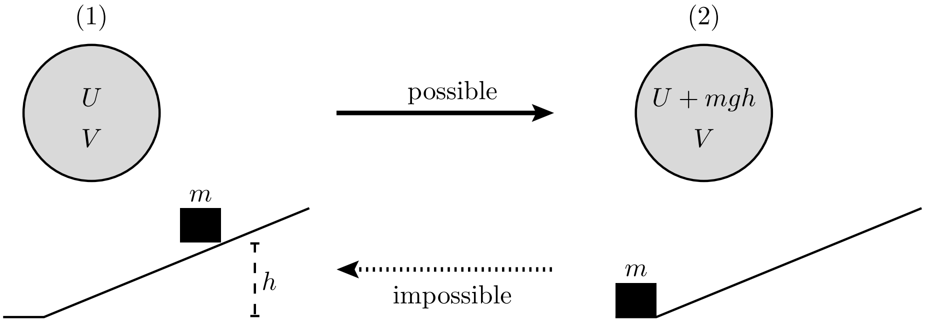
1.5 Second Law of Thermodynamics

The second law of thermodynamics allows us to calculate the distribution of internal energy between two subsystems for systems in thermal contact. It does much more than that. A consequence of the second law is the definition of an absolute temperature scale. Furthermore, it specifies that irreversible processes can only proceed in one direction. This allows us to distinguish whether a video recording is played forwards or backwards. The second law, with *entropy* as the associated state variable, is the cornerstone of thermodynamics.

First, let's consider the second law (postulate) in Kelvin's formulation:

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

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

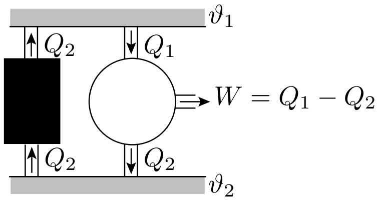


With Kelvin's formulation, everything is said for a single heat bath. It is more interesting to look at heat engines between two heat baths with $\vartheta_2 < \vartheta_1$.

Consequence 1: (Clausius' Formulation)

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

> To see that this formulation is equivalent to Kelvin's formulation, one can link Clausius' process (Black Box) with the Carnot process. This connects Clausius' machine to 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 not allowed according to Kelvin. (As an exercise, one can show the reverse direction.)



Consequence 2: (Carnot's Theorem)

The Carnot efficiency is the maximum efficiency for a cycle process between two heat baths.

To prove this, one connects the (imaginary) machine (Black Box) with an efficiency $\eta > \eta_C$ to the Carnot machine, which operates as a heat pump $(W/Q_1 = \eta_C, W/Q_1' = \eta)$. No work is done externally, but the amount of heat $Q = Q_1 - Q_1' = Q_2 - Q_2' = W(\eta_C^{-1} - \eta^{-1}) > 0$ is transferred from the cold to the warm heat bath.

Consequence 3: (Universality of reversible cycle processes)

Since reversible cycles can also be operated in reverse as heat pumps, it follows immediately from Carnot's theorem that the efficiency of a reversible cycle is always η_C. Otherwise, one could run the process backwards in the sketch of the conclusion 2 and thus violate Clausius' formulation. Thus, the Carnot efficiency is universal for all reversible cycles with two heat baths. The construction of the Carnot process using the ideal gas in Section 1.4 is only there to show that $\eta_C > 0$, meaning that a non-trivial reversible cycle exists. With the second law, one can show that real gases also have the same efficiency when operated reversibly (without additional friction losses). All reversible cycles are referred to as Carnot processes.

Consequence 4: (Absolute Temperature Scale)

For the function $f(\vartheta_1, \vartheta_2) = Q_2/Q_1$ in the Carnot efficiency $\eta = 1 - f(\vartheta_1, \vartheta_2)$ for reversible cycles, it holds (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 from the concatenation of 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. This effectively creates 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 setting the temperature T_0 of a standard bath 0, the *absolute temperature* (or thermodynamic temperature) $T = T_0 f(\vartheta_0, \vartheta)$ of any other heat bath (with the phenomenological temperature ϑ) is determined. Thus, $T > 0$ and

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

The Carnot efficiency thus has the simple form

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

as a function of absolute temperatures.

Please note that the temperature scale defined in this way has only one degree of freedom (given by the specification of T_0). In particular, the different temperature scales only differ by a multiplicative constant. As a result, and due to the inequality $T > 0$, the *temperature zero point* is absolutely anchored (more on this in the third law). Conventionally, the Kelvin scale, as an absolute temperature scale, is defined such that there are exactly 100 Kelvin between the freezing and boiling points of water. The conversion formula from the phenomenological to the absolute scale is therefore

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

From the comparison of (1.42) with (1.38), we find $U \propto T$ for the ideal gas. Furthermore, U is proportional to the number of particles N, which leads us to the *caloric equation of state*[6]

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

where the Boltzmann constant is

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

experimentally determinable by the choice of temperature unit. Using (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 number of particles in units of the Avogadro constant[7]

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

which leads to

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

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

Consequence 5: (Clausius' Theorem)

For any cyclic process, we have

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

---

[6] The factor $\frac{3}{2}$ is a convention and ensures that the thermal equation of state (1.47) does not require a factor.

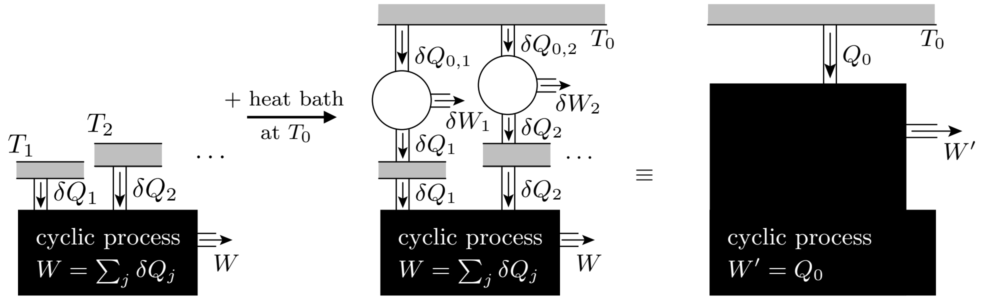
[7] This number is chosen so that a mole indicates the ratio of atomic mass u to one gram.

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

To prove this, we introduce an additional heat bath with temperature $T_0 \geq T_j$ and consider the entire system as a thermodynamic system. We then carry out the process step by step with Carnot engines between T_0 and each T_j with $\delta Q_j / \delta Q_{0,j} = T_j / T_0$. At the end of the cyclic process, we have only extracted the heat to the heat bath T_0

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

According to the first law, this heat has been completely converted into work $W = Q_0$. This is only permissible according to the second law if $Q_0 \leq 0$ (meaning that work has actually been converted into heat), which proves the theorem.



Consequence 6: (Irreversibility)

A reversible cyclic process can also be carried out in reverse. However, all heat quantities are reversed. With Clausius' theorem, we have $-\oint \delta Q/T \leq 0$ and thus (we indicate with subscript 'rev' that we are restricting ourselves to reversible processes)

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

Cyclic processes with $\oint \frac{\delta Q}{T} < 0$ are called *irreversible*, as they cannot be operated in reverse in time. The inequality determines a direction of time, the *thermodynamic arrow of time.*

Therefore, if one restricts oneself 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 only depends on the initial and final states.

This directly leads to the definition of a new state quantity, the *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 any reversible process from the fixed state $\boldsymbol{Z}_0$ to $\boldsymbol{Z}$ and S_0 is an undetermined integration constant. Thus, $dS = \delta Q/T$ is a complete differential, allowing us to interpret the temperature T as an *integrating factor*. Through the second law, the entropy is determined up to the additive constant S_0.

From the combination of the first and second law, one obtains the *Gibbs fundamental equation*

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

With this, one can obtain the complete thermodynamics from the state function $S(\boldsymbol{Z}) = S(U, Z_1, \dots)$. In particular, we have

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

In the case where volume is the only working coordinate, we obtain from

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

by rearranging 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. Additionally, we find the (thermal) Maxwell relation

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

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

In a thermally isolated system, entropy cannot decrease. It is also said that only such processes can occur *spontaneously.* Because from Clausius' theorem it follows for a process from (1) to (2)

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

with the equality sign in reversibility. For the proof, we complete the (thermally isolated) process to a cyclic process, performing the return from (2) to (1) reversibly (not necessarily adiabatically). This gives us

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

from which the result follows. The adiabatic process in a thermally isolated system is therefore not equivalent to isentropic ($dS = 0$). Only a reversible adiabatic process is isentropic.

Example 5: (Entropy of the ideal gas)

With these considerations, we can calculate 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) through a sequence of an adiabatic process ($V^{2/3}U = \text{const.}$) and an isothermal process (with the temperature T determined by (1.45)). On the adiabatic process, the entropy remains constant, and the gas expands to the volume $V_1 = (U_0/U)^{3/2} V_0$.

On the isothermal process, we have (with Eq. (1.34))

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

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

The second law provides a connection between the thermal $p(V, T)$ and the caloric $U(V, T)$ equation of state. To do this, consider S as a function of (V, T) and obtain

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

or $T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$ and $p = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial U}{\partial V}\right)_T$. From the first relationship, $T\left(\frac{\partial^2 S}{\partial V \partial T}\right) = \left(\frac{\partial^2 U}{\partial V \partial T}\right)$ (derivative with respect to V). Differentiating the second relationship with respect to T yields

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

Thus, the thermodynamic relationship holds

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

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

The thermal equation of state $pV = N k_B T$ (1.47) combined with (1.64), implies that

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

In this case, the internal energy $U(T)$ is independent of the gas volume V.

Example 7: (Relative Objectivity of Heat/Entropy)

> To understand the relative objectivity, we consider the thermodynamic system from Example 1, where all particle coordinates are extensive variables. 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. Therefore, $dU = \delta W$. For this system, there is no heat ($\delta Q = 0$) because all degrees of freedom are controlled externally. Furthermore, $S(U, \boldsymbol{x}_1, \dots) = S_0$. Thus, entropy becomes a constant (by the 3rd law $S = 0$). In reality, it is impossible to control all particle positions. However, the rule holds that with more extensive variables, the amount of heat typically decreases (because more internal energy is transformed into work in a process) and thus entropy decreases. Although entropy is a state quantity, it does not make sense to consider the 'entropy of a gas' as an absolute quantity. In fact, entropy depends on the extensive variables and therefore on the experimental possibilities. We will delve deeper into 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 with $\Delta S \to 0$ ($T \to 0$). This observation was further refined by Planck:

> *(Nernst's Heat Theorem)*
>
> For every system, entropy approaches a finite value independent of the extensive coordinates Z_α as $T \to 0$.

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

Note: The third law does not apply to the (classical) ideal gas (1.62). One can also take the opposite standpoint and conclude: every real gas deviates from ideal behavior as $T \to 0$. In fact, at low temperatures, it is important to consider quantum mechanics, which keeps the third law valid.

Consequence 1: (Unattainability of absolute zero)

> We consider a thermodynamic system with $\boldsymbol{Z} = (U, V)$, where V represents any working coordinate. A general process can be described with any precision by a sequence of isothermal and adiabatic processes. Isotherms naturally do not change the temperature. The adiabats are given by $S(\boldsymbol{Z}) = \text{const.}$ and do

not intersect. Now, states with $T = 0$ themselves form an adiabat (at $S = 0$). Thus, the zero point (starting from a state with $T > 0$) cannot be reached on either an adiabat or an isotherm.

Consequence 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 increase the temperature by one Kelvin. The heat capacities must vanish as $T \to 0$. 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 $C_V, C_p \to 0$ as $T \to 0$.

Chapter 2

Thermodynamic Potentials

In the last chapter, we have already found the thermodynamic potential $S(\boldsymbol{Z})$. In principle, the entire thermodynamics can be determined from the properties of entropy S as a function of the additive quantities $\boldsymbol{Z}$. We summarize the formalism in the following. 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 other potentials can be determined through Legendre transformations. Although all formulations are equivalent, trivial statements in one formulation can be highly nontrivial in another formulation. The art of thermodynamics is to formulate each question with a thermodynamic potential in such a way that the solution becomes as simple as possible.

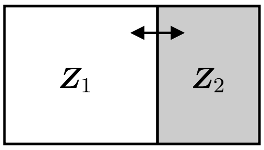
2.1 Entropy

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

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

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

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



We have already shown property (a) in (1.60). The other properties follow directly: property (b) follows when we consider two subsystems that are constrained by a partition. In the initial state, $S(\boldsymbol{Z}_1, \boldsymbol{Z}_2) = S(\boldsymbol{Z}_1) + S(\boldsymbol{Z}_2)$, since the constrained

The state in the two subsystems can be independently reached, and the amounts of heat in (1.54) are additive. After removing the constraints, the *complete equilibrium* is established, which is determined only by the total quantities $\boldsymbol{Z}_1 + \boldsymbol{Z}_2$. Since the removal of the partition (idealized) occurs without work and heat exchange, we have $S(\boldsymbol{Z}_1, \boldsymbol{Z}_2) = S(\boldsymbol{Z}_1) + S(\boldsymbol{Z}_2) \leq S(\boldsymbol{Z}_1 + \boldsymbol{Z}_2)$ according to (2.1a).

Through constrained equilibria, a class of non-equilibrium states is represented in thermodynamics. The *principle of maximum entropy*, property (c), states that in a closed system (with fixed $\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2$), the system is in complete equilibrium if and only if S is maximum, i.e.

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

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

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

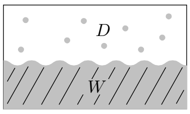
$$\begin{aligned} dS &= \frac{1}{T_1} dU_1 - \frac{1}{T_1}\sum_\alpha g_{1,\alpha} dZ_{1,\alpha} + \frac{1}{T_2}\overbrace{dU_2}^{-dU_1} - \frac{1}{T_2}\sum_\alpha g_{2,\alpha}\overbrace{dZ_{2,\alpha}}^{-dZ_{1,\alpha}} \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \sum_\alpha \left(\frac{1}{T_2}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

the equilibrium conditions follow

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

The condition that $\partial^2 S \leq 0$ (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 extensive variables are (V, N). The water surface is the partition. The separation is reversible (without surface tension) and therefore the entropies are additive, $S_\text{total} = S_W + S_D$. 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, but are connected by the vapor pressure curve $p(T)$, see later.

Example 2: (Heat Transport)

Consider two subsystems that are only in mechanical equilibrium, but where $T_1 > T_2$. By removing the constraints in U_1, U_2, the exchange of energy in the form of heat is made possible. If we keep the total system thermally isolated, we have $dU_1 = -dU_2$. Therefore, we have

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

With $T_1 > T_2$, we have $dU_2 \geq 0$, meaning that heat flows from the hotter to the colder part of the system in order to reach equilibrium.

Example 3 (Incomplete equilibrium)

One can remove constraints successively. In particular, we consider a *diathermic wall*, which allows heat exchange but prevents mechanical exchange. In equilibrium, we have $T_1 = T_2$ (but not necessarily $p_1 = p_2$). On the other hand, a movable adiabatic wall leads to the mechanical equilibrium that 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 composed of λ equivalent subsystems in complete equilibrium. Due to homogeneity, each subsystem is determined by the state variables $\boldsymbol{Z}/\lambda$, so that $\boldsymbol{Z} = (\boldsymbol{Z}/\lambda) + (\boldsymbol{Z}/\lambda) + \cdots$. Therefore, we have[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 $f(\lambda \boldsymbol{x}) = \lambda^\alpha f(\boldsymbol{x})$. Therefore, the entropy of a homogeneous system is homogeneous of degree 1, or also *extensive*. Extensive quantities are therefore S, U, V, Z_α. The equilibrium quantities like T, p, μ as the first derivatives of S with respect to $\boldsymbol{Z}$ are *intensive*, meaning 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 relationship $xS(\boldsymbol{Z}_1) + (1-x)S(\boldsymbol{Z}_2) = S(x\boldsymbol{Z}_1) + S((1-x)\boldsymbol{Z}_2)$. Additionally, the Eulerian homogeneity relationship holds[2]

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

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

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

---

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

[2] This can be derived directly by differentiating the relationship (2.6) with respect to λ and then setting $\lambda = 1$.

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

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

This relationship shows that the intensive variables are not independent.

2.2 Response Variables

The response of a thermodynamic system to changes in external conditions is determined by *response variables*. For the important case with volume V as the working variable, the following measured quantities are defined:

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

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

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

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

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

The response variables are all intensive and therefore (material-)specific. There are relationships between the variables. For example, we have

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

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 variables are independent.

Example 4 (Ideal Gas)

For the ideal gas with $pV = Nk_BT$ and $S(U,V)$ from (1.62), we determine through direct calculation

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

Example 5 (Perfect Gas)

For a (thermally) perfect gas, the thermal equation of state is $pV = Nk_BT$. From (1.64), we know that U and therefore c_V can only depend on T. We refer to a gas (thermally and calorically) as perfect if c_V is constant. The calorimetric equation of state is given by

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

It holds that

$$\delta Q = dU + pdV \overset{(dp=0)}{=} d(U + pV) = Nd(c_VT + k_BT)\,. \tag{2.20}$$

Therefore, for the specific heat at constant pressure

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

For an adiabatic process (see (1.35)), it holds that

$$\frac{c_V}{k_B}(Vdp + pdV) = dU = -pdV \tag{2.22}$$

and thus the adiabatic equation

$$pV^\gamma = \text{const.} \tag{2.23}$$

with the *adiabatic exponent*

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

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

Example 6: (TdS Equations)

It holds $TdS = dU + pdV = C_VdT + [(\partial U/\partial V)_T + p]dV$. From the relation (1.64) follows the TdS equation

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

A similar calculation with (T, p) as independent variables yields the second TdS equation

$$TdS = C_pdT - \alpha TVdp\,. \tag{2.26}$$

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

2.3 Internal Energy

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

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

Thus, the partial derivatives provide the thermodynamic quantities [cf. (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 thus provides the same information as $S(\boldsymbol{Z})$. Therefore, U is a thermodynamic potential with the *natural variables* (S, Z_α).

Example 7: (ideal gas)

The change in entropy is given by $TdS = C_V dT + [(\partial U/\partial V)_T + p]dV$, see example 6. By integration, we obtain the entropy of the perfect gas (cf. (1.62))

$$\begin{aligned} S &= \int \frac{(C_V dT + pdV)}{T} = C_V \ln(T/T_0) + N k_B \ln(V/V_0) \\ &= N[c_V \ln(U/U_0) + k_B \ln(V/V_0)] \,. \end{aligned} \tag{2.29}$$

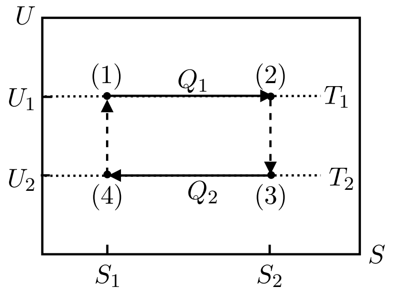
By reversing this, we obtain the internal energy (as a thermodynamic potential)

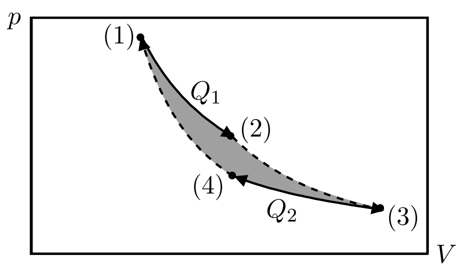
$$U(S, V) = U_0 \left(\frac{V_0}{V}\right)^{k_B/c_V} e^{S/Nc_V} = c_V N T \tag{2.30}$$

from which we can determine the entire thermodynamics. The result for the ideal gas is obtained with $c_V = \frac{3}{2} k_B$.

Example 8: (Carnot Cycle)

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





The work $W = \oint p dV = Q_1 - Q_2$ follows from the first law and corresponds to the area in the p-V diagram. The heat quantities $Q_{1,2} = \Delta S / T_{1,2}$ are determined by the second law through the entropy difference $\Delta S = S_2 - S_1$ and the respective temperature $T_{1,2}$. It holds $Q_1/T_1 = \Delta S = Q_2/T_2$ and thus $W = Q_1 - Q_2 = Q_1(1 - Q_2/Q_1) = \eta_C Q_1$. If we replace the U-S diagram with a T-S diagram, we see that the Carnot efficiency depends not on the medium but only on the temperature.

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

$$\Delta U \leq 0, \tag{2.31}$$

meaning that the internal energy can only decrease. To prove this, we complete the process, as in (1.60), by adding a reversible process to form a cycle with

$$0 \geq \oint \frac{\delta Q}{T} = \int_{(1)}^{(2)} \frac{\overbrace{\delta Q}^{=dU}}{T} + \overbrace{\int_{(2)}^{(1)} \frac{\delta Q_{\text{rev}}}{T}}^{=\Delta S = 0} = \int_{(1)}^{(2)} \frac{dU}{T} \overset{3}{\geq} \frac{1}{T_{\text{min}}} \Delta U \,. \tag{2.32}$$

An argument analogous to that 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 variables is in complete equilibrium if and only if the internal energy is minimal. Therefore, for a stable equilibrium, $dU = 0$ and $\partial^2 U \geq 0$.

Example 9: (Stability Conditions)

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

$$0 \leq \frac{\partial^2 U}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \quad \text{and} \quad 0 \leq \frac{\partial^2 U}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V \kappa_S} \,. \tag{2.33}$$

This leads to the conditions

$$c_V > 0 \quad \text{and} \quad \kappa_S > 0 \,, \tag{2.34}$$

meaning that with increasing temperature, entropy increases and an increase in volume leads to a decrease in pressure.

---

[3] Since $0 \geq \int dU/T$, we need to estimate T from below 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 be stable). Therefore, $U(S + dS, V + dV) + U(S - dS, V - dV)$ should be a minimum with respect to dS, dV, from which $\partial^2 U \geq 0$ follows.

The conditions (2.33) are necessary but not sufficient for the Hessian matrix $\partial^2 U$ to be positive semidefinite. The additional condition

$$0 \leq \mathrm{Det}(\partial^2 U) = \frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 \tag{2.35}$$

yields $\kappa_T > 0$, as we will show in Example 13. Together with (2.17), we obtain the stability conditions $c_p \geq c_V > 0$ and $\kappa_T \geq \kappa_S > 0$.

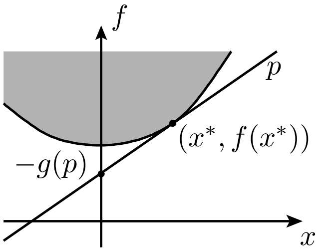
The internal energy is useful when considering a closed system that is both thermally and mechanically isolated, as the principle of minimal energy applies in that case. However, in applications, one is often interested in *open systems* that allow for heat and/or work exchange. To describe such systems, we want to recall the Legendre transformation in the next section, which we already know from the mechanics lecture. We will mostly focus on volume V as the only working coordinate. However, the results can easily be generalized to magnetization $\mathcal{M}$, ... In particular, we will explicitly discuss the grand potential Ω, which describes systems with particle exchange. From now on, we will focus on homogeneous systems. Thus, we use the terms 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]

$$g(p) = \max_x [xp - f(x)], \tag{2.36}$$

which is again convex. The Legendre transformation is an involution, i.e., its own inverse function, 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. As a result, the Legendre-transformed $g(p, y)$ of a convex function $f(x, y)$ becomes concave in y while remaining convex in p. However, in thermodynamics, one usually wants $g(p, y)$ to remain convex in the untransformed variable y. Therefore, one typically defines $-g(p, y)$ as the Legendre transform of $f(x, y)$ with

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

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

For a differentiable function, one can determine the Legendre transformation by differentiation. Since the derivative vanishes at the maximum x^*, we have

$$p = f'(x^*) \tag{2.37}$$

which determines $x = x^*(p)$ in terms of p. It is said that the Legendre transformation from x to $p = f'(x)$ changes the independent variable.

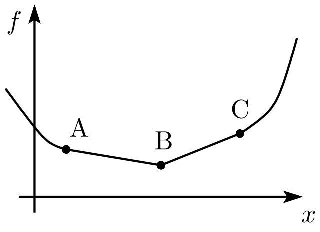
Considering how $g(p)$ behaves under small changes, we obtain

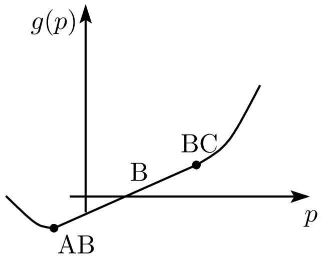
$$dg = d(x^*p - f(x^*)) = \overbrace{(p - f'(x^*))}^{0}\, dx^* + x^*dp = x^*dp. \tag{2.38}$$

Thus, we have

$$g'(p) = \frac{dg}{dp}(p) = x^*(p) = x \tag{2.39}$$

and we obtain the value of x of the original variable by differentiating g with respect to the new variable p. If the function f is not strictly convex but has straight segments, then 'straight lines of f' turn into 'corners of g':





Since $\mathcal{L}$ is an involution, this property holds true in reverse as well. We will further explore this property in the chapter on phase transitions.

2.5 Enthalpy

When heating a system at constant volume, the complete heat δQ according to the first law leads to an increase in internal energy $dU = \delta Q$. In chemical applications, the volume is often not kept constant but the pressure is. In this case, part of the heat is converted into work $\delta W = -pdV$. Changing the internal energy $U(S,V)$ from V to $p = -(\partial U/\partial V)_S$ as an independent variable, we obtain the *enthalpy*

$$H(S,p) = U + pV \tag{2.40}$$

i.e. $-H$ is the Legendre transform of U with respect to $-V$. It holds that

$$dH = \overbrace{dU}^{\delta Q - pdV} + pdV + Vdp = TdS + Vdp\,, \tag{2.41}$$

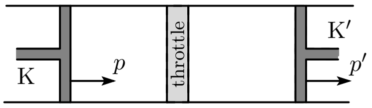


Fig. 2.1: Joule-Kelvin process: Pistons K and K′ are moved in such a way that the gas is pushed through the throttle. The pressure p and p' in the respective chambers are maintained. The throttle generates a pressure gradient $\Delta p = p - p' > 0$ and the process is irreversible.

thus heating a system at constant pressure p leads to an increase in enthalpy with $dH = \delta Q$. Furthermore, due to (2.41) we have

$$T = \left(\frac{\partial H}{\partial S}\right)_p, \qquad V = \left(\frac{\partial H}{\partial p}\right)_S. \tag{2.42}$$

The enthalpy is convex in S with $H(S_1 + S_2, p) \leq H(S_1, p) + H(S_2, p)$. The concavity in p is not as important, as constraints cannot be imposed on intensive variables. Therefore, in equilibrium, H is minimal with respect to constraints in S and $\Delta H \leq 0$ for processes at constant S and p.

Example 10: (Reaction Heat)

Chemical reactions are typically carried out at constant pressure. For a reaction, the change in enthalpy ΔH per amount of substance is given. From the previous considerations, we know that at constant pressure, the change in enthalpy directly corresponds to the change in heat. Therefore, we have:

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

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

Example 11: (Joule-Thomson process[6])

Gay-Lussac's overflow experiment showed that for an ideal gas, the internal energy is only a function of temperature T. The experimental setup was refined by Joule and Thomson. The experiment is carried out adiabatically with $\delta Q = 0$. The left piston K compresses the gas with constant pressure p through the cotton plug, which acts as a throttle, see Fig. 2.1. The right piston K′ retreats with constant pressure $p' < p$. Due to the pressure difference, the process is irreversible. We consider the steady state that occurs after some time when the

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

pistons are moved uniformly. We denote with u, u' the internal energy of the gas per volume on the left and right side (far away from the throttle).

Let us now consider a (arbitrary) time interval during which the left piston covers the volume V and the right piston covers the volume V'. Since no heat is exchanged, the 1st law requires that the work done $\Delta W = pV - p'V'$ corresponds to the change in internal energy $\Delta U = u'V' - uV$. By rearranging, we obtain

$$H = pV + uV = pV' + u'V' = H' \,, \tag{2.43}$$

meaning that the enthalpy remains constant.

We now inquire about the change in temperature when the gas flows over. In particular, we introduce the Joule-Thomson coefficient

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H \tag{2.44}$$

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

$$\mu_{\mathrm{JT}} = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} = -\frac{T(\partial S/\partial p)_T + V}{C_P} \,. \tag{2.45}$$

In (2.55), we will show that $(\partial S/\partial p)_T = -(\partial V/\partial T)_p = -\alpha V$ holds. Thus, we obtain

$$\mu_{\mathrm{JT}} = \frac{V}{C_P}(\alpha T - 1) \,. \tag{2.46}$$

For an ideal gas, $\alpha = 1/T$ and therefore $\mu_{\mathrm{JT}} = 0$. For real gases, at low temperatures $\mu_{\mathrm{JT}} > 0$ (the gas cools down) and at high temperatures $\mu_{\mathrm{JT}} < 0$ (the gas heats up). The temperature with $\mu_{\mathrm{JT}} = 0$ is called the *inversion temperature*. For nitrogen (N_2), for example, the inversion temperature is 621 K.

2.6 Free Energy

Solids are relatively rigid, and therefore 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 adapted to this system is the *free energy* $F(T, V)$, which we obtain as a Legendre transformation

$$F(T, V) = U - TS, \qquad dF = -SdT - pdV \tag{2.47}$$

from S to T with $T = (\partial U/\partial S)_V$.

The free energy gets 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 corresponds to the maximum work that can be performed during the process. The proof follows from

$$\Delta S \overset{(1.61)}{\geq} \int_{\boldsymbol{Z}_1}^{\boldsymbol{Z}_2} \frac{\delta Q}{T} = \frac{\Delta Q}{T} \tag{2.48}$$

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

$$-\Delta W = -\Delta U + \Delta Q \leq -\Delta U + T\Delta S = -\Delta F\,. \tag{2.49}$$

Here, $-\Delta W$ is the work done by the system on its surroundings, and equality holds for a reversible process. As a corollary, it follows that 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 in V.

Example 12: (Maxwell Relation)

From the interchange of the second derivatives, we obtain the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial p}{\partial T}\right)_V,, \tag{2.50}$$

which we will use in the following example.

Example 13: (Stability)

From the principle of minimum we obtain the stability condition

$$0 \leq \frac{\partial^2 F}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{V\kappa_T} \tag{2.51}$$

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

$$\begin{aligned}\frac{\partial^2 F}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_T &\overset{(1.6)}{=} -\overbrace{\left(\frac{\partial p}{\partial V}\right)_S}^{-\partial^2 U/\partial V^2} - \overbrace{\left(\frac{\partial p}{\partial S}\right)_V}^{-\partial^2 U/\partial V \partial S} \overbrace{\left(\frac{\partial S}{\partial V}\right)_T}^{(\partial p/\partial T)_V} \\ &= \frac{\partial^2 U}{\partial V^2} + \frac{\partial^2 U}{\partial S \partial V} \underbrace{\left(\frac{\partial p}{\partial S}\right)_V}_{-\partial^2 U/\partial S \partial V} \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{(\partial^2 U/\partial S^2)^{-1}} = \frac{\mathrm{Det}(\partial^2 U)}{\partial^2 U/\partial S^2}\,.\end{aligned} \tag{2.52}$$

Thus, the stability condition on F corresponds exactly to the condition on the determinant of the Hessian matrix (together with (2.33)). This corresponds to the fact that we have discussed before: all thermodynamic potentials contain essentially the same information. However, ‘simple’ insights in one formulation are often very complicated in another. Just consider the many steps in the derivation of (2.52).

2.7 Gibbs Energy

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

$$G(T,p) = U - TS + pV = F + pV = H - TS, \qquad dG = -SdT + Vdp \tag{2.53}$$

as a Legendre transformation of H or F. By coupling to a working medium at constant pressure p, work $-\Delta W = p\Delta V$ is done externally. From (2.49) we obtain

$$\Delta G = \Delta F - \Delta W \leq 0\,. \tag{2.54}$$

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

Example 14: (Continuation of Example 10)

When considering only volume work, no inhibitions can be introduced to G. Therefore, in this example, we consider a chemical reaction at constant pressure and temperature, where the number of particles acts as a work coordinate. The chemical transformations change the amounts of the individual substances (thus lifting the inhibition 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 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 the gaseous phase is stable at high temperatures.

As already seen, Maxwell's equations simply follow from the fact that the second derivatives commute. Each potential leads to its own Maxwell relation, with the Maxwell relations all being equivalent, of course. In particular, the relationship (1.64) between the thermal and the caloric equation of state is an expression of the Maxwell relation. For the Gibbs energy, we obtain the Maxwell relation

$$-\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 G}{\partial T \partial p} = \left(\frac{\partial V}{\partial T}\right)_p = V\alpha, \tag{2.55}$$

thus, 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 for F,

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial p}{\partial T}\right)_V = p\beta \tag{2.56}$$

we find equivalently that $p\beta$ must also vanish.[7] We will encounter the relationship

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[7] If the pressure remains finite, the stress coefficient must also vanish for $T \to 0$.

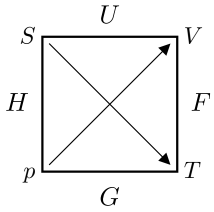


Fig. 2.2: The Guggenheim square shows the four potentials next to their respective natural variables. The partial derivatives of the potential with respect to a variable are opposite, resulting in a minus sign when moving against the arrow. So, $(\partial F/\partial T)_V = -S$ but $(\partial U/\partial S)_V = T$.

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

One can remember the four potentials with their respective natural variables using the Guggenheim square in Fig. 2.2.

2.8 Particle Exchange and Grand Potential

We have only looked at volume work so far. Of course, one can generalize the procedure to general work coordinates and perform a Legendre transformation with respect to each coordinate to obtain new thermodynamic potentials. In addition to volume, the exchange of particles dN is the most important work coordinate in applications. It allows for the description of transport and chemical reactions. We start with 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 $V = V_1+V_2$, $N = N_1+N_2$. The equilibrium quantity μ (chemical potential) is associated with N. Due to convexity, one can transition from F to the *grand canonical* potential

$$\Omega(T,V,\mu) = F - \mu N = U - TS - \mu N, \qquad d\Omega = -SdT - pdV - Nd\mu\,. \tag{2.57}$$

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

Example 15: (Compressibility relationship)

For homogeneous systems, there is an alternative expression that often appears in applications. Due to the Gibbs-Duhem relationship (2.10), we have $Vdp = Nd\mu$ at constant temperature. This leads to the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\frac{1}{N}\left(\frac{\partial V}{\partial \mu}\right)_{T,N} = -\left(\frac{\partial (V/N)}{\partial \mu}\right)_{T,N}\,. \tag{2.58}$$

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

$$\kappa_T = -\left(\frac{\partial n^{-1}}{\partial \mu}\right)_T = \frac{1}{n^2}\left(\frac{\partial n}{\partial \mu}\right)_T = \frac{V}{N^2}\left(\frac{\partial N}{\partial \mu}\right)_{T,V}\,. \tag{2.59}$$

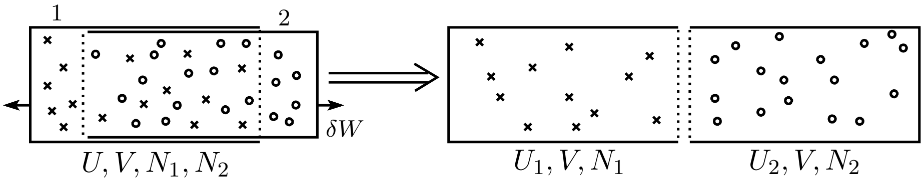


Fig. 2.3: Reversible demixing: the two substances correspond to the crosses (1) and the circles (2). The semi-permeable walls are shown in a dotted pattern.

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

2.9 Multi-component Systems

We consider a thermodynamic system consisting of r components (substances). Initially, we do not allow chemical reactions. The generalized coordinates are $Z_\alpha \in V, N_1, \dots, N_r$ with the state variables

$$\boldsymbol{Z} = (U, V, N_1, \dots, N_r) = (U, V, \boldsymbol{N}) \,. \tag{2.60}$$

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

$$TdS = dU + pdV - \sum_{i=1}^{r} \mu_i dN_i = dU + pdV - \boldsymbol{\mu} \cdot d\boldsymbol{N}, \tag{2.61}$$

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

To determine the entropy, we consider the reversible process of demixing, see Fig. 2.3. This requires semi-permeable walls. Let's consider the adiabatic demixing of two components. When we separate the two containers (demixing), we need to perform the work $\Delta W(U, V, N_1, N_2)$. At the end of the reversible process, we have two containers each with only one component. Therefore,

$$S(U, V, N_1, N_2) = S_1(U_1, V, N_1) + S_2(U_2, V, N_2) \tag{2.62}$$

with $U = U_1 + U_2 + \Delta W$ and $T_1(U_1, V, N_1) = T_2(U_2, V, N_2) = \tilde{T}$ (since S is maximal with respect to constraints in U); $\tilde{T}$ is the temperature after the adiabatic demixing.

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

$$S(U, V, N_1, \dots, N_r) = \sum_i S_i(U_i, V, N_i), \qquad U = \sum_i U_i, \qquad T_i = \tilde{T} \,. \tag{2.63}$$

Thermodynamics is thus fully described by that of the pure components. By rearranging, we obtain the internal energy

$$U(S, V, \boldsymbol{N}) = \sum_i U_i(S_i, V, N_i), \qquad S = \sum_i S_i, \qquad T_i = \tilde{T}_i \,. \tag{2.64}$$

Microscopically, $\Delta W = 0$ only when the components do not interact with each other. Ideal adiabatic demixing is carried out isothermally, as the temperature T before demixing is given by

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{N}} = \sum_i \left(\frac{\partial U_i}{\partial S_i}\right)_{V,N_i} \left(\frac{\partial S_i}{\partial S}\right)_{V,\boldsymbol{N}} = \tilde{T} \sum_i \left(\frac{\partial S_i}{\partial S}\right)_{V,\boldsymbol{N}} = \tilde{T} \, . \tag{2.65}$$

Since the temperature is fixed during ideal demixing, it is useful to switch to the free energy with

$$F(T, V, \boldsymbol{N}) = U - TS = \sum_i F_i(T, V, N_i) \, . \tag{2.66}$$

This leads to the *additivity of partial pressures*

$$p(T, V, \boldsymbol{N}) = -\left(\frac{\partial F}{\partial V}\right)_{T,\boldsymbol{N}} = -\sum_i \left(\frac{\partial F_i}{\partial V}\right)_{T,N_i} = \sum_i p_i(T, V, N_i) \tag{2.67}$$

and the fact that the chemical potential

$$\mu_i(T, V, \boldsymbol{N}) = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_j \neq N_i} = \left(\frac{\partial F_i}{\partial N_i}\right)_{T,V} = \mu_i^0(T, V) \tag{2.68}$$

is given by the chemical potential μ_i^0 of the pure substance.

Example 16: (Mixing of perfect gases)

For perfect gases (with $p_i V_i = N_i k_B T_i$) holds (from (2.29) and (2.30))

$$S(T, V, \boldsymbol{N}) = \sum_i S_i(T, V, N_i) = \sum_i N_i [c_{V,i} \ln(T/T_0) + k_B \ln(V/V_0)] \, . \tag{2.69}$$

From the additivity of partial pressures follows

$$p = \sum_i \frac{N_i k_B T}{V} = \frac{N k_B T}{V} \qquad \text{with} \qquad N = \sum_i N_i \, . \tag{2.70}$$

Starting from the demixed state with $p_i = p$ and $T_i = T$ with the entropy $S_0 = \sum_i S_i(T, V_i, N_i)$, $V_i = N_i k_B T/p$, $V = \sum_i V_i$ the interdiffusion of gases leads to the increase in entropy (*mixing entropy*)

$$\begin{aligned} S_\mathrm{m} = S - S_0 &= \sum_i [S_i(T, V, N_i) - S_i(T, V_i, N_i)] = k_B \sum_i N_i \ln(V/V_i) \\ &= k_B \sum_i N_i \ln(N/N_i) \geq 0 \, . \end{aligned} \tag{2.71}$$

The mixing of gases is thus irreversible and the gases do not demix spontaneously.

The process is carried out at constant pressure p and temperature T. The mixture occurs spontaneously and thus leads to a decrease in Gibbs energy

$$\begin{aligned} G(T,p,\boldsymbol{N}) &= U - TS + pV = U - TS_0 + pV - T(S - S_0) \qquad (2.72)\\ &= \sum_i \underbrace{[U_i(T,V_i,N_i) - TS_i(T,V_i,N_i) + pV_i]}_{G_i(T,p,N_i)} + \underbrace{k_BT\sum_i N_i \ln(N_i/N)}_{-TS_\mathrm{m}} . \end{aligned}$$

The first term corresponds to the Gibbs energy in the unmixed state. The second term is negative and describes the decrease in Gibbs energy due to the mixture.

Note: The mixture of perfect gases is called *ideal mixtures*, as 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 the mixture.

Therefore, if one imagines the diversity of substances as a continuously changing parameter, the mixing entropy disappears discontinuously when the substances become equivalent. This effect is also called the *Gibbs paradox*, although there is nothing paradoxical about it, because diversity is not a continuous parameter (either the particles are equal for all possible 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 (substance 0). The remaining substances $\nu = 1, 2, \ldots$ are the *solute substances*. To describe the solution, we introduce the *concentrations* $c_i = N_i/N \ll 1$ (with $c_0 \approx 1$). From (2.72) we obtain

$$\begin{aligned} \mu_0(T,p,c_1,\ldots) &= \left(\frac{\partial G}{\partial N_0}\right)_{T,p,N_i\neq N_0} = \left(\frac{\partial G_0}{\partial N_0}\right)_{T,p} + k_BT\ln(c_0)\\ &= \mu_0^0(T,p) - k_BT\sum_\nu c_\nu \qquad (2.73) \end{aligned}$$

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

$$d\sum_i N_i \ln(N_i/N) = \sum_i \ln(c_i)dN_i + \overbrace{\sum_i dN_i - \frac{\sum_i N_i}{N}dN}^{0} . \qquad (2.74)$$

Analogously, we obtain the expression

$$\mu_\nu(T,p,\boldsymbol{c}) = \left(\frac{\partial G}{\partial N_\nu}\right)_{T,p,N_i\neq N_\nu} = \mu_\nu^0(T,p) + k_BT\ln(c_\nu) \qquad (2.75)$$

for the chemical potential of the solute substances.

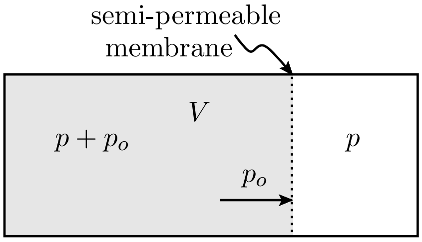


Fig. 2.4: Osmotic pressure using the example of sugar and water: Sugar water is in the left region, pure water in the right region. The regions are separated by a semi-permeable membrane on which the osmotic pressure p_o acts.

Example 18: (Osmotic Pressure)

The osmotic pressure occurs in systems where the dissolved substances are enclosed in a partial area by a semi-permeable membrane, while the solvent can freely distribute itself, see Fig. 2.4. Since the solvent can move through the membrane, the equilibrium condition is given by

$$\mu_0(T, p+p_o, \boldsymbol{c}) = \mu_0(T, p, 0) = \mu_0^0(T, p)\,. \tag{2.76}$$

From (2.73) we obtain

$$\mu_0^0(T, p+p_o) - \mu_0^0(T, p) = k_B T \sum_\nu c_\nu \tag{2.77}$$

for a dilute solution. Assuming that $p_o \ll p$, we can linearize the left side. It holds $(\partial\mu_0^0/\partial p)_T = 1/N_0(\partial G_0/\partial p)_T = V_0/N_0 \approx V/N$ and thus the *osmotic pressure* follows

$$p_o = \frac{N k_B T}{V}\sum_\nu c_\nu = \frac{k_B T}{V}\sum_\nu N_\nu\,. \tag{2.78}$$

Therefore, the rule applies: the dissolved substances 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 pressure p_{fl} in the liquid phase being equal to the pressure p_{g} in the gas phase. The equilibrium condition demands

$$\mu_{\mathrm{fl}}^0(T, p) = \mu_{\mathrm{g}}^0(T, p)\,, \tag{2.79}$$

see Example 1.

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

$$\mu_{\mathrm{fl}}(T, p-\Delta p, \boldsymbol{c}) = \mu_{\mathrm{g}}^0(T, p-\Delta p)\,. \tag{2.80}$$

For dilute solutions, we obtain

$$k_B T\sum_\nu c_\nu \overset{(2.73)}{=} \mu_{\mathrm{fl}}^0(T, p-\Delta p) - \mu_{\mathrm{fl}}(T, p-\Delta p, \boldsymbol{c}) \overset{(2.80)}{=} \mu_{\mathrm{fl}}^0(T, p-\Delta p) - \mu_{\mathrm{g}}^0(T, p-\Delta p).$$

Expanding μ^0 as in the previous example in Δp, we obtain

$$k_B T \sum_\nu c_\nu = \left(\frac{V_\mathrm{g}}{N_\mathrm{g}} - \frac{V_\mathrm{fl}}{N_\mathrm{fl}} \right) \Delta p \,. \tag{2.81}$$

Typically, for the specific volume $V_\mathrm{g}/N_\mathrm{g} \gg V_\mathrm{fl}/N_\mathrm{fl}$. Additionally, using the ideal gas law $V_\mathrm{g}/N_\mathrm{g} = k_B T/p$, we obtain the *Raoult's law*

$$\frac{\Delta p}{p} = \sum_\nu c_\nu \,. \tag{2.82}$$

2.10 Chemical reactions

In this final section, we investigate the possibility that substances can transform into each other through chemical reactions. In this case, the number of particles of each substance is not conserved. Consider, for 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 is established, in which N_C, N_O, and N_{CO_2} are determined by thermodynamic considerations.

Let us consider r substances with the chemical symbols S_i. The s chemical reactions that can take place are described by the symbolic equations

$$\sum_{i=1}^{r} \nu_i^k \mathrm{S}_i = 0, \qquad k = 1, \ldots, s, \tag{2.83}$$

with the *stoichiometric coefficients* $\nu_i^k \in \mathbb{Z}$. As an example, let's consider the combustion reaction $2\mathrm{H}_2 + \mathrm{O}_2 \rightleftharpoons 2\mathrm{H}_2\mathrm{O}$ (with $s = 1$). It involves the substances H_2, O_2, and $\mathrm{H}_2\mathrm{O}$. The stoichiometric equation is given by

$$-2\mathrm{H}_2 - \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} = 0, \qquad (\text{thus } \nu_{\mathrm{H}_2} = -2, \nu_{\mathrm{O}_2} = -1, \nu_{\mathrm{H}_2\mathrm{O}} = 2) \,. \tag{2.84}$$

The chemical transformations can change the number of particles in a system without particle exchange. This is governed by

$$dN_i = \sum_{k=1}^{s} \nu_i^k d\lambda_k \tag{2.85}$$

with arbitrary $d\lambda_1, \ldots, d\lambda_s$. The quantity $d\lambda_k$ indicates how 'often' the reaction k (in terms of the formula conversion $\sum_{i=1}^{r} \nu_i^k \mathrm{S}_i$) has been carried out, with λ_i being the *conversion variables*. With the initial conditions $N_1^0, \ldots, N_r^0$, the number of particles can be obtained as

$$N_i = N_i^0 + \sum_{k=1}^{s} \nu_i^k \lambda_k \tag{2.86}$$

by carrying out the s reactions. These numbers of particles form an s-dimensional plane on which the chemical equilibrium is established.

Chemical reactions usually occur at constant pressure p and temperature T. In this case, chemical equilibrium corresponds to the minimum of the Gibbs energy $G(T, p, \boldsymbol{N})$, see section 2.7. Therefore, we have

$$0 = dG = \sum_{i}^{r} \mu_i dN_i \tag{2.87}$$

for all stoichiometrically allowed dN_i from (2.85). This leads to the equilibrium conditions

$$\sum_{i=1}^{r} \nu_i^k \mu_i = 0, \qquad \text{for } k = 1, \ldots, s\,. \tag{2.88}$$

The equilibrium conditions thus correspond exactly to the symbolic equations (2.83), where the chemical symbol is replaced by the corresponding chemical potential of the substance.

Law of Mass Action: We consider a single reaction $\sum_{i=1}^{r} \nu_i \mathrm{S}_i = 0$ between perfect gases. The chemical potential is then given by (2.73). The equilibrium condition (2.88) thus takes the form

$$\sum_{i=1}^{r} \nu_i \mu_i(T, p, \boldsymbol{c}) = \sum_{i=1}^{r} \mu_i^0(T, p) + k_B T \sum_{i=1}^{r} \ln(c_i)\,, \tag{2.89}$$

with $\mu_i^0(T, p)$ being the chemical potentials of the pure substances. After dividing by $k_B T$ and subsequent exponentiation, we obtain the *Law of Mass Action*

$$\prod_{i=1}^{r} c_i^{\nu_i} = \exp\left[-\frac{1}{k_B T} \sum_{i=1}^{r} \nu_i \mu_i^0(T, p)\right] = K(T, p)\,. \tag{2.90}$$

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: (Combustion Reaction)

> The equilibrium constant for the combustion reaction is given by $K \approx 10^{83}$ at standard conditions. Considering that there are approximately 10^{50} atoms on Earth and about 10^{80} in the visible universe, the equilibrium is completely on the product side. Conventionally, one writes $2H_2 + O_2 \to 2H_2O$. The reverse reaction (electrolysis) does not occur spontaneously and requires the addition of additional energy.

Example 21: (pH Value)

There is another reaction involving water that much more frequently proceeds in reverse. This is the dissociation $H_2O \leftrightharpoons H^+ + OH^-$ of water into a proton and a hydroxyl molecule. At standard conditions, $K \approx 10^{-14}$. Due to electrical neutrality, $c_{\mathrm{H}} = c_{\mathrm{OH}}$. Thus, from the law of mass action, it follows

$$K = \frac{c_{\mathrm{H}}\, c_{\mathrm{OH}}}{\underbrace{c_{\mathrm{H_2O}}}_{1-2c_{\mathrm{H}}}} = c_{\mathrm{H}}^2(1 + O(c_{\mathrm{H}})), \tag{2.91}$$

that the concentration of protons $c_{\mathrm{H}} = 10^{-7}$. The pH value is defined as

$$\mathrm{pH} = -\log_{10} c_{\mathrm{H}}\,. \tag{2.92}$$

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

Chapter 3

Phase Transitions

3.1 Evaporation

Unlike chemical reactions, phase transitions are processes in which the substances do not change, but transition from one *phase* to another. Typical phases of substances are gaseous (g), liquid (fl), and solid (s). As an introductory example, let's consider the transition from liquid to gaseous (evaporation) or vice versa (condensation). As seen in the example 1, in the transition region, part of the system is in the liquid phase while another part is already in the gas phase. In the following, we neglect surface effects due to the separating surface. Since the phases are in both thermal and mechanical contact, in equilibrium we have $p = p_{\mathrm{fl}} = p_{\mathrm{g}}$ and $T = T_{\mathrm{fl}} = T_{\mathrm{g}}$. We use the Gibbs energy as the thermodynamic potential and obtain

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

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

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

Solving this equation for $p(T)$ provides the vapor pressure curve, see example 1.

The functions μ_{g} and μ_{fl} are not equal, as they describe different phases. In a *first-order phase transition*, the first derivatives differ. On the vapor pressure curve, we have

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

because indeed the *specific volume* $v = V/N$ (volume per particle) in the gas phase is greater than in the liquid phase. 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 Fig. 3.1.

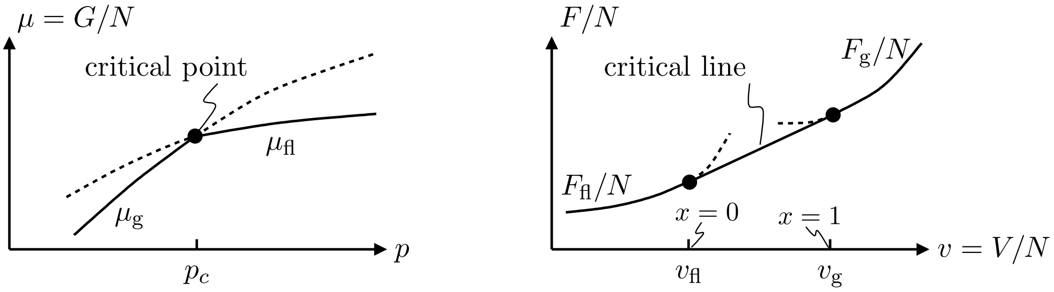


Fig. 3.1: Left: Chemical potential $\mu = G/N$ as a function of pressure p. The chemical potentials μ_{g} and μ_{fl} of the respective phases intersect. The equilibrium state corresponds to the minimum of the Gibbs energy. The gas phase (high specific volume) is at low pressures. Right: Through the Legendre 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_{fl}, F_{g}.

The Gibbs energy $G(p, T, N)$ carries all the thermodynamic information. However, it is not possible to determine the particle numbers N_{g}, N_{fl} in the respective phases from it. For this purpose, one must switch to the free energy (per particle)

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

which only depends on T and the specific volume v. The phase transition corresponds to the critical line in Fig. 3.1. Starting from a specific volume $v = v_{\mathrm{g}}$ (gas phase), an increase in the number of particles (or a decrease in volume) transfers more and more particles to the liquid phase. At the value $v = v_{\mathrm{fl}}$, the entire system is in the liquid phase. The individual points on the critical line describe different mixing ratios $0 \le x \le 1$ with

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

Denoting the free energies in the respective phases as F_{g}, F_{fl}, then

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

is the straight line of the *convex hull* of the two curves, see Fig. 3.1.

Beside the jump in specific volume (derivative of μ with respect to p), there is also a jump in specific entropy $s = S/N$ (derivative of μ with respect to $-T$). These derivatives are linked to the vapor pressure curve $p(T)$ through the Gibbs-Duhem relationship (2.10). Along the vapor pressure curve, we have

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

This leads to the *Clausius-Clapeyron relationship*

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

Typically, $\Delta s, \Delta v > 0$ and thus the slope of the vapor pressure curve is positive. During the transformation 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 $\Delta\mu = \mu_{\mathrm{g}} - \mu_{\mathrm{fl}} = 0$). For the water-vapor transition at normal pressure, for example, $\ell = 40\,\mathrm{kJ/mol}$. An anomaly occurs during the ice-water transition: for temperatures between 0 and 4°C, $\Delta v < 0$. This makes the phase line between ice and water inclined backwards.

Example 1: (Vapor Pressure Formula)

> We use the following approximation to integrate the Clausius-Clapeyron relationship. Firstly, let the latent heat ℓ be temperature-independent. Secondly, assume $\Delta v \approx v_{\mathrm{g}}$ with the ideal gas law $v_{\mathrm{g}} = k_BT/p$ in the gas phase. Under these assumptions, the Clausius-Clapeyron relationship $dp/dT = \ell/v_gT = \ell p/k_BT^2$ leads to the vapor pressure formula
>
> $$p(T) \propto e^{-\ell/k_BT}\,. \tag{3.10}$$

3.2 Gibbs Phase Rule

Let us consider r components (substances) that are distributed in ν phases in a more general sense. We denote the respective chemical potentials as $\mu_{i\alpha}$, 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 phase α. Due to the constraint $\sum_j c_{j\alpha} = 1$, only $r - 1$ of these concentrations are independent. This results in a total of $2 + \nu(r - 1)$ independent variables. In equilibrium, the conditions hold

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

These are exactly $r(\nu - 1)$ equations with i arbitrary and $\alpha \neq \beta$. Therefore, the remaining degrees of freedom (*Gibbs phase rule*) are obtained as

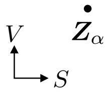
$$f = 2 + \nu(r - 1) - r(\nu - 1) = 2 + r - \nu\,. \tag{3.12}$$

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

Single-component system: In a system with only one component, a pure phase ($\nu = 1$) has two degrees of freedom. Therefore, both p and T must be specified. On the other hand, when two phases coexist ($\nu = 2$), only one degree of freedom remains. Thus, the coexistence only occurs along a line $p(T)$ in the p-T diagram. We have already encountered this relationship in the example 1 as the vapor pressure curve. Three phases can only coexist at a point (the *triple point*). The coexistence of four phases cannot occur in a single-component system.

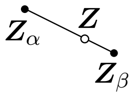
As shown, the coexistence of phases cannot be described using the Gibbs energy $G(T, p)$. Therefore, we switch to the internal energy $U(S, V)$. The states are then completely determined by $\boldsymbol{Z} = (S, V)$ (with N remaining constant). Depending on the number of coexisting phases ν, the following scenario arises for fixed (T, p)

$\nu = 1$:



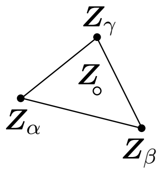
Pure phase: the state $\boldsymbol{Z}_\alpha$ is uniquely determined by (T, p).

$\nu = 2$:



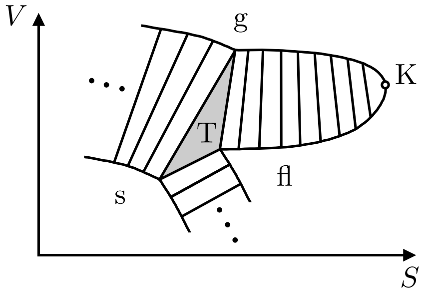
Coexistence of two phases α, β: at the phase transition, a point (T, p) corresponds to the entire line. The endpoints are the pure phases. Any state $\boldsymbol{Z}$ is characterized by the mixing ratio $x_\alpha = N_\alpha/(N_\alpha + N_\beta)$.

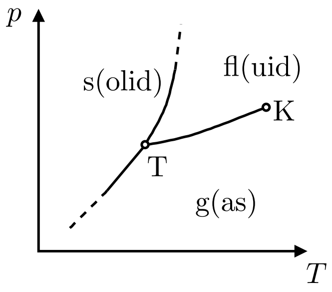
$\nu = 3$:



At the coexistence of three phases α, β, γ, two mixing ratios are needed to determine a general state $\boldsymbol{Z}$. All states form a triangle with the pure phases as vertices and the two-phase mixtures as edges.

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





On the left side, the lines correspond to the transition curves at fixed (T, p). Depending on the transition, the curves are referred to as melting curve (s–fl), sublimation curve (s–g), and vapor pressure curve (fl–g). At the triple point (T), all three phases meet. The triple point thus uniquely determines the critical temperature T_c and the critical pressure p_c. For water (H_2O), for example, $p_c = 611\,\text{Pa}$ and $T_c = 273\,\text{K}$. For higher temperatures, the transition curves between gaseous and liquid become shorter and

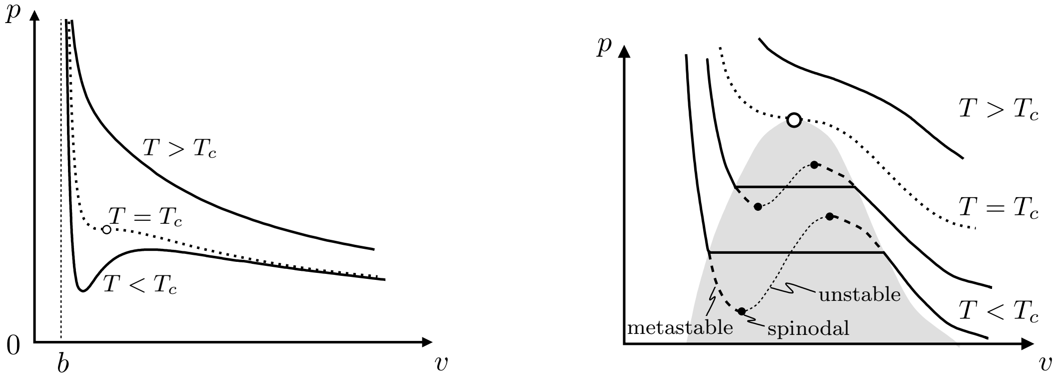


Fig. 3.2: Isotherms of the van der Waals gas.

disappear at the critical point (K) completely with $\Delta s = \Delta v = 0$. At the critical point, the first derivatives of $\mu(T, p)$ are continuous and the discontinuity only occurs in higher derivatives (*second-order phase transition*). The white area corresponds to the pure phases, where the assignment to (T, p) is unique. The designations 'liquid' and 'gaseous' only have a strict meaning along the vapor pressure curves. Because above the critical point, the transition from liquid to gaseous can be carried out without a phase transition.

3.3 Van der Waals Gas

Gases behave as ideal gases only at very high temperatures and low pressures. In his dissertation, van der Waals proposed a phenomenological modification of the ideal gas law $pv = k_B T$ which is able to describe the gas-liquid transition. For this, he was awarded the Nobel Prize in 1910. The idea is that due to the strong short-range repulsion between atoms, each atom only has the reduced volume $V - b$ available. $b \geq 0$ is called the *co-volume*. He took into account the long-range attraction by reducing the external pressure by a term $-a/v^2$, with $a \geq 0$ the *cohesion pressure parameter*. The effect arises from the fact that the particles near the wall are pulled inward by the other particles (the environment is not isotropic). The reduction per particle (near the wall) is proportional to the density N/V, and therefore proportional to $(N/V)^2 = 1/v^2$ overall. The equation of state of the van der Waals gas thus has 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 Fig. 3.2 are similar to those of the ideal gas. At the critical temperature T_c, the isotherm has a saddle point with $(\partial p/\partial V)_T =$

$(\partial^2 p/\partial V^2)_T = 0$. From

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

we find the values

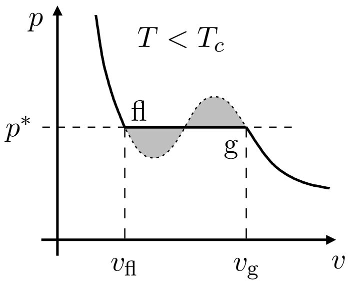
$$v_c = 3b, \qquad k_B T_c = \frac{8}{27}\frac{a}{b} \qquad \text{and} \quad p_c = \frac{1}{27}\frac{a}{b^2}\,. \tag{3.15}$$

In particular, the quantity

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

has a universal value independent of the parameters a, b of the gas. Experimentally, a relatively good agreement is found with slightly reduced values in the range of 0.28 to 0.33.

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



The vapor pressure $p^* = p(T)$ is sought, which completes the isotherm. It is determined by the equilibrium condition $\mu_{\mathrm{fl}}(p^*, T) = \mu_{\mathrm{g}}(p^*, T)$. 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 temperature. Along the isotherms, one can calculate the difference in chemical potential. We obtain

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

Through partial integration, we obtain the *Maxwell construction*

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

meaning the shaded areas are equal in size.

3.4 Universality, Critical Exponents

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

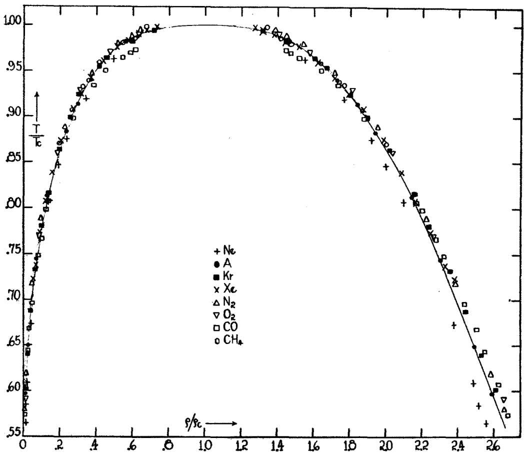


Fig. 3.3: Density $\rho = 1/v$ of the liquid phase (ρ_{fl}) and the gas phase (ρ_{g}) as a function of temperature for different gases. For the reduced quantities, all data points lie on the same curve. From E.A. Guggenheim, '*The Principle of Corresponding States*', J. Chem. Phys. **13**, 253 (1945).

states)

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

Therefore, it is expected that all gases exhibit the same behavior when pressure, volume, and temperature are divided by the values at the critical point. For similar gases, this works quite reasonably, as shown in Fig. 3.3.

The universality works even better for the so-called critical exponents. To do this, we develop $\tilde{p}(\tilde{T}, \tilde{v})$ around $(T, v) = (T_c, v_c)$ 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, we obtain

$$\begin{aligned} \left(\frac{\partial^3\tilde{p}}{\partial\tilde{v}^3}\right)_c &= \left(\frac{72}{\tilde{v}^5} - \frac{16\cdot 81\tilde{T}}{(3\tilde{v}-1)^4}\right)_c = -9, & \left(\frac{\partial\tilde{p}}{\partial\tilde{T}}\right)_c &= \left(\frac{8}{3\tilde{v}-1}\right)_c = 4, \\ \left(\frac{\partial^2\tilde{p}}{\partial\tilde{T}\partial\tilde{v}}\right)_c &= -\left(\frac{24}{(3\tilde{v}-1)^2}\right)_c = -6 & \left(\frac{\partial^2\tilde{p}}{\partial\tilde{T}^2}\right)_c &= 0, \,. \end{aligned} \tag{3.21}$$

Thus, the expansion of $p(T, v)$ around the critical point takes 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 from high temperatures along an isochore (with $v = v_c$). It holds

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

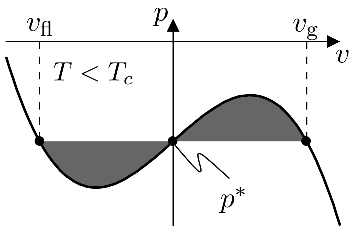
with the critical exponent $\gamma = 1$.

(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, the expression (3.22) must be complemented by the Maxwell construction. This is facilitated by the fact that the quantity $\tilde{p} - 1 - 4(\tilde{T} - 1) = \tilde{p} - 4\tilde{T} + 3$ is an odd function in $v - v_c$. Thus, the Maxwell construction yields $\tilde{p}^* = 4\tilde{T} - 3$ and therefore



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

The solution with $v^* = v_c$ is unstable (for $T < T_c$), the other two solutions correspond to v_{g} and v_{fl}. We obtain

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

Thus, for the volume change along the vapor pressure curve, we have

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

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

Experimentally, it is found that the universality of the critical exponents β, γ, δ is very nicely observable. However, the exponents are different with $\beta \approx 0.3$, $\gamma \approx 1.3$, and $\delta \approx 5.0$. The reason is that near the critical point, our naive theory breaks down as fluctuations become more important. The explanation of both the universality and the specific values of the critical exponents through the renormalization group theory is one of the most important successes of theoretical physics in the second half of the 20th century.

Chapter 4

Statistical Mechanics

Statistical mechanics aims to relate the results of thermodynamics to the microscopic laws of physics. This approach sacrifices generality (statistical mechanics in quantum mechanics is different from statistical mechanics in classical physics) but gains predictive power; in particular, the thermodynamic potentials can be calculated from the microscopic laws. To derive thermodynamics from the microscopic laws, one must derive the two main laws. The first law is unproblematic, as the concept of (internal) energy already exists at the microscopic level. The key point is therefore to anchor the entropy S microscopically. The solution goes back to Boltzmann, who recognized that for every thermodynamic state $\boldsymbol{Z}$ (macrostate), there are many microscopic states. If the number of microscopic states is denoted by $\Gamma(\boldsymbol{Z})$, one obtains $S = k_B \ln \Gamma$, as we will see later. It is clear that entropy is not a property of the microstate but is only determined by specifying the macrostate. This is linked to the statement that entropy depends on the working coordinates and is therefore (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, as fluctuations then disappear.

4.1 Entropy

Let's start with the definition (Boltzmann)

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

where the factor k_B only sets the temperature scale to the Kelvin scale.[1] More importantly, the fact that S is linked to $\ln \Gamma$ is crucial. 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 taking the logarithm, the entropy becomes additive as desired. Equation (4.1) shifts

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[1] Note that the factor k_B is independent of the base of the logarithm and a 'normalization factor' of Γ, as they only additively change the entropy.

the problem of a statistical definition of entropy from S to Γ. Let $\Gamma(\boldsymbol{Z}) \geq 1$ be a measure of microscopic states with

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

then the main theorems of thermodynamics follow. Condition (i) implies that S is a state quantity (depends only on the state $\boldsymbol{Z}$ and not on the preparation).

Let us now consider a system composed of two subsystems with $\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2$. The entropy of the system is constrained by

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

In the equilibrium state $\boldsymbol{Z}$ (without constraint), one must consider all states with $\boldsymbol{Z}_1, \boldsymbol{Z}_2$ arbitrary, only restricted by $\boldsymbol{Z} = \boldsymbol{Z}_1 + \boldsymbol{Z}_2$. The total number of states is given by[2]

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

and thus the entropy is found to be

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

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

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

Thus, (2.1b) follows and by reversing the arguments in Section 1.5, the impossibility of a second law of thermodynamics (2nd Law) is also established. For a homogeneous system, as seen in Section 2.1, the entropy even becomes a concave function.

By removing the constraints, the entropy always increases due to superadditivity. From thermodynamics, we expect that in complete equilibrium the equality sign holds in

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

with the state variables $\boldsymbol{Z}_1^*, \boldsymbol{Z}_2^*$ of the two subsystems. This is only approximately fulfilled in statistical physics. 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 $\propto N$ terms.

---

[2] Here, one needs the intuitive property that the total number of states for disjoint possibilities is simply the sum of the individual states.

For example, for the energy $U = U_1 + U_2$, it holds that $U \propto N$ and $0 \leq U_1, U_2 \leq U$. The sum thus has $U/\Delta \propto N$ terms with energy resolution Δ. Thus, from (4.4), the upper bound estimation is obtained as

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

From (4.6), it follows that

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

and from (iii), it can be seen that the term $O(\ln N)$ can be neglected in the thermodynamic limit.

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

From $S(\boldsymbol{Z}) = S(\boldsymbol{Z}_1^*) + S(\boldsymbol{Z}_2^*)$, the thermal (and mechanical) equilibrium follows (zeroth law), see (2.4). In particular, the equilibrium quantities 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 obtained from

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

In particular, heat in statistical physics is identified as usual with

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

The third law requires that $\Gamma = 1$ for $T \to 0$ and is only valid 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 properties $(i), (ii), (iii)$.

4.2 Quantum Mechanics

In the following, we want to focus on the working coordinates V, N. With the volume, for example, we can describe the work of a gas, and the number of particles is useful for describing chemical processes or a particle reservoir. The results can of course be generalized quite directly to other working coordinates (note that then the entropy is different because the number of microscopic states for a macroscopic state naturally changes).

First, let's consider quantum mechanics. A system of N particles is described by the Schrödinger equation $i\hbar\partial_t\Psi(q,t) = H\Psi(q,t)$ with $q = (\boldsymbol{q}_1, \boldsymbol{q}_2, \dots)$ being the $3N$ coordinates of the particles. The restriction to the volume V is achieved by a box potential (so that $\Psi(q) = 0$ at the boundary). The energy eigenstates $|n\rangle$ with $H\Psi_n = E_n\Psi_n$ are stationary states in quantum mechanics. In fact, $\Psi_n(t) = U_t\Psi_n = e^{-iE_nt/\hbar}\Psi_n$ under time evolution, so that the probability that the system is in state $|n\rangle$ does not change.

Now it is important that the entropy S only considers states that have an (internal) energy U. Due to the discreteness of the energy levels, we cannot demand this condition exactly, but we only require $U - \Delta \leq E_n \leq U$. It turns out that for large systems (in the TDG) the choice of $\Delta > 0$ is irrelevant. In particular, for large systems, one can also choose $\Delta = U$.

With these considerations, we define

$$\Gamma(U) = \sum_n \delta_\Delta(U - E_n) = \langle \delta_\Delta(U - H)\rangle_{\text{qm}} \tag{4.12}$$

with

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

Thus, $\Gamma(\boldsymbol{Z})$ is simply the number of states that are compatible with the state variables $\boldsymbol{Z}$. The work variables V and N are set by restrictions of the Hilbert space. We therefore neglect the dependence of Γ on V and N in the following and simply add a subscript if necessary.

The property (i) follows by construction with $U_t = \exp(-iHt/\hbar)$ and

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

Now to property (ii): a composite system is described by the Hamiltonian operator $H = H_1 + H_2$ (energy is approximately additive) on the Hilbert space $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$. The Hilbert spaces describe the inhibition in the working coordinates V and N ($\mathcal{H}_1$ corresponds to N_1 particles in volume V_1). Thus, we have

$$\begin{aligned}\Gamma(U) &= \text{Tr}_{\mathcal{H}}\,\delta_\Delta(U - H) = \text{Tr}_{\mathcal{H}_1}\text{Tr}_{\mathcal{H}_2}\,\delta_\Delta(U - H_1 - H_2) \\ &= \text{Tr}_{\mathcal{H}_1}\Gamma_2(U - H_1) \overset{3}{=} \text{Tr}_{\mathcal{H}_1}[\Gamma_2(U - U_1)\delta_\Delta(U_1 - H_1)] + O(\Delta) \\ &= \Gamma_2(U - U_1)\,\text{Tr}_{\mathcal{H}_1}\delta_\Delta(U_1 - H_1) + O(\Delta) = \Gamma_1(U_1)\Gamma_2(U - U_1) + O(\Delta)\,.\end{aligned} \tag{4.15}$$

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

In quantum mechanics, at low temperatures T which means low energies U, there is often only a single ground state. However, the system must be in a state such that $\Gamma \to 1^+$ for $T \to 0^+$, which explains the third law.

Example 1: (Particles in a box potential)

We consider a particle of mass m with Hamiltonian $H = \boldsymbol{p}^2/2m$ in a box of size $L \times L \times L$ as a thermodynamic system. For the number of states (4.12), we only need the spectrum. For completeness, we note that the wave functions (with the boundary condition $\Psi_{\delta V} = 0$) have 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

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

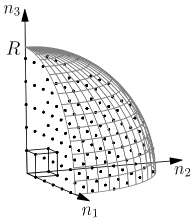
In applications, it is often useful to use the relationship $\delta_\Delta(x) = \Theta(x) - \Theta(x-\Delta)$, with $\Theta(x)$ being the step function. It holds

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

This leaves the evaluation of the sum

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

with the volume $\Omega_3(R) = \frac{4\pi}{3}R^3$ of the sphere with radius R. The factor $\frac{1}{8}$ comes from the fact that the restriction $n_j \ge 0$ implies that only one octant of the sphere contributes.
In the thermodynamic limit (TDG), the boundary conditions are unimportant. Therefore, one usually uses *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 the 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 calculate the volume of the entire sphere, but only with half the radius. Due to

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

---

[3] We use that $\delta_\Delta(x-y) = 1$ also for $|x-y| < \Delta$.

indeed, both boundary conditions lead to the same result ($h = 2\pi\hbar$ is the Planck constant, $V = L^3$)

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

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

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

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

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

and the pressure

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

It can be seen that in the thermal and caloric equations of state, Δ drops out, as hoped. The thermal equation of state is that of the classical ideal gas with only one particle.

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 are looking for a measure $\Gamma(U)$ that remains invariant under time evolution. The rescue comes from the Liouville theorem in the mechanics lecture: the phase volume of a subset $\Omega \in \mathbb{R}^{6N}$ remains preserved under time evolution. As a reminder, we consider the mapping ϕ_t (canonical flow), which maps the 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 Jacobian matrix $J = \partial(\bar{q},\bar{p})/\partial(q,p)$ with $\operatorname{Det} J = 1$ (see for example Landau-Lifshitz Vol. 1, §47). This leads to the Liouville theorem

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

With these considerations, we define the ‘number of states’ as ($q_j \in V$ for all j)

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

and with the Liouville theorem, we obtain that $\Gamma(U)$ is stationary (condition (i)). We have introduced the additional factor f_N, which we will determine immediately.

Let us now consider a constrained system with N_1 particles in volume V_1 and N_2 particles in volume V_2. For the spatial integrals, we have (q_1 are the N_1 spatial coordinates in volume V_1 and q_2 are the remaining spatial coordinates in volume V_2)

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

where the binomial coefficient counts the ways to distribute the coordinates into the two containers. We immediately recognize (by dividing the equation by $N!$) that the definition (4.26) can only be multiplicative if we choose the Gibbs factor

$$f_N = \frac{1}{N!\,h^{3N}}, \qquad d\Gamma_N = \frac{d^{3N}q d^{3N}p}{h^{3N}N!} \tag{4.28}$$

[4] The additional factor h^{-3N} with h being the Planck constant follows from the Bohr-Sommerfeld quantization (one state per h phase space volume). It is unimportant in the classical description (only changes the entropy by an additive constant per particle) but ensures that the quantum mechanical entropy transitions into the classical entropy in the large temperature limit T, see example 2. With the Gibbs factor, we have $\int_V d\Gamma_N = \int_{V_1} d\Gamma_{N_1}\int_{V_2} d\Gamma_{N_2}$ and we obtain (cf. (4.15))

$$\begin{aligned}\Gamma(U,V,N) &= \int_V d\Gamma_N\,\delta_\Delta(U-H) = \int_{V_1} d\Gamma_{N_1}\int_{V_2} d\Gamma_{N_2}\,\delta_\Delta(U-H_1-H_2)\\ &= \int_{V_1} d\Gamma_{N_1}\Gamma(U-H_1,V_2,N_2)\\ &= \Gamma(U-U_1,V_2,N_2)\int_{V_1} d\Gamma_{N_1}\delta_\Delta(U_1-H_1) + O(\Delta)\\ &= \Gamma(U_1,V_1,N_1)\Gamma(U_2,V_2,N_2) + O(\Delta)\,. \end{aligned} \tag{4.29}$$

Thus, the entropy in classical statistical mechanics is superadditive as desired.

Note: The Gibbs factor arises because the constraint only determines the number of particles in the subvolumes, but does not specify which particles they are. In a system where we know that the N_1 particles with coordinates $q \in \mathbb{R}^{3N_1}$ are in volume V_1 and the N_2 particles with coordinates $q' \in \mathbb{R}^{3N_2}$ are in volume V_2, we have directly

$$\int_V d^{3N_1}dq_1\, d^{3N_2}dq_2 = \int_{V_1} d^{3N_1}dq_1 \int_{V_2} d^{3N_2}dq_2\,, \tag{4.30}$$

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[4] 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).

without the Gibbs factor. However, in this description of the system (since we know which particles are in which subvolume), it is no longer possible to subsequently lift the constraint on the number of particles.

Example 2: Classical particle in a box

We consider the classical version of the example 1. In this case, we need to determine $\Gamma(U,V)$ from (4.26) ($N=1$). It holds

$$\begin{aligned}\Gamma(U,V) &= \frac{1}{h^3}\overbrace{\int d^3x}^{V}\overbrace{\int d^3p\,\delta_\Delta(U-\boldsymbol{p}^2/2m)}^{\Omega_3(\sqrt{2mU})-\Omega_3(\sqrt{2m(U-\Delta)})}\\ &= \frac{V}{h^3}\left[\Omega_3(\sqrt{2mU})-\Omega_3(\sqrt{2m(U-\Delta)})\right]\,. \qquad (4.31)\end{aligned}$$

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

Example 3: Ideal gas

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

$$H=\sum_{j=1}^{N}\frac{\boldsymbol{p}_j^2}{2m}\,. \qquad (4.32)$$

We calculate the phase space volume

$$\Gamma=\frac{1}{h^{3N}N!}\underbrace{\int d^{3N}x}_{V^N}\int d^{3N}p\,\delta_\Delta(U-H)\,. \qquad (4.33)$$

As an auxiliary quantity, we introduce the function

$$\Omega_{3N}(R)=\int_{\sum_j \boldsymbol{p}_j^2\le R^2} d^{3N}p=\text{Volume of the }3N\text{-dimensional sphere of radius }R \qquad (4.34)$$

Thus, we have

$$\Gamma(U,V,N)=\frac{V^N}{h^{3N}N!}\left[\Omega_{3N}(\sqrt{2mU})-\Omega_{3N}(\sqrt{2m(U-\Delta)})\right]. \qquad (4.35)$$

The volume of a sphere is given by

$$\Omega_d(R)=\frac{\pi^{d/2}}{(d/2)!}R^d\,. \qquad (4.36)$$

The volume grows very rapidly with R. This means that the majority of the volume is located at the surface.[5] We obtain

$$\Omega_d(R)-\Omega_d(R_0)=\frac{\pi^{d/2}}{(d/2)!}(R^d-R_0^d)=\frac{\pi^{d/2}}{(d/2)!}R^d\left[1-(R_0/R)^d\right]. \qquad (4.37)$$

---

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

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

With this, we have

$$\Gamma(U,V,N) \approx \frac{V^N}{h^{3N} N!} \Omega_{3N}(\sqrt{2mU}) = \frac{V^N}{N!} \frac{(2\pi m U/h^2)^{3N/2}}{(3N/2)!} \,. \tag{4.38}$$

In the thermodynamic limit, we also use the Stirling formula

$$\ln N! = N(\ln N - 1) + O(\ln N) \tag{4.39}$$

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

$$S(U,V,N) = k_B \ln \Gamma = N k_B \ln \left[\frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right] + \frac{5}{2} N k_B \,, \tag{4.40}$$

which is 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 is obtained from

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{3}{2} \frac{N k_B}{U} \qquad \text{or} \qquad U = \frac{3}{2} N k_B T \,. \tag{4.41}$$

For the pressure, we find

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{U,N} = \frac{N k_B}{V} \qquad \text{or} \qquad pV = N k_B T \,. \tag{4.42}$$

Thus, we have derived the thermal and caloric equations of state of the ideal gas from a microscopic perspective.

4.4 Probability Theory

With the Boltzmann prescription $S = k_B \ln \Gamma$ and the definition $\Gamma = \langle \delta_\Delta(U - H) \rangle$, which holds in both the classical and quantum mechanical cases, we have microscopically founded thermodynamics. To gain a deeper insight, however, it is useful to illuminate the whole 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

$$p_i \geq 0 \qquad \text{and} \qquad \sum_{i \in \Omega} p_i = 1 \,. \tag{4.43}$$

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

$$P(A) = \sum_{i \in A} p_i \,. \tag{4.44}$$

Thus, the probabilities range from $P(E) = 0$ (impossible event E) to $P(E) = 1$ (certain event). It is useful in statistical mechanics to interpret probabilities in a *Bayesian sense*. We are familiar with this from statements like: 'There is a 25% probability of rain tomorrow.' In this case, the probability expresses the degree of belief.

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

$$\overline{f(X)} = \sum_i p_i f(x_i) = \sum_x P(X = x) f(x)\,. \tag{4.45}$$

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

$$P(a \le X \le b) = \int_a^b dx\, p(x), \qquad \text{meaning} \quad p(x) = \frac{d}{dx} P(a \le X \le x)\,. \tag{4.46}$$

Thus, the expectation value is given by

$$\overline{f(X)} = \int dx\, p(x) f(x)\,. \tag{4.47}$$

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

$$P(X = x, Y = y) = P(X = x) P(Y = y) \tag{4.48}$$

which implies, for example, $\overline{XY} = \overline{X}\,\overline{Y}$.

The expectation value $\overline{X}$ describes the probability distribution $p(x)$ with only one value. In application, it is important to also know something about possible deviations from $\overline{X}$. For this, the *variance* is used

$$(\delta X)^2 = \overline{(X - \overline{X})^2} = \overline{X^2} - \overline{X}^2\,. \tag{4.49}$$

This tells us that the values of X are likely to lie in the range $\overline{X} \pm \delta X$ with high probability.[6] Probability theory becomes a deterministic theory for $\delta X \to 0$. This corresponds exactly to the thermodynamic limit, in which statistical mechanics transitions into thermodynamics. The covariance of two random variables is defined as

$$\delta X\, \delta Y = \overline{(X - \overline{X})(Y - \overline{Y})} = \overline{XY} - \overline{X}\,\overline{Y}\,. \tag{4.50}$$

It holds that $\delta X\, \delta Y = 0$ if X and Y are independent.

An important result is the *central limit theorem*: for random variables X_j, $j = 1, \ldots, N$, that are uncorrelated with identical mean $\overline{X} = \overline{X_j}$ and variance $(\delta X)^2 = (\delta X_j)^2 < \infty$, the sample mean is defined as

$$\mu = \frac{1}{N} \sum_j X_j \qquad \text{with} \quad \overline{\mu} = \overline{X}\,. \tag{4.51}$$

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[6] For example, Chebyshev's inequality holds $P(|X - \overline{X}| \ge k) \le (\delta X)^2 / k^2$.

For the variance of the sample mean, one obtains

$$(\delta\mu)^2 = \frac{1}{N^2}\sum_{i,j} \overbrace{\overline{\delta X_i\, \delta X_j}}^{\delta_{ij}(\delta X)^2} = \frac{(\delta X)^2}{N}\,. \tag{4.52}$$

The central limit theorem holds

$$\delta\mu = \frac{\delta X}{\sqrt{N}} \sim \frac{1}{\sqrt{N}} \overset{(N\to\infty)}{\to} 0\,. \tag{4.53}$$

This shows that the sample mean becomes deterministic for a large sample size N.

We will also often use generating functions. For a random variable X, the generating function is defined as the expectation value

$$Z(\lambda) = \overline{\exp(\lambda X)} = \sum_i p_i e^{\lambda x_i}\,. \tag{4.54}$$

It holds that $Z(0) = \sum_i p_i = 1$ and the expectation value is obtained by

$$\overline{X} = \sum_i p_i x_i = \sum_i p_i \frac{d}{d\lambda} e^{\lambda x_i}\Big|_{\lambda=0} = Z'(0)\,. \tag{4.55}$$

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

Moving on to the *cumulant generating function* $F(\lambda) = \ln Z(\lambda)$, we obtain

$$F(0) = 0, \quad F'(0) = \frac{Z'(0)}{Z(0)} = \overline{X}\,, \quad F''(0) = \frac{Z''(0)}{Z(0)} - \frac{Z'(0)^2}{Z(0)^2} = (\delta X)^2; \tag{4.56}$$

meaning that the first coefficient in the Maclaurin series of $F(\lambda)$ is the expectation value and the second is the variance.[7]

Shannon Entropy: We have seen that an event with $P = 1$ occurs with certainty while an event with $P = 0$ does not occur at all. Looking for a measure of uncertainty, one realizes that it should vanish for $P = 0$ or $P = 1$ and be maximal for $P = \frac{1}{2}$. Therefore, as a measure of uncertainty of a random distribution p_i, $i = 1, \ldots, M$, the *Shannon Entropy*[8]

$$S_{\text{Shannon}} = -\sum_i p_i \log_2 p_i \geq 0 \tag{4.57}$$

is introduced. Conventionally, the logarithm to the base 2 is used, so S_{Shannon} is measured in ‘bits’. For two events with $p_1 = p$ and $p_2 = q = 1 - p$, we have

$$S_{\text{Shannon}} = -p\log_2 p - q\log_2 q\,. \tag{4.58}$$

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[7] More generally, the n-th cumulant is defined as $d^n F(0)/d\lambda^n$.

[8] The convention is to define $x \ln x = 0$ for $x = 0$.

The function vanishes for $p = 0$ or $p = 1$, is symmetric $p \leftrightarrow q$, and has 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): Taking $N \gg 1$ independent samples from the distribution p_i, one expects to obtain the result x_i $\bar{n}_i$ times for a typical sequence with $\bar{n}_i = p_i N$. The number of typical configurations is given by the multinomial coefficient

$$\Gamma(\bar{n}_1, \ldots, \bar{n}_M) = \frac{N!}{\bar{n}_1! \cdots \bar{n}_M!} \,. \tag{4.59}$$

Using the Stirling formula $N! \sim (N/e)^N$, we obtain for large N the result

$$\Gamma(\bar{n}_1, \ldots, \bar{n}_M) \sim \frac{2^{N \log_2 N}}{2^{\bar{n}_1 \log_2 \bar{n}_1} \ldots 2^{\bar{n}_M \log_2 \bar{n}_M}} = 2^{-\sum_i \bar{n}_i \log_2(\bar{n}_i/N)} = 2^{N S_{\text{Shannon}}} \,. \tag{4.60}$$

Therefore, for large N, one needs $(N S_{\text{Shannon}})$ bits of information to store which of the typical sequences has been obtained. Furthermore, it can be shown that with overwhelming probability, a typical sequence is obtained. A general sequence occurs with the probability

$$P(n_1, \ldots, n_M) = \frac{N!}{n_1! \cdots n_M!} p_1^{n_1} \cdots p_M^{n_M} \sim 2^{\sum_i n_i \log_2(N p_i/n_i)} \tag{4.61}$$

Now, if we set $n_i = \bar{n}_i + dn_i$, with the deviation $dn_i \ll \bar{n}_i$ from the typical sequence, then we obtain

$$n_i \log_2(N p_i/n_i) = -\frac{1}{\ln(2)} \left(dn_i + \frac{dn_i^2}{2\bar{n}_i} \right) + O(dn_i/\bar{n}_i)^3 \tag{4.62}$$

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

$$P(n_1, \ldots, n_M) \sim 2^{-N \sum_i p_i (dn_i/\bar{n}_i)^2/\ln(4)} \tag{4.63}$$

Thus, a typical sequence occurs with probability 1 in the limit $N \to \infty$. The Shannon result provides a deterministic statement (probability 1) 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, the *density matrix* is usually used:

$$\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i| \,. \tag{4.64}$$

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

- $\rho = \rho^\dagger$ (Hermitian),
- $\rho \geq 0$, i.e., $\langle\psi|\rho|\psi\rangle \geq 0$ for all $|\psi\rangle$ (Semidefinite),
- $\mathrm{Tr}(\rho) = 1$ (Trace 1).

Due to Hermiticity, the density matrix can be diagonalized in an orthonormal basis $|\psi_i\rangle$ with eigenvalues $p_i \in \mathbb{R}$. It holds that $p_i \geq 0$ (due to point 2) and $\sum_i p_i = 1$ (due to point 3). Therefore, for a general density matrix, we have the representation in (4.64) where p_i is the probability of finding the system in the state $|\psi_i\rangle$. Pure states are exactly the cases where ρ is a projector with $\rho^2 = \rho$ (which means there is an i such that $p_i = 1$ and $p_{j\neq i} = 0$).

The expectation value of any observable A in the state ρ is then given by

$$\overline{A} = \sum_i p_i \langle\psi_i|A|\psi_i\rangle = \mathrm{Tr}(\rho A)\,. \tag{4.65}$$

Starting from the state ρ_0 at time $t = 0$, the time evolution of the individual wave functions under the Hamiltonian operator H according to the Schrödinger equation is given by $U_t|\psi_i\rangle = e^{-iHt/\hbar}|\psi_i\rangle$. Thus, at time t the state is

$$\rho_t = \sum_i p_i\, U_t|\psi_i\rangle\langle\psi_i|U_t^\dagger = e^{-iHt/\hbar}\rho_0 e^{iHt/\hbar}\,. \tag{4.66}$$

The density matrix thus follows the *von Neumann equation*

$$\frac{d\rho_t}{dt} = -\frac{i}{\hbar}[H, \rho_t]\,. \tag{4.67}$$

With the density matrix, one can express the Shannon entropy independently of the basis. It holds (von Neumann entropy)

$$S_{\text{von-Neumann}} = -\mathrm{Tr}(\rho \log_2 \rho) = -\sum p_i \log_2 p_i = S_{\text{Shannon}}\,. \tag{4.68}$$

For pure states, of course, $S_{\text{Shannon}} = 0$. Mixed states lead to $S_{\text{Shannon}} > 0$. In the following, we denote with the probability density ρ both a density matrix in quantum mechanics and a probability density $\rho(q, p)$ in phase space in classical mechanics.

Insert: (Entanglement)

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

$$\rho_A : \mathcal{H}_A \to \mathcal{H}_A, \qquad \rho_A = \mathrm{Tr}_B(\rho) \tag{4.69}$$

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

$$\langle M_A\rangle = \mathrm{Tr}(\rho M_A) = \underbrace{\mathrm{Tr}_A\,\mathrm{Tr}_B}_{=\mathrm{Tr}_{A\otimes B}}(\rho M_A) = \mathrm{Tr}_A(\rho_A M_A)\,. \tag{4.70}$$

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

First, let's consider 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

$$\rho_1 = |\uparrow\uparrow\rangle\langle\uparrow\uparrow| \,. \tag{4.71}$$

For measurements on Alice's subsystem, the knowledge of the reduced density matrix is sufficient

$$\rho_{1,A} = \mathrm{Tr}_B(\rho_1) = \sum_{m_B=\pm} \big(1 \otimes \langle m_B|\big)\, |\uparrow\uparrow\rangle\langle\uparrow\uparrow|\, \big(1 \otimes |m_B\rangle\big) = |\uparrow\rangle\langle\uparrow| \,. \tag{4.72}$$

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

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

$$\rho_2 = \frac{1}{2}\big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big)\big(\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\big) = \frac{1}{2}\Big(|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + |\downarrow\uparrow\rangle\langle\downarrow\uparrow| - |\uparrow\downarrow\rangle\langle\downarrow\uparrow| - |\downarrow\uparrow\rangle\langle\uparrow\downarrow|\Big) \,. \tag{4.73}$$

In this case, the reduced state is

$$\rho_{2,A} = \frac{1}{2}\big(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|\big) = \frac{1}{2}\, I_2 \tag{4.74}$$

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

The different behavior of $|\Psi_1\rangle$ and $|\Psi_2\rangle$ is related to the fact that $|\Psi_1\rangle = |\uparrow\rangle \otimes |\uparrow\rangle$ is a *product state*. It can be shown 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, the reduced density matrix

$$\rho_A = \mathrm{Tr}_B\big(|\psi_A\rangle \otimes |\psi_B\rangle\langle\psi_A| \otimes \langle\psi_B|\big) = \big(\mathrm{Tr}_B\, |\psi_B\rangle\langle\psi_B|\big)|\psi_A\rangle\langle\psi_A| = |\psi_A\rangle\langle\psi_A| \tag{4.75}$$

corresponds to the pure state $|\psi_A\rangle$. This gives us the following simple criterion for any pure state $|\Psi\rangle$ on $\mathcal{H}_A \otimes \mathcal{H}_B$:

$$|\Psi\rangle \text{ can be written as a product state} \quad \Leftrightarrow \quad \rho_A \text{ is a pure state.} \tag{4.76}$$

One calls states that cannot be written as product states *entangled* states. In particular, we obtain the result that the singlet state $|\Psi_2\rangle$ is an entangled state and therefore 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

$$(U_A \otimes U_B)|\Psi_2\rangle = |\psi_A\rangle \otimes |\psi_B\rangle \tag{4.77}$$

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

4.5 Microcanonical Ensemble

We want to give a statistical interpretation of the Boltzmann formula $S = k_B \ln \Gamma$ with $\Gamma = \langle \delta_\Delta(U - H)\rangle$, which holds with the respective definition of $\langle\cdot\rangle$ in both the classical and quantum cases. The bracket $\langle\cdot\rangle$ provides 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 where $U = H$ holds (as we have already seen, the specific value of uncertainty $\Delta > 0$ is unimportant). The other constraints are implicit in the formalism (we only allow states with given V, N).

The state variables U, V, N only determine a macrostate, to which $\propto \Gamma = e^{S/k_B}$ microstates belong. With limited access/knowledge about the system, we cannot precisely determine which of the microstates will be realized. The most natural assumption (see the Gibbsian variational principle later) is that we assign the same probability to all states. The equal distribution in phase space over the states allowed by the constraints is called the *microcanonical ensemble* (or the *microcanonical ensemble*) with the probability density $\rho_{\text{mk}} = c\,\delta_\Delta(U-H)$. The normalization c is obtained from

$$1 = \langle c\,\delta_\Delta(U-H)\rangle = c\langle\delta_\Delta(U-H)\rangle = c\,\Gamma(U)\,. \tag{4.78}$$

This results in the probability density (*microcanonical distribution*)

$$\rho_{\text{mk}} = \frac{1}{\Gamma(U)}\delta_\Delta(U-H), \qquad \Gamma(U) = \langle\delta_\Delta(U-H)\rangle, \tag{4.79}$$

where the denominator

$$\Gamma(U) = \begin{cases} \sum_n \delta_\Delta(U-E_n) & \text{(quantum mechanically)}, \\ \int d\Gamma_N\,\delta_\Delta(U-H) & \text{(classically)}, \end{cases} \tag{4.80}$$

is called the *microcanonical partition function.*

For the measure of disorder/entropy, one then calculates the Shannon entropy,

$$S = -k_B \sum_i p_i \ln p_i \tag{4.81}$$

which is called Gibbs entropy with the new normalization; it holds that $S_{\text{Gibbs}} = k_B \ln(2) S_{\text{Shannon}}$. We obtain

$$S = -k_B\langle\rho_{\text{mk}}\ln\rho_{\text{mk}}\rangle = k_B\frac{\ln\Gamma(U)}{\Gamma(U)}\langle\delta_\Delta(U-H)\rangle = k_B\ln\Gamma(U), \tag{4.82}$$

which exactly corresponds to the Boltzmann definition.

Landauer Principle: The relationship $S_{\text{Gibbs}} = k_B \ln(2) S_{\text{Shannon}}$ between thermodynamics and information theory leads to the following result: when deleting a bit on a hard drive, the Shannon entropy is reduced by 1 bit (initially $p_0 = p_1 = \frac{1}{2}$, in the end $p_0 = 1, p_1 = 0$.) Translated to thermodynamics, this corresponds to a reduction in entropy of

$$S_{\text{Landauer}} = k_B \ln(2) = 9.57 \times 10^{-24}\,\text{J/K} \tag{4.83}$$

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

$$\Delta Q = T S_{\text{Landauer}} = 4 \times 10^{-21}\,\text{J} = 4\,\text{zJ} \tag{4.84}$$

If one were to delete a hard drive with $1\,\text{TB} = 8 \times 10^{12}$ Bit, the heat in the room would increase by at least

$$\Delta Q \geq 3 \times 10^{-8}\,\text{J}\,. \tag{4.85}$$

With the statistical description, one can extend the second law to systems that are not in the thermodynamic limit and where fluctuations are not negligible. It holds that

> *(Second Law statistical formulation)*
>
> In a closed system, it is impossible to deterministically (with probability 1) reduce entropy only by manipulating the extensive variables.

It is important to understand (as we have mentioned many times) that entropy is a quantity that depends on the available extensive variables. If one has control over the spatial coordinates of all particles, one can of course reach any state. However, in this case, there is no heat and entropy disappears. For a deeper understanding of the second law, I recommend the comic 'Max the Demon Vs Entropy of Doom' by Auerbach and Codor.

The statistical mechanics also makes a statement about the probability of achieving a decrease in entropy $\Delta S < 0$ (from $S \to S' = S + \Delta S$). A decrease in entropy corresponds to a reduction in the microcanonical partition function (and thus the number of states). One starts with $\Gamma = e^{S/k_B}$ states and ends with $\Gamma' = e^{S'/k_B} < \Gamma$. The number of states, however, remains unchanged, both in quantum mechanics (due to unitarity) and in classical mechanics (due to Liouville's theorem). Therefore, at most Γ' out of Γ states lead to the decrease in entropy, and thus we obtain the probability

$$P(\Delta S < 0) \leq \frac{\Gamma'}{\Gamma} = e^{\Delta S/k_B} \tag{4.86}$$

for a decrease in entropy. In the thermodynamic limit, $\Delta S \propto N$ and thus the probability vanishes, and statistical mechanics transitions to deterministic thermodynamics, see Eq. (4.63). For a microscopic change of 1 bit, $\Delta S = -S_{\text{Landauer}}$ and we obtain a decrease in entropy with probability

$$P(\Delta S = -S_{\text{Landauer}}) \leq e^{-\ln 2} = \frac{1}{2}\,. \tag{4.87}$$

A change in entropy of the order of S_{Landauer} is therefore not forbidden in statistical mechanics and not even so unlikely.

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 focus on the state variable U, as the work variables are constrained. The total system is closed with $U_{\text{tot}} = U_1 + U_2$. The microcanonical partition function of the total system is given by

$$\Gamma(U_{\text{tot}}) = \Gamma(U_1^*)\Gamma(U_2^*) \tag{4.88}$$

The energies U_1^*, U_2^* in equilibrium are determined by the condition $\partial S_1(U_1^*)/\partial U_1 = \partial S_2(U_2^*)/\partial U_2 = 1/T$. However, we now want to allow for fluctuations and set $U_1 = H$ arbitrarily with H being the Hamiltonian of the system. Furthermore, we are only interested in the system, so we write $U = U_1$ and $S = S_1$.

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

$$\rho_{\text{k}}(H) = \frac{\Gamma(U_2)}{\Gamma(U_{\text{tot}})} = \frac{1}{\Gamma(U^*)}\frac{\Gamma(U_2)}{\Gamma(U_2^*)} = e^{-S(U^*)/k_B}\frac{e^{S_2(U_{\text{tot}}-H)/k_B}}{e^{S_2(U_{\text{tot}}-U^*)/k_B}}\,. \tag{4.89}$$

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

Since $H \ll U_{\text{tot}}$, we can expand the exponent and obtain

$$S_2(U_{\text{tot}} - H) = S_2(U_{\text{tot}}) - \frac{1}{T}U + O(1/N_{\text{tot}})\,, \tag{4.90}$$

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 $N_2 \approx N_{\text{tot}}$. This gives us the *canonical distribution*

$$\rho_k(H) = e^{-S(U^*)/k_B + (U^*-H)/k_BT} = e^{(F-H)/k_BT}, \quad F(T) = U^* - TS(U^*)\,. \tag{4.91}$$

We define the *canonical partition function* (we implicitly leave out the dependence on V by assuming that the N particle positions are restricted within the volume V)

$$Z_N(\beta) = \langle e^{-\beta H}\rangle, \qquad \beta = \frac{1}{k_BT}, \tag{4.92}$$

$$= \begin{cases} \sum_n e^{-\beta E_n} & \text{(quantum mechanical)},\\ \int d\Gamma_N\, e^{-\beta H} & \text{(classical)}, \end{cases} \tag{4.93}$$

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

$$F(T, V, N) = -k_BT \ln Z_N(T),. \tag{4.94}$$

The canonical partition function describes a system that is in thermal contact with a heat bath. From a statistical point of view, it is also evident that the free energy is the correct potential to describe this system. In the thermodynamic limit, the microcanonical distribution (closed system) and the canonical distribution (system in contact with a heat bath) yield the same result. However, for small systems, the fluctuations differ, which 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

$$U = \overline{H} = \langle \rho_k H\rangle = \frac{1}{Z_N}\langle He^{-\beta H}\rangle = -\frac{1}{Z_N}\frac{\partial Z_N}{\partial\beta} = -\frac{\partial \ln Z_N}{\partial\beta} = \frac{\partial(\beta F)}{\partial\beta}\,. \tag{4.95}$$

The expectation value corresponds exactly to the Gibbs-Helmholtz relationship

$$\frac{\partial(\beta F)}{\partial\beta} = F + \beta\frac{\partial F}{\partial\beta} = F - T\frac{\partial F}{\partial T} = F + TS = U \tag{4.96}$$

from thermodynamics. Statistical mechanics extends this result to fluctuations. We calculate the square of fluctuations ($Z_N(\beta)$ is, up to an unimportant factor, the generating function)

$$\begin{aligned}(\delta U)^2 &= \frac{\partial^2 \ln Z_N(\beta)}{\partial\beta^2} = -\frac{\partial^2(\beta F)}{\partial\beta^2} = -\left(\frac{\partial U}{\partial\beta}\right)_{V,N} = k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{V,N} \\ &= k_B T^2 N c_V \,.\end{aligned} \tag{4.97}$$

Thus, for the relative deviation ($u = U/N$ is the internal energy per particle)

$$\frac{\delta U}{U} = \sqrt{\frac{k_B T^2 c_V}{u^2 N}} \sim \frac{1}{N^{1/2}} \,. \tag{4.98}$$

It is important to note that the derivation of the canonical ensemble only requires that the heat bath is large ($N_{\text{tot}} \to \infty$). In statistical mechanics, systems with finite N can be studied (one can even set $N = 1$). These systems undergo fluctuations. Only in the thermodynamic limit do the *relative deviations* disappear and the theory becomes deterministic.

The relationship (4.97) is the first example of a *fluctuation-dissipation relationship*. It connects the fluctuations (here of U) with response quantities (here c_V). In computer simulations, it is often easier to determine δU and then calculate the specific heat through

$$c_V = \frac{(\delta U)^2}{k_B T^2 N} \tag{4.99}$$

Calculating the canonical partition function is typically much simpler than calculating the microcanonical partition function due to the lack of restriction to a single energy. Therefore, the canonical approach is usually chosen in applications.

Example 4: (Configurational Integral)

> In classical statistical mechanics of N particles, the Hamiltonian usually has the form $H = \sum_i \boldsymbol{p}_i^2/2m + U_{\text{pot}}(\boldsymbol{x}_1, \dots)$, see (1.7). The integral over momenta can thus be performed for any potential. This yields
>
> $$Z_N = \frac{Q}{h^{3N}} \overbrace{\int d^{3N}p\, e^{-\beta\sum_i \boldsymbol{p}_i^2/2m}}^{(2\pi m k_B T)^{3N/2}} = \frac{Q}{\lambda^{3N}} \tag{4.100}$$
>
> with the *configurational integral*
>
> $$Q = \frac{1}{N!}\int d^{3N}x\, e^{-\beta U_{\text{pot}}(x)} \tag{4.101}$$

and the *thermal wavelength*

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}\,. \tag{4.102}$$

For an electron, for example, we have

$$\lambda = \frac{74.5\,\mathrm{nm}}{\sqrt{T[\mathrm{K}]}}\,. \tag{4.103}$$

Example 5: (Ideal Gas)

Back to the ideal gas once again. In this case, the configuration integral is trivial with

$$Q = \frac{V^N}{N!}\,. \tag{4.104}$$

This results in the free energy

$$F = -k_B T \ln Z_N = -N k_B T \ln\left(\frac{V}{N\lambda^3}\right) - N k_B T\,. \tag{4.105}$$

From this, for example, the entropy (4.40) follows by differentiating with respect to $-T$.

Example 6: (Maxwell-Boltzmann Distribution)

For a classical ideal gas in an external potential U_{ext}, we obtain the distribution

$$\rho_k = \frac{1}{Z_N} \exp\left[-\beta \sum_i \left(\frac{\boldsymbol{p}_i^2}{2m} + U_{\mathrm{ext}}(\boldsymbol{x}_i)\right)\right]. \tag{4.106}$$

If we are only interested in the position $\boldsymbol{x}$ and the momentum $\boldsymbol{p}$ of a particle, we only need 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. This gives us the Maxwell-Boltzmann distribution

$$\rho_{\mathrm{MB}}(\boldsymbol{x},\boldsymbol{p}) d^3x\, d^3p = \frac{1}{Z_1} \exp\left[-\beta\left(\frac{\boldsymbol{p}^2}{2m} + U_{\mathrm{ext}}(\boldsymbol{x})\right)\right]. \tag{4.107}$$

Example 7: (Equipartition Theorem)

We consider a (classical) Hamiltonian system with f degrees of freedom. Let $(x_1, ..., x_{2f}) = (q_1, p_1, \ldots, q_f, p_f)$ with q and p being the conjugate variables. Then the *equipartition theorem* holds

$$\begin{aligned} \overline{x_i \frac{\partial H}{\partial x_j}} &= \int \frac{d\Gamma_N}{Z_N} x_i \frac{\overbrace{\partial e^{-\beta H}}^{(\partial_{x_j} H) e^{-\beta H}}}{(-\beta)\,\partial x_j} = \overbrace{\int \frac{d\Gamma_N}{Z_N} \frac{\partial(x_i e^{-\beta H})}{(-\beta)\,\partial x_j}}^{0} - \int \frac{d\Gamma_N}{Z_N} e^{-\beta H} \frac{\partial x_i}{(-\beta)\,\partial x_j} \\ &= k_B T \delta_{ij}\,, \end{aligned} \tag{4.108}$$

where we have neglected the boundary terms, assuming that the Hamiltonian function restricts the system to a finite part of the phase space.

For the Hamiltonian function $H = K + U_{\text{pot}} = \sum_{i=1}^{3N} p_i^2/2m + U_{\text{pot}}(q)$ from the example 4, we can apply the equipartition theorem to the kinetic energy. We obtain

$$k_B T \delta_{ij} = \overline{p_i \frac{\partial H}{\partial p_j}} = \frac{\overline{p_i p_j}}{m} \,. \tag{4.109}$$

This means that the average kinetic energy $\overline{p_i^2/2m}$ of each degree of freedom is given by $k_B T/2$. Therefore, overall we have

$$\overline{K} = \frac{3}{2} N k_B T = \frac{1}{2} f k_B T \tag{4.110}$$

with $f = 3N$ being the number of degrees of freedom. Using the virial theorem (1.32) for the ideal gas, we obtain the thermal equation of state

$$N k_B T = pV \,. \tag{4.111}$$

For an interacting system, (1.33) leads to the thermal equation of state

$$N k_B T = pV + \sum_j \overline{\boldsymbol{x}_j \cdot \frac{\partial U_{\text{ww}}}{\partial \boldsymbol{x}_j}(\boldsymbol{x}_1, \dots)} \,. \tag{4.112}$$

Thus, the ideal gas equation is extended by the virial as an additional term. Developing the virial in powers of the particle density $n = N/V$ yields the so-called virial expansion.

Example 8: (Degrees of Freedom)

For a classical, harmonic system with the Hamiltonian (per particle) $H = \sum_{i=1}^{f_p} p_i^2/2m_i + \sum_{i=1}^{f_q} k_i q_i^2/2$, the equipartition theorem states that each of the $f = f_p + f_q$ degrees of freedom carries an average 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 applies to the more general kinetic energy $p^2/2m(q)$ where the mass depends on the coordinates $q_1, \dots$. It follows

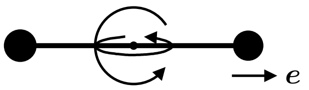
$$U = \overline{H} = \frac{1}{2} f k_B T \tag{4.113}$$

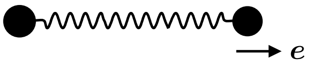
with f being the number of degrees of freedom. Therefore, for the specific heat $c_V = \frac{1}{2} f k_B$ and the system becomes a perfect gas with adiabatic exponent

$$\gamma = \frac{c_V + k_B}{c_V} = \frac{f+2}{f} = 1 + \frac{2}{f} \,. \tag{4.114}$$

Example 9: (Diatomic Molecules, Ideal Gas)

For (light) diatomic molecules (H_2, N_2, O_2) without interactions, in addition to the three kinetic degrees of freedom, rotational degrees of freedom are also present. The system has two rotational degrees of freedom with quadratic kinetic energy $L^2/2I = (p_\theta^2 + p_\phi^2/\sin^2\theta)/2I$, where p_θ, p_ϕ are conjugate to the variables (θ, ϕ) that parameterize the unit vector of the bond line $\boldsymbol{e} = (\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta)$. Therefore, the system is a perfect gas with $f = 5$ degrees of freedom.





Of course, there are still vibrational degrees of freedom, but these are frozen out for light molecules at room temperature due to quantum effects, see later. For heavy molecules (Br_2) or high temperatures, there is the possibility of vibration along the bond line. This vibration contributes two degrees of freedom (potential and kinetic energy), and thus the number of degrees of freedom in this case increases to $f = 7$.

Statistical Interpretation of Heat: In statistical mechanics (canonical ensemble), entropy is determined by the Gibbs (Shannon) expression

$$S = -k_B \sum_i p_i \ln p_i , \qquad p_i = e^{-\beta H_i}/Z_N = e^{\beta(F-H_i)} \tag{4.115}$$

Each microstate i corresponds to a specific value $H_i = E_i$ of the energy in the closed system. The internal energy of thermodynamics corresponds to the expectation value

$$U = \overline{H} = \sum_i p_i H_i \,. \tag{4.116}$$

We can rewrite the entropy a bit by using $\ln p_i = \beta(F - H_i)$. We obtain

$$TS = -k_B T \sum_i p_i \beta(F - H_i) = -F + U \,, \tag{4.117}$$

which exactly corresponds to the thermodynamic relationship between U (or S) and F.

Now, considering small changes, we get ($\sum_i dp_i = 0$ since $\sum_i p_i = 1$)

$$\begin{aligned} TdS &= -k_B T \sum_i (1 + \ln p_i) dp_i = \sum_i H_i dp_i \\ dU &= \sum_i p_i dH_i + \sum_i H_i dp_i = \sum_i p_i dH_i + \underbrace{TdS}_{\delta Q} = \delta W + \delta Q \,. \end{aligned} \tag{4.118}$$

The work δW corresponds to reversible changes in internal energy (without changing the probabilities). The change in heat is given by $\delta Q = \sum_i H_i dp_i$.

Gibbs' Variational Principle: We motivated the microcanonical distribution by the fact that we have knowledge about the macrostate, but are completely ignorant about the microstate. One can specify this 'principle of insufficient reason', initially formulated by Laplace, more precisely. To do this, we want to determine the probability distribution p_i on the microstates i which maximizes the Gibbs/Shannon entropy (Gibbs' variational principle). To do this, we determine the extremum of $S = -k_B \sum_i p_i \ln p_i$ under the constraint $\sum_i p_i = 1$. This implies (λ is the Lagrange multiplier)

$$0 = d(S/k_B - \lambda \sum_i p_i) = -\sum_i (\ln p_i + 1 + \lambda) dp_i \tag{4.119}$$

Thus, we have

$$p_i = e^{-1-\lambda} = \text{const.}, \tag{4.120}$$

which corresponds exactly to the microcanonical distribution (equal distribution on the microstates). The fact 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 for energy exchange. However, the constraint holds

$$U = \overline{H} = \sum_i p_i H_i\,. \tag{4.121}$$

To find the extremum of S, we therefore need a second Lagrange multiplier β. We obtain

$$0 = d(S/k_B - \lambda \sum_i p_i - \beta \sum_i H_i p_i) = -\sum_i (\ln p_i + 1 + \lambda + \beta H_i) dp_i \tag{4.122}$$

with the result

$$p_i = e^{-1-\lambda-\beta H_i} \propto e^{-\beta H_i}, \tag{4.123}$$

which corresponds exactly to the canonical distribution with $\beta = 1/k_B T$.

This way, one can understand statistical mechanics with the 'principle of insufficient reason' more deeply. Since one cannot uniquely determine the microstate by solely accessing the macroscopic quantities, it is simply assumed that the system is in the state with the highest entropy (given the knowledge about the system). This corresponds exactly to the typical configurations of Shannon. Even though there is no knowledge about the microstate, statements about observables can still be made. In particular, there are quantities whose relative fluctuations vanish in the thermodynamic limit of large systems, allowing deterministic statements to be made.

One can easily extend the Gibbs variational principle by allowing fluctuations in other work coordinates. For example, one can imagine that the system is in contact with a working medium that allows volume changes and only sets the pressure on average. It is directly seen that the additional Lagrange multipliers correspond exactly to the

$$\begin{tikzcd}
\text{thermodyn. potential} & f(x) \arrow[rr, "\mathcal{L}\text{ (Legendre)}"] \arrow[d, dotted, leftrightarrow, "F(x) = e^{-f(x)}"] & & g(p) \arrow[d, dotted, leftrightarrow, "G(p) = e^{g(p)}"'] \\
\text{partition function} & F(x) \arrow[rr, "G(p) = \int dx\, F(x) e^{xp}\text{ (Laplace)}"'] & & G(p)
\end{tikzcd}$$

Fig. 4.1: Relationship between the Legendre transformation in thermodynamics and the Laplace transformation in statistical mechanics: a change from x to p as the natural variable corresponds to a Laplace transformation on the corresponding partition functions; except for corrections that vanish in the thermodynamic limit.

equilibrium quantities g_α. For the work coordinate Z with the equilibrium quantity g, the probability distribution is then obtained as

$$p_i \propto e^{-\beta(H_i - g Z_i)} \,. \tag{4.124}$$

The fact that in the thermodynamic limit this corresponds exactly to a change from Z to g with a Legendre transformation and thus is equivalent to thermodynamics, follows in the next section.

4.7 Equivalence of Ensembles

We first present a general result that links Legendre transformation with Laplace transformation. The application of this result shows, among other things, that in the thermodynamic limit, the microcanonical ensemble yields the same results as the canonical ensemble.

Given an extensive quantity $x \propto N$ for $N \to \infty$, let $f(x)$ be a convex function that is also extensive. Furthermore, we define the corresponding 'partition function' $F(x) = e^{-f(x)}$. Then, in the thermodynamic limit $N \to \infty$, a Laplace transformation of $F(x)$ to $G(p)$ corresponds exactly to a Legendre transformation of $f(x)$ to $g(p) = \ln G(p)$ (up to subdominant corrections of $O(\ln N)$), see Fig. 4.1. In formulas, we have

$$G(p) = \int dx\, F(x) e^{xp} \quad \Rightarrow \quad g = \mathcal{L}f \text{ with } F(x) = e^{-f(x)}, G(p) = e^{g(p)} \,. \tag{4.125}$$

Now for the proof: The function $xp - f(x)$, due to the convexity of f, has a well-defined maximum at x^* for each p, see (2.4). Therefore, the integrand $e^{xp - f(x)}$ is dominated by values near this maximum. In second order, we obtain

$$xp - f(x) = \overbrace{x^* p - f(x^*)}^{\mathcal{L}f} + \overbrace{(p - f'(x^*))}^{0}(x - x^*) - \frac{1}{2} f''(x^*)(x - x^*)^2 \,. \tag{4.126}$$

Furthermore, from the extensivity, we have $f'' \propto 1/N$. With this approximation (saddle point approximation), the Laplace transformation can be explicitly carried out with the result

$$G(p) = e^{\mathcal{L}f} \int dx \, e^{-\frac{1}{2} f''(x^*)(x-x^*)^2} = e^{\mathcal{L}f} \, O(1/f''(x^*)^{1/2}) = e^{\mathcal{L}f} \, O(N^{1/2}) \,. \qquad (4.127)$$

We obtain

$$g(p) = \ln G(p) = \overbrace{\mathcal{L}f}^{O(N)} + O(\ln N) \,, \qquad (4.128)$$

which completes the proof.

Note: The saddle point approximation restricts the integral to a range $\delta x = x - x^* \simeq N^{1/2}$. Furthermore, $x^* \propto N$ due to extensivity. This means that the fluctuations in x are not small, but only the relative fluctuations are small, see (4.53) and (4.98).

Note: In applications, the integral is often not over all real numbers, but only over a subset. As long as $x^* \pm \delta x$ is within the integration range, the result still holds. For a similar reason, the integral can be replaced by a sum over integers (in the thermodynamic limit, many integers are within the range $x^* \pm \delta x$ and the integrand changes slowly).

Microcanonical and canonical ensemble: The relationship

$$\int dU \, \frac{\Gamma(U)}{\Delta} e^{-\beta U} = \int dU \, \frac{\overbrace{\langle \delta_\Delta(U-H) e^{-\beta U} \rangle}^{\approx \delta_\Delta(U-H)e^{-\beta H}}}{\Delta} = \langle e^{-\beta H} \rangle = Z_N(\beta) \qquad (4.129)$$

between canonical and microcanonical partition functions holds, where we have 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, as it only corresponds to a constant shift $\ln \Delta$ on the potentials).

Now it is only a matter of choosing the functions f, F, g, G and the variables x, p from equation (4.125) correctly, in order to show that

$$(-\beta)F(\beta) = \max_U \Big((-\beta)U - \frac{-S(U)}{k_B} \Big) = \max_U \Big(\frac{S(U)}{k_B} - \beta U \Big) \,. \qquad (4.130)$$

which (after dividing by $(-\beta)$) is equivalent to the (standard) result

$$F(\beta) = \min_S \Big(U(S) - \frac{-S}{(-\beta)k_B} \Big) = \min_S \Big(U(S) - TS \Big) \qquad (4.131)$$

from (2.47). Thus, in the thermodynamic limit, F and S are linked by a Legendre transformation and the two ensembles yield the same results. It is also said that the ensembles are *equivalent*.

The necessary connection is provided by $(x \mapsto U, p \mapsto -\beta)$

$$\begin{aligned} f(x) &\mapsto -S(U)/k_B = -\ln\Gamma(U), & F(x) &\mapsto \Gamma(U), \\ g(p) &\mapsto (-\beta)F(\beta) = \ln Z_N(\beta), & G(p) &\mapsto Z_N(\beta)\,, \end{aligned} \tag{4.132}$$

thus we have shown the equivalence of the ensembles in the thermodynamic limit.

4.8 Grand Canonical Ensemble

As we have seen in the last section, we 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, which is why we explicitly carry out the procedure for this case.

Let us consider a system that is coupled to both a heat bath (at temperature T) and a particle reservoir (with chemical potential μ). Physically, the two reservoirs can of course be realized by the same system. We can obtain the *grand canonical distribution* analogously to the derivation of Equation (4.89). Equivalently, from the Gibbs variational principle (4.124) (with $g \mapsto \mu, Z \mapsto N$) we obtain the result

$$\rho_{\text{gk}} = \frac{e^{-\beta(H-\mu N)}}{\mathcal{Z}}\,. \tag{4.133}$$

The grand canonical partition function

$$\mathcal{Z}(\beta, z) = \sum_N z^N Z_N(\beta) = \langle e^{-\beta(H-\mu N)}\rangle, \qquad \text{with the } \textit{fugacity } z = e^{\beta\mu} \tag{4.134}$$

is linked to the grand potential by

$$\Omega(\beta, z) = -k_B T \ln \mathcal{Z}(\beta, z)\,. \tag{4.135}$$

The partition function $\mathcal{Z}(\beta, z)$ is the generating function for the (internal) energy (with respect to $-\beta$) and the number of particles (with respect to $\ln z$). We obtain

$$U = \overline{H} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \quad \text{and} \quad N = \overline{N} = \frac{\partial \ln \mathcal{Z}}{\partial \ln z} = z\frac{\partial \ln \mathcal{Z}}{\partial z} \tag{4.136}$$

In the grand canonical ensemble, the number of particles is only fixed on average. For the variance, we obtain

$$(\delta N)^2 = \frac{\partial^2 \ln \mathcal{Z}}{\partial \ln z^2} = \left(\frac{\partial N}{\partial(\beta\mu)}\right)_{\beta,V} = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{\beta,V} \overset{(2.59)}{=} \frac{N^2}{V}\kappa_T k_B T\,. \tag{4.137}$$

In the thermodynamic limit, the relative fluctuations vanish with $\delta N/N \propto 1/N^{1/2}$, as already known from the equivalence of ensembles.

Note: The grand canonical ensemble requires that the partition function be calculated over systems with any number of particles N. In quantum mechanics, this corresponds to the trace over the *Fock space*

$$\mathcal{F} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N \,. \tag{4.138}$$

The direct sum goes over the vacuum state $\mathcal{H}_0 = \mathbb{C}$, the one-particle Hilbert space $\mathcal{H}_1 = \mathcal{H}$, the two-particle Hilbert space $\mathcal{H}_2$, and so on. In nature, not all states in the product space

$$\mathcal{H}_N = \mathcal{H}^{\otimes N} = \underbrace{\mathcal{H} \otimes \cdots \otimes \mathcal{H}}_{N \text{ factors}} \tag{4.139}$$

are realized. Only the symmetric (for bosons) or antisymmetric (for fermions) subspaces are allowed, with

$$\psi_N(\dots, \boldsymbol{x}_i, \dots, \boldsymbol{x}_j, \dots) = \psi(\dots, \boldsymbol{x}_j, \dots, \boldsymbol{x}_i, \dots) \qquad \text{(bosons)}, \tag{4.140}$$

$$\psi_N(\dots, \boldsymbol{x}_i, \dots, \boldsymbol{x}_j, \dots) = -\psi_N(\dots, \boldsymbol{x}_j, \dots, \boldsymbol{x}_i, \dots) \qquad \text{(fermions)}. \tag{4.141}$$

A general state in Fock space has the form

$$\Psi = (\psi_0, \psi_1, \psi_2, \dots) \tag{4.142}$$

with the scalar product

$$\langle \Psi | \Phi \rangle = \sum_N \langle \psi_N | \phi_N \rangle_{\mathcal{H}_N} \,. \tag{4.143}$$

Here, $|\psi_0|^2$ is the probability of the system being in the vacuum state. The probability density of finding N particles in the system at positions $\boldsymbol{x}_1, \dots, \boldsymbol{x}_N$ is accordingly $|\psi_N(\boldsymbol{x}_1, \dots, \boldsymbol{x}_N)|^2$.

For the calculation of 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

$$N|\Psi\rangle = (0, \psi_1, 2\psi_2, \dots) \tag{4.144}$$

and the Hamiltonian operator on the Fock space

$$H|\Psi\rangle = (0, H_1\psi_1, H_2\psi_2, \dots) \tag{4.145}$$

as a function of the Hamiltonian operators H_N on the N-particle Hilbert space.

Chapter 5

Quantum Gases

5.1 Rotations of Diatomic Molecules

In Example 9, we have seen that the rotations of a diatomic molecule with $H = L^2/2I$ classically contribute k_B to the specific heat. The equipartition theorem is no longer valid in quantum statistics. The reason is that degrees of freedom can *freeze out*, as we will see below.

Quantum mechanically, the Hamiltonian operator has the spectrum

$$\begin{aligned} H|l,m\rangle &= E_l|l,m\rangle, \qquad\qquad |m| \leq l,\ l \in \{0,1,\dots\} \\ E_l &= \frac{\hbar^2}{2I}l(l+1)\,. \end{aligned} \tag{5.1}$$

We now calculate 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, we obtain 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 we have

$$Z(\alpha) \simeq 1 + 3e^{-2\alpha}, \qquad c_V \simeq 12k_B\alpha^2 e^{-2\alpha}\,. \tag{5.4}$$

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[1] Since we only have one particle, there is of course no distinction between canonical and grand canonical.

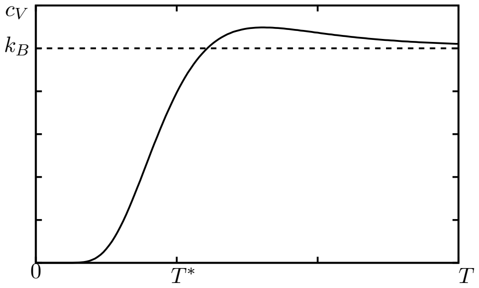

Fig. 5.1: Specific heat of a diatomic molecule as a function of temperature. For low temperatures, it is exponentially suppressed and approaches the result k_B from the equipartition theorem for high temperatures. The temperature dependence is anomalous with a non-monotonic behavior.

Thus, at low temperatures, the rotations freeze out exponentially with $c_V \sim e^{-T^*/T}$. At high temperatures, the sum becomes a Riemann integral with

$$Z = \int_0^\infty (2l+1)e^{-\alpha l(l+1)}\,dl = -\frac{1}{\alpha}\underbrace{\int_0^\infty \frac{d}{dl}e^{-\alpha l(l+1)}\,dl}_{-1}\,. \tag{5.5}$$

Therefore, $Z \simeq 1/\alpha$ and $c_V \simeq k_B$, which corresponds exactly to 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 is not monotonic. 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* in the specific heat: it first increases before being suppressed.

5.2 Phonon Gas

Consider a solid with N atoms. The atoms with mass M are arranged in the equilibrium position $\boldsymbol{r}_i$ ($i = 1, \ldots, N$) in a crystal lattice. Small deviations $\boldsymbol{u}_i = (u_{i,\alpha})_{\alpha=1,2,3}$ from the equilibrium position can be used to develop the energy in quadratic order. The Hamiltonian is obtained as

$$H = \sum_i \frac{\boldsymbol{p}_i^2}{2M} + \frac{1}{2}M \sum_{\substack{i,j \\ \alpha,\beta}} D_{\alpha\beta}(\boldsymbol{r}_i - \boldsymbol{r}_j)u_{i,\alpha}u_{j,\beta} \tag{5.8}$$

with $\boldsymbol{p}_i = M\dot{\boldsymbol{u}}_i$ being the canonical momentum corresponding to $\boldsymbol{u}_i$. The *dynamic matrix* D is symmetric $D_{\alpha\beta}(\boldsymbol{r}) = D_{\beta\alpha}(-\boldsymbol{r})$, positive-semidefinite, and due to translational symmetry, depends only on $\boldsymbol{r}_i - \boldsymbol{r}_j$.

Important are the eigenmodes and eigenfrequencies, which diagonalize the problem. To 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 the eigenfrequencies ω_ν. The eigenmodes are linked to the original degrees of freedom by an orthogonal principal axis transformation. With respect to the eigenmodes, the Hamiltonian operator 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 thus 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 calculate 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 consisting of non-interacting subsystems. As a result, the (free) energy becomes a sum of the subsystems.

We now only need to calculate the partition function Z_ν of an eigenmode (harmonic oscillator), with the result

$$Z_\nu = \sum_{n_\nu=0}^{\infty} e^{-\beta\hbar\omega_\nu(n_\nu + \frac{1}{2})} = e^{-\beta\hbar\omega_\nu/2} \frac{1}{1 - e^{-\beta\hbar\omega_\nu}} = \left[2\sinh\left(\frac{\hbar\omega_\nu}{2k_B T} \right) \right]^{-1}\,. \tag{5.14}$$

---

[2] Due to the orthogonality of the transformation, $\sum_i \boldsymbol{u}_i^{(\nu)} \cdot \boldsymbol{u}_i^{(\nu')} = \delta_{\nu\nu'}$.

The internal energy is given by

$$\begin{aligned}U &= -\frac{\partial \ln Z}{\partial \beta} = \sum_\nu \frac{\partial}{\partial \beta} \ln\left[2\sinh(\beta\hbar\omega_\nu/2)\right] = \sum_\nu \frac{1}{2}\hbar\omega_\nu \coth\left(\frac{\hbar\omega_\nu}{2k_BT}\right) \\ &= \sum_\nu \hbar\omega_\nu \left(\overline{n_\nu} + \frac{1}{2}\right) \qquad (5.15)\end{aligned}$$

with the mean occupation number (*Bose-Einstein distribution*)

$$\overline{n_\nu} = \frac{1}{e^{\hbar\omega_\nu/k_BT} - 1}\,. \qquad (5.16)$$

At high temperatures $k_BT \gg \hbar\omega_\nu$, the occupation number becomes

$$\overline{n_\nu} = \frac{k_BT}{\hbar\omega_\nu}\,. \qquad (5.17)$$

In this limit, we obtain the heat capacity (*Dulong-Petit law*)

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} k_BT \sum_{\nu=1}^{3N} = 3Nk_B\,. \qquad (5.18)$$

Thus, at high temperatures, we obtain the result from the equipartition theorem.

At low temperatures, some degrees of freedom are frozen out. To calculate the heat capacity, we need the eigenfrequencies ω_ν. Due to translational invariance, the eigenvalue problem in Fourier space is already diagonal, so only the diagonalization of the 3×3 matrix remains

$$\tilde{D}_{\alpha\beta}(\boldsymbol{k}) = \sum_i e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_i} D_{\alpha\beta}(\boldsymbol{r}_i) \qquad (5.19)$$

Thus, the system 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 during a homogeneous displacement $\boldsymbol{u}_i = \boldsymbol{d}$ of the crystal. It follows that

$$0 = \sum_i D(\boldsymbol{r}_i) = \tilde{D}(\boldsymbol{k} = 0) \qquad (5.20)$$

and thus also the Goldstone theorem $\omega_\lambda(\boldsymbol{k} \to 0) \to 0$. This means that the excitations are (linear) sound modes

$$\omega_\lambda(\boldsymbol{k}) = \begin{cases} s_\parallel |\boldsymbol{k}|, & \text{longitudinal mode with } \boldsymbol{u} \parallel \boldsymbol{k}, \\ s_\perp |\boldsymbol{k}|, & \text{transverse mode with } \boldsymbol{u} \perp \boldsymbol{k}, \end{cases} \qquad (5.21)$$

where the sound velocities $s_\perp$ of the two transverse modes are equal due to symmetry.[3] The linear dispersions are only valid for small $\boldsymbol{k}$.

We consider the system in a box with volume $V = L^3$. The quantization of the $\boldsymbol{k}$ modes is $\boldsymbol{k} = (2\pi/L)\boldsymbol{n}$, as in the example 1 (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 corresponds to the zero-point energy. We determine the excitation energy with respect to U_0 by changing from $k = |\boldsymbol{k}|$ to ω as the integration variable. 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 being the ‘average’ speed of sound defined by

$$\frac{1}{s^3} = \frac{1}{3} \sum_\lambda \frac{1}{s_\lambda^3} = \frac{2}{3s_\perp^3} + \frac{1}{3s_\parallel^3} \,. \quad (5.24)$$

Thus, the heat capacity of the phonon gas (at low temperatures) is given by

$$C_V = \frac{\partial U}{\partial T} = \frac{2\pi^2}{5} k_B V \left(\frac{k_B T}{\hbar s} \right)^3 \,. \quad (5.25)$$

The linearization of the spectrum in (5.21) is of course only valid for small energies and thus low temperatures. In fact, (5.25) is found to exceed the classical value of the Dulong-Petit law for high temperatures. The issue is that frequencies are included in the integral (5.23) where the linearization is no longer valid. Debye therefore proposed to replace the upper limit of the integral by the *Debye frequency*

$$\omega_D = \left(\frac{6\pi^2 s^3 N}{V} \right)^{1/3} \quad (5.26)$$

which is chosen such that for $T \gg \hbar\omega_D/k_B$, the Dulong-Petit law holds as desired.[5] The Debye energy $\hbar\omega_D$ plays an analogous role in the phonon gas to the Fermi energy ε_F in the theory of the Fermi gas, separating the high-temperature range (classical theory) from the low-temperature range (quantum theory).

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[3] The dynamic 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 constant term vanishes. The linear term is forbidden due to semidefiniteness ($D \geq 0$). The quadratic term can be parameterized by the two (Lamé) constants μ, λ with $\lambda \geq 0$ and $\lambda + \mu \geq 0$ due to $D \geq 0$. The sound velocities are thus 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] The result is obtained 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 Cavity Radiation

The theory of cavity radiation, also known as blackbody radiation, has many similarities with the phonon gas discussed in the previous section. The system consists of a cavity (vacuum) surrounded by walls at temperature T. Through absorption and emission of photons, the walls thermalize with the photon gas inside the cavity. The photons correspond to the quantized modes of the wave equation, which can be obtained from the Maxwell equation in vacuum. Each eigenfrequency ω_ν corresponds to a harmonic oscillator, which in equilibrium has an average occupation $\overline{n_\nu} = 1/(\exp(\hbar\omega_\nu/k_BT) - 1)$.

There are significant differences between the phonon gas and the photon gas. Firstly, the speed of photons is always the speed of light c, and secondly, due to $\boldsymbol{\nabla} \cdot \boldsymbol{E} = 0$, there are only two transverse modes. Therefore, in this case, we obtain for the mean speed (from (5.24))

$$\frac{1}{s^3} = \frac{2}{3c^3}, \qquad \text{and thus} \qquad s = \left(\frac{3}{2}\right)^{1/3} c\,. \tag{5.27}$$

The spectrum is linear without a cutoff frequency ω_D. From (5.27) and (5.23), we obtain 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 increases 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 thermodynamics. In particular, we still need the thermal equation of state $p(T)$. It should be noted that due to the lack of conservation of particle number, the pressure p can only depend on the single intensive quantity 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 relationship $pV = U/3$, which is satisfied by the phonon gas, is the (ultra-)relativistic extension of (1.32).

From the relationship $u(T) = \int d\omega\, \tilde{u}(\omega, T)$ in (5.23), we further obtain the *spectral energy density*

$$\tilde{u}(\omega, T) = \frac{\omega^2}{\pi^2c^3}\frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}\,. \tag{5.31}$$

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[6] The linear term $\propto T$ must vanish due to (2.56).

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 cavity radiation dates back to Max Planck. From the experimentally known results for a and $\omega_0(T)$, he determined the constants $\hbar$ and k_B. With knowledge of the value of the universal gas constant R, he also determined the then most accurate value of Avogadro's number R/k_B.

5.4 Ideal Quantum Gases

We have now seen in some 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 a change in 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 operator $H_N = \sum_{i=1}^N \boldsymbol{p}_i^2/2m$ with exclusively kinetic energy, the properties of bosonic gases at low temperatures are fundamentally different from those of fermionic gases.

The eigenfunctions of the single-particle problem $H_1 = \boldsymbol{p}^2/2m$ are given by plane waves (considering periodic boundary conditions again)

$$\psi_{\boldsymbol{k},\sigma}(\boldsymbol{r}, m) \propto \delta_{\sigma m} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \qquad \boldsymbol{k} = \frac{2\pi}{L}\boldsymbol{n}, \quad \sigma \in \{-s, -s+1, \ldots, s\} \tag{5.33}$$

with spin s and momentum $\hbar\boldsymbol{k}$ of the particle. The single-particle energies are given by

$$\varepsilon_{\boldsymbol{k},\sigma} = \frac{\hbar^2 \boldsymbol{k}^2}{2m}, \qquad \text{with} \quad H_1 \psi_{\boldsymbol{k},\sigma}(\boldsymbol{r}, m) = \varepsilon_{\boldsymbol{k},\sigma} \psi_{\boldsymbol{k},\sigma}(\boldsymbol{r}, m). \tag{5.34}$$

Since there is no interaction in the problem, one can consider the many-particle wave functions (initially without statistics) as product wave functions

$$\psi_N(x_1, \ldots, x_N) \propto \psi_{\alpha_1}(x_1) \cdots \psi_{\alpha_N}(x_N) \tag{5.35}$$

with $\alpha = (\boldsymbol{k}, \sigma)$ and $x = (\boldsymbol{r}, m)$. This wave function has the eigenenergy $E_N = \sum_i \varepsilon_{\alpha_i}$.

In the following, it is useful to introduce the *occupation number basis*. Due to 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 subspace and $\mathcal{P}_-$ onto the fermionic subspace. For fermionic states, the *Pauli principle* applies, restricting the occupation numbers to the values 0 or 1. In fact,

$$\mathcal{P}_-\Big[\varphi_\alpha(x_1)\varphi_\alpha(x_2)\Big] \propto \varphi_\alpha(x_1)\varphi_\alpha(x_2) - \varphi_\alpha(x_2)\varphi_\alpha(x_1) = 0 \,, \tag{5.38}$$

so that no states with $n_\alpha \geq 2$ exist.

Since the results of all ensembles coincide in the thermodynamic limit, it is easiest 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

$$n_\alpha = \begin{cases} 0, 1, 2, 3, \dots & \text{(bosons)}, \\ 0, 1 & \text{(fermions)}, \end{cases} \tag{5.39}$$

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 of each other, the partition function is a product of the individual contributions.

The logarithm transforms the product into a sum with the result

$$\ln \mathcal{Z} = \sum_\alpha \begin{cases} -\ln\Big(1 - e^{\beta(\mu-\varepsilon_\alpha)}\Big) & \text{(bosons)}, \\ \ln\Big(1 + e^{\beta(\mu-\varepsilon_\alpha)}\Big) & \text{(fermions)}. \end{cases} \tag{5.42}$$

From this, one finds the average occupation number $\overline{n_\alpha}$

$$\overline{n_\alpha} = -\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \varepsilon_\alpha}\right)_{\mu,\beta,\varepsilon_{\beta\neq\alpha}} = \begin{cases} \dfrac{1}{e^{\beta(\varepsilon_\alpha-\mu)} - 1} & \text{(bosons)}, \\ \dfrac{1}{e^{\beta(\varepsilon_\alpha-\mu)} + 1} & \text{(fermions)}, \end{cases} \tag{5.43}$$

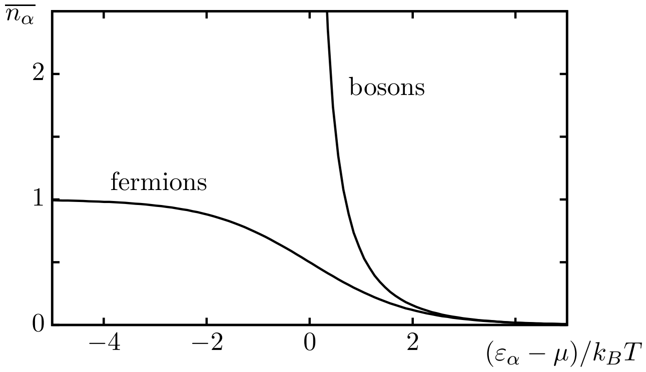

Fig. 5.2: Bose-Einstein and Fermi-Dirac distributions

see Fig. 5.2. The distribution of bosons is called *Bose-Einstein distribution.* We have already seen this in the example of the phonon and photon gases with $\mu = 0$ (without conservation of particle number). The distribution of fermions is called *Fermi-Dirac distribution.*

From the average occupation number, one can obtain the different thermodynamic quantities for an ideal quantum gas. For example, the average number of particles is given by

$$N = \sum_\alpha \overline{n_\alpha}\,. \tag{5.44}$$

The internal energy is obtained from

$$U = \overline{\sum_\alpha \varepsilon_\alpha n_\alpha} = \sum_\alpha \varepsilon_\alpha \overline{n_\alpha}\,. \tag{5.45}$$

From the relationship $\Omega = -k_BT \ln \mathcal{Z} = -pV$, one can finally determine the pressure

$$\frac{pV}{k_BT} = \ln \mathcal{Z} = \sum_\alpha \begin{cases} \ln(1+\overline{n_\alpha}) & \text{(Bosons)}\,, \\ -\ln(1-\overline{n_\alpha}) & \text{(Fermions)} \end{cases} \tag{5.46}$$

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

$$e^{\beta(\varepsilon_\alpha-\mu)} = \begin{cases} (1+\overline{n_\alpha})/\overline{n_\alpha} & \text{(Bosons)}\,, \\ (1-\overline{n_\alpha})/\overline{n_\alpha} & \text{(Fermions)}\,, \end{cases} \tag{5.48}$$

the factor $\beta(\varepsilon_\alpha - \mu)$ can be expressed in terms of the occupation numbers. The result is

$$S = -k_B \sum_\alpha \begin{cases} \overline{n_\alpha}\ln\overline{n_\alpha} - (1+\overline{n_\alpha})\ln(1+\overline{n_\alpha}) & \text{(Bosons)}\,, \\ \overline{n_\alpha}\ln\overline{n_\alpha} + (1-\overline{n_\alpha})\ln(1-\overline{n_\alpha}) & \text{(Fermions)}\,. \end{cases} \tag{5.49}$$

The fermionic result can be interpreted with (4.81) 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: considering the state α with energy ε_α, the system has the probability

$$p_{n_\alpha} = \frac{1}{\mathcal{Z}_\alpha} e^{-\beta n_\alpha (\varepsilon_\alpha - \mu)} \overset{(5.48)}{=} \frac{1}{1+\overline{n_\alpha}} \left(\frac{\overline{n_\alpha}}{1+\overline{n_\alpha}} \right)^{n_\alpha} \tag{5.50}$$

of having the occupation number n_α with $\mathcal{Z}_\alpha$ from (5.41) and the average occupation number $\overline{n_\alpha} = [e^{\beta(\varepsilon_\alpha - \mu)} - 1]^{-1}$. The occupation number is thus 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, $\varepsilon_\alpha = \hbar^2 \boldsymbol{k}^2 / 2m$. 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)

$$\frac{p}{k_B T} = \pm \frac{1}{V} \sum_{\boldsymbol{k},\sigma} \ln(1 \pm z e^{-\beta \varepsilon_{\boldsymbol{k},\sigma}}) = \pm \frac{g_s}{(2\pi)^3} \int d^3k \, \ln(1 \pm z e^{-\beta \varepsilon_{\boldsymbol{k},\sigma}}) \tag{5.52}$$

with spin degeneracy $g_s = 2s + 1$. Now we use the substitution (λ is the thermal wavelength from (4.102))

$$x^2 = \beta \varepsilon_{\boldsymbol{k},\sigma} = \frac{\hbar^2 k^2}{2 m k_B T} = \frac{\lambda^2 k^2}{4\pi}, \qquad d^3k = 4\pi k^2 dk = \frac{(4\pi)^{5/2}}{\lambda^3} x^2 \, dx \tag{5.53}$$

and obtain

$$\frac{p}{k_B T} = \frac{g_s}{\lambda^3} f^{\pm}_{5/2}(z) \qquad \text{with} \qquad f^{\pm}_{5/2}(z) = \pm \frac{4}{\sqrt{\pi}} \int_0^\infty dx \, x^2 \ln(1 \pm z e^{-x^2}) \,. \tag{5.54}$$

Using $\ln(1 - z) = -\sum_{n=1}^\infty z^n / n$, ($|z| < 1$) and

$$\frac{4}{\sqrt{\pi}} \int_0^\infty dx \, x^2 e^{-n x^2} = \frac{1}{n^{3/2}} \tag{5.55}$$

we get the power series expansion

$$f^{\pm}_{5/2}(z) = \mp f_{5/2}(\mp z) \qquad \text{with} \qquad f_{5/2}(z) = \sum_{l=1}^\infty \frac{z^l}{l^{5/2}} \,. \tag{5.56}$$

Furthermore, we define

$$f^{\pm}_{3/2}(z) = \mp f_{3/2}(\mp z) \qquad \text{with} \qquad f_{3/2}(z) = \sum_{l=1}^\infty \frac{z^l}{l^{3/2}} = z \frac{d}{dz} f_{5/2} = \frac{d}{d \ln z} f_{5/2} \,, \tag{5.57}$$

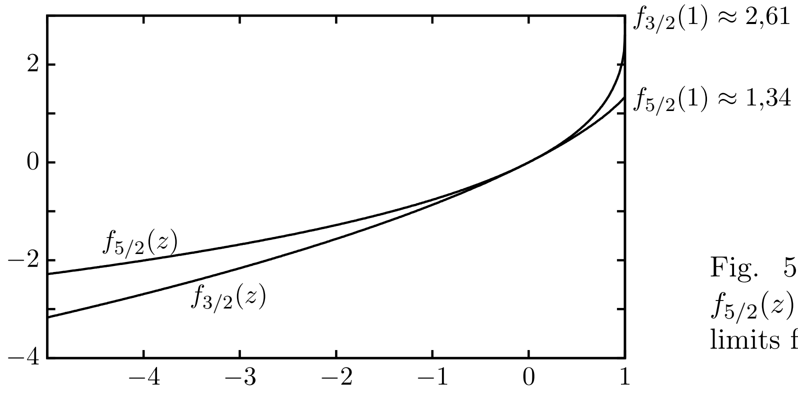

Fig. 5.3: The functions $f_{5/2}(z)$ and $f_{3/2}(z)$ with the limits for $z \to 1^-$.

see Fig. 5.3.

The equation (5.54) is analogous to the thermal equation of state of the (classical) ideal gas. However, the fugacity z is related to the (average) number of particles N through the relationship $N = z(\partial \ln \mathcal{Z}/\partial z)_{T,V}$. Therefore, for ideal quantum gases, the following relationships hold:

$$\frac{p}{k_B T} = \frac{g_s}{\lambda^3} f^{\pm}_{5/2}(z), \tag{5.58}$$

$$\frac{N}{V} = \frac{g_s}{\lambda^3} f^{\pm}_{3/2}(z) \qquad \Big(= \partial(p/k_B T)/\partial \ln z \Big), \tag{5.59}$$

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 constant z, $\beta p \propto \lambda^{-3} \propto \beta^{-3/2}$. With $\ln \mathcal{Z} = pV/k_B T$, we obtain:

$$\frac{U}{V} = -\left(\frac{\partial(\beta p)}{\partial \beta}\right)_z = \frac{3}{2} p\,. \tag{5.61}$$

Therefore, the result:

$$U = \frac{3}{2} pV \tag{5.62}$$

from the virial theorem (1.32) also holds in quantum mechanics. All effects due to exchange symmetry are thus contained in the (thermal) equation of state:

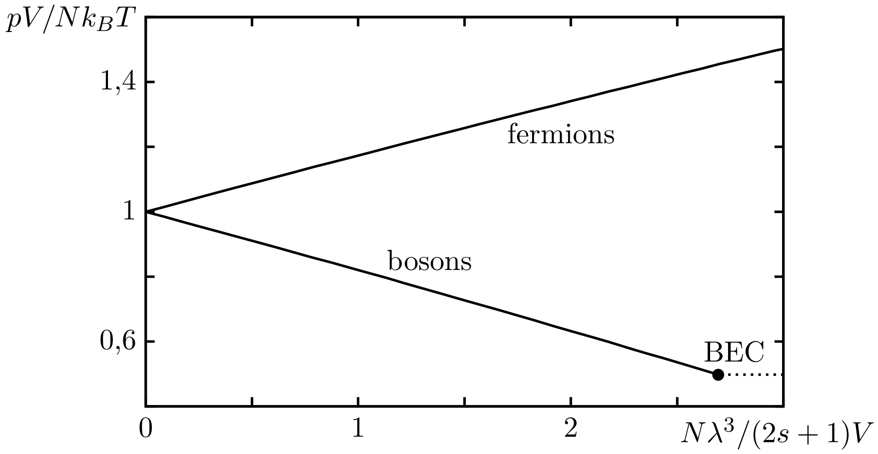

Fig. 5.4: Deviation of the thermal equation of state pV/Nk_BT from the classical result 1 as a function of $N\lambda^3/V$ of the particles in the volume λ^3.

$$\frac{pV}{Nk_BT} = \frac{f^{\pm}_{5/2}(z)}{f^{\pm}_{3/2}(z)}\,, \tag{5.63}$$

or, in other words, in the deviation of the right-hand side from the classical value of 1. Using (5.59) to express z in terms of the particle density, we obtain the result from Fig. 5.4.

Classical Limit: The classical limit is reached for

$$\frac{V}{N} \gg \lambda^3\,, \tag{5.64}$$

which means that the typical particle spacing is greater than the thermal wavelength λ. Here, λ describes the de Broglie wavelength of a particle with energy k_BT. The classical limit corresponds to low densities or high temperatures. From (5.59) it follows that $z \ll 1$ and we can focus on the terms with $l = 1$ in the expansion of $f^{\pm}_{\alpha}(z)$. It then holds that

$$\frac{f^{\pm}_{5/2}(z)}{f^{\pm}_{3/2}(z)} = 1 + O(z) \tag{5.65}$$

and we obtain the relationships $pV = Nk_BT$ and $U = \frac{3}{2}Nk_BT$ of the classical ideal gas.

The next order in z gives $f^{\pm}_{5/2}(z)/f^{\pm}_{3/2}(z) = 1 \pm z/2^{5/2}$ and thus the first exchange effects. From (5.59) we obtain

$$\frac{1}{g_s}\frac{\lambda^3 N}{V} = z + O(z^2)\,. \tag{5.66}$$

and therefore

$$pV = Nk_BT\left(1 \pm \frac{1}{g_s}\frac{\lambda^3 N}{2^{5/2}V} + O(z^2)\right) . \tag{5.67}$$

The Fermi gas has a higher pressure (due to the Pauli exclusion principle) and the Bose gas has a lower pressure than the classical gas.

5.5 Degenerate Fermi Gas

In a degenerate gas, the case $\lambda^3 \gg V/N$ is referred to, where exchange effects dominate due to quantum mechanics. This corresponds to the limit 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 through the relationship

$$\frac{N}{V} = \frac{1}{V}\sum_{\boldsymbol{k},\sigma}\overline{n_{\boldsymbol{k},\sigma}} = g_s\int\frac{d^3k}{(2\pi)^3}\overbrace{\Theta(\varepsilon_F - \hbar^2k^2/2m)}^{\text{sphere with radius } k_F = \sqrt{2m\varepsilon_F}/\hbar} = \frac{g_s}{(2\pi)^3}\frac{4\pi k_F^3}{3} \tag{5.69}$$

where g_s is the spin degeneracy, and k_F is the Fermi wave vector. This leads to

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 N}{g_s V}\right)^{2/3} . \tag{5.70}$$

The ground state energy $E_0 = U(T = 0)$ is given by

$$\begin{aligned} E_0 &= \sum_{\boldsymbol{k},\sigma}\varepsilon_{\boldsymbol{k},\sigma}\overline{n_{\boldsymbol{k},\sigma}} = g_sV\int\frac{d^3k}{(2\pi)^3}\frac{\hbar^2k^2}{2m}\Theta(\varepsilon_F - \hbar^2k^2/2m) \\ &= \frac{3}{5}N\varepsilon_F \end{aligned} \tag{5.71}$$

The *zero-point pressure* (pressure in the ground state) is given by

$$p_0 = -\left(\frac{\partial E_0}{\partial V}\right)_N = -\frac{3}{5}N\left(\frac{\partial\varepsilon_F}{\partial V}\right)_N = \frac{2}{5}\frac{N}{V}\varepsilon_F . \tag{5.72}$$

Electrons in a metal have a density $N/V \simeq 10^{22}\,\text{cm}^{-3}$. Therefore, $\varepsilon_F/k_B \simeq 10^4\,\text{K}$. This means that metals are degenerate even at room temperature. The electrons exert a zero-point pressure $p_0 \simeq 10^4\,\text{atm}$. As a function of V at constant particle number N, the zero-point pressure is given by $p_0 \propto V^{-5/3}$.

Sommerfeld Expansion: In order to obtain results at finite temperatures, we need the expansion of $f^+_{5/2}(z)$ for $z \to \infty$. The asymptotic expansion (*Sommerfeld Expansion*) is given by

$$f^+_{5/2}(z) = \frac{8}{15\sqrt{\pi}}\left(\ln^{5/2} z + \frac{5\pi^2}{8}\ln^{1/2} z + O(\ln^{-3/2} z)\right) . \tag{5.73}$$

From this, we also have

$$f^+_{3/2}(z) = \frac{d}{d\ln z} f^+_{5/2}(z) = \frac{4}{3\sqrt{\pi}}\left(\ln^{3/2} z + \frac{\pi^2}{8}\ln^{-1/2} z + O(\ln^{-5/2} z)\right) . \tag{5.74}$$

Substituting the Sommerfeld expansion into (5.59), we obtain the relationship

$$\ln^{3/2} z + \frac{\pi^2}{8}\ln^{-1/2} z \simeq \frac{3\sqrt{\pi}\lambda^3 N}{4g_s V} = (\varepsilon_F/k_B T)^{3/2} , \tag{5.75}$$

or equivalently

$$\ln z \times \left(1 + \frac{\pi^2}{8\ln^2 z}\right)^{2/3} \simeq \frac{\epsilon_F}{k_B T} . \tag{5.76}$$

We iteratively solve this equation for $\ln z$ and obtain the result

$$\mu = k_B T \ln z = \varepsilon_F \left(1 - \frac{\pi^2}{12}(k_B T/\varepsilon_F)^2 + O(k_B T/\varepsilon_F)^4\right) . \tag{5.77}$$

For a fixed particle density, this implies $\mu \to \varepsilon_F$ as $T \to 0$.

Furthermore, using (5.58), we find

$$\begin{aligned}\frac{pV}{Nk_B T} = \frac{f^+_{5/2}(z)}{f^+_{3/2}(z)} &= \frac{2}{5}\left(\ln z + \frac{\pi^2}{2\ln z} + O(\ln^{-2} z)\right) \\ &= \frac{2}{5}\frac{\varepsilon_F}{k_B T}\Big(1 + \underbrace{\frac{5\pi^2}{12}}_{\pi^2/2-\pi^2/12}(k_B T/\varepsilon_F)^2 + O(k_B T/\varepsilon_F)^4\Big) . \end{aligned} \tag{5.78}$$

Therefore, the pressure (at constant number of particles and volume) is higher at finite temperature than at zero temperature.

In addition, we obtain the specific heat

$$c_V = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3V}{2N}\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{\pi^2}{2}\frac{k_B T}{\varepsilon_F} k_B , \tag{5.79}$$

which increases linearly in T for low temperatures. In particular, $c_V \to 0$ as $T \to 0$, as required by the third law of thermodynamics.

5.6 Degenerate Bose Gas

As we have already seen, the pressure for bosonic exchange statistics is lowered compared to the classical gas. However, the functions $f^-_{3/2}(z)$ and $f^-_{5/2}(z)$ reach 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 $\mu = 0$, see Fig. 5.3. In fact, the curve ends at the point BEC in Fig. 5.4 with

$$\left(\frac{\lambda^3 n}{g_s}\right)_c = f^-_{3/2}(1) \approx 2.61 \quad \text{and} \quad \left(\frac{p}{nk_BT}\right)_c = \frac{f^-_{5/2}(1)}{f^-_{3/2}(1)} \approx 0.514 \tag{5.80}$$

Thus, at the critical point, of the three intensive quantities $T, p, n = N/V$, only one is independent.[7] At a fixed temperature, this results in a critical particle density

$$n_c(T) = \frac{1}{v_c(T)} = \frac{2.61\, g_s}{\lambda^3} \propto T^{3/2} \tag{5.81}$$

and a critical pressure

$$p_c(T) = 0.514\, n_c k_B T \propto T^{5/2}\,. \tag{5.82}$$

The relationships (5.58) and (5.59) for the Bose gas are only valid for $p \leq p_c$ and thus $n \leq n_c$. A phase transition occurs at the pressure p_c, known as the *Bose-Einstein condensation* (BEC).

Superfluid ^{4}He: At a fixed pressure p, one finds from the condition $p = p_c(T_c)$ that the Bose-Einstein condensation (BEC) occurs at the *critical temperature*

$$T_c = \frac{1}{k_B}\left(\frac{h^3 p}{1.34\, g_s (2\pi m)^{3/2}}\right)^{2/5} \tag{5.83}$$

The critical temperature is highest for light atoms. Considering the example of ^{4}He, which consists of two protons and two neutrons, making it a boson with spin $s = 0$ (an even number of bound fermions has bosonic statistics). The mass is $m = 4\,\mathrm{u} = 6.6 \times 10^{-27}\,\mathrm{kg}$. At a typical pressure of $p = 1\,\mathrm{atm}$, one would therefore expect a BEC at

$$T_c \approx 1.7\,\mathrm{K}, \qquad\qquad (\text{with } n_c \approx 8.5\,\mathrm{nm}^{-3})\,. \tag{5.84}$$

This value is close 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, $s = \frac{1}{2}$), it is observed that at these temperatures, helium-3 remains liquid. The reason is that ^{3}He is a fermi gas and therefore does not undergo BEC. Only at a much lower temperature of $\simeq 2\,\mathrm{mK}$ does ^{3}He also become a superfluid. The physical mechanism in this case is based on pair formation (to form bosons from ^{3}He) followed by condensation of the pairs.

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[7] This corresponds to the Gibbs phase rule with 2 phases and 1 component, see later.

The Bose gas (bg) has the maximum particle density $n_c(T)$. Therefore, it can accommodate a maximum of $N_{\mathrm{bg}} = n_c V$ particles in the volume V. This raises the question of what happens for $N > n_c V$. To keep the particle number fixed, we need to switch to the free energy. We have (for $N > N_{\mathrm{bg}}$, so $\mu = 0$)

$$F(T,V,N) = \min_{\mu}(\Omega + \mu N) = V \min_{\mu}(\mu n - p) \overset{(\mu=0)}{=} -p_c(T)V\,. \tag{5.85}$$

Since $\mu = 0$, the free energy naturally does not depend on N.

One can alternatively write the free energy as

$$\frac{F}{N} = x f_{\mathrm{bg}} + (1-x) f_{\mathrm{BEK}}, \qquad x = \frac{v}{v_c} = \frac{N_{\mathrm{bg}}}{N} = \left(\frac{T}{T_c}\right)^{3/2} \tag{5.86}$$

with

$$f_{\mathrm{bg}}(T, v_c) = -p_c v_c \overset{(5.82)}{=} -0.514\, k_B T \qquad \text{and} \qquad f_{\mathrm{BEK}}(T, 0) = 0 \tag{5.87}$$

In the language of Chapter 3 (cf. Fig. 3.1), this corresponds to a coexistence of the ideal Bose gas (bg) (with specific volume v_c) with the Bose-Einstein condensate (with specific volume $v_{\mathrm{BEK}} = 0$). The unrealistic property of the vanishing specific volume of the BEK (corresponding to an infinite density) is due to the fact that we have not taken interactions into account. The Bose-Einstein condensate is thus an idealized system with $s_{\mathrm{BEK}} = u_{\mathrm{BEK}} = v_{\mathrm{BEK}} = 0$.

We have seen that the equation (5.59) only considers the particles $N_{\mathrm{bg}} = n_c V < N$ that form the ideal Bose gas. The question is, where in the derivation we have 'lost' the other particles. Mathematically, below the Bose-Einstein condensation (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

$$\overline{n_0} = N_{\mathrm{BEC}} = N - N_{\mathrm{bg}} = (1-x)N = \left(1 - \frac{v}{v_c}\right) N \tag{5.88}$$

Therefore, (5.52) in general must be replaced by the relationship

$$\begin{aligned} \frac{p}{k_B T} &= -\frac{g_s}{V}\ln(1-z) - \frac{g_s}{(2\pi)^3}\int d^3k\, \ln(1 - z e^{-\beta\varepsilon_{\boldsymbol{k},\sigma}}) \\ &= -\frac{g_s}{V}\ln(1-z) + \frac{g_s}{\lambda^3} f^{-}_{5/2}(z) \end{aligned} \tag{5.89}$$

Normally, in the thermodynamic limit $V \to \infty$, the contribution of the Bose-Einstein condensate (first term) 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 the remaining states.

To obtain a more precise interpretation of the critical temperature as a phase transition, we calculate the entropy from the free energy $F = -p_c V$ in (5.85) (with $p_c \propto T^{5/2}$ for $T < T_c$):

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = V\frac{\partial p_c}{\partial T} = \frac{5}{2}\frac{Vp_c}{T} \propto T^{3/2}\,. \tag{5.90}$$

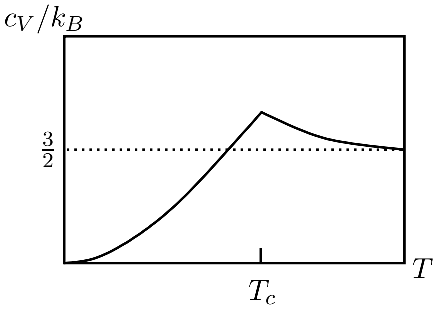
This fulfills the third law of thermodynamics for the ideal Bose gas. If we rewrite the entropy as $S = s_{\mathrm{bg}}N_{\mathrm{bg}}$, we see that the entropy is only carried by the particles in the Bose gas with $s_{\mathrm{bg}} = 0.514\,\frac{5}{2}k_B$. The entropy difference between the two phases in the phase mixture is then given by $\Delta s = s_{\mathrm{bg}}$. Therefore, the system has latent heat

$$\ell = T\Delta s = 0.514\,\frac{5}{2}k_B T\,. \tag{5.91}$$

Furthermore, there is a jump $\Delta v = v_c$ in the specific volume. The Clausius-Clapeyron relationship (3.8), which can be directly verified, connects the ratio of these jumps with the derivative $\partial p_c/\partial T$ of the vapor pressure curve (5.82). This allows us to identify the transition as a first-order phase transition. The specific heat below the critical temperature is given by

$$c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V = \frac{15}{4}\frac{vp_c}{T} \overset{(5.82)}{=} \frac{15}{4} \times 0.514 k_B \frac{v}{v_c} = 1.93\,k_B\left(\frac{T}{T_c}\right)^{3/2}\,. \tag{5.92}$$

The specific heat thus increases at low temperatures as $T^{3/2}$. At the critical temperature, the specific heat has a value of $1.93\,k_B$, which is greater than the value of $\frac{3}{2}k_B$ at high temperatures. Overall, the specific heat has a maximum at the critical temperature.



Chapter 6

Magnetism

Magnetic systems are a test environment to verify the results of statistical physics. On the one hand, the systems are simple enough to obtain theoretical results (partly exact), and on the other hand, there are experimental methods, such as neutron scattering, that can determine magnetic properties of materials very accurately. Another advantage is that in most materials, the typical energy of magnetism is on the order of 100-1000 K and that the magnetic degrees of freedom are relatively decoupled from other degrees of freedom, allowing them to be understood separately.

Within classical physics, magnetism cannot be explained. In fact, it is the statement of the *Bohr-van-Leeuwen theorem* that there is no classical magnetism. Quantum mechanics leads to charged particles generating a diamagnetic response to applied magnetic fields due to orbital degrees of freedom. Additionally, there is an intrinsic angular momentum, the spin, which generates a magnetic dipole and leads to a paramagnetic response. In quantum mechanics, there are many different magnetic phases (para-, ferro-, antiferro-, spin glass magnetism, . . .) with various phase transitions in between. In this chapter, we will only be able to explain some basics. For more information, refer to further literature, such as the book by Chaikin and Lubensky.

6.1 General

In magnetic systems, the working coordinate is the magnetization $\mathcal{M}$ along the magnetic field with the corresponding equilibrium quantity B_0, see example 1.4. In the following, we consider the spin of N particles, keeping N fixed. The (reversible) work is then given by

$$\delta W = B_0 \, d\mathcal{M} \,. \tag{6.1}$$

In comparison to the liquids and gases that we studied in Chapter 1, the relationship $(V, -p) \leftrightarrow (\mathcal{M}, B_0)$ holds. Through this analogy, we name 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

$$F = U - TS \qquad \text{and} \qquad G = U - TS - B_0\mathcal{M}\,. \tag{6.2}$$

The fundamental equations are

$$dF = -SdT + B_0\,d\mathcal{M} \qquad \text{and} \qquad dG = -SdT - \mathcal{M}\,dB_0\,. \tag{6.3}$$

The magnetic analogue to compressibility is the magnetic *susceptibility*

$$\chi_x = \left(\frac{\partial\mathcal{M}}{\partial B_0}\right)_x, \qquad \text{isothermal (for } x = T\text{) and adiabatic (for } x = S\text{)}\,. \tag{6.4}$$

The 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 constant $x = B_0, \mathcal{M}$. For *paramagnetic* substances, $\chi_T > 0$ and thus $C_{B_0} \geq C_{\mathcal{M}}$. For *diamagnetic* substances with $\chi_T < 0$, on the other hand, $C_{B_0} \leq C_{\mathcal{M}}$.

Example 1: (Stability conditions)

The minimum principle on the potentials $U(S,\mathcal{M})$, $H(S,B_0)$ leads in particular to

$$\frac{T}{C_{\mathcal{M}}} = \frac{\partial^2 U}{\partial S^2} \geq 0, \; \frac{T}{C_{B_0}} = \frac{\partial^2 H}{\partial S^2} \geq 0.$$

Thus, the specific heats satisfy the stability conditions $C_{\mathcal{M}}$, $C_{B_0} > 0$.[1]

Example 2: (Adiabatic Demagnetization)

When a body is adiabatically magnetized, its temperature changes. This follows from the relationship

$$\left(\frac{\partial T}{\partial B_0}\right)_S = -\left(\frac{\partial\mathcal{M}}{\partial S}\right)_{B_0} = -\left(\frac{\partial\mathcal{M}}{\partial T}\right)_{B_0}\left(\frac{\partial T}{\partial S}\right)_{B_0} = -\frac{T}{C_{B_0}}\left(\frac{\partial\mathcal{M}}{\partial T}\right)_{B_0}\,. \tag{6.6}$$

In the first equation, 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] The stability conditions for χ_S, χ_T follow from the second derivatives of $U^{\text{em}}(S,\mathcal{M})$, $F^{\text{em}}(T,\mathcal{M})$ with respect to $\mathcal{M}$. However, it must be considered that $B_0 d\mathcal{M}$ is only the magnetostatic energy of the magnetic substance, to which the field energy term $d(\frac{1}{2}B_0^2) = B_0\,dB_0$ must be added. Thus, $dF^{\text{em}} = dF + B_0\,dB_0 = -SdT + B_0(dB_0 + d\mathcal{M}) = -SdT + B_0(\chi_T^{-1} + 1)d\mathcal{M}$. The stability condition $\partial^2 F^{\text{em}}/\partial\mathcal{M}^2 \geq 0$ thus reads $\chi_T \geq -1$. Analogously, for U^{em}, the condition $\chi_S \geq -1$ is obtained.

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 changed. This is the so-called *magneto-caloric effect*. At room temperature, it is small, but at low temperatures it can become substantial. For paramagnetic substances, the Curie's law $\mathcal{M} \propto T^{-1}$ applies, see below. Thus, $\partial\mathcal{M}/\partial T \propto -T^{-2} < 0$ and we obtain $(\partial T/\partial B_0)_S > 0$. In adiabatic *demagnetization* ($dB_0 < 0$), the temperature of the body decreases.

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 the external field $\boldsymbol{B}_0$. We further assume that the magnetic moments of magnitude $\mu = |\boldsymbol{m}_i|$ can only take two possibilities with $\boldsymbol{m}_i \cdot \boldsymbol{B}_0 = m_i B_0 = s_i \mu B_0$ with $s_i = \pm 1$ (Ising spin): either they align in the field ($s_i = +1$) or they point in the opposite direction ($s_i = -1$). This gives a total of 2^N possible configurations. The partition function (at fixed B_0) is then given by[2]

$$\begin{aligned} Z_B &= \sum_{s_1,\ldots,s_N} e^{-\beta H_B} = \sum_{s_1,\ldots,s_N} e^{\beta\mu B_0 \sum_i s_i} = \Big(\sum_{s_1} e^{\beta\mu B_0 s_1}\Big)\cdots\Big(\sum_{s_N} e^{\beta\mu B_0 s_N}\Big) \\ &= \Big(\sum_{s} e^{\beta\mu B_0 s}\Big)^N = 2^N \cosh^N(\beta\mu B_0)\,. \end{aligned} \tag{6.8}$$

From the partition function, we obtain the Gibbs free energy

$$G(T,B_0) = -k_B T \ln Z_B = -N k_B T \ln[2\cosh(\mu B_0/k_B T)]\,. \tag{6.9}$$

This allows us to calculate 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

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{B_0} = N k_B \ln 2 + N k_B \ln\cosh(\mu B_0/k_B T) - \frac{B_0}{T}\mathcal{M} \\ &= -N k_B (p_+ \ln p_+ + p_- \ln p_-)\,. \end{aligned} \tag{6.11}$$

---

[2] In comparison to gas, Z_B corresponds to the isothermal-isobaric partition function. The term H_B corresponds to the Laplace transformation of $\mathcal{M}$ to B_0, see (4.124).

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[3]

$$\overline{H_B} = -B_0 \mathcal{M} = -N\mu B_0 \tanh(\mu B_0/k_B T) \tag{6.12}$$

is proportional to the magnetization.

In the high-temperature limit ($k_B T \gg \mu B_0$), the *Curie's law* follows from (6.10) as

$$\mathcal{M} = \frac{N\mu^2 B_0}{k_B T} \,. \tag{6.13}$$

At low temperatures with $k_B T \ll \mu B_0$, the magnetization saturates

$$\mathcal{M} = N\mu(1 - 2e^{-2\mu B_0/k_B T}) \tag{6.14}$$

to the maximum value $N\mu$ except for exponential corrections.

In the presence of a finite magnetic field B_0, both the heat capacity[4]

$$C_{B_0} = T\left(\frac{\partial S}{\partial T}\right)_{B_0} = \frac{N\mu^2 B_0^2}{k_B T^2 \cosh^2(\mu B_0/k_B T)} \tag{6.15}$$

and the susceptibility

$$\chi_T = \left(\frac{\partial \mathcal{M}}{\partial B_0}\right)_T = \frac{N\mu^2}{k_B T \cosh^2(\mu B_0/k_B T)} = \frac{T C_{B_0}}{B_0^2} \tag{6.16}$$

have a maximum at $\mu B_0 \sim k_B T$ before the degrees of freedom freeze out at low temperatures (exponentially), see Fig. 6.1. At low temperatures, we find the behavior $C_{B_0} \propto T^{-2} e^{-2\mu B_0/k_B T}$ and $\chi_T \propto T^{-1} e^{-2\mu B_0/k_B T}$. For high temperatures, on the other hand, cosh → 1, so that $C_{B_0} \propto T^{-2}$ and $\chi_T \propto T^{-1}$.

For $B_0 = 0$, Curie's law holds

$$\chi_T = \frac{N\mu^2}{k_B T} \tag{6.17}$$

at all temperatures.

6.3 Ising Model

The ideal paramagnet does not take into account interactions between the magnetic moments and therefore cannot describe phase transitions. By adding an interaction

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[3] 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 the formalism, but corresponds to the Legendre transformation of $\mathcal{M}$ with respect to B_0. Thus, $U = 0$ and $\overline{H_B} = G + TS = -B_0\mathcal{M} = \partial(\beta G)/\partial\beta$. This is because for the present system without interaction, the energy is proportional to the magnetization. Therefore, $S(U, \mathcal{M})$ and $U(S, \mathcal{M})$ are not well defined.

[4] Since the average energy is fixed for a fixed magnetization, the degenerate result $C_{\mathcal{M}} = 0$ holds.

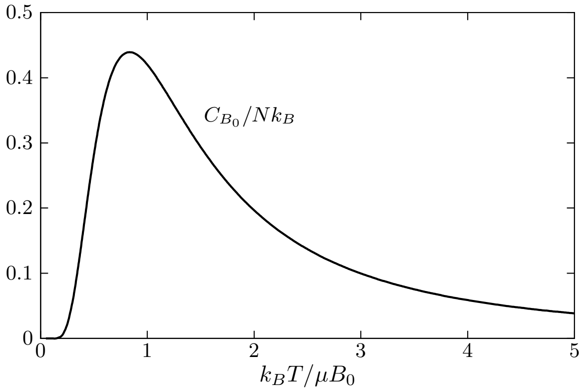

Fig. 6.1: The heat capacity of an ideal paramagnet exhibits the Schottky anomaly. The value is small for both high and low temperatures. It has a maximum $C^*_{B_0} \approx 0.44Nk_B$ at $k_BT \approx 0.83\mu B_0$.

energy of the form

$$H = -\frac{1}{2}\sum_{i,j} J_{ij}s_is_j - h\sum_i s_i, \qquad h = \mu B_0, \tag{6.18}$$

we obtain the *Ising model*. The factor $\frac{1}{2}$ ensures that each pair of spins is counted only once.

The coupling constants J_{ij} have units of 'energy' and describe the interaction between spin i and spin j. Note that due to $s_i^2 = 1$, 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} random). Typically, the origin of the interaction J is the *exchange interaction*, i.e. the combination of the electrostatic Coulomb interaction with the Pauli exclusion principle. Typical orders of magnitude are $|J|/k_B \simeq 100$–$1000\,\mathrm{K}$.

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 through the partition function

$$Z_B = \sum_{s_1,\dots,s_N} e^{-\beta H} = e^{-\beta G}\,. \tag{6.20}$$

In general, this partition function is not analytically solvable. A useful approximation is the *mean field approximation*. In this approach, the interaction term s_is_j is replaced by the interaction of s_i with the (uniform) mean spin $m = \overline{s}$ (mean field). We write

$$s_i = m + (s_i - m) = m + \delta_i\,. \tag{6.21}$$

The energy is then given by (summing over $\langle i,j\rangle$ for 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 $z = 2d$ describes the number of nearest neighbors. Except for the last term, the spins are independent. Therefore, we want to neglect the last term. For this, we need the correlations to be small, with

$$\frac{\overline{\delta s_i\,\delta s_j}}{m^2} = \frac{\overline{\delta_i\delta_j}}{m^2} \ll 1 \tag{6.23}$$

Since the mean field theory neglects correlations, it breaks down especially near a phase transition, as will be discussed later.

Without the last term, the energy has the form

$$H_{\text{MF}} = -h_{\text{eff}}\sum_i s_i + \frac{z}{2}NJm^2\,. \tag{6.24}$$

This is the energy of an ideal paramagnet in the effective field $h_{\text{eff}} = h + zJm$. A similar calculation as in the last chapter leads to, see Eq. (6.9),

$$G(T,h,m) = \frac{z}{2}NJm^2 - Nk_BT\ln[2\cosh(\beta h_{\text{eff}})]\,. \tag{6.25}$$

In equilibrium, the Gibbs energy is minimized with respect to the inhibition m. Thus,

$$0 = \frac{\partial G}{\partial m} = zNJm - zNJ\tanh(\beta h_{\text{eff}})\,. \tag{6.26}$$

This equation corresponds to the *self-consistency equation*

$$m = \overline{s_i} = \frac{\sum_{s_i=\pm1} s_i e^{\beta h_{\text{eff}} s_i}}{\sum_{s_i=\pm1} e^{\beta h_{\text{eff}} s_i}} = \tanh(\beta h_{\text{eff}}) = \tanh\Big[\beta(h+zJm)\Big] = -\frac{1}{N}\frac{\partial G}{\partial h} \tag{6.27}$$

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) provides the thermodynamics. In particular, one is interested in the susceptibility

$$\chi_T = -\mu^2\frac{\partial^2 G(T,h)}{\partial h^2} \overset{(6.26)}{=} -\mu^2\frac{\partial}{\partial h}\left(\frac{\partial G(T,h,m)}{\partial h}\bigg|_{m=m^*}\right) \overset{(6.27)}{=} N\mu^2\frac{\partial m(T,h)}{\partial h} \tag{6.28}$$

With the self-consistency equation $m^* = \tanh(\beta h_{\text{eff}})$, we obtain

$$\frac{\chi_T}{N\mu^2} = \frac{\overbrace{\partial\tanh(\beta h_{\text{eff}})}^{\beta[1-\tanh^2(\beta h_{\text{eff}})]}}{\partial h_{\text{eff}}}\frac{\partial h_{\text{eff}}}{\partial h} = \beta(1-m^{*2})\left(1 + zJ\frac{\partial m^*}{\partial h}\right) = \beta(1-m^{*2})\left(1 + \frac{zJ\chi_T}{N\mu^2}\right)$$

and thus 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 $m^* = \overline{s_i}$.

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 leads to the solution

$$m^* = \frac{h}{k_B T - zJ} \tag{6.30}$$

In particular, $m^* = 0$ for $B_0 = h = 0$. In this case, the Curie law is modified 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 the ferromagnetic case with $J > 0$)

$$T_c = \frac{zJ}{k_B}\,. \tag{6.32}$$

The divergence indicates that the paramagnetic solution at $m^* = 0$ becomes unstable for $T \leq T_c$.

We investigate this instability using the self-consistency equation. For $h = 0$, we look for a solution of

$$m = \tanh(\beta zJm) = \tanh(T_c m/T)\,. \tag{6.33}$$

The value $m = 0$ is always a solution. As can be seen from the graph in Fig. 6.2, for $T < T_c$ there are additional solutions $\pm m(T, 0)$. These solutions are degenerate and minimize G. $N\mu\, m(T, 0)$ is called the *spontaneous magnetization*, as it occurs without a corresponding external field. Thus, the system is in a *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, $m^* \to 1^-$, so one can use $\tanh x \approx 1 - 2e^{-2x}$. This leads to the approximation

$$m^*(T, 0) \begin{cases} = 0, & T \geq T_c\,, \\ \approx \sqrt{3(1 - T/T_c)}, & T \lesssim T_c\,, \\ \approx 1 - 2e^{-2T_c/T}, & T \ll T_c \end{cases} \tag{6.34}$$

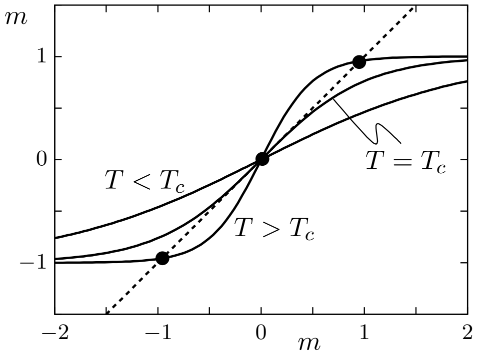

Fig. 6.2: Graphical solution of the self-consistency equation for $h = 0$: The intersection between the dashed line ($m = m$) and the curve $\tanh(T_c m/T)$ gives the solutions. In the ferromagnetic phase ($T < T_c$), there are 3 solutions, while in the paramagnetic phase ($T > T_c$) there is only 1 solution.

for the magnetization. The magnetization exhibits a non-analytic behavior at $T = T_c$, signaling the phase transition. In the presence of 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 $T = T_c$. Using 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 related to 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 differentiating with respect to T. Only the explicit T dependence needs to be used, since G is a minimum with respect to m^*. We get

$$\begin{aligned} S(T, h = 0) = -\left(\frac{\partial G}{\partial T}\right)_h &= N k_B \ln\big[2\cosh(T_c m^*/T)\big] - \frac{N k_B T_c m^*}{T} \overbrace{\tanh(T_c m^*/T)}^{m^*} \\ &= N k_B \ln\big[2\cosh(T_c m^*/T)\big] - \frac{N k_B T_c m^{*2}}{T} \,. \end{aligned} \tag{6.39}$$

At low temperatures, $\cosh(x) \approx \frac{1}{2}e^x$. Thus, the system satisfies the third law of thermodynamics with

$$S(T \ll T_c, h = 0) \approx N k_B T_c \frac{m^*(1-m^*)}{T} \overset{(6.34)}{\approx} \frac{2 N k_B T_c e^{-2T_c/T}}{T} \tag{6.40}$$

and the degrees of freedom freeze out at low temperatures. For temperatures around T_c, we can expand the entropy for small m^* with the result

$$S = N k_B \ln(2) + \frac{N k_B T_c (T_c - 2T)}{2T^2} m^{*2} + O(m^{*4})\,. \tag{6.41}$$

For $T > T_c$, $m^* = 0$ and we obtain $S(T > T_c, h = 0) = N k_B \ln(2)$ from N disordered Ising spins. Overall, we have

$$S(T, h=0) \begin{cases} = N k_B \ln(2), & T > T_c, \\ \approx N k_B \ln(2) - \frac{3}{2} N k_B (1 - T/T_c), & T \lesssim T_c, \\ \approx 2 N k_B T_c e^{-2T_c/T}/T, & T \ll T_c\,. \end{cases} \tag{6.42}$$

The entropy thus exhibits a non-analytic behavior at $T = T_c$ signaling the phase transition. Similarly, the heat capacity

$$C_{B_0}(T, h=0) = T \left(\frac{\partial S}{\partial T}\right)_h \begin{cases} = 0, & T > T_c, \\ \approx \frac{3}{2} N k_B, & T \lesssim T_c, \\ \approx 4 N k_B T_c^2 e^{-2T_c/T}/T^2, & T \ll T_c\,. \end{cases} \tag{6.43}$$

exhibits a jump of height $\frac{3}{2} N k_B$ at the phase transition, see Fig. 6.3.

Near the critical point $(T, h) = (T_c, 0)$, the behavior of the system is described by critical exponents. These are

$$C_{B_0} \propto |T - T_c|^{-\alpha}, \quad m^*_{h=0} \propto (T_c - T)^{\beta}, \quad \chi_{T,h=0} \propto |T - T_c|^{-\gamma}, \quad m^*_{T=T_c} \propto h^{1/\delta}\,.$$

The results from (6.43), (6.34), (6.37), and (6.36) provide the values $\alpha = 0$, $\beta = \frac{1}{2}$, $\gamma = 1$, $\delta = 3$. These are the same values we 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 changes T_c but not the nature of the phase transition. However, it turns out that the molecular field approximation is only valid for $d \geq 4$, since the condition (6.23) is not applicable for lower dimensions near the phase transition. In particular, there is no phase transition for $d = 1$. In other dimensions, we find:

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)

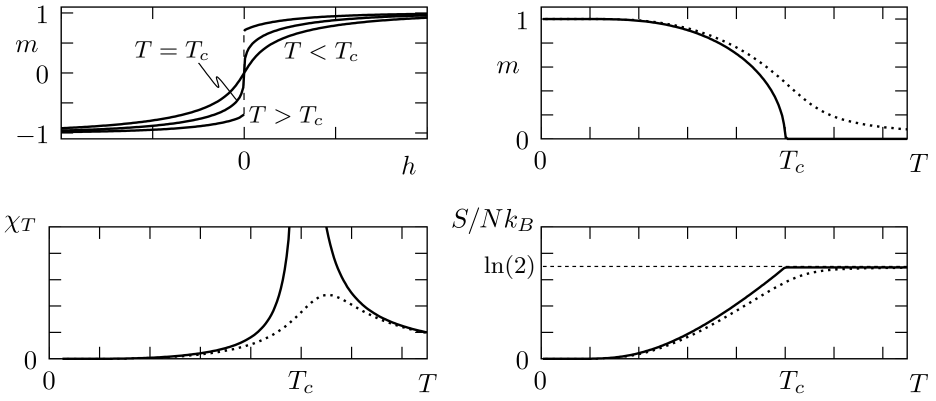

Fig. 6.3: Results of the molecular field approximation for the ferromagnetic Ising model for the magnetization $\mathcal{M} = N\mu m$, the isothermal susceptibility χ_T, and the entropy S. The solid lines represent results for an external magnetic field $B_0 = \mu h$. The dashed curves apply for $h > 0$. The problem has a critical point at $(T, B_0) = (T_c, 0)$. The singularities are softened by a finite magnetic field.

These exponents are called the Ising exponents. The liquid-gas phase transition is in the same *universality class* and therefore has the same exponents. However, there are also other universality classes with different exponents. For example, if we consider classical unit vectors $\boldsymbol{e} \in \mathbb{R}^2$ in the plane instead of Ising spins, then we are in the XY universality class. Unit vectors in 3D space are called the Heisenberg universality class, see also the book by Chaikin-Lubensky.

It turns out that of the four critical exponents, only two are independent. In general, the following inequalities hold:

$$\begin{aligned} &\alpha' + 2\beta + \gamma' \geq 2 && \text{(Rushbrooke)},\\ &\gamma' \geq \beta(\delta - 1) && \text{(Widom)}, \end{aligned} \tag{6.44}$$

where α', γ' indicate the exponents when approaching the critical point from the low-temperature phase.[5] For example, the Rushbrooke inequality follows from the relationship

$$C_{B_0}(T, h=0) \overset{(6.5)}{=} \frac{T}{\chi_T}\left(\frac{\partial \mathcal{M}}{\partial T}\right)^2_{B_0} + \overbrace{C_{\mathcal{M}}}^{\geq 0} \geq \frac{N\mu^2 T}{\chi_T}\left(\frac{\partial m^*}{\partial T}\right)^2_{h=0} . \tag{6.45}$$

For $T \lesssim T_c$, $C_{B_0} \propto (T_c - T)^{-\alpha'}$, $\chi_T \propto (T_c - T)^{-\gamma'}$, $m^*_{h=0} \propto (T_c - T)^{\beta}$. From (6.45), we obtain (as $T \to T_c^-$)

$$(T_c - T)^{-\alpha' - \gamma' - 2(\beta - 1)} \geq \text{const.} \tag{6.46}$$

Thus, the Rushbrooke inequality holds in the form $0 \geq -\alpha' - \gamma' - 2(\beta - 1)$.

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[5] Such a distinction does not exist for β and δ.

The *scaling hypothesis* $G(\lambda^a t, \lambda^b h) = \lambda G(t,h)$, which follows from the renormalization group theory, reduces all critical exponents to a and b. For example, for the magnetization, the scaling behavior is obtained as

$$\lambda M(t,h) \propto -\lambda \left(\frac{\partial G}{\partial h}\right)_t = \lambda^b M(\lambda^a t, \lambda^b h)\,. \tag{6.47}$$

Setting $h = 0$ and $\lambda = (-t)^{-1/a}$ (for $t < 0$) here, we obtain

$$M(t,0) \propto (-t)^{(1-b)/a} M(-1,0)\,. \tag{6.48}$$

This gives $\beta = (1-b)/a$. Furthermore, choosing $t = 0$ and $\lambda = h^{-1/b}$ leads to the relationship $1/\delta = 1/b - 1$. Continuing these considerations to the second derivatives, we obtain the relationships

$$\alpha = \alpha' = 2 - \frac{1}{a}, \qquad \beta = \frac{1-b}{a}, \qquad \gamma = \gamma' = \frac{2b-1}{a}, \qquad \delta = \frac{b}{1-b}\,. \tag{6.49}$$

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 equations. The exponents a, b are not measurable. Therefore, β, γ are usually treated as 'free' critical exponents. Solving the equations in (6.44) for α, δ then leads to the relationship

$$\alpha = 2(1-\beta) - \gamma \qquad \text{and} \qquad \delta = 1 + \frac{\gamma}{\beta}\,. \tag{6.50}$$

It is easy to verify that the critical exponents of the Ising model satisfy these relationships.

6.5 Peierls' Argument

We have seen that the results of the molecular field approximation are mostly incorrect 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. Therefore, an alternative approach is needed to understand low-dimensional systems. We discuss the Peierls' argument, which in particular shows that the Ising model does not exhibit a phase transition in one dimension.

1D: We want to show that in one dimension, for $T > 0$, there is no spontaneous magnetization. Therefore, at finite temperatures, there is 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 exists at small $T > 0$, if typical configurations from the canonical ensemble are still predominantly aligned. However, it disappears if large domains of reversed spins become probable.

Let us now consider the probability of a configuration with a domain wall. The energy difference is $\Delta E = 2J > 0$. Thus, the probability of a *specific* 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)

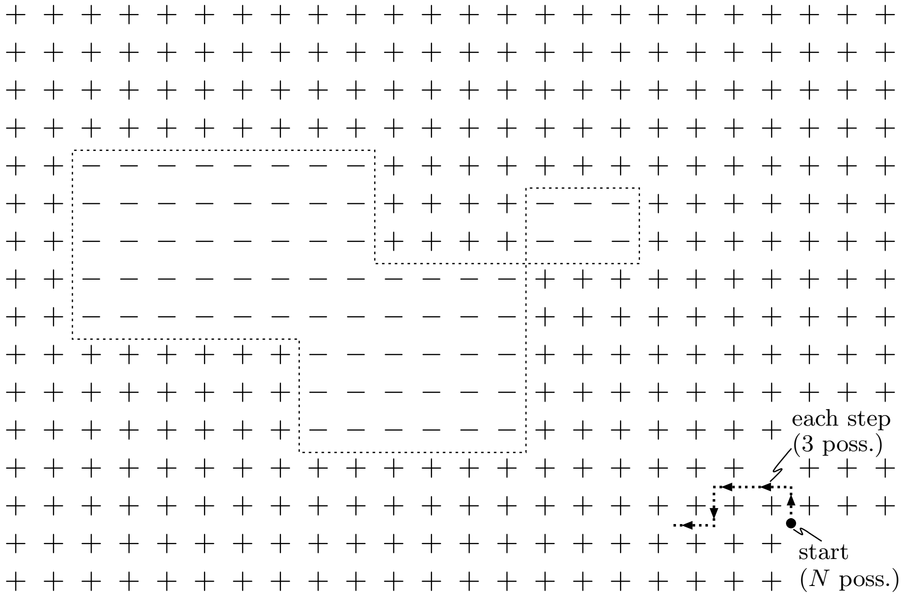
$$p_{\text{wall}} = p_0(N-1)e^{-\beta\Delta E} = p_0 e^{-\beta\Delta F} \tag{6.51}$$

with the difference in 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 $-T\Delta S$ the entropy difference $\Delta S = k_B \ln(N-1)$ due to the $N-1$ possibilities for the domain wall. In the thermodynamic limit $N \to \infty$, the entropic term dominates. Thus, $p_{\text{wall}} \gg p_0$ and the spontaneous magnetization of the ground state is destroyed at any finite temperature.

2D: Also in two dimensions, we consider a domain of $-$ embedded in the ground state $+$. The energy difference from the ground state is $\Delta E = 2JL$ with L being 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 any plaquette (N possibilities) and then going in any direction (4 possibilities). At each further step, one then has a maximum of 3 possibilities (since one cannot go back the same way).



This gives 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 $L^2 \propto N$. This results in the difference in free energy

$$\Delta F \gtrsim L\big[2J - \ln(3) k_B T\big]\,. \tag{6.54}$$

For temperatures with $k_B T \leq 2J/\ln(3) \approx 1.8J$, $\Delta F \geq 0$ and domain walls are suppressed. Thus, the spontaneous magnetization of the ground state persists even at finite temperatures. The Peierls' argument is quite good for simplicity, as the exact transition point is at $k_B T_c = 2J/\ln(1+\sqrt{2}) \approx 2.27\,J$.

Chapter 7

Non-equilibrium and Transport

So far, we have studied systems in equilibrium without considering how equilibrium is actually reached. In this final chapter, we want to provide a brief overview of systems that are not in equilibrium. We will focus on systems that have only been slightly perturbed from equilibrium. In particular, we will assume that there are fast processes that bring a system into a *local equilibrium*. Such equilibrium is described by local equilibrium quantities $T(\boldsymbol{r},t), p(\boldsymbol{r},t), \mu(\boldsymbol{r},t), \ldots$. However, in complete equilibrium, T, p, μ are constants. The achievement of complete equilibrium is facilitated by the *hydrodynamic* modes.

7.1 Heat Conduction

We start with heat conduction in a homogeneous system. Away from equilibrium, the state variables become dependent on position. 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

$$\frac{\partial u}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}^q = 0 \,. \tag{7.1}$$

Here, u is the energy density ($[u]$ = energy/volume) and $\boldsymbol{j}^q$ is the heat flux density ($[j^q]$ = power/area). Here, $\boldsymbol{j}^q \cdot \boldsymbol{n}\, dA$ is the heat flux flowing through the area dA with the normal vector $\boldsymbol{n}$. A spatial dependence of the temperature $T(\boldsymbol{r},t)$ leads to a heat flux density $\boldsymbol{j}^q$. For small temperature gradients, the *Fourier's law* holds

$$\boldsymbol{j}^q = -\kappa \boldsymbol{\nabla} T \tag{7.2}$$

with the thermal conductivity κ. The thermal conductivity κ must be positive so that heat flows from the hotter to the colder location.

To obtain a closed system of equations, we still need to use the thermodynamic relation

$$du = nc_V dT \tag{7.3}$$

with $n = N/V$ being the particle density and c_V the specific heat per particle. Here, we have assumed that we are describing heat conduction in a solid, so we can neglect thermal expansion effects (n remains constant). By substituting the relationships (7.2) and (7.3) into the continuity equation, we obtain the *heat conduction equation* ($\kappa = \text{const.}$)

$$\frac{\partial T}{\partial t} = D\,\Delta T \tag{7.4}$$

with the diffusion constant

$$D = \frac{\kappa}{nc_V}\,. \tag{7.5}$$

Starting from a temperature distribution $T_0(\boldsymbol{r}) \leq T_{\text{max}}$ at time $t = 0$, the solution of the heat conduction 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, the following estimate holds for the gradient

$$\begin{aligned} |\boldsymbol{\nabla} T(\boldsymbol{r}, t)| &= \frac{1}{(4\pi Dt)^{3/2}(2Dt)} \left| \int d^3r'\,(\boldsymbol{r}' - \boldsymbol{r}) e^{-|\boldsymbol{r}-\boldsymbol{r}'|^2/4Dt}\, T_0(\boldsymbol{r}') \right| \\ &\leq \frac{T_{\text{max}}}{(4\pi Dt)^{3/2}(2Dt)} \underbrace{\int d^3x\, x\, e^{-x^2/4Dt}}_{=4\pi \int_0^\infty dx\, x^3 e^{-x^2/4Dt} = 32\pi D^2 t^2} = \frac{2T_{\text{max}}}{\sqrt{\pi Dt}}\,. \end{aligned} \tag{7.7}$$

Therefore, diffusion leads to a decrease in the temperature gradient, which vanishes in the limit $t \to \infty$. Thus, the heat conduction 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 compensate for a typical gradient T_{max}/L.

Note: The heat conduction equation is only valid in the hydrodynamic regime for lengths $L \gg \ell$ with ℓ being the *mean free path* and times $\gg \tau$ with $\tau = v\ell$ being the *scattering time* (v is the typical speed of the particles). 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 reaches a local equilibrium on the length scale ℓ and time scale τ. This is followed by 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. Therefore, it is accompanied by a change in entropy. With the definition $du = Tds$ (no expansion $dv = 0$), we find from the continuity equation (7.1) the relationship

$$\frac{\partial s}{\partial t} = -\frac{1}{T}\boldsymbol{\nabla}\cdot\boldsymbol{j}^q = -\boldsymbol{\nabla}\cdot\frac{\boldsymbol{j}^q}{T} - \frac{1}{T^2}\boldsymbol{j}^q\cdot\boldsymbol{\nabla}T\,. \tag{7.8}$$

The term $\boldsymbol{j}^s = \boldsymbol{j}^q/T$ is the entropy flux density. Entropy is not conserved. Therefore, entropy does not satisfy a source-free continuity equation, but instead

$$\frac{\partial s}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}^s = \dot{\mathsf{s}} \tag{7.9}$$

with the *entropy production rate* (per volume)

$$\dot{\mathsf{s}} = -\frac{\boldsymbol{j}^q\cdot\boldsymbol{\nabla}T}{T^2} \overset{(7.2)}{=} \kappa\frac{(\boldsymbol{\nabla}T)^2}{T^2} \geq 0\,. \tag{7.10}$$

It is important to note that the local entropy production is always positive, in accordance with the second law of thermodynamics. In equilibrium, $\boldsymbol{\nabla}T = 0$, and therefore no new entropy is produced. The entropy flux 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 want to generalize the considerations. To do this, 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, …). In equilibrium, these have the value $\alpha_{0,i}$ with entropy S_0. Now consider a fluctuation α_i with entropy change

$$\Delta S = S - S_0 = \frac{1}{2}\sum_{i,j}(\partial^2 S)_{ij}\alpha_i\alpha_j, \tag{7.11}$$

where $\partial^2 S \leq 0$. The probability density of finding the system in a state with deviations α_i is given by

$$\rho(\boldsymbol{\alpha}) = \rho(\alpha_1, \ldots, \alpha_f) = \rho(0, \ldots, 0)e^{\Delta S/k_B}\,. \tag{7.12}$$

It is helpful to introduce the *thermodynamically conjugate quantities*

$$\gamma_i = \frac{\partial S}{\partial \alpha_i} = \sum_j (\partial^2 S)_{ij}\alpha_j \tag{7.13}$$

In equilibrium, S is maximal and therefore $\gamma_j = 0$. γ_i is also called the *thermodynamic forces.* This leads to the correlations

$$\begin{aligned}\overline{\alpha_i\gamma_j} &= \int d^f\alpha\,\alpha_i\gamma_j\rho(\boldsymbol{\alpha}) = k_B\int d^f\alpha\,\alpha_i\frac{\partial\rho(\boldsymbol{\alpha})}{\partial\alpha_j} = -k_B\int d^f\alpha\,\rho(\alpha)\frac{\partial\alpha_i}{\partial\alpha_j}\\ &= -k_B\delta_{ij}\,.\end{aligned} \tag{7.14}$$

It is often easiest to determine the conjugate quantities using the following 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 associated with the force γ_i.

Example 1: We determine the quantity conjugate to $\alpha = U$ for the heat transport from Chapter 7.1. Consider two systems in thermal contact. The entropy S is given by $dU = TdS$ (without expansion). The entropy generation is given by, see (2.5) with $\dot{U} = \dot{U}_2 = -\dot{U}_1$,

$$\dot{S} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \dot{U} = \Delta\left(\frac{1}{T}\right) \dot{U} \,. \tag{7.16}$$

Thus, the thermodynamic force is $\gamma = \Delta(1/T) = 1/T_2 - 1/T_2$.

Example 2: In applications, a local version of the last example is often used. Here, the energy density u plays the role of the local state variable. The entropy density can change according to (7.9) due to both an entropy flow (heat flow without temperature difference) and entropy generation $\dot{\mathsf{s}}$. The local version of the entropy generation (7.16) is

$$\dot{\mathsf{s}} \overset{(7.10)}{=} -\frac{\boldsymbol{j}^q \cdot \boldsymbol{\nabla} T}{T^2} = \left(\boldsymbol{\nabla} \frac{1}{T}\right) \cdot \boldsymbol{j}^q \,. \tag{7.17}$$

The entropy generation is due to a heat flow from a hot to a cold temperature. A comparison with (7.15) shows that $\gamma_i = \partial_i(1/T)$ are the conjugate forces to the current densities $d\alpha_i/dt = j^q_i$.

In equilibrium, $\alpha_i = \gamma_j = 0$. If the deviations from equilibrium are small, the quantities α_i satisfy linear equations of motion

$$\frac{d\alpha_i(t)}{dt} = \sum_j L_{ij}\gamma_j(t) = \sum_{j,k} L_{ij}\,(\partial^2 S)_{jk}\,\alpha_k(t) \tag{7.18}$$

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 do not change under time reversal. Then, for microscopic fluctuations ($\tau > 0$), we have

$$\overline{\alpha_i(t)\alpha_j(t+\tau)} \overset{(\tau\mapsto-\tau)}{=} \overline{\alpha_i(t)\alpha_j(t-\tau)} \overset{(t\mapsto t+\tau)}{=} \overline{\alpha_j(t)\alpha_i(t+\tau)} \tag{7.19}$$

Differentiating this relationship 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 the *Onsager reciprocity relation* with (7.14)

$$L_{ji} = L_{ij}\,. \tag{7.21}$$

This relationship can be generalized with a similar 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 reciprocity relation holds

$$L_{ij}(\boldsymbol{B}_0) = \epsilon_i \epsilon_j L_{ji}(-\boldsymbol{B}_0)\,. \tag{7.23}$$

Note that α_i and γ_i have the same parity, while the current $d\alpha_i/dt$ has the opposite parity. This breaks the (macroscopic) equations of motion (7.18) time-reversal invariance and leads (in general) to irreversible dynamics.

Example 3: (Electrical reciprocity)

Electric transport is described by Ohm's law

$$j_i = \sum_{j=1}^{3} \sigma_{ij}\,E_j\,. \tag{7.24}$$

The conductivity tensor σ_{ij} relates the electric field strength $\boldsymbol{E}$ to the electric current density $\boldsymbol{j}$. The current generates the electric power density

$$\dot{u} = \boldsymbol{E}\cdot\boldsymbol{j} = \sum_{i,j} \sigma_{ik} E_i E_k \geq 0\,. \tag{7.25}$$

At the (fixed) temperature T, this leads to entropy generation (per volume)

$$\dot{\mathsf{s}} = \frac{\dot{u}}{T} = \frac{1}{T}\boldsymbol{E}\cdot\boldsymbol{j}\,. \tag{7.26}$$

Thus, $\gamma_i = E_i/T$ is the thermodynamic force for the electric current density $d\alpha_i/dt = j_i$.

A comparison of (7.24) with (7.18) shows that the Onsager transport coefficients are given by

$$L_{ij} = T\sigma_{ij}\,. \tag{7.27}$$

For electric transport, the reciprocity relation holds

$$\sigma_{ij}(\boldsymbol{B}_0) = \sigma_{ji}(-\boldsymbol{B}_0)\,. \tag{7.28}$$

For an isotropic material, $\sigma_{ij} = \delta_{ij}\sigma$. Therefore, σ is necessarily an even function of the magnetic field $\boldsymbol{B}_0$.

The conductivity σ_{yx} is determined in an experimental setup where the voltage is applied in the x direction and the current is measured in the y direction. Without an applied magnetic field ($\boldsymbol{B}_0 = 0$), reciprocity requires that the result is the same when switching the voltage and current measurements (and thus measuring σ_{xy}).

Example 4: (dissipative and reactive transport coefficients)

The generation of entropy takes the form

$$\dot{S} = \sum_{i,j} L_{ij}(\boldsymbol{B}_0)\gamma_i\gamma_j = \sum_{i,j} \tilde{L}_{ij}(\boldsymbol{B}_0)\gamma_i\gamma_j \tag{7.29}$$

with the symmetric matrix

$$\tilde{L}_{ij}(\boldsymbol{B}_0) = \frac{1}{2}\left[L_{ij}(\boldsymbol{B}_0) + L_{ji}(\boldsymbol{B}_0)\right] = \frac{1}{2}\left[L_{ij}(\boldsymbol{B}_0) + \epsilon_i\epsilon_j L_{ij}(-\boldsymbol{B}_0)\right]\,. \tag{7.30}$$

In order for the entropy generation (as demanded by the 2nd law) to always be positive, the matrix $\tilde{L}_{ij}$ must be positive definite. $\tilde{L}$ is referred to as the *dissipative* part of the transport coefficients. If the degrees of freedom i and j have the same parity ($\epsilon_i\epsilon_j = 1$), $\tilde{L}_{ij}$ 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

$$\hat{L}_{ij} = \frac{1}{2}\left[L_{ij}(\boldsymbol{B}_0) - L_{ji}(\boldsymbol{B}_0)\right] = \frac{1}{2}\left[L_{ij}(\boldsymbol{B}_0) - \epsilon_i\epsilon_j L_{ij}(-\boldsymbol{B}_0)\right] \tag{7.31}$$

with $L_{ij} = \tilde{L}_{ij} + \hat{L}_{ij}$ is called the *reactive* transport coefficients, which have the opposite parity as a function of the magnetic field $\boldsymbol{B}_0$.

Example: (Electric transport in 2D)

The electric transport in 2D is described by the conductivity tensor (B_0 is the magnetic field strength in 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 $\sigma_{xy} = -\sigma_{yx}$ hold, as only the two (real) matrices $I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and $J = i\sigma_2 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$ under a general rotation $R = e^{\phi J}$ in the plane remain invariant with $R(\alpha I + \beta J)R^T = \alpha I + \beta J$.

With the results from the last 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. 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 function. The quantization of the problem leads to Landau levels and to $\sigma_{xy} = ne^2/h$ with $n \in \mathbb{Z}$ (*Quantum Hall Effect*).

7.4 Thermoelectric Effects

We apply the results from the last chapter to thermoelectric processes. We consider a system of charged particles with charge q. Unlike in Chapter 7.1, we now allow for both energy transport and particle transport. The change in the number of particles leads to 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, $\mu_{\mathrm{e}}(\boldsymbol{r}) = \text{const.}$ in equilibrium.

Note: In a metal, the chemical potential μ is usually determined by the positive background charge and cannot be significantly changed. For this reason, in a metal we can replace the electrochemical force $\boldsymbol{\nabla}\mu_e = -q\boldsymbol{\mathcal{E}}$ with the electric force $q\boldsymbol{\nabla}\Phi = -q\boldsymbol{E}$.

The change in entropy is described by $Tds = du - \mu_e dn$ (we neglect thermal expansion effects again). This leads to the relationship

$$T\frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \mu_e \frac{\partial n}{\partial t}\,. \tag{7.34}$$

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 $\boldsymbol{j}^n$. Analogously for energy, we have

$$\frac{\partial u}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}^e = 0 \tag{7.36}$$

with the energy current density $\boldsymbol{j}^e$. In comparison to Equation (7.1), due to the electrochemical work, not the entire energy current is a heat current. Rather, we have

$$\boldsymbol{j}^q = T\boldsymbol{j}^s = \boldsymbol{j}^e - \mu_e \boldsymbol{j}^n \tag{7.37}$$

due to the fundamental equation $Tds = du - \mu_e dn$. For a better understanding of the heat current $\boldsymbol{j}^q$, we consider a particle exchange where each particle carries energy $\varepsilon = \mu_e$. In this case, $\boldsymbol{j}^e = \mu_e \boldsymbol{j}^n$ and the process occurs reversibly without heat exchange. A finite heat current 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

$$\frac{\partial s}{\partial t} = -\frac{1}{T}\boldsymbol{\nabla}\cdot\boldsymbol{j}^e + \mu_e\boldsymbol{\nabla}\cdot\boldsymbol{j}^n = -\boldsymbol{\nabla}\cdot\boldsymbol{j}^s + \underbrace{\boldsymbol{\nabla}\frac{1}{T}\cdot\boldsymbol{j}^e - \boldsymbol{\nabla}\frac{\mu_e}{T}\cdot\boldsymbol{j}^n}_{\dot{\mathsf{s}}} \tag{7.38}$$

A comparison with (7.9) shows that the last two terms are the entropy generation rate. Therefore, we have

$$\dot{\mathsf{s}} = \boldsymbol{\nabla}\frac{1}{T}\cdot\boldsymbol{j}^e - \boldsymbol{\nabla}\frac{\mu_e}{T}\cdot\boldsymbol{j}^n = \boldsymbol{\nabla}\frac{1}{T}\cdot\boldsymbol{j}^q - \frac{1}{T}\boldsymbol{\nabla}\mu_e\cdot\boldsymbol{j}^n\,. \tag{7.39}$$

As shown before, the first term corresponds to entropy generation by heat flow from a high to a lower temperature. The second term corresponds to the Joule heat $\boldsymbol{\mathcal{E}}\cdot\boldsymbol{j}$ with the electric current density $\boldsymbol{j} = q\boldsymbol{j}^n$. It arises from the conversion of electrochemical work into heat.

A comparison of (7.39) with (7.15) shows that $\boldsymbol{\nabla}(1/T)$ and $-(\boldsymbol{\nabla}\mu_e)/T$ are the thermodynamic forces for the currents $\boldsymbol{j}^q$ and $\boldsymbol{j}^n$.[1] The reciprocity relations (for $\boldsymbol{B}_0 = 0$) are

$$\begin{aligned} \boldsymbol{j}^n &= -L_{11}\frac{1}{T}\boldsymbol{\nabla}\mu_e + L_{12}\boldsymbol{\nabla}\frac{1}{T} = -\frac{L_{11}}{T}\boldsymbol{\nabla}\mu_e - \frac{L_{12}}{T^2}\boldsymbol{\nabla}T\,,\\ \boldsymbol{j}^q &= -L_{12}\frac{1}{T}\boldsymbol{\nabla}\mu_e + L_{22}\boldsymbol{\nabla}\frac{1}{T} = -\frac{L_{12}}{T}\boldsymbol{\nabla}\mu_e - \frac{L_{22}}{T^2}\boldsymbol{\nabla}T\,. \end{aligned} \tag{7.40}$$

We now want to relate the three transport quantities L_{11}, L_{12}, L_{22} to already known quantities. For heat and charge transport, the standard form is

$$\boldsymbol{j}^q = -\kappa\,\boldsymbol{\nabla}T + \Pi\,\boldsymbol{j}\,, \qquad\qquad \boldsymbol{\mathcal{E}} = \frac{1}{\sigma}\boldsymbol{j} + \epsilon\,\boldsymbol{\nabla}T\,, \tag{7.41}$$

with the Peltier coefficient Π and the thermopower ϵ. The reason for this notation is that experimentally the electric current $\boldsymbol{j} = q\,\boldsymbol{j}^n$ and the temperature gradient $\boldsymbol{\nabla}T$ can be most easily measured. A comparison of (7.40) and (7.41) provides relationships between the coefficients. For example, considering the case $\boldsymbol{\nabla}T = 0$, we obtain

$$\sigma = \frac{q^2 L_{11}}{T} \qquad \text{and} \qquad \sigma\Pi = \frac{qL_{12}}{T}\,. \tag{7.42}$$

Analogously, for $\boldsymbol{\nabla}\mu_e = -q\boldsymbol{\mathcal{E}} = 0$, we find the relations

$$\sigma\epsilon = \frac{qL_{12}}{T^2} \qquad \text{and} \qquad \kappa + \sigma\epsilon\Pi = \frac{L_{22}}{T^2}\,. \tag{7.43}$$

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[1] Alternatively, one could consider $\boldsymbol{j}^e$ and $\boldsymbol{j}^n$ as independent currents. In this case, the forces would be $\boldsymbol{\nabla}(1/T)$ and $-\boldsymbol{\nabla}(\mu_e/T)$.

A comparison of the two expressions for L_{12} yields the reciprocity relation

$$\Pi = \epsilon T \tag{7.44}$$

between the Peltier coefficient and the thermopower.

We want to better understand the equations (7.41) with a few examples.

Example 5: (Electrical conduction)

For a system without a temperature gradient $\boldsymbol{\nabla} T = 0$, Ohm's law applies

$$\boldsymbol{j} = \sigma \boldsymbol{\mathcal{E}} \,, \tag{7.45}$$

where $\boldsymbol{\mathcal{E}} = \boldsymbol{E} - (1/q)\boldsymbol{\nabla}\mu$ takes into account the complete electrochemical force. Note that even without a temperature gradient, heat is still transported with

$$\boldsymbol{j}^q = \Pi \, \boldsymbol{j} \,. \tag{7.46}$$

Example 6: (Heat conduction)

The heat conduction from Chapter 7.1 results in the case where no electric current/particle flow is flowing, $\boldsymbol{j} = 0$. We then obtain Fourier's law

$$\boldsymbol{j}^q = -\kappa \boldsymbol{\nabla} T \,. \tag{7.47}$$

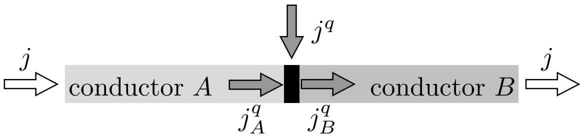
Note that in this case, the electrochemical force does not vanish but

$$\boldsymbol{\mathcal{E}} = \epsilon \boldsymbol{\nabla} T \tag{7.48}$$

applies. For this reason, the coefficient ϵ is called the *thermoelectric power*.

Example 7: (Peltier Effect)

We consider two different metals (A and B) at a homogeneous temperature T. We drive an electric current j through the contact.

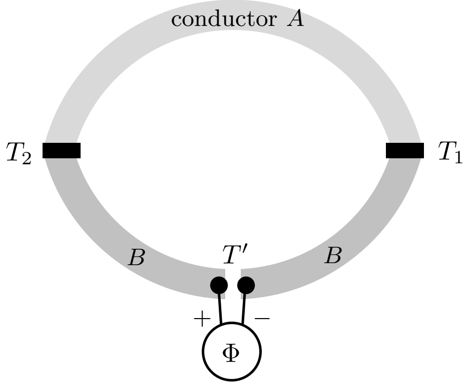


The heat flow is then given by (7.46). At the contact point, there is a discontinuity of size

$$j^q = j_B^q - j_A^q = (\Pi_B - \Pi_A) j \,. \tag{7.49}$$

In the steady state system, this heat must be added to the contact when the current j is driven from conductor A to conductor B. If the direction of the current is reversed, the sign of j^q also changes. For one direction of the current, the contact cools down, in the other direction it heats up.

Example 8: (Seebeck Effect)



The Seebeck effect is closely related to the Peltier effect. However, now an (electrically) open circuit with $\boldsymbol{j} = 0$ is considered. Two metals are connected through two contacts at different temperatures T_1, T_2. The resulting voltage Φ can then be determined with a voltmeter at temperature T'.

In an open circuit, equation (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 only contributes at the contacts.[2] Therefore, we have

$$\Phi = T_1(\epsilon_A - \epsilon_B) + T_2(\epsilon_B - \epsilon_A) = (\epsilon_B - \epsilon_A)(T_2 - T_1) \,. \tag{7.51}$$

Example 9: (Thomson Effect)

The continuity equation for energy has the form

$$\frac{\partial u}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{j}^e \overset{(7.37)}{=} -\boldsymbol{\nabla} \cdot \boldsymbol{j}^q - \boldsymbol{\nabla} \cdot \left(\frac{\mu_e}{q} \boldsymbol{j} \right) = -\boldsymbol{\nabla} \cdot \boldsymbol{j}^q + \boldsymbol{\mathcal{E}} \cdot \boldsymbol{j} - \frac{\mu_e}{q} \underbrace{\boldsymbol{\nabla} \cdot \boldsymbol{j}}_{=\,0,\ \text{since stationary}}$$

Substituting the relationships (7.41) yields the result

$$\frac{\partial u}{\partial t} = \boldsymbol{\nabla} \cdot (\kappa \boldsymbol{\nabla} T) + \frac{1}{\sigma} \boldsymbol{j}^2 + \underbrace{\left(\epsilon - \frac{d\Pi}{dT} \right)}_{-T d\epsilon/dT} \boldsymbol{\nabla} T \cdot \boldsymbol{j} \,. \tag{7.52}$$

The first term describes heating due to sources in the heat flow $-\kappa \Delta T$, driven by the temperature gradient. The second term is the Joule heat $\boldsymbol{j} \cdot \boldsymbol{E}$. The last term is the *Thomson heat*

$$\delta \dot{q}_{\text{Thomson}} = \tau \boldsymbol{\nabla} T \cdot \boldsymbol{j}, \qquad \text{Thomson coefficient } \tau = T \frac{d\epsilon}{dT} \,. \tag{7.53}$$

It occurs when there is both a temperature gradient and an electric current.

Note: The Thomson coefficient τ is important because it can be directly measured 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.

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[2] We assume that the temperature dependence of ϵ within a material is much smaller than the difference between the materials.

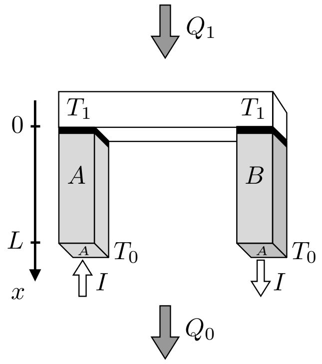

Fig. 7.1: Structure of a Peltier Element. It consists of three conductors. Two columns made of conductor materials A and B connected by a crossbar. The lower end of the columns at $x = L$ is at room temperature T_0. A current I is driven clockwise through the system. We denote the Peltier coefficients of the two contacts as Π_A, Π_B. Due to the experimental setup (with $\Pi_B > \Pi_A$), the crossbar is cooled to the temperature $T_1 < T_0$.

Peltier Element: Finally, we consider a Peltier Element as a typical example of a non-equilibrium 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 to two contacts on a conductor that is being cooled, see Fig. 7.1. The system is driven by an electric current I. The conductors have cross-section A with electric current densities $j_B = -j_A = I/A$ along the x-axis. We consider the steady state that occurs after a certain time. We simplify the problem by assuming that the material constants κ, σ and $\epsilon = \Pi/T$ are temperature-independent.

The electrical problem is solved by specifying the current density. The thermal problem is determined by equations (7.52) and (7.41). In the steady state, due to (7.52) in conductor A, we have

$$0 = \boldsymbol{\nabla} \cdot (\kappa_A \boldsymbol{\nabla} T_A) + \frac{1}{\sigma_A} \boldsymbol{j}^2 = \kappa_A T_A''(x) + \frac{I^2}{\sigma_A A^2} \,. \tag{7.54}$$

The temperature distribution with boundary conditions $T_A(L) = T_0$ and $T(0) = T_1$ is given by

$$T_A(x) = T_1 + \frac{(T_0 - T_1)x}{L} + \frac{I^2}{2A^2 \sigma_A \kappa_A} x(L - x) \,. \tag{7.55}$$

The same relationship applies in conductor B with $\sigma_A, \kappa_A \mapsto \sigma_B, \kappa_B$.

The heat output $\dot{Q}_0$ 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

$$\begin{aligned} \dot{Q}_0 &= -A\kappa_A T_A'(L) + A\epsilon_A T_0 j_A - A\kappa_B T_B'(L) + A\epsilon_B T_0 j_B \\ &= \epsilon T_0 I + \frac{1}{2} R I^2 - K \Delta T \end{aligned} \tag{7.56}$$

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, the cooling power is obtained

$$\dot{Q}_1 = A\big[j_A^q(0) + j_B^q(0)\big] = \epsilon T_1 I - \frac{1}{2} R I^2 - K \Delta T \tag{7.57}$$

With the first law of thermodynamics, we have

$$\dot{W} = \dot{Q}_0 - \dot{Q}_1 = RI^2 + \epsilon I \Delta T \,. \tag{7.58}$$

This power must be provided by the voltage source that drives the current I. The electrical power is $\dot{W} = IV$. Therefore, we obtain that the voltage

$$V = RI + \epsilon \Delta T \tag{7.59}$$

drops 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 has a maximum as a function of the current. Solving the condition $\partial\eta/\partial I = 0$ for I, we obtain

$$I^* = \frac{\epsilon \Delta T}{R(\sqrt{1 + Z\overline{T}} - 1)} \tag{7.61}$$

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, so the Peltier element operates with a lower efficiency. For a high efficiency, the dimensionless figure of merit $Z\overline{T}$ must be as large as possible. This requires materials with low resistance and low thermal conductivity.

In metals, the figure of merit is limited 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 contribution of phonons. Overall, we have the estimate

$$Z\overline{T} \lesssim \frac{3e^2\epsilon^2}{\pi^2 k_B^2} \approx 4 \times 10^{-5} \left(\epsilon \, [\mu\mathrm{V/K}] \right)^2 . \tag{7.65}$$

Typically, metals have a thermoelectric power ϵ on the order of a few μV/K. Therefore, metals are unsuitable as Peltier elements.

In semiconductor heterostructures, the Wiedemann-Franz law does not apply. Although there is no thermodynamic limit for $Z\overline{T}$, all known materials have values $\lesssim 3$. Finding a system with $Z\overline{T} \gg 1$ is an active research field. This is particularly important technologically, as a Peltier element can also be operated in reverse (as a heat engine) to generate electrical power from a temperature difference. The idea is to use such elements in electrical circuits for heat recovery. However, the problem is that the efficiency η^* depends very weakly (through the square root) on the figure of merit.

For a cooling element, the minimum temperature $T_1 = T_{\text{min}}$ that can be reached is given by the point where $\eta^* = 0$. We obtain

$$T_{\text{min}} = \frac{T_0}{\sqrt{1 + Z\overline{T}}}, \qquad \text{or equivalently} \qquad T_{\text{min}} = \frac{\sqrt{1 + 2ZT_0} - 1}{Z}\,. \tag{7.66}$$

The current required to reach this minimum temperature is given by

$$I_{\text{max}} \overset{(7.61)}{=} \frac{\epsilon \Delta T}{R(T_0/T_{\text{min}} - 1)} = \frac{\epsilon\, T_{\text{min}}}{R}\,. \tag{7.67}$$

This current is supplied at a voltage

$$V_{\text{max}} = RI_{\text{max}} + \epsilon(T_0 - T_{\text{min}}) = \epsilon\, T_0 \tag{7.68}$$

Instead of maximizing the efficiency, it is often more helpful in practice to obtain a maximum cooling power $\dot{Q}_1$ (at given temperatures T_0, T_1). The expression (7.57) is optimized with a current

$$I_{\text{KL}} = \frac{\epsilon\, T_1}{R} \tag{7.69}$$

It can be seen that this corresponds to expression (7.67) exactly for $T_1 = T_{\text{min}}$. At the minimum temperature, the maximum cooling power corresponds to the maximum efficiency. However, at this point $\eta^* = 0$, and the cooling power disappears. In general, at a temperature T_1, the maximum cooling power can be achieved as

$$\begin{aligned} \dot{Q}_{\text{max}} = \dot{Q}_1\Big|_{I=I_{\text{KL}}} &= \frac{\epsilon^2 T_1^2}{2R} - K\Delta T = K\left(\frac{ZT_1^2}{2} - \Delta T\right) \\ &= \frac{\epsilon^2}{2R}(T_1^2 - T_{\text{min}}^2) + K(T_1 - T_{\text{min}}) \end{aligned} \tag{7.70}$$

It can be seen that the cooling power is proportional to K and decreases as the cold temperature approaches the minimum temperature T_{min}.

Notation

dU	complete 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, number of particles (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
$\boldsymbol{Z}$	all (extensive) quantities $(U, Z_1, Z_2, \dots)$ that define 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
$(\delta X)^2$	variance of X
$v = V/N$	specific volume
$n = v^{-1}$	particle density
λ	thermal wavelength
$c_i = N_i/N$	concentrations of substance i