Statistical Physics

– Lecture Notes[1] –

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[1] These lecture notes are intended as supplementary material to a lecture given at the Ludwig-Maximilians-Universität München during summer term 2005. These notes borrow from many books, some of them will explicitly be mentioned in the text. Also note that this is work in progress and may contain errors. I highly recommend that you study one of the standard texts on statistical mechanics in detail!

Contents

Chapter 2

Classical Statistical Physics

The physical systems discussed in this chapter are assumed to obey the laws of classical mechanics.

2.1 Phase Space and Liouville Theorem

The dynamical state of a classical system of N point particles is completely determined by specifying the $3N$ canonical coordinates $(q_1, q_2, \cdots, q_{3N})$ and their conjugate momenta $p_1, p_2, \cdots, p_{3N}$. Such a *microstate* may either be represented by a point in $6N$-dimensional phase space (Γ-space)

$$\vec{X} = (p, q) = (p_1, \cdots, p_{3N},\, q_1, \cdots, q_{3N}) \tag{2.1}$$

or a set of N points $\{\mathbf{p}_i, \mathbf{q}_i\}$ in the 6-dimensional μ-space.

2.1.1 Hamiltonian formulation of classical mechanics

The time evolution of a representative point in Γ-space is determined by the Hamiltonian equations of motion

$$\frac{d}{dt}\vec{X} = (\dot{p}, \dot{q}) = \left(-\frac{\partial \mathcal{H}(p,q)}{\partial q}, \frac{\partial \mathcal{H}(p,q)}{\partial p}\right) \tag{2.2}$$

with the Hamiltonian $\mathcal{H}(p, q)$, which is assumed not to depend on any time derivative of p and q [1]. The Hamilton equations are then invariant under time reversal and uniquely determine the motion of a representative point for all times, when the position of the representative point is given at any time. As a consequence the trajectory of a representative point in phase space is either a simple closed curve or a curve that never intersects itself.

The equation of motion for an observable $A(\vec{X}(t), t)$ is given by

$$\frac{d}{dt}A = \{\mathcal{H}, A\} + \frac{\partial}{\partial t}A \tag{2.3}$$

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[1] See any standard book on classical mechanics, e.g. Goldstein.

with the Possion brackets defined as

$$\{\mathcal{H}, A\} := \sum_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) . \tag{2.4}$$

Upon introducing the Liouville operator $\mathcal{L}A = i\{\mathcal{H}, A\}$ this can also be written as

$$\frac{d}{dt} A = -i\mathcal{L}A + \frac{\partial}{\partial t} A \tag{2.5}$$

2.1.2 The Liouville Theorem

A collection of points in Γ-space is called an *ensemble* and is characterized by a density function $\rho(p, q, t)$. The temporal evolution is determined by

$$\frac{d}{dt}\rho(p, q, t) = \frac{\partial}{\partial t}\rho + \{\mathcal{H}, \rho\} = 0 \tag{2.6}$$

known as the Liouville theorem. It can be interpreted geometrically. If one follows the motion of a representative point in phase space, the density of representative points in its neighborhood stays constant. In other words, the density of points in phase space moves likes an incompressible fluid. Note that one can also write the Liouville equation in the form of a continuity equation

$$\frac{\partial}{\partial t}\rho(p, q, t) + \nabla \cdot (\mathbf{v}\rho) = 0 \tag{2.7}$$

with $\mathbf{v} = (\dot{p}, \dot{q})$ the velocity of a respresentative point in phase space.

2.1.3 The Ergodicity Theorem and Ensemble Theory

Consider a single given physical system on the energy surface $\mathcal{H} = E$ and let's ask which points on the energy surface are traced out by its phase space trajectory. This is a fundamental and extremely difficult question and there is an ongoing debate on whether and how it can be answered in general.

Instead of giving an answer, L. Boltzmann, postulated in 1887 the ergodicity theorem as follows:
The trajectory of a system in phase space will pass through every configuration on the energy surface.
As a consequence a time average of an observable measured over a sufficiently long time period would be equal to an ensemble average (Note that the concept of ensembles was not introduced by Boltzmann but by Gibbs much later!). Actually, Boltzmann's formulation of the ergodicity theorem is not quite right. The volume of the energy surface is typically of the order e^N. Hence for a macroscopic number of particles $N \sim 10^{23}$ a practically infinite amount of time would be needed to actually pass through all points on the energy surface in phase space. P. and T. Ehrenfest gave a different formulation in 1911:
The trajectory of a system in phase space will come arbitrarily close to any

point on the energy surface.
The ergodicity theorem is certainly not valid for every possible classical system. There are counter examples, like a system of particles in a perfectly rectangular box which are all moving exaclty parallel to one of the edges of the box. But, of course, this is also a quite singular case. If there is the smallest perturbation on just one of the particles, it will soon start to collide with other particles and generate "disorder" in the box. It is generally believed that the ergodicity theorem is valid for all practical purposes. Then, one can replace time averages[2] on a single system by ensemble averages, i.e. averages over many systems in phase space which are distributed according to some density $\rho(p, q)$. In order to describe an equilibrium situation these densities must then be stationary (time independent).

The question that remains is how to choose these ensembles. The Liouville theorem gives us a first hint. It tells us that any stationary distribution has to be a function of the integrals of motion. In particular, all functions $\rho = \rho(\mathcal{H})$ are possible candidates for an equilibrium ensemble.

2.2 Microcanonical Ensemble

We consider an isolated (macroscopic) system with N particles, confined to a volume of size V and an energy in the interval $[E, E + \Delta]$ with $\Delta \ll E$. There is an infinite number of microstates which satisfy these macroscopic constraints. The set of all these microstates is called an ensemble [3]. Following Gibbs one may think of this set as an infinite number of mental copies of the same macroscopic system (Gibbsian ensemble).

2.2.1 The Postulate of equal a priori Probability

We are interested in a describtion of the macroscopic properties of the system in equilibrium. To this end we introduce a probability measure on the microcanonical ensemble by assuming that all microstates compatible with the macroscopic conditions are equally likely (*postulate of equal a priori probability*). The corresponding microcanonical probability density function reads

$$\rho(p, q) = \begin{cases} \rho_0 & \text{if } E < \mathcal{H}(p, q) < E + \Delta \\ 0 & \text{else,} \end{cases} \tag{2.8}$$

where ρ_0 is determined such that $\int d^{3N}p\, d^{3N}q\, \rho(p, q) = 1$.

The *most probable value* $\overline{A}$ of an observable $A(p, q)$ is the value of A posessed by the largest number of systems in the ensemble. The *ensemble*

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[2] These time averages have to be over a time interval large enough such that the system can come sufficiently close to any point on the energy surface. This time is called the "relaxation time". These times depend on the particular system one is studying and can vary over an extremlely wide range.

[3] In the language of probability theory this set is the sample space and the microstates are the outcomes.

average of A is defined by

$$\langle A\rangle := \int d^{3N}p\, d^{3N}q\, A(p,q)\rho(p,q)\,. \tag{2.9}$$

Since we have assumed all microstates to be equally probably the volume of the energy shell $[E, E+\Delta]$ is a measure for the number of allowed microstates. We define the volume in Γ-space occupied by the microcanonical ensemble as

$$\Gamma(E) = \int_{E<\mathcal{H}(p,q)<E+\Delta} d^{3N}p\, d^{3N}q\,. \tag{2.10}$$

The volume in phase space enclosed by the energy surface $\mathcal{H}(p,q) = E$ is

$$\Sigma(E) = \int_{\mathcal{H}(p,q)<E} d^{3N}p\, d^{3N}q = \int d^{3N}p\, d^{3N}q\, \Theta(E-\mathcal{H}(p,q))\,. \tag{2.11}$$

Then a Taylor expansion gives to leading order

$$\Gamma(E) = \Sigma(E+\Delta) - \Sigma(E) \approx \omega(E)\Delta \tag{2.12}$$

with the density of states

$$\omega(E) = \frac{\partial}{\partial E}\Sigma(E)\,. \tag{2.13}$$

In the limit $\Delta \to 0$ one can also write

$$\omega(E) = \int d^{3N}p\, d^{3N}q\, \delta(E-\mathcal{H}(p,q)) \tag{2.14}$$

and hence the microcanonical probability density can be written as

$$\rho(p,q) = \frac{1}{\omega(E)}\,\delta(E-\mathcal{H}(p,q))\,. \tag{2.15}$$

Example: To illustrate the magnitude of these quantities in phase space we consider an ideal gas of identical particles described by the Hamiltonian $\mathcal{H}(p,q) = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m}$; see the problem sets.

$$\begin{aligned}\Sigma(E) &= \int d^{3N}p\, d^{3N}q\, \Theta(E-\mathcal{H}(p,q)) \sim V^N E^{3N/2} && (2.16)\\ \omega(E) &= \int d^{3N}p\, d^{3N}q\, \delta(E-\mathcal{H}(p,q)) \sim V^N E^{3(N-1)/2} && (2.17)\end{aligned}$$

Obviously the difference between ω and Γ does not matter for $N \sim 10^{23}$. Also note that the volume in phase space grows exponentially with N. The bizzare geometrical properties of high-dimensional spaces have important implications. Let us, for example, allow for all energie values in the interval $[0, E]$ and ask, what is the probability of finding the system with an energy less than xE where $0 \leq x \leq 1$:

$$P[\text{energy } \leq xE] = \Sigma(xE)/\Sigma(E) = x^{3N/2}\,. \tag{2.18}$$

For $x = 0.999999$ and $N = 10^{23}$ this is

$$\ln P[\text{energy } \leq 0.999999E] = 1.5 \cdot 10^{23} \ln(1 - 10^{-6}) \approx -1.5 \cdot 10^{23-6}\,. \tag{2.19}$$

and hence the probability that the energy is very close to E is as good as 1

$$P[0.999999E \leq \text{ energy } \leq E] = 1 - e^{-1.5 \cdot 10^{17}} \tag{2.20}$$

We conclude, that even if we allow for energy values in the whole interval $[0, E]$ the by far most likely values will be confined to a tiny shell close to E.

Note: Since the phase space volumes grow exponentially with the number of particles, we have up to terms which scale as $\ln N$,

$$\ln \omega = \ln \Gamma = \ln \Sigma. \tag{2.21}$$

This can be seen by the following order of magnitude estimates

$$\begin{aligned} \Gamma &\sim \frac{\partial \Sigma}{\partial E}\Delta \sim \frac{\Sigma\Delta}{E} && (2.22) \\ \rightarrow \underbrace{\ln \Gamma}_{\sim N} &\sim \underbrace{\ln \Sigma}_{\sim N} + \underbrace{\ln(\Delta/E)}_{\sim \ln N} && (2.23) \end{aligned}$$

Hence all three quantities ω, Γ and Σ can be used equally well for a description of the equilibrium state of a macroscopic system in the thermodynamic limit $N \rightarrow \infty$.

2.2.2 Statistical Weight and Boltzmann Entropy

We now define a *statistical weight* $W(E)$ in phase space

$$W(E) = \frac{c_N}{h^{3N}} \Gamma(E) \tag{2.24}$$

which is proportional to the volume of the microcanonical ensemble in phase space. We make $W(E)$ a dimensionless quantity by choosing the unit of h to be that of an angular momentum. The constant of proportionality c_N is chosen such that the Boltzmann entropy defined below is an extensive quantity; see Gibbs paradox below. In classical mechanics the quantity h is completely undetermined! There is no classical principle which would fix an elementary “unit cell” in phase space. Hence any discretization in a classical calculation will have an arbitrary factor $(\text{unit})^N$ which depends on ones choice of discretization. These ambiguities have to drop out in any physical observable calculated from classical statistical mechanics. It will turn out (see the ideal gas) that if we identify h with Planck’s constant the results derived from classical statistical mechanics will be identical to the classical limit of a quantum statistcial mechanics calculation.

The **Boltzmann entropy** is defined by

$$S(E) := k_{\mathrm{B}} \ln W(E) \tag{2.25}$$

where k_{B} is Boltzmann’s constant, a universal number to be determined later[4].

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[4] Here there is no need to introduce the Boltzmann constant k_{B}. It will be used later to introduce a convention about the units of temperature.

2.2.3 The Laws of Thermodynamics

The Boltzmann entropy has the following properties:

1. **Extensivity:** We have *defined* the Boltzmann entropy such that the entropy of m identical non-interacting systems equals the sum of the entropies of the individual systems.

$$\begin{aligned} \Gamma(mE, mV, mN) &= \prod_{i=1}^{m} \Gamma(E, V, N) && (2.26) \\ \to S(mE, mV, mN) &= mS(E, V, N)\,. && (2.27) \end{aligned}$$

   This property is called extensivity of the entropy. If we now start from a system characterized by (E, V, N) and divide it into m identical subsystems, which are still macroscopic, extensivity of the entropy will hold as long as the subsystems can be considered as (almost) statistically independent (central limit theorem). This will hold for systems with interactions, which are not too long range and for partitions where the surface energy is small compared to the bulk energy. In the following we will only consider the extensive parts of the Boltzmann entropy as relevant for the description of a macroscopic system.

2. 0^{th} **law of thermodynamics**. There is an (intensive) quantitity T (temperature) which characterizes the thermodynamic equilibrium between two systems which are allowed to exchange energy (are in thermal contact). Similar conclusions can be reached if we allow for the exchange of volume or particles.

3. 1^{st} **law of thermodynamics**. This is just the fundamental law of energy conservation in a formulation which applies for quasi-static changes of the thermodynamic state of a macroscopic system.

4. 2^{nd} **law of thermodynamics**. If an isolated system undergoes a change in thermodynamic state (i.e. we change the macroscopic constraints on a system) such that the initial and final state are thermal equilibrium states, the entropy of the final state is not smaller than the entropy of the initial state:

$$S_f \geq S_i,\,. \qquad (2.28)$$

The existence of a temperature. We decompose a macroscopic isolated system in thermodynamic equilibrium - described in terms of the microcanonical ensemble - into two subsystems with macroscopic parameters (E_1, V_1, N_1) and (E_2, V_2, N_2), respectively. We keep particle numbers N_α and volumes V_α for both subsystems fixed, but allow the energies of the subsystems to have a range of values,

$$E < E_1 + E_2 < E + 2\Delta\,. \qquad (2.29)$$

Sampling energies in bins of size Δ (and choosing the lower bound in energy to be 0) the volume in phase space occupied by the total system is

$$\Gamma(E) = \sum_{i=1}^{E/\Delta} \Gamma_1(E_1^{(i)})\Gamma_2(E - E_1^{(i)}) \,. \tag{2.30}$$

A key feature of a macroscopic system in thermal equilibrium is that out of the large number of terms in the above sum only one is dominant. This can be seen as follows. Let the largest term in the sum be $\Gamma_1(\overline{E}_1)\Gamma_2(\overline{E}_2)$. Then it is obvious that

$$\Gamma_1(\overline{E}_1)\Gamma_2(\overline{E}_2) \leq \Gamma(E) \leq \frac{E}{\Delta}\,\Gamma_1(\overline{E}_1)\Gamma_2(\overline{E}_2) \tag{2.31}$$

or equivalently

$$k_\mathrm{B} \ln\big(\Gamma_1(\overline{E}_1)\Gamma_2(\overline{E}_2)\big) \leq S(E) \leq k_\mathrm{B} \ln\big(\Gamma_1(\overline{E}_1)\Gamma_2(\overline{E}_2)\big) + k_\mathrm{B} \ln \frac{E}{\Delta} \tag{2.32}$$

Since both entropy and energy are extensive quantities, i.e. both scale with the number of particles in the (sub)system, $S \propto N$ and $E \propto N$, we finally get (note that Δ is a constant independent of N):

$$S(E) = S_1(\overline{E}_1) + S_2(\overline{E}_2) + \mathcal{O}(\ln N) \,. \tag{2.33}$$

This looks like the extensive property of the entropy, but actually we have shown a much more dramatic property of equilibrium systems. We have shown that out of the many possible energy values the subsystems actually have definite values $\overline{E}_1$ and $\overline{E}_2$, which maximize the phase space volume $\Gamma(E_1)\Gamma(E_2)$ under the constraint $E = E_1 + E_2$. This results in a *variational principle*

$$d\,[\Gamma(E_1)\Gamma(E_2)] = 0 \quad \text{with} \quad d(E_1 + E_2) = 0 \,. \tag{2.34}$$

It states that the *equilibrium state* of two subsystems (contained in a larger isolated system), which are allowed to exchange energy with each other, is actually also the *most probable state*! Since $S \sim \ln \Gamma$ and ln is a monotonically increasing function, the above variational principle is also equivalent to finding the state of maximum entropy under a given constraint.

Temperature. An immediate consequence of the above variational principle is that all (macroscopic) parts of a macroscopic system described by the microcanonical ensemble have the same temperature T, defined by

$$\frac{1}{T} := \frac{\partial S(E)}{\partial E} \,. \tag{2.35}$$

With the temperature T we have found a first quantity which is characteristic for macroscopic systems in equilibrium.

Chemical Potential. Similarly, we can consider two subsystems which are allowed to exchange energy and particles. Then our variational pinciple reads

$$d(E_1 + E_2) = 0$$

$$\begin{aligned} &d(N_1 + N_2) = 0 \\ &d(\Gamma_1(E_1, N_1)\,\Gamma(E_2, N_2)) = 0 \end{aligned} \tag{2.36}$$

Upon defining the chemical potential by

$$\frac{\mu}{T} := -\frac{\partial S(E,N)}{\partial N}\,, \tag{2.37}$$

one finds

$$\begin{aligned} T_1 &= T_2\,, \\ \mu_1 &= \mu_2\,. \end{aligned} \tag{2.38}$$

Hence we conclude that not only the temperature but also the chemical potential is the same in all (macroscopic) parts of an isolated system in thermal equilibrium.

External Parameters, Pressure. Let the Hamiltonian $\mathcal{H} = \mathcal{H}(p, q; x)$ depend on an external parameter x. Then we have

$$\Sigma(E, x) = \int d^{3N}p\, d^{3N}q\, \theta(E - \mathcal{H}(p, q; x)) \tag{2.39}$$

Consider the differential

$$\begin{aligned} d\Sigma(E, x) &= \int d\Gamma\, \delta(E - \mathcal{H}) \left(dE - \frac{\partial \mathcal{H}}{\partial x} dx \right) \\ &= \omega(E) \left(dE - \langle \frac{\partial \mathcal{H}}{\partial x} \rangle dx \right) \end{aligned} \tag{2.40}$$

Note that here we have used the following definition for the average in the microcanonical ensemble

$$\langle A \rangle = \frac{1}{\omega(E)} \int d\Gamma \delta(E - \mathcal{H}) A(p, q) \tag{2.41}$$

Then

$$d \ln \Sigma = \frac{\omega}{\Sigma} \left(dE - \langle \frac{\partial \mathcal{H}}{\partial x} \rangle dx \right) \tag{2.42}$$

With $\omega = \partial\Sigma/\partial E$ one finds $\omega/\Sigma = \partial \ln \Sigma/\partial E$. This finally gives for the entropy $S = k_{\mathrm{B}} \ln(c_N \Sigma/h^{3N})$

$$dS = \underbrace{\frac{\partial S}{\partial E}}_{=1/T} \left(dE - \langle \frac{\partial \mathcal{H}}{\partial x} \rangle dx \right) \tag{2.43}$$

(Note that in the thermodynamic limit $\ln \Sigma = \ln \Gamma = \ln \omega$). The quantity

$$X = \langle \frac{\partial \mathcal{H}}{\partial x} \rangle \tag{2.44}$$

is called the conjugate field to the external parameter x. Repeating the above argument for a set of independent external parameters $\{x_i\}$ one finds

$$dE = TdS + \sum_i X_i dx_i \,, \tag{2.45}$$

which is the **first law of thermodynamics** for quasistatic processes. If we take $x_1 = V$ and $x_2 = N$ as the only external parameters, then the corresponding conjugate fields are

$$\begin{aligned} \langle \frac{\partial \mathcal{H}}{\partial N} \rangle &= \frac{\partial E}{\partial N}\Big|_S = -\frac{\partial S}{\partial N}\Big|_E \frac{\partial E}{\partial S}\Big|_N = \mu && (2.46) \\ \langle \frac{\partial \mathcal{H}}{\partial V} \rangle &:= -P && (2.47) \end{aligned}$$

where we have introduced the pressure P as the field conjugate to the volume V. This results in the following (maybe more familiar form) of the first law of thermodynamics

$$dE = TdS - PdV + \mu dN \,, \tag{2.48}$$

where $\delta W = -PdV$ is the external work done on the system (PdV is the net amount of work done by the system). Since dE is the change in total energy (sometimes also called internal energy) the quantity $\delta Q = TdS$ can be interpreted as a “non-mechanic” way to change the total energy of a system (“heat”).

The above definition of the pressure is a *mechanical definition*. We can also define the pressure *thermodynamically* using our variational principle for two subsystems contained in a larger isolated system which are allowed to exchange energy and volume. One finds that the pressure defined by

$$P := T\frac{\partial S(E,V)}{\partial V} \tag{2.49}$$

is the same in all (macroscopic) parts of an isolated system in thermal equilibrium. By comparing with the exact differential of the entropy, Eq. 2.48, we immediately see that both the mechanical and thermodynamic definitions are consistent.

The 2$^{\text{nd}}$ law of thermodynamics. We start from an initial macroscopic state described by the macroscopic variables (E, V, N) and a microcanonical ensemble with the statistical weight $W(E, V, N)$ (thermal equilibrium state). More generally, we could think of a set of macroscopic variables $\{Y_i\}$. Now imagine that we relax one or some of these macroscopic constraints, e.g. allow for a larger volume V'. Then all the microscopic states, which were initially accessible for the macroscopic system, are still accessible. But, there will obviously also be many more other microscopic states accessible to the system. In short, if we relax a constraint the accessible phase space volume will increase. If we now *assume* that the final equilibrium state is again described by a microcanonical ensemble, then an increase in phase space is equivalent to an increase in entropy. In that sense the 2$^{\text{nd}}$ law of thermodynamics follows by defnition of the Boltzmann entropy and the assumption that both initial and final equilibrium states are described by a microcanonical ensemble.

Equilibrium statistical mechanics does not tell us how one gets from one equilibrium state to another. The actual question we have to answer is a dynamic one, namely how and in what sense does the microcanonical probability density of the initial state evolve towards a microcanonical ensemble of the final state. Just think of the time evolution of the phase space volume of a single particle confined between two walls moving in a one dimensional world. Consider the time evolution of the phase space volume with $-L_i \leq q \leq L_i$ and $-\sqrt{2mE} \leq p \leq \sqrt{2mE}$, where we suddenly relax the volume constraint by enlarging the accessible volume: $L_i \to L_f$. Liouville's theorem tells us that the volume does not change! So why should upon relaxing the constraint the above statement of a larger accessible phase space be true? This puzzle can be resolved if one considers the time evolution of the initial phase space volume in the larger box. As time evolves the initial rectangular shaped phase space volume will shear and for long times develop a filamentous structure which will "fill" the larger phase space such that it comes arbitrarily close to any point in this phase space (ergodicity!). **to be completed**.

2.2.4 Fluctuations

What about fluctuations around the most probable value? In our discussion of thermal equilibrium between two systems we have seen that the energies adjust themselves to the most probable values $\bar{E}_1$ and $\bar{E}_2$. But, what about fluctuations around the most probable energy values? How large and how likely are those? For illustration, we come back to the example of an ideal gas with a phase space volume scaling as

$$\Gamma(E) \sim \left(\frac{V}{N}\right)^N \left(\frac{E}{N}\right)^{3N/2} \tag{2.50}$$

Let us now consider two subsystems of an isolated ideal gas which can exchange energy but not particles. Then the equilibrium condition states that temperatures in these subsystems have to be equal

$$\frac{\partial S_1(E_1)}{\partial E_1}\Big|_{\overline{E}_1} = \frac{\partial S_2(E_2)}{\partial E_2}\Big|_{\overline{E}_2 = E - \overline{E}_1} \tag{2.51}$$

This immediately gives us the most probable values for the energies of the two subsystems as

$$\overline{E}_1 = E \frac{N_1}{N_1 + N_2}, \quad \overline{E}_2 = E - \overline{E}_1 \tag{2.52}$$

Now we ask a more ambitious question: "What is the probability $P(E_1)$ to find subsystem 1 with an energy E_1?" This is obviously given by

$$P(E_1) = \frac{\Gamma_1(E_1)\,\Gamma_2(E - E_1)}{\Gamma(E)} \tag{2.53}$$

Using the result for the ideal gas and performing a saddle point expansion around the most probable value one finds (see problem sets)

$$\begin{aligned} P(E_1) &\sim \frac{(E_1/N_1)^{3N_1/2}(E_2/N_2)^{3N_2/2}}{(E/N)^{3N/2}} \\ &\approx P(\overline{E}_1)\exp\left[-\frac{3}{4}\frac{N_1+N_2}{\overline{E}_1\overline{E}_2}(E_1-\overline{E}_1)^2\right] \end{aligned} \tag{2.54}$$

For the relative width of the distribution one finds (for $N_1 \approx N_2$)

$$\frac{\Delta E_1}{\overline{E}_1} \sim \frac{1}{\sqrt{N}} \tag{2.55}$$

i.e. a distribution which becomes extremly narrow for a macroscopic system with $N \sim 10^{23}$ particles.

Example: Statistical Mechanics of an Ideal Gas.
With $\Gamma(E,V,N) \sim V^N E^{3N/2}$ we immediately find

$$S(E,V,N) = k_\mathrm{B}\ln\Gamma(E,V,N) + c = k_\mathrm{B}N\left(\ln V + \frac{3}{2}\ln E\right) + c' \tag{2.56}$$

and hence

$$\begin{aligned} \tfrac{1}{T} = \tfrac{\partial S}{\partial E} = \tfrac{3}{2}k_\mathrm{B}N/E \quad &\Rightarrow E = \frac{3}{2}Nk_\mathrm{B}T \\ \tfrac{P}{T} = \tfrac{\partial S}{\partial V} = k_\mathrm{B}N/V \quad &\Rightarrow PV = Nk_\mathrm{B}T \end{aligned} \tag{2.57}$$

These are the well known equations of state for an ideal gas.

2.3 Canonical Ensemble

In many applications of statistical mechanics one considers a small but still somehow macroscopic subsystem embedded in a larger system (often called reservoir), e.g. a piece of condensed matter in an experimental apparatus or a polymer in solution. One would like to understand the equilibrium properties of the subsystem. The subsystem is constantly exchanging energy with the larger resevoir and hence can certainly not be described as a microcanonical ensemble with a fixed energy. But, as we have learned from the previous section, any macroscopic part of a system described by a microcanonical ensemble is characterized by the same temperature T. This naturally leads us to ask: *"What is the statistical ensemble of a small subsystem characterized by the macroscopic variables* (T,V,N)*?"*

2.3.1 Distribution Function and Partition Sum

Consider an isolated composite system made up of two subsystems whose dynamics is characterized in terms of the Hamiltonians $\mathcal{H}_1(p_1,q_1)$ and

$\mathcal{H}_2(p_2,q_2)$. We describe the composite system as a microcanonical ensemble with a constant probability density $\rho_{mc}(p,q)=\rho_0$ on the energy shell

$$E \leq \mathcal{H}_1 + \mathcal{H}_2 \leq E + 2\Delta\,. \tag{2.58}$$

We assume that system 2 is much larger than system 1: $N_2 \gg N_1$, $\bar{E}_2 \gg \bar{E}_1$.

The probability density $\rho(p_1,q_1)$ to find system 1 in the phase space volume element $d\Gamma_1 = d^{3N_1}p\ d^{3N_1}q$ is obtained from the microcanonical probability density by integrating out the degrees of freedom of the reservoir,

$$\rho(p_1,q_1) \sim \int_{E-\mathcal{H}_1 \leq \mathcal{H}_2 \leq E+2\Delta-\mathcal{H}_1} d\Gamma_2 \approx \omega_2(E-\mathcal{H}_1)\,2\Delta\,. \tag{2.59}$$

In other words, the probability density at the phase space point (p_1,q_1) for subsystem 1 is proportional to the phase space volume of the reservoir at the energy $E_2 = E - \mathcal{H}_1(p_1,q_1)$:

$$\rho(p_1,q_1) \sim \omega_2(E-\mathcal{H}_1(p_1,q_1))\,. \tag{2.60}$$

If we are interested in the probabilty density to find the energy of subsystem 1 in the energy interval between E_1 and $E_1+\Delta$, we have, in addition, to integrate over the representative points of system 1 in the energy shell $E_1 \leq \mathcal{H}_1(p_1,q_1) \leq E_1+\Delta$,

$$\rho(E_1) \sim \omega_1(E_1)\omega_2(E-E_1)\,. \tag{2.61}$$

We now use the fact that subsystem 2 is much larger than subsystem 1. This implies that $\mathcal{H}_1$ is typically much smaller than E and suggests that we try a Taylor expansion with a small parameter $\mathcal{H}_1/E$. How should we perform such a Taylor expansion? Let's take the ideal gas as a guidance. For the classical ideal gas one finds

$$\omega(E-\mathcal{H}_1) \sim (E-\mathcal{H}_1)^\nu \quad \text{with } \nu = 3N/2 \gg 1\,. \tag{2.62}$$

This gives

$$\omega(E-\mathcal{H}_1) \sim E^\nu \left(1 - \nu\frac{\mathcal{H}_1}{E} + \frac{\nu(\nu-1)}{2}\frac{\mathcal{H}_1^2}{E^2} + \cdots\right) \tag{2.63}$$

For the second term in the brackets to be smaller than the first one we have to require that $\mathcal{H}_1 \ll \frac{2}{\nu-1}E$, i.e. $\mathcal{H}_1$ would have to be much smaller than the typical energy of a single particle. This is far too restrictive! The way out is to expand $\ln\omega(E-\mathcal{H}_1)$ instead.

$$\ln(E-\mathcal{H}_1)^\nu = \nu\ln(E-\mathcal{H}_1) \approx \ln E^\nu - \nu\left(\frac{\mathcal{H}_1}{E} + \frac{1}{2}\frac{\mathcal{H}_1^2}{E^2} + \cdots\right)\,. \tag{2.64}$$

Here, we only need that $\mathcal{H}_1 \ll E$. A Taylor expansion of $\ln\omega_2(E-\mathcal{H}_1)$ gives

$$\ln\omega_2(E-\mathcal{H}_1) = \ln\omega_2(E) - \underbrace{\frac{\partial\ln\omega_2(E_2)}{\partial E_2}\Big|_{E_2\approx E}}_{=\beta=1/k_{\mathrm{B}}T} \mathcal{H}_1(p_1,q_1) + \cdots \tag{2.65}$$

and hence the following probability densities (with $\beta = 1/k_{\mathrm{B}}T$)

$$\begin{aligned} \rho(p,q) &\sim e^{-\beta\mathcal{H}_1(p_1,q_1)}\,, && (2.66) \\ \rho(E_1) &\sim \omega_1(E_1)e^{-\beta E_1}\,. && (2.67) \end{aligned}$$

Note that T is the temperature of the larger system, which is frequently also called a “heat bath” or “heat reservoir”.

In summary, we can now define the following canonical probability density function in phase space (dropping the index “1”)

$$\rho(p,q) = \frac{1}{Z}\, e^{-\beta\mathcal{H}(p,q)}\,, \tag{2.68}$$

which is normalized to one when integrated over phase space

$$\int \frac{d^{3N}p\; d^{3N}q}{N!\; h^{3N}}\; \rho(p,q) = 1\,. \tag{2.69}$$

Hence the normalization factor, termed *partition integral*, is

$$Z(T,V,N) = \int \frac{d^{3N}p\; d^{3N}q}{N!\; h^{3N}}\; e^{-\beta\mathcal{H}(p,q)}\,. \tag{2.70}$$

Averages are calculated by

$$\langle A\rangle = \int \frac{d^{3N}p\; d^{3N}q}{N!\; h^{3N}}\; \rho(p,q)A(p,q)\,. \tag{2.71}$$

We will frequently use the shorthand notation $\int d\gamma = \int \frac{d^{3N}p\; d^{3N}q}{N!\; h^{3N}}$.

We can rewrite the partition integral over the phase space volume element $d\gamma$ as an integral over the energy E upon defining a density of states $D_N(E)$ by

$$D_N(E)dE = \frac{1}{N!\, h^{3N}}\, \omega(E)dE\,. \tag{2.72}$$

Then the partition integral reads

$$Z(T,V,N) = \int dE\, D_N(E)e^{-\beta E} \tag{2.73}$$

For an ideal gas $D_N(E) \sim E^{3N/2}$ (see problem sets). Hence the integrand has very sharp maximum at some value $\overline{E}$ such that $\ln Z \approx \ln\Gamma(\overline{E}) - \beta\overline{E}$ and hence $k_{\mathrm{B}}\ln Z = TS_{mc} - \beta\overline{E}$, where S_{mc} is the Boltzmann entropy defined with the statistical weight of the microcanonical ensemble.

2.3.2 Statistical Thermodynamics

Now we make contact with thermodynamics, i.e. show how the partition integral $Z(T,V,N)$ of the canonical ensemble is related to macroscopic observables like the average internal energy $\langle\mathcal{H}\rangle$ and the pressure P. With

$$\langle\mathcal{H}\rangle = \int d\gamma\rho(p,q)\mathcal{H}(p,q) \tag{2.74}$$

where $\rho = \exp[-\beta\mathcal{H}]/Z$ and $Z = \int d\gamma\rho$ it is easy to show that

$$\langle\mathcal{H}\rangle = -\frac{\partial}{\partial\beta}\ln Z \tag{2.75}$$

Similarily one finds

$$P = -\langle\frac{\partial\mathcal{H}}{\partial V}\rangle = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z \tag{2.76}$$

We define the **free energy** as

$$F(T,V,N) := -k_{\mathrm{B}}T\ln Z(T,V,N) \tag{2.77}$$

Then we immediately find

$$P = -\frac{\partial F}{\partial V} \tag{2.78}$$

and

$$\langle\mathcal{H}\rangle = -\frac{\partial}{\partial\beta}(-\beta F) = F + \beta\frac{\partial F}{\partial\beta} \tag{2.79}$$

We define the **entropy** in the canonical ensemble as

$$S := -k_{\mathrm{B}}\langle\ln\rho\rangle = -k_{\mathrm{B}}\int d\gamma\rho\ln\rho \tag{2.80}$$

The free energy and the entropy are related by

$$F = \langle E\rangle - TS\,. \tag{2.81}$$

This can be seen as follows

$$\begin{aligned}
S &= -k_{\mathrm{B}}\int d\gamma\rho\ln\rho && (2.82)\\
&= k_{\mathrm{B}}\int d\gamma\frac{1}{Z}e^{-\beta\mathcal{H}}(\ln Z + \beta\mathcal{H}) && (2.83)\\
&= k_{\mathrm{B}}(\ln Z + \beta\mathcal{H}) && (2.84)\\
&= \frac{1}{T}(k_{\mathrm{B}}\ln Z + \langle\mathcal{H}\rangle) && (2.85)\\
&= \frac{1}{T}(-F + \langle E\rangle) && (2.86)
\end{aligned}$$

With Eq. (2.79) this gives

$$S = \frac{1}{k_{\mathrm{B}}T^2}\frac{\partial F}{\partial\beta} = -\frac{\partial F}{\partial T} \tag{2.87}$$

In summary, one finds for the differential of the free energy $F(T,V,N)$

$$dF = -SdT - PdV + \frac{\partial F}{\partial N}dN \tag{2.88}$$

with

$$S = -\frac{\partial F}{\partial T} \tag{2.89}$$

$$P = -\frac{\partial F}{\partial V} \tag{2.90}$$

With Eq. 2.81 this can also be written as

$$d\langle E\rangle = TdS - PdV + \frac{\partial F}{\partial N}dN \tag{2.91}$$

We can find $\frac{\partial F}{\partial N}$ by comparing the latter expression with the first law of thermodynamics obtained in the microcanonical ensemble

$$dS_{\text{MK}} = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \tag{2.92}$$

If we identify the canonical and the microcanonical entropy and the energy in the microcanonical ensemble with the average energy in the canonical ensemble[5], then one gets

$$\mu = \frac{\partial F}{\partial N}\,, \tag{2.93}$$

such that the differential of the free energy $F(T, V, N)$ reads

$$dF = -SdT - PdV + \mu dN \tag{2.94}$$

2.3.3 Energy Fluctuations in the Canonical Ensemble

In this section we show that the canonical ensemble is mathematically equivalent to the microcanonical ensemble in the sense that although the canonical ensemble contains systems of all energies the overwhelming majority of them have the same energy.

We start with a calculation of the first two cummulants of the Hamiltonian in the canonical ensemble. The average energy is by definition

$$\langle\mathcal{H}\rangle = \langle E\rangle = \int d\gamma \rho \mathcal{H} \tag{2.95}$$

$$= \int d\gamma \frac{1}{Z} e^{-\beta\mathcal{H}}\mathcal{H} \tag{2.96}$$

$$= \int d\gamma \exp[-\beta\mathcal{H} + \beta F]\mathcal{H} \tag{2.97}$$

Hence

$$\int d\gamma \exp[-\beta\mathcal{H} + \beta F](\mathcal{H} - \langle\mathcal{H}\rangle) = 0 \tag{2.98}$$

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[5] Later we will show that this is valid in the thermodynamic limit $N \to \infty$.

Differentiating both sides with respect to β, we obtain

$$\int d\gamma\,(\mathcal{H}-\langle\mathcal{H}\rangle)\left(F-\mathcal{H}+\beta\frac{\partial F}{\partial\beta}\right)\exp[-\beta\mathcal{H}+\beta F]-\frac{\partial\langle\mathcal{H}\rangle}{\partial\beta}=0 \quad (2.99)$$

By Eq. (2.79) we obtain

$$\frac{\partial\langle\mathcal{H}\rangle}{\partial\beta}+\langle(\mathcal{H}-\langle\mathcal{H}\rangle)^2\rangle=0 \quad (2.100)$$

Therefore the mean square fluctuations of energy is

$$\Delta E^2=\mathrm{Var}[\mathcal{H}]=\langle(\mathcal{H}-\langle\mathcal{H}\rangle)^2\rangle=-\frac{\partial\langle\mathcal{H}\rangle}{\partial\beta}=k_{\mathrm{B}}T^2\frac{\partial\langle E\rangle}{\partial T} \quad (2.101)$$

For a macroscopic system we have $\langle\mathcal{H}\rangle\sim N$ and $C_V=\frac{\partial\langle E\rangle}{\partial T}\sim N$ and hence

$$\frac{\Delta E}{\langle E\rangle}\sim\frac{1}{\sqrt{N}} \quad (2.102)$$

Therefore out of the many possible energies allowed in the canonical ensemble only the average energy makes a sizeable contribution to the partition integral.

Another way of illustrating the same point is to ask for the most important contribution to the partition integral

$$Z(T,V,N)=\int dE D_N(E)e^{-\beta E}=\int dE e^{-\beta E+S_{mc}(E,V,N)/k_{\mathrm{B}}}\,, \quad (2.103)$$

where we have used the relation between the density of states and the microcanonical entropy $S_{mc}=k_{\mathrm{B}}\ln D_N(E)$. The exponential function varies with E extremely rapidly since both E and S_{mc} are extensive functions and hence scale with particle number N. Or in other words, since the density of states grows fast with E (in general like a power law in N) and the Boltzmannn factor decreases with E there must be a sharp maximum at some energy $\bar{E}$, where

$$E/T-S_{mc}=\mathrm{Min}\,,\quad \text{thus}\quad \frac{1}{T}=\frac{\partial S_{mc}}{\partial E}|_{E=\bar{E}}\,; \quad (2.104)$$

i.e. an overwhelming contribution to the integral comes from the neighborhood of the most probable value $\bar{E}$ in the canonical ensemble. The exponent in the integral is expanded in this neighborhood as

$$\exp\left[-\beta\bar{E}+S_{mc}(\bar{E},V,N)/k_{\mathrm{B}}-\frac{1}{2k_{\mathrm{B}}T^2C_V}(E-\bar{E})^2\right] \quad (2.105)$$

where the relations

$$\frac{\partial^2 S_{mc}}{\partial E^2}=\frac{\partial T^{-1}}{\partial E}=-\frac{1}{T^2C_V} \quad (2.106)$$

have been used (E in all these expressions should be put equal to $\bar{E}$). To the extent that the difference $E-\bar{E}$ is small, or more precisely, of the order of $\mathcal{O}(N^{1/2})$ in magnitude, the higher order terms in the expansion are of the order of $(E-\bar{E})^m \times \mathcal{O}(N^{-m+1}) = \mathcal{O}(N^{1-m/2})$ and can be ignored as $N \to \infty$. Hence the partition integral can well be approximated by

$$Z(T,V,N) = \sqrt{2\pi k_{\rm B} T^2 C_V}\,\delta E^{-1} \exp[-\beta \bar{E} + S_{mc}(\bar{E},V,N)/k_{\rm B}] \quad (2.107)$$

the logarithm of which gives to leading order in N

$$F(T,V,N) = \bar{E} - TS_{mc}(\bar{E},V,N) \quad (2.108)$$

from which we conclude that the canonical and microcanonical definition of the entropy are equivalent in the thermodynamic limit, $S_{\rm MK} = S$ (if we use instead of the fixed energy E in the microcanonical energy the most likely energy $\bar{E}$ or the average energy $\langle E \rangle$).

2.3.4 Maximum Entropy Principle

This section will highlight the idea of a canonical ensemble from a different angle. We consider an actual ensemble (i.e. collection of mental copies) of $\mathcal{N}$ identical systems. The ensemble of systems is supposed to share the available energy $\mathcal{E}$ such that the energy of a given system is only fixed on average, i.e. $\langle E \rangle = \mathcal{E}/\mathcal{N}$. Now let E_r with $r = 0,1,2,\cdots$ denote the possible energy values of each system. You may regard these values either as an arbitrary partition of the allowed energy interval into shells of size Δ (classical mechanics) or as the eigenvalues of the Hamiltonian (quantum mechanics). Note that in some model systems there is a discrete set of allowed energies even in classical systems (see problem sets). Then a given realization of the ensemble is characterized by a set of numbers $\{n_r\} \equiv \{n_0, n_1, n_2, \cdots\}$, where n_r is the number of systems in the ensemble with energy E_r (in short: "occupation numbers"). These numbers have to satisfy the constraints

$$\sum_r n_r = \mathcal{N}\,, \quad (2.109)$$

$$\sum_r n_r E_r = \mathcal{E}\,. \quad (2.110)$$

There are

$$W(\{n_r\}) = \frac{\mathcal{N}!}{n_0! n_1! n_2! \cdots} \quad (2.111)$$

possible realization of a given set $\{n_r\}$ corresponding to the number of different ways to assign the set of energies $(E_0, E_1, \cdots)$ to $\mathcal{N}$ systems such that each E_r is chosen n_r times[6].

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[6] Compare with the corresponding problem in probability theory, where the task is to distribute balls with different colors r among $\mathcal{N}$ boxes such that n_r boxes will receive a ball with color r. We do not count the order in which the balls are placed into the boxes.

We now assume that all possible state in the ensemble are equally likely to occur (*postulate of equal 'a priori' probability*). This implies that frequency $W(\{n_r\})$ of a given tupel $\{n_r\}$ is a direct measure of its probability (up to normalization)! The most probable realization $\{\bar{n}_r\}$ is then given by

$$W(\{n_r\}) = Max \Leftrightarrow \ln W(\{n_r\}) = Max \tag{2.112}$$

such that the constraints in Eqs. 2.109-2.110 are obeyed. Since we are interested in the thermodynamic limit $\mathcal{N} \to \infty$ we approximate the statistical weight using the Stirling formula

$$\ln W = \ln \mathcal{N}! - \sum_r \ln n_r! \approx \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r \,. \tag{2.113}$$

Upon introducing the Lagrangian multipliers α and β the condition which determines $\{\bar{n}_r\}$ reads

$$\delta(\ln W) - \alpha \sum_r \delta n_r - \beta \sum_r E_r \delta n_r = 0 \tag{2.114}$$

where

$$\delta(\ln W) = \ln W(\{n_r + \delta n_r\}) - W(\{n_r\}) = -\sum_r (\ln n_r + 1)\delta n_r \tag{2.115}$$

Since the variations δn_r are arbitrary we conclude

$$\ln \bar{n}_r = -(\alpha + 1) - \beta E_r \to \bar{n}_r = Ce^{-\beta E_r} \tag{2.116}$$

The parameters C (or equivalently α) and β are determined by the constraints in Eqs. 2.109-2.110. This gives for C

$$\frac{\bar{n}_r}{\mathcal{N}} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \tag{2.117}$$

and the parameter β has to be determined from the implicit relation

$$\langle E \rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{\sum E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \tag{2.118}$$

Hence we have found that the Lagrange multiplier β, which takes care that the average energy is fixed, corresponds to $\beta = 1/k_{\mathrm{B}}T$ introduced earlier by our thermodynmic considerations, where we considered a smaller system in contact with a large heat bath.

Suggested reading: One can show (see e.g. R.K. Pathria, "Statistical Mechanics", chap. 3.2) that $\{\bar{n}_r\}$ is by far the most likely contribution to any average and that fluctuations around this most likely value can safely be ignored in the thermodynamic limit. Hence the maximum entropy principle, as formulated above, together with the postulate of equal a priori probability can be used as a quite general starting point in statistical mechanics. In the problem sets you will use this principle to derive the statistical weights in the grand canonical ensemble.

2.3.5 Equipartition Theorem

Upon using the defnition of canonical averages one can easily show that

$$\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = k_{\mathrm{B}} T \delta_{ij} \,. \tag{2.119}$$

For

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(q) \tag{2.120}$$

this implies

$$\langle q_i \frac{\partial V}{\partial q_j} \rangle = k_{\mathrm{B}} T \quad \text{(Virial Theorem)} \tag{2.121}$$

In particular, one finds for a set of harmonic oscillators with

$$V = \sum_{i=1}^{3N} V_i = \sum_{i=1}^{3N} \frac{m}{2} \omega_i^2 q_i^2 \tag{2.122}$$

that each degree of freedom has on average a potential energy

$$\langle V_i \rangle = \frac{1}{2} k_{\mathrm{B}} T \,. \tag{2.123}$$

For

$$E_{\mathrm{kin}} = \sum_{i,k} a_{ik} p_i p_k \quad \text{with} \quad a_{ik} = a_{ki} \tag{2.124}$$

one can show along similar lines that each degree of freedom has on average a kinetic energy of $\frac{1}{2} k_{\mathrm{B}} T$

$$\langle E_{\mathrm{kin}} \rangle = \frac{3}{2} k_{\mathrm{B}} T \,. \tag{2.125}$$

2.4 Grand Canonical Ensemble

The grand canonical ensemble describes the equilibrium statistical mechanics of a system at fixed volume which is in contact with a large reservoir such that it can exchange both energy and particles. We have already learned that in such a situation thermal equilibrium is characterized by two intensive thermodynamic parameters, the temperature T and chemical potential μ, which are constant in any macroscopic subsystem.

2.4.1 Distribution Function and Partition Sum

We consider a large system characterized by macroscopic variables (E, V, N) whose equilibrium state is described by a microcanonical ensemble. As in the derivation of the canonical ensemble we split this system into a larger reservoir 2 and a smaller subsystem 1, whose statistical properties we would like to describe. The density distribution function $\rho_1(p_1, q_1)$ for the smaller subsystem 1 characterized by (E_1, V_1, N_1) is obtained by summing over all allowed micro-states of the reservoir. This gives

$$\rho_1(p_1, q_1) \sim \omega_2(E - \mathcal{H}_1, N - N_1) \sim e^{S_{mc}(E - \mathcal{H}_1, N - N_1)/k_\mathrm{B}} \,, \tag{2.126}$$

where S_{mc} is the microcanonical entropy of the reservoir. We now assume $\mathcal{H}_1/E \ll 1$ and $N_1/N \ll 1$ and perform a Taylor expansion of the entropy (neglecting terms of second order and higher)

$$\begin{aligned} \rho_1(p_1, q_1) \quad &\sim \quad \exp\left[\frac{1}{k_\mathrm{B}}\left(S_{mc}(E, N) - \frac{\partial S_{mc}}{\partial E}\mathcal{H}_1 - \frac{\partial S_{mc}}{\partial N} N_1\right)\right] \\ &\sim \quad \exp\left[-\beta(\mathcal{H}_1(p_1, q_1) - \mu N_1)\right] \,. \end{aligned} \tag{2.127}$$

Note that both the chemical potential μ and the temperature T are those of the reservoir. Hence the name "reservoir".

In summary we get for the *grand canonical phase space density distribution function*

$$\rho_G(p, q) = \frac{1}{Z_G}\, e^{-\beta(\mathcal{H} - \mu N)} \,, \tag{2.128}$$

where from now on we will omit the subscript 1 identifying the volume under consideration. The normalization constant is the *grand canonical partition integral*

$$Z_G(T, V, \mu) = \sum_{N=0}^{\infty} z^N \int d\gamma e^{-\beta\mathcal{H}(p,q)} = \sum_{N=0}^{\infty} z^N Z(N, V, T) \,, \tag{2.129}$$

where we have introduced the fugacity $z = \exp(\beta\mu)$.[7] Note also that we have employed the thermodynamic limit and set the upper bound in the particle number to infinity.

We can now calculate averages of an observable $A(p, q)$ as

$$\langle A \rangle = \sum_{N=0}^{\infty} \int \frac{d^{3N}p \; d^{3N}q}{N! \; h^{3N}} \, \rho_G(p, q) \, A(p, q) \,. \tag{2.130}$$

As an example we calculate the average particle number

$$\langle N \rangle = \frac{\partial}{\partial(\beta\mu)} \ln Z_G(T, V, \mu)\big|_{T,V} = k_\mathrm{B}T \frac{\partial}{\partial\mu} \ln Z_G(T, V, \mu)\big|_{T,V} \,. \tag{2.131}$$

Solving this implicit equation gives $\mu = \mu(\langle N \rangle, T, V)$ for the chemical potential. Since the chemical potential is an intensive quantity we have the following homogeneity relation if we rescale the system size by a factor α: $\mu(\alpha\langle N \rangle, T, \alpha V) = \mu(\langle N \rangle, T, V)$.

---

[7] The grand canonical partition sum can regarded as the discrete Laplace transform of the canonical partition integral.

2.4.2 Thermodynamic Quantities

Similar to the canonical ensemble we now define the *grand canonical potential* as

$$\Phi(T,V,\mu) := -k_{\mathrm{B}}T\ln Z_G(T,V,\mu)\,. \tag{2.132}$$

The entropy in the grand canonical ensemble is defined by

$$S_G := -k_{\mathrm{B}}\langle \ln\rho_G\rangle\,. \tag{2.133}$$

This implies

$$\begin{aligned} S_G &= -k_{\mathrm{B}}\sum_{N=0}^{\infty}\int d\gamma\rho_G\left[-\ln Z_G-\beta\mathcal{H}+\beta\mu N\right] &(2.134)\\ &= k_{\mathrm{B}}\ln Z_G+\frac{\langle\mathcal{H}\rangle}{T}-\frac{\mu}{T}\langle N\rangle &(2.135)\end{aligned}$$

and hence

$$\Phi = \langle E\rangle - TS_G - \mu\langle N\rangle \tag{2.136}$$

Now we are left with the task to determine the exact differential of the grand canonical potential $\Phi(T,V,\mu)$,

$$d\Phi = \left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu}dT+\left(\frac{\partial\Phi}{\partial V}\right)_{\mu,T}dV+\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V}d\mu \tag{2.137}$$

One obtains

$$\begin{aligned}\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu} &= \frac{\partial}{\partial T}(-k_{\mathrm{B}}T\ln Z_G)\\ &= \frac{\partial\beta}{\partial T}\frac{\partial}{\partial\beta}\left(-\frac{1}{\beta}\ln Z_G\right)=\frac{1}{k_{\mathrm{B}}T^2}\left[-\frac{1}{\beta^2}\ln Z_G+\frac{1}{\beta}\frac{\partial\ln Z_G}{\partial\beta}\right]\\ &= \frac{\Phi}{T}-\frac{1}{T}\langle\mathcal{H}-\mu N\rangle = -S_G\\ \left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu} &= \frac{\partial}{\partial V}(-k_{\mathrm{B}}T\ln Z_G)\\ &= -k_{\mathrm{B}}T\langle-\beta\frac{\partial\mathcal{H}}{\partial V}\rangle = \langle\frac{\partial\mathcal{H}}{\partial V}\rangle = -P\\ \left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} &= \frac{\partial}{\partial\mu}(-k_{\mathrm{B}}T\ln Z_G)\\ &= -k_{\mathrm{B}}T\beta\langle N\rangle = -\langle N\rangle\end{aligned}$$

In summary, this gives

$$d\Phi = -S_G dT - PdV - \langle N\rangle d\mu \tag{2.138}$$

and with Eq. (2.136)

$$d\langle E\rangle = TdS_G - PdV + \mu d\langle N\rangle \tag{2.139}$$

2.4.3 Fluctuations

Finally, we consider fluctuations in the particle number **to be completed**

2.5 The isobaric-isothermal ensemble

Again, we consider a small subsystem of a larger reservoir. But now we allow for energy and volume exchange. Then the proper statistical distribution function is (see problem sets)

$$\rho_{\mathrm{P}}(p,q) = \frac{1}{Z_{\mathrm{P}}}\,\exp[-\beta(\mathcal{H}+PV)]\,, \tag{2.140}$$

with the partition sum

$$\begin{aligned} Z_{\mathrm{P}} &= \int dV e^{-\beta PV} Z(N,V,T) \qquad (2.141) \\ &= \int dV \int dE\, D_N(E)\exp[-\beta(E+PV)]\,. \qquad (2.142) \end{aligned}$$

Upon defining the thermodynamic potential, *free enthalpy* (Gibbs free energy),

$$G(T,P,N) := -k_{\mathrm{B}}T\ln Z_{\mathrm{P}} \tag{2.143}$$

with $G = E - TS + PV$, one can show that the corresponding exact differential reads

$$dG = -SdT + VdP + \mu dN\,. \tag{2.144}$$

Chapter 3

Quantum Statistical Physics

3.1 Quantum states of macroscopic systems

We have seen in chapter 2 that the (microscopic) state of a classical system can be described by a representative point (p, q) in phase space (Γ-space). In order to describe the equilibrium properties of macroscopic systems we have then formulated a statistical describtion of classical systems in terms of ensembles which are characterized by density distribution functions $\rho(p, q)$ in phase space. Here we would like to describe the quantum state of a system and again find a proper statistical describtion of an equilibrium state. It will turn out that the quantity analogous to the density distribution will be a density operator.

3.1.1 Hilbert spaces and pure states

In quantum mechanics one associates with a given physical system a Hilbert space $\mathcal{E}$ with elements (kets) denoted by $|\psi\rangle$, and a corresponding dual space $\mathcal{E}^*$ with elements (bras) denoted by $\langle\psi|$. The Hilbert space is a linear vector space[1]. With a complete orthonormal basis (ONB) set $\{|m\rangle\}$ characterized by the orthogonality relation

$$\langle m|n\rangle = \delta_{mn} \tag{3.1}$$

and the closure relation

$$\sum_m |m\rangle\langle m| = \mathbf{1} \tag{3.2}$$

one can write for any state $|\psi\rangle \in \mathcal{E}$

$$|\psi\rangle = \sum_m |m\rangle\langle m|\psi\rangle \equiv \sum_m c_m |m\rangle\,, \tag{3.3}$$

and any operator A

$$A = \sum_{m,n} |m\rangle\langle m|A|n\rangle\langle n| \equiv \sum_{m,n} A_{mn}|m\rangle\langle n|\,. \tag{3.4}$$

---

[1] For simplicity we will consider only those Hilbert spaces which are spanned by countable basis sets, i.e. separable Hilbert spaces.

This implies that an operator A acting on a state $|\psi\rangle$ may be considered as a matrix multiplication

$$
\begin{aligned}
A|\psi\rangle &= \sum_{m,n} A_{mn} c_n |m\rangle && (3.5)\\
\langle m|A|\psi\rangle &= \sum_{n} A_{mn} c_n \,. && (3.6)
\end{aligned}
$$

Expectation values of operators in a quantum state $|\psi\rangle$ are defined as

$$\langle A\rangle = \langle \psi|A|\psi\rangle \,. \tag{3.7}$$

Upon defining a density operator ρ by

$$\rho := |\psi\rangle\langle\psi| \tag{3.8}$$

and the trace operator $\mathsf{Tr}\,(A)$ acting on an operator A as a sum over all diagonal elements of A in a ONB $\{|m\rangle\}$

$$\mathsf{Tr}\,(A) = \sum_m \langle m|A|m\rangle \tag{3.9}$$

we can rewrite this average also as[2]

$$\langle A\rangle = \mathsf{Tr}\,(\rho A)\ . \tag{3.10}$$

A state $|\psi\rangle \in \mathcal{E}$ is also called a pure state. The density operator of such a state has the characteristic property that $\rho^2 = \rho$, i.e. it can be considered as a projection operator onto the pure state $|\psi\rangle$. In the ONB $\{|m\rangle\}$ the density operator can be written as

$$\rho = |\Psi\rangle\langle\Psi| = \sum_{m,n} c_m c_n^\star |m\rangle\langle n| = \sum_{m,n} \rho_{mn} |m\rangle\langle n| \tag{3.11}$$

with the *density matrix* $\rho_{mn} = \langle m|\rho|n\rangle = c_m c_n^\star$. The density matrix of a pure state is uniquely determined by the set of coefficients (complex probability amplitudes) $\{c_m\}$ in the basis $\{|m\rangle\}$. This is the quantum analogue of a representative point in phase space for a classical system.

---

[2] Upon exploiting the definition of the trace it is obvious that the trace has the following properties:

- $\mathsf{Tr}\,(A)$ is invariant under base transfomations.
- $\mathsf{Tr}\,(|\phi\rangle\langle\psi|) = \langle\phi|\psi\rangle$.
- The trace is cyclically invariant, i.e. $\mathsf{Tr}\,(AB) = \mathsf{Tr}\,(BA)$, if both $\mathsf{Tr}\,(AB)$ and $\mathsf{Tr}\,(BA)$ actually exist.
- For $X \to X + \delta X$ one finds $\delta\mathsf{Tr}\,(f(X)) = \mathsf{Tr}\,(\delta X f'(X))$, i.e. we can take the derivatives as if $[X, \delta X] = 0$.
- If the Hilbert space is a direct product $\mathcal{E} = \mathcal{E}_a \otimes \mathcal{E}_b$, then the trace factorizes, $\mathsf{Tr}\,(AB) = \mathsf{Tr}_a\,(A) \cdot \mathsf{Tr}_b\,(B)$, if A and B are operators acting in the Hilbert spaces $\mathcal{E}_a$ and $\mathcal{E}_b$, respectively.

3.1.2 Mixed states and density operators

We start with a simple example to illustrate that a description of quantum systems in terms of state vectors in Hilbert space may not always be appropriate or even possible. Consider two spin-$\frac{1}{2}$ particles with a Hilbert space $\mathcal{E} = \mathcal{E}_1 \otimes \mathcal{E}_2$ coupled into a singlet state

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left(|+-\rangle - |-+\rangle \right) , \tag{3.12}$$

where $|\pm\rangle$ refers to a spin up/down state. We are interested in expectation values of observables A_1 acting on the first spin only and would like to find a describtion in terms of a density matrix, which only contains information about the first spin irrespective of the orientation of the second spin. The reduced density operator is found by performing a partial trace over the Hilbert space $\mathcal{E}_2$,

$$\rho_1 = \mathsf{Tr}_2 \left(|\psi\rangle\langle\psi| \right) = \frac{1}{2} \left(|+\rangle\langle+| + |-\rangle\langle-| \right) \tag{3.13}$$

which describes an unpolarized spin which has equal probability to be in the spin up or down state. The expectation value of an obervable A_1 can then be written as

$$\langle A_1 \rangle = \mathsf{Tr}_1 \left(\rho_1 A_1 \right) = \frac{1}{2} (\langle+|A_1|+\rangle + \langle-|A_1|-\rangle) , \tag{3.14}$$

i.e. as a incoherent sum of two independent events (spin up or down). In measuring properties of the first spin only we have obviously lost some information on the entangled nature of the singlet state. The situation encountered in this simple example is actually quite generic. A proper describtion of subsystems is in many instances only possible if one uses the concept of density operators (see the problem sets!).

This leads us to consider *mixed states* described by density operators

$$\rho = \sum_\lambda q_\lambda |\lambda\rangle\langle\lambda| , \tag{3.15}$$

where $\{|\lambda\rangle\}$ is a set of possible (normalized) quantum states of a given system, and q_λ are *weights* with $0 \le q_\lambda \le 1$ and $\sum_\lambda q_\lambda = 1$. Note that we can not interpret the numbers q_λ as probabilities for the states $|\lambda\rangle$ if those are not mutually orthogonal; orthogonality is needed for the states to be mutually exclusive.

The density operator has the following properties:

(i) The density operator is hermitean: $\rho^\dagger = \rho$. This is simply due to the fact that $q_\lambda \in \mathbb{R}$. As a consequence the expectation value of all observables $A = A^\dagger$ are real: $\langle A \rangle^* = \mathsf{Tr}\left((\rho A)^\dagger \right) = \mathsf{Tr}\left(A^\dagger \rho^\dagger \right) = \mathsf{Tr}\left(A\rho \right) = \mathsf{Tr}\left(\rho A \right) = \langle A \rangle$.

(ii) The density operator has unit trace: $\mathsf{Tr}\,(\rho) = 1$. This follows from the normalization of the states $|\lambda\rangle$ and the weights: $\mathsf{Tr}\,(\rho) = \sum_\lambda q_\lambda \langle\lambda|\lambda\rangle = \sum_\lambda q_\lambda = 1$.

(iii) The density matrix is non-negative: $\langle\phi|\rho|\phi\rangle \geq 0$ for any $|\phi\rangle \in \mathcal{E}$. This follows from the fact that the amplitudes q_λ are positive: $\langle\phi|\rho|\phi\rangle = \sum_\lambda q_\lambda |\langle\phi|\lambda\rangle|^2 \geq 0$.

The hermicity of the density operator implies that we can find a orthonormal basis set $\{|m\rangle\}$ such that the density matrix becomes diagonal with real and non-negative eigenvalues p_m,

$$\rho = \sum_m p_m |m\rangle\langle m| \quad \text{with} \quad 0 \leq p_m \leq 1 \quad \text{and} \quad \sum_m p_m = 1\,. \tag{3.16}$$

Since now the set of states $\{|m\rangle\}$ are mutually exclusive we can regard p_m as the probability for the (micro-)states $|m\rangle$. Hence the representation of the density operator in terms of its eigenstates plays a special role amongst the various possible equivalent representation. It allows for a probabilistic interpretation, where the random variables are observables A (hermitean operators, which are possibly non-commuting) and the probability densities are density operators ρ.

The time evolution of the density operator can be obtained from the Schrödinger equation

$$i\hbar\partial_t|\psi\rangle = \mathcal{H}|\psi\rangle\,, \tag{3.17}$$

and its hermitean conjugate

$$-i\hbar\partial_t\langle\psi| = \langle\psi|\mathcal{H}\,. \tag{3.18}$$

Then a simple calculation

$$\begin{aligned} i\hbar\partial_t\rho &= \sum_\lambda q_\lambda \big[(i\hbar\partial_t|\lambda\rangle)\langle\lambda| + |\lambda\rangle(i\hbar\partial_t\langle\lambda|)\big] \\ &= \sum_\lambda q_\lambda \big[(\mathcal{H}|\lambda\rangle)\langle\lambda| - |\lambda\rangle(\langle\lambda|\mathcal{H})\big] \\ &= [\mathcal{H},\rho] \end{aligned}$$

gives the *von Neumann equation*

$$\boxed{i\hbar\partial_t\rho = [\mathcal{H},\rho]}\,, \tag{3.19}$$

which governs the time evolution of the density operator in the Schrödinger picture. This equation should not be confused with the differential equation describing the time evolution of operators in the Heisenberg picture; the corresponding Heisenberg equation differs by a sign. Note also that the derivation goes through even for Hamiltonians with some explicit time dependence; this will be important later. From the von Neumann equation we conclude that density operators which depend on the Hamiltonian $\mathcal{H}$ only are stationary (and hence possible candidates for a describtion of equilibrium ensembles).

The time evolution of the expectation value of an observable is

$$\begin{aligned} \partial_t \mathsf{Tr}\,(\rho A) &= \mathsf{Tr}\,(\partial_t \rho A) = \frac{1}{i\hbar}\mathsf{Tr}\,([\mathcal{H},\rho]A) \\ &= \frac{1}{i\hbar}\mathsf{Tr}\,(\mathcal{H}\rho A - \rho\mathcal{H}A) = \frac{1}{i\hbar}\mathsf{Tr}\,(\rho A\mathcal{H} - \rho\mathcal{H}A) \\ &= \frac{1}{i\hbar}\mathsf{Tr}\,(\rho[A,\mathcal{H}]) \end{aligned}$$

which gives the *Ehrenfest equation* for the time evolution of the expectation value of A

$$i\hbar\partial_t\langle A\rangle = \langle[A,\mathcal{H}]\rangle\,. \tag{3.20}$$

Compare this with the Heisenberg equation $i\hbar\partial_t A(t) = [A(t),\mathcal{H}]$ for an operator $A(t)$ in the Heisenberg picture.

In the energy basis set the von Neumann equation has a particulary simple form ,

$$\frac{d\rho_{mn}}{dt} = \frac{i}{\hbar}(E_n - E_m)\rho_{mn}\,. \tag{3.21}$$

Hence, stationarity of the density matrix, $d\rho_{nm}/dt = 0$, implies that it is diagonal in the energy basis. This is, of course, consistent with the fact that the density matrix ρ and the Hamiltonian $\mathcal{H}$ are diagonal in the same basis set if they commute with each other.

3.2 The statistical entropy

We define the statistical entropy of a quantum state described the density operator ρ as (von Neumann, 1927)

$$S(\rho) := -k_{\mathrm{B}}\langle\ln\rho\rangle = -k_{\mathrm{B}}\mathsf{Tr}\,(\rho\ln\rho)\ . \tag{3.22}$$

This definition is analgous to classical mechanics with the only difference that here the average is a trace over a complete orthonormal basis set in Hilbert space instead of an integral over phase space. The purpose of this section is to study the general properties of the statistical entropy for any arbitrary density operator, i.e. our results are not restricted to equilibrium phenomena but will apply to non-equilibrum situations as well.

Lemma: For any pair of non-negative operators X and Y we have

$$\mathsf{Tr}\,(X\ln Y) - \mathsf{Tr}\,(X\ln X) \leq \mathsf{Tr}\,(Y) - \mathsf{Tr}\,(X)\ . \tag{3.23}$$

The equal sign holds only if $X = Y$. The right hand side vanishes if X and Y are normalized density operators with $\mathsf{Tr}\,(X) = \mathsf{Tr}\,(Y) = 1$.[3]

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[3] Note that the lemma is trivially true in classical mechanics!

Proof: Let $|m\rangle$ and X_m be the eigenvectors and eigenvalues of X, and $|q\rangle$ and Y_q those of Y. Let us first assume that the X_m and Y_q are positive. By writing X and Y in their respective eigenbasis we can write the left hand side of Eq.(3.23) as

$$\sum_{m,q} X_m \langle m|q\rangle \ln Y_q \langle q|m\rangle - \sum_m X_m \ln X_m = \sum_{m,q} |\langle m|q\rangle|^2 X_m \ln(Y_q/X_m)\,,$$

where we have inserted $1 = \sum_q \langle m|q\rangle\langle q|m\rangle$ in the second term. Upon using $\ln x \leq x - 1$ we finally get for the left hand side of Eq.(3.23)

$$\begin{aligned} \text{l.h.s.} &\leq \sum_{m,q} |\langle m|q\rangle|^2 (Y_q - X_m) \\ &= \sum_q Y_q - \sum_m X_m = \mathsf{Tr}\,(Y) - \mathsf{Tr}\,(X)\ , \end{aligned}$$

where we have used the closure relation for the ONB's $\{|m\rangle\}$ and $\{|q\rangle\}$. Using continuity we can extend the results to non-negative operators X and Y; if some of the eigenvalues Y_q are zero and the left hand side becomes $-\infty$. The equal sign holds when $Y_q = X_m$ for all pairs (m, q) such that $|\langle m|q\rangle|^2 \neq 0$; note that $\ln x = x - 1$ only if $x = 0$. This implies that $\langle m|q\rangle(Y_q - X_m) = 0$ for all pairs (m, q), whence $\sum_{m,q} |m\rangle\langle m|q\rangle(Y_q - X_m)\langle q| = 0$ and $X = Y$.

Properties of the statistical entropy:

(a) *Maximum.* If the possible kets are those of a finite W-dimensional subspace $\mathcal{E}_W \subset \mathcal{E}$, the statistical entropy is a maximum and equal to

$$S = k_\mathrm{B} \ln W \tag{3.24}$$

if the probabilities of all the kets in the subspace are equal to one another.

Proof: Take $Y = \mathbf{1}_W/W$ and X arbitrary with $\mathsf{Tr}\,(X) = \mathsf{Tr}\,(Y) = 1$. Then the lemma reads $\mathsf{Tr}\,(X \ln(\mathbf{1}_W/W)) - \mathsf{Tr}\,(X \ln X) \leq 0$, which immediately implies

$$S_X = -k_\mathrm{B} \mathsf{Tr}\,(X \ln X) \leq -k_\mathrm{B} \mathsf{Tr}\,(X \ln(\mathbf{1}_W/W)) = k_\mathrm{B} \ln W\,.$$

This property of the statistical entropy implies that the density operator corresponding to the state of maximum disorder in the space $\mathcal{E}_W$ is this $\rho = \mathbf{1}_W/W$, where we measure disorder in terms of the magnitude of the statistical entropy S. Hence the assumption of equal a priori probability is equivalent to choosing the state with maximum disorder. For example the most disordered state of a spin-$\frac{1}{2}$ particle is the unpolarized state.

(b) *Minimum.* The statistical entropy S is a minimum and equal to zero in a pure state. The proof for this statement is obvious since a pure state means that out of the set $\{p_m\}$ only one is nonzero and hence identical to 1, i.e. $S = -k_\mathrm{B} 1 \ln 1 = 0$. Inversely, the vanishing of S can be used to characterize a pure state as $\sum_m p_m \ln p_m$ is zero only if all p_m vanish except one. The pure states, the ones where our knowledge is best, even though they involve quantum mechanics uncertainties, are those for which the degree of disorder is zero.

(c) *Additivity.* Consider a composite system $\mathcal{E} = \mathcal{E}_a \otimes \mathcal{E}_b$ where $\mathcal{E}_a$ and $\mathcal{E}_b$ are statistically independent with density operators ρ_a and ρ_b, respectively. Then the statistical entropy of the composite system is the sum of the entropies of its parts.

$$S(\rho) = S(\rho_a) + S(\rho_b)\,. \tag{3.25}$$

Proof: Statistical independence of the subspaces means that we can write the density operator of $\mathcal{E}$ as the direct product of the density operators for the subspaces, $\rho = \rho_a \otimes \rho_b$. Now let $|m_a, n_b\rangle = |m_a\rangle|n_b\rangle$ be a factorized base which diagonalizes the density operator in $\mathcal{E} = \mathcal{E}_a \otimes \mathcal{E}_b$. Then

$$\begin{aligned}
-k_\mathrm{B}\mathsf{Tr}\,(\rho \ln \rho) &= \sum_{m_a,n_b} \langle m_a, n_b|\rho \ln \rho|m_a n_b\rangle = \sum_{m_a,n_b} p_{m_a} p_{n_b} \ln(p_{m_a} p_{n_b}) \\
&= \sum_{m_a,n_b} p_{m_a} p_{n_b} (\ln p_{m_a} + \ln p_{n_b}) = \sum_{m_a} p_{m_a} \ln p_{m_a} + \sum_{n_b} p_{n_b} \ln p_{n_b} \\
&= S(\rho_a) + S(\rho_b)\,.
\end{aligned}$$

The amount of disorder contained in the system consisting of two statistically independent parts is just the sum of the amounts of disorder of each of the parts.

(d) *Correlations.* If a composite system is described be the density operator ρ in the space $\mathcal{E} = \mathcal{E}_a \otimes \mathcal{E}_b$, the statistical entropies of its parts satisfy the *sub-additivity* inequality

$$S(\rho) \leq S(\rho_a) + S(\rho_b)\,, \tag{3.26}$$

where the equal sign holds only when $\rho = \rho_a \otimes \rho_b$. This means that ρ_a and ρ_b together contain less information than ρ, which describes the correlations between subsystems a and b.

Proof: The density operator for the subspace $\mathcal{E}_a$ is $\rho_a = \mathsf{Tr}_b\,(\rho)$, and the density operator for the subspace $\mathcal{E}_b$ is $\rho_b = \mathsf{Tr}_a\,(\rho)$.[4] Define a density operator $\rho' = \rho_a \otimes \rho_b$, which is equivalent to ρ for all measurements carried out on subsystems a and b separately and represented by operators which have the factorized form $A \otimes B$; but it does not contain information included in ρ about correlations between the subsystems.

We have

$$\begin{aligned}
S(\rho_a) &= -k_\mathrm{B}\mathsf{Tr}_a\,(\rho_a \ln \rho_a) = -k_\mathrm{B}\mathsf{Tr}\,(\rho \ln(\rho_a \otimes \mathbf{1}_b)) \\
S(\rho_b) &= -k_\mathrm{B}\mathsf{Tr}_b\,(\rho_b \ln \rho_b) = -k_\mathrm{B}\mathsf{Tr}\,(\rho \ln(\mathbf{1}_a \otimes \rho_b))\ .
\end{aligned}$$

With

$$\ln(\rho_a \otimes \mathbf{1}_b) + \ln(\mathbf{1}_a \otimes \rho_b) = \ln(\rho_a \otimes \rho_b)$$

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[4] Let A be an operator which acts in subspace $\mathcal{E}_a$ only. Then the average of A reads $\langle A\rangle = \mathsf{Tr}\,(\rho A) = \sum_{m_a,n_b} \langle m_a|\langle n_b|\rho A|n_b\rangle|m_a\rangle = \sum_{m_a} \langle m_a|A\left(\sum_{n_b} \langle n_b|\rho|n_b\rangle\right)|m_a\rangle = \mathsf{Tr}_a\,((\mathsf{Tr}_b\,(\rho))A) = \mathsf{Tr}_a\,(\rho_a A)$. Hence the density operator for operators acting in subspace $\mathcal{E}_a$ only are $\rho_a = \mathsf{Tr}_b\,(\rho)$.

this gives

$$\begin{aligned} S(\rho') &= S(\rho_a) + S(\rho_b) \\ &= -k_{\mathrm{B}}\mathsf{Tr}\left(\rho \ln(\rho_a \otimes \mathbf{1}_b)\right) - k_{\mathrm{B}}\mathsf{Tr}\left(\rho \ln(\mathbf{1}_a \otimes \rho_b)\right) \\ &= -k_{\mathrm{B}}\mathsf{Tr}\left(\rho \ln \rho'\right) \end{aligned}$$

Now with $X = \rho$ and $Y = \rho'$ the lemma tells us that

$$S(\rho) = -k_{\mathrm{B}}\mathsf{Tr}\left(\rho \ln \rho\right) \leq -k_{\mathrm{B}}\mathsf{Tr}\left(\rho \ln \rho'\right) = S(\rho')$$

Note that reciprocally, one can prove that the statistical entropy is the only function of the density operator which is invariant under a unitary transformation and which satisfies the sub-additivity condition.

(e) *Concavity.* The statistical entropy is a concave function on the set of density operators in a given Hilbert space $\mathcal{E}$. For any pair ρ_1 and ρ_2 and a parameter $0 < \lambda < 1$ we have

$$S(\lambda\rho_1 + (1-\lambda)\rho_2) \geq \lambda S(\rho_1 + (1-\lambda)S(\rho_2) \tag{3.27}$$

where the equal sign holds only if $\rho_1 = \rho_2$.
Proof: Define $\rho = \lambda\rho_1 + (1-\lambda)\rho_2$. Then for the choices $X = \rho_{1/2}$ and $Y = \rho$ the lemma gives $S(\rho_{1/2}) \leq -k_{\mathrm{B}}\mathsf{Tr}\left(\rho_{1/2} \ln \rho\right)$. Hence $\lambda S(\rho_1) + (1-\lambda)S(\rho_2) \leq -k_{\mathrm{B}}\left[\lambda \mathsf{Tr}\left(\rho_1 \ln \rho\right) + (1-\lambda)\mathsf{Tr}\left(\rho_2 \ln \rho\right)\right] = \mathsf{Tr}\left(\rho \ln \rho\right) = S(\rho)$.
Combining two states of the same system in a single statistical mixture increases the disorder as measured by the statistical entropy. The above results can be generalized to

$$S(\sum_j \mu_j S_j) \geq \sum_j \mu_j S(\rho_j) \tag{3.28}$$

for $\mu_j > 0$ and $\sum_j \mu_j = 1$.

3.3 Equilibrium ensembles

The expectation value of an observable A in a quantum statistical ensemble is obtained by taking the trace of the operator product with the density operator $\langle A \rangle = \mathsf{Tr}\left(\rho A\right)$. We expect that this quantity will be a constant independent of time for a system in thermal equilibrium, $d\langle A \rangle / dt = 0$. Since this statement has to be true for any observable we conclude that density operators for an equilibrium state need to be stationary,

$$\frac{d\rho}{dt} = 0\,. \tag{3.29}$$

From the von Neumann equation it follows that the density operator must commute with the Hamiltonian

$$[\mathcal{H}, \rho] = 0\,, \tag{3.30}$$

i.e. the equilibrium density operator must be a constant of the motion. Analogous to classical mechanics, one possible solution are density operators which are functions of the Hamiltonian

$$\rho = \rho(\mathcal{H})\,. \tag{3.31}$$

These operators are not the most general ones. In principle, any function of the form $\rho(\mathcal{H}, C_1, C_2, \cdots)$, where C_i are constants of motion, is a stationary solution. As a consequence we are facing similar problems as in classical mechanics if we would like to derive statistical mechanics from the full dynamics of the system. We will not enter this discussion here, but rather take a pragmatic point of view. Among the solutions of the von Neumann equation there is a class that is compatible with our macroscopic knowledge about the system, for instance, all distributions that correspond to a specified value of the total energy. This class still contains an enormous number of functions. In the absence of further information we have no a priori reason for favoring one of these more han any other. Hence we shall naturally construct the equilibrium density operator by assigning equal statistical weight to all functions compatible with the requirements:

$$\rightarrow \quad \textbf{principle of equal a priori probabilities}\,. \tag{3.32}$$

Clearly this principle is *not* a mechanical but a statistical assumption. The following discussion is then parallel to classical statistical mechanics. In particular, we do not have to repeat the arguments connecting statistical mechanics with thermodynamics. They are indeed identical.

3.3.1 Microcanonical ensemble

We consider an isolated system with an energy in the interval $[E, E{+}\Delta]$ with $\Delta \ll E$. We work in the basis $\{|n\rangle\}$ of the eigenstates of the Hamiltonian: $\mathcal{H}|n\rangle = E_n|n\rangle$. Then a density operator $\rho(\mathcal{H})$ will be diagonal

$$\rho = \sum_n p_n |n\rangle\langle n|\,. \tag{3.33}$$

We postulate equal probabilities for all eigenstates $|n\rangle$ with energy eigenvalues in the interval $[E, E + \Delta]$:

$$p_n = \frac{1}{W}\begin{cases} 1 & \text{if } E < E_n < E + \Delta, \\ 0 & \text{else.}\end{cases} \tag{3.34}$$

The density operator is normalized, $\mathsf{Tr}\,(\rho) = 1$, such that $W = \sum_n 1$ is the number of *states* whose energy eigenvalues lie in the interval $[E, E + \Delta]$, or short the number of accessible states (= statistical weight).

The statistical entropy (Boltzmann entropy) is defined as in classical mechanics

$$S(E) := k_{\mathrm{B}} \ln W(E)\,. \tag{3.35}$$

Note that this definition is equivalent to

$$S(E) := -k_{\mathrm{B}} \mathsf{Tr}\,(\rho \ln \rho)\;. \tag{3.36}$$

3.3.2 Canonical ensemble

Upon using the same reasoning as in classical mechanics one can derive the probability $p(E_n)$ for a given energy eigenvalue E_n of a subsystems embedded in a larger reservoir (Boltzmann factor)

$$p(E_n) = \frac{1}{Z}\, e^{-\beta E_n} \tag{3.37}$$

Again Z is determined such that the density operator

$$\rho = p(E_n) |n\rangle\langle n| \tag{3.38}$$

is normalized, $\sum_n p(E_n) = 1$. This gives for the canonical partition sum

$$Z = \sum_n e^{-\beta E_n}\,. \tag{3.39}$$

Note that the *sum is over states* and not over energy eigenvalues! These results can also be written in a form which is idependent of the set of basis functions

$$\rho = \frac{1}{Z}\, e^{-\beta \mathcal{H}} \quad \text{with} \quad Z = \mathsf{Tr}\left(e^{-\beta\mathcal{H}}\right) \tag{3.40}$$

The statistical entropy is defined as

$$S := -k_{\mathrm{B}} \mathsf{Tr}\left(\rho \ln \rho\right)\,, \tag{3.41}$$

which reads in a basis of energy eigenfunctions

$$S = -k_{\mathrm{B}} \sum_n p(E_n) \ln p(E_n)\,. \tag{3.42}$$

Upon defining the free energy as

$$F := -k_{\mathrm{B}} T \ln Z \tag{3.43}$$

all further conclusions are identical to the classical case.

3.3.3 Grand canonical ensemble

In the grand canonical ensemble we consider an open subsystem, which can exchange both energy and particles with a large reservoir. Since we are no longer dealing with fixed particle numbers and their associated Hilbert spaces $\mathcal{E}_N$ but with variable particle numbers, we must associate with the system a Hilbert space, called *Fock space*, which is constructed as the direct sum $\oplus_{N=0}^{\infty}\mathcal{E}_N$ of N-particle spaces $\mathcal{E}_N$. In this space we introduce a particle operator $\hat{N}$ in order to treat the energy and the particle number on the same footing. Its eigenvalues are the integers N and its eigenvectors the kets for which the system has well defined number of particles[5].

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[5] In the following we will skip the "hat" on operators again, since the context should usually make clear whether we are working with operators or numbers.

Again, similar reasoning as for the canonical ensemble gives for the density operator in a basis independent form

$$\rho_G = \frac{1}{Z_G} \exp\left[-\beta(\mathcal{H} - \mu N)\right] \tag{3.44}$$

with the grand canonical partition sum

$$Z_G = \sum_{N=0}^{\infty} z^N \, Z(N, V, T)\,, \tag{3.45}$$

and fugacity $z = e^{\beta\mu}$. The entropy is again defined as $S := -k_{\mathrm{B}} \mathsf{Tr}\,(\rho \ln \rho)$ and statistical thermodynamics follows as in classical mechanics.

3.4 The maximum entropy principle

Instead of deriving the various ensembles starting from the equal probability assumption for all energy eigenstates in the microcanonical ensemble, all of statistical mechanics can be derived from the *maximum entropy principle*:

The density operator ρ describing the equilibrium state of a macroscopic system is given by the maximum of the statistical entropy $S(\rho)$ such that the constraints $\mathsf{Tr}\,(\rho) = 1$ and $\mathsf{Tr}\,(\rho A_i) = \langle A_i \rangle$ for the set of macroscopic constants of motion $\{A_i\}$ are satisfied.

In order to account for the constraints we introduce the Lagrange multipliers ν for $\mathsf{Tr}\,(\rho) = 1$ and λ_i for $\mathsf{Tr}\,(\rho A_i) = \langle A_i \rangle$. Then the stationarity condition reads

$$0 = d\left(\frac{1}{k_{\mathrm{B}}} S(\rho) - \sum_i \lambda_i \mathsf{Tr}\,(\rho A_i) - \nu \mathsf{Tr}\,(\rho)\right) \tag{3.46}$$

$$= -\mathsf{Tr}\left(d\rho\left(\ln\rho + 1 + \nu + \sum_i \lambda_i A_i\right)\right) \tag{3.47}$$

Since all the variations $d\rho$ are independent[6] we get

$$\ln\rho + 1 + \nu + \sum_i \lambda_i A_i = 0 \tag{3.50}$$

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[6] To make this more explicit let us introduce a ONB $\{|n\rangle\}$. Then

$$\sum_{n,m} \langle n|d\rho|m\rangle\langle m| \left(\ln\rho + 1 + \nu + \sum_i \lambda_i A_i\right) |n\rangle \tag{3.48}$$

In this expression we can choose as the real independent variations the matrix elements $\langle n|d\rho|m\rangle$, $\langle n|d\rho|m\rangle + \langle m|d\rho|n\rangle$, $\langle n|d\rho|m\rangle - i\langle m|d\rho|n\rangle$, the coefficients of which much vanish ($n < m$). This implies for the matrix elements

$$\langle m| \left(\ln\rho + 1 + \nu + \sum_i \lambda_i A_i\right) |n\rangle = 0 \tag{3.49}$$

and hence the operator must be identical to 0.

or equivalently

$$\rho = \exp\left[-\sum_i \lambda_i A_i - \nu - 1\right] \tag{3.51}$$

Upon defining $Z = e^{\nu+1}$ we get

$$\boxed{\rho = \frac{1}{Z}\exp\left[-\sum_i \lambda_i A_i\right] .} \tag{3.52}$$

We can now determine the Lagrange multiplier ν or equivalently Z such that $\mathsf{Tr}\,(\rho) = 1$. This gives

$$\boxed{Z = \mathsf{Tr}\left(\exp\left[-\sum_i \lambda_i A_i\right]\right) .} \tag{3.53}$$

The *Gibbs-Boltzmann distribution* (GB), Eq.3.52 and its associated *partition sum*, Eq.3.53, represent the general form of a distribution function and partition sum in thermodynamic equilibrium for a system where the averages of the constants of motion A_i are held constant.

Up to now we have shown only that the GB distribution is stationary. We still need to show that it is actually a maximum. To show this we again use the lemma with $X = \tilde{\rho}$ and $Y = \rho$, where both ρ is the GD distribution and $\tilde{\rho}$ is a normalized density operator with the same averages for A_i as ρ

$$\begin{aligned} S(\tilde{\rho}) &= -k_{\mathrm{B}}\mathsf{Tr}\,(\tilde{\rho}\ln\tilde{\rho}) \le -k_{\mathrm{B}}\mathsf{Tr}\,(\tilde{\rho}\ln\rho) \\ &= k_{\mathrm{B}}\ln Z\,\underbrace{\mathsf{Tr}\,(\tilde{\rho})}_{=1} + k_{\mathrm{B}}\sum \lambda_i\,\underbrace{\mathsf{Tr}\,(\tilde{\rho}A_i)}_{=\langle A_i\rangle} \\ &= k_{\mathrm{B}}\ln Z + \sum_i (k_{\mathrm{B}}\lambda_i)A_i = S(\rho) \end{aligned}$$

In conclusion, the GB distribution gives a description of the equilibrium state of a system with the largest possible entropy satisfying the given macroscopic constraints.

Note that this proof also implies a variational principle: for any density operator $\tilde{\rho}$ we have

$$\frac{1}{k_{\mathrm{B}}} S(\tilde{\rho}) - \sum \lambda_i \mathsf{Tr}\,(\tilde{\rho}A_i) \le \ln Z \tag{3.54}$$

where the maximum of the left hand side is $\ln Z$ for $\tilde{\rho} = \rho$. We can now choose a class of density operators $\tilde{\rho}$ (trial operators) and determine the ones which maximize the left hand side of Eq.3.54.

Let us now turn to a discussion of the *partition sum*. It is a function of the Lagrange multipliers, $Z(\{\lambda_i\})$, and has the form of a moment generating function. Indeed,

$$\begin{aligned}\langle A_i\rangle &= \frac{1}{Z}\mathsf{Tr}\left(e^{-\sum_j \lambda_j A_j} A_i\right)\\ &= -\frac{1}{Z}\frac{\partial}{\partial\lambda_i}\mathsf{Tr}\left(e^{-\sum_j \lambda_j A_j}\right)\\ &= -\frac{1}{Z}\frac{\partial}{\partial\lambda_i}Z = -\frac{\partial}{\partial\lambda_i}\ln Z \qquad (3.55)\end{aligned}$$

We have found an implicit equation

$$\boxed{\langle A_i\rangle = -\frac{\partial}{\partial\lambda_i}\ln Z} \qquad (3.56)$$

for the Lagrange multipliers λ_i, which we could solve for λ_i and eliminate them in favor of $\langle A_i\rangle$. This is not, what is done in practice. One usually takes the Lagrange parameters as the quantities characterizing the equilibrium state.

We can also derive the *correlations* and the *statistical fluctuations* of the constants of motion A_i from the partition function in the most common case where the observables A_i commute with each other. One finds

$$\frac{\partial^2 Z}{\partial\lambda_i\partial\lambda_j} = \mathsf{Tr}\left(e^{-\sum_k \lambda_k A_k} A_i A_j\right) \qquad (3.57)$$

and hence

$$\frac{\partial^2 \ln Z}{\partial\lambda_i\partial\lambda_j} = \langle A_i A_j\rangle - \langle A_i\rangle\langle A_j\rangle \equiv C_{ij} \qquad (3.58)$$

The correlation matrix C_{ij} is positive since for arbitrary coefficients x_i we have

$$\sum_{ij} C_{ij}x_i x_j = \langle|\sum_i (A_i - \langle A_i\rangle)x_i|^2\rangle \qquad (3.59)$$

This implies that $\ln Z$ is a *convex* function of its variables λ_i; as a consequence the implicit equation Eq.3.56 has a unique solution.

There is an interesting relation between the equilibrium entropy and the logarithm of the partition sum. According to its definition the statistical entropy in equilibrium reads

$$\begin{aligned}\frac{1}{k_{\mathrm{B}}}S &= -\langle\ln\rho\rangle = -\langle-\ln Z - \sum_i \lambda_i A_i\rangle\\ &= \ln Z + \sum_i \lambda_i\langle A_i\rangle\\ &= \ln Z - \sum \lambda_i \frac{\partial}{\partial\lambda_i}\ln Z\,. \qquad (3.60)\end{aligned}$$

In other words, S/k_{B} is the Legendre transform (see also chapter 4.2) of $\ln Z$ with respect to the Lagrange multipliers: $\ln Z(\{\lambda_i\}) \rightarrow S(\{\langle A_i\rangle\})$. Since

$$d\ln Z = -\sum_i \langle A_i\rangle\, d\lambda_i\,, \quad \text{with} \quad \langle A_i\rangle = -\frac{\partial \ln Z}{\partial\lambda_i} \qquad (3.61)$$

we get from Eq.3.60

$$dS = \sum_i (k_\mathrm{B}\lambda_i)\, d\langle A_i\rangle\,, \quad \text{with} \quad k_\mathrm{B}\lambda_i = \frac{\partial S}{\partial\langle A_i\rangle} \tag{3.62}$$

These relations show that the *natural variables* for $\ln Z$ are the Lagrange multipliers λ_i, whereas for S they are the macroscopic averages $\langle A_i\rangle$.

For the matrix of the second derivatives we hence get

$$\frac{\partial^2 Z}{\partial\lambda_i\partial\lambda_j} = -\frac{\partial\langle A_i\rangle}{\partial\lambda_j} = -\frac{\partial\langle A_j\rangle}{\partial\lambda_i} \tag{3.63}$$

$$\frac{1}{k_\mathrm{B}}\frac{\partial^2 S}{\partial\langle A_i\rangle\partial\langle A_j\rangle} = \frac{\partial\lambda_i}{\partial\langle A_j\rangle} = \frac{\partial\lambda_j}{\partial\langle A_i\rangle} \tag{3.64}$$

This explicitely shows that the matrices of the second derivatives of $\ln Z$ and $-S/k_\mathrm{B}$ are the inverse of each other. Since $\ln Z$ is convex, this implies that S a *concave* function of the variables $\langle A_i\rangle$.

Examples:

1. **Canonical ensemble for a fluid:** We introduce the Lagrange parameter β for $\mathsf{Tr}\,(\rho\mathcal{H}) = \langle E\rangle = U$ and get

$$\rho_C = \frac{1}{Z_C}e^{-\beta\mathcal{H}}\,, \quad \text{with} \quad Z_C = \mathsf{Tr}\left(e^{-\beta\mathcal{H}}\right) \tag{3.65}$$

   Then the equilibrium entropy reads

$$S_C = k_\mathrm{B}\ln Z_C + k_\mathrm{B}\beta U \tag{3.66}$$

   with

$$U = -\frac{\partial}{\partial\beta}\ln Z_C \tag{3.67}$$

   and

$$\beta = \frac{1}{k_\mathrm{B}}\frac{\partial S_C}{\partial U} \tag{3.68}$$

   Upon introducing the notation $\beta = 1/k_\mathrm{B}T$ we can then write the free energy as

$$F_C = -k_\mathrm{B}T\ln Z_C = U - TS_C \tag{3.69}$$

2. **Grand canonical ensemble for a fluid:** Consider the direct sum of Hilbert spaces $\mathcal{E}_N$ for a fixed number of particles: $\mathcal{E} = \oplus_{N=0}^{\infty}\mathcal{E}_N$ (Fock space). Then, the trace operation in the Fock space reads, $\mathsf{Tr}\,(.) = \sum_{N=0}^{\infty}\mathsf{Tr}_N\,(.)$, a sum over traces in the N-particle subspaces $\mathcal{E}_N$. Introduce a Lagrange multiplicator β for $\mathsf{Tr}\,(\rho H) = U$ and $(-\alpha)$ for $\mathsf{Tr}\,(\rho N) = \langle N\rangle$. Then according to our general rules we find

$$\rho_G = \frac{1}{Z_G}e^{-\beta\mathcal{H}_N + \alpha N} \tag{3.70}$$

with

$$\begin{aligned} Z_G &= \sum_{N=0}^{\infty} e^{\alpha N} \mathsf{Tr}_N \left(e^{-\beta \mathcal{H}_N} \right) \\ &= \sum_{N=0}^{\infty} e^{\alpha N} Z_C(\beta; N) \end{aligned} \tag{3.71}$$

such that the grand canonical partition sum is the discrete Legendre transform of the canonical partition sum.

For the Lagrange multipliers we have the implicit equations

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_G \tag{3.72}$$

$$\langle N \rangle = \frac{\partial}{\partial \alpha} \ln Z_G \tag{3.73}$$

The entropy reads

$$S_G(\langle E \rangle, \langle N \rangle) = k_{\mathrm{B}} \ln Z_G + k_{\mathrm{B}} \beta \langle E \rangle - k_{\mathrm{B}} \alpha \langle N \rangle \tag{3.74}$$

with

$$k_{\mathrm{B}} \beta = \frac{\partial}{\partial \langle E \rangle} S_G \tag{3.75}$$

$$-k_{\mathrm{B}} \alpha = \frac{\partial}{\partial \langle N \rangle} S_G \tag{3.76}$$

and

$$dS_G = (k_{\mathrm{B}} \beta) d\langle E \rangle - (k_{\mathrm{B}} \alpha) d\langle N \rangle \tag{3.77}$$

Upon defining new Lagrange parameters T and μ, which we call temperature and chemical potential, respectively,

$$\beta = \frac{1}{k_{\mathrm{B}} T}, \quad \text{and} \quad \alpha = \frac{\mu}{T} \tag{3.78}$$

this can also be written in the form

$$dS_G = \frac{1}{T} d\langle E \rangle - \frac{\mu}{T} d\langle N \rangle \tag{3.79}$$

The fluctuations in energy and particle number read

$$\langle (\mathcal{H} - \langle E \rangle)^2 \rangle = \frac{\partial^2 \ln Z_G}{\partial \beta^2} = \frac{-k_{\mathrm{B}} \frac{\partial^2 S}{\partial N^2}}{\frac{\partial^2 S}{\partial N^2} \frac{\partial^2 S}{\partial U^2} - \left(\frac{\partial^2 S}{\partial N \partial U} \right)^2} \tag{3.80}$$

$$\langle (N - \langle N \rangle)^2 \rangle = \frac{\partial^2 \ln Z_G}{\partial \alpha^2} = \frac{-k_{\mathrm{B}} \frac{\partial^2 S}{\partial U^2}}{\frac{\partial^2 S}{\partial N^2} \frac{\partial^2 S}{\partial U^2} - \left(\frac{\partial^2 S}{\partial N \partial U} \right)^2} \tag{3.81}$$

Chapter 4

Statistical Thermodynamics

The goal of this chapter is twofold. First, we will derive the laws of thermodynamics from the maximum entropy principle alone (!). Second, we will explore the consequences of the laws of thermodynamics without any reference to the nature of the constituent molecules and their interactions. In this sense thermodynamics is a universal theory which is (to a large extent) independent of any molecular details. Note that the laws of thermodynamics were developed at a time where matter was considered rather as a continuum than an assembly of atoms or molecules.

4.1 The laws of thermodynamics

4.1.1 The 0^{th} law of thermodynamics

In its *thermodynamic formulation* the **zeroth law** has the form: *Two systems, which are in thermal equilibrium with a third system, are also in equilibrium with each other.*

This is an equivalence relation between systems in thermal equilibrium. Consider a system in a reference equilibrium state. Then the 0^{th} law says that all systems brought successively (or simultaneously) into thermal equilibrium with the reference state (across diathermal boundaries) will have a common property, that of being in equilibrium with each other. This property is called the empirical temperature ϑ. Of course one needs an experimental procedure which assigns a scale to this empirical temperature. This can be done by measuring a certain property of the reference system and assigning an empirical temperature scale to it. For now we do not need to specify this. We only need to know that the 0^{th} law allows for the definition of an empirical temperature which measures the equivalence of thermal equilibrium states ("Vergleichsmaßstab"). The 0^{th} law was added to the axiomatic system of thermodynamics as an afterthought to make the concept of thermal equilibrium more precise and introduce the notion of a temperature.

For the *proof of the 0^{th} law in statistical mechanics* we consider two thermally isolated systems a and b, described by Hamiltonians $\mathcal{H}_a$ and $\mathcal{H}_b$ such that $[\mathcal{H}_a, \mathcal{H}_b] = 0$. Then there are two separate constants of motion, the total energy of the two systems, E_a and E_b, respectively. Then each of these systems $i = a, b$ can be described by density operators for the canonical ensemble

$$\rho_i = \frac{1}{Z_i(\beta_i)} e^{-\beta_i \mathcal{H}_i} \tag{4.1}$$

with the partion sums

$$Z_i(\beta_i) = \mathsf{Tr}_i \left(e^{-\beta_i \mathcal{H}_i} \right) \tag{4.2}$$

such that the Lagrange multipliers β_i are obtained from the solution of the implicit equations

$$\langle E_i \rangle = -\frac{\partial}{\partial \beta_i} \ln Z_i(\beta_i) \,. \tag{4.3}$$

Since there are no correlations between the two systems a and b the density operator for the total system, $a + b$, is simply given by the tensor product of the density operator of the individual systems,

$$\rho = \rho_a \otimes \rho_b = \frac{1}{Z_a(\beta_a) Z_b(\beta_b)} \exp\left[-\beta_a \mathcal{H}_a - \beta_b \mathcal{H}_b\right] \,. \tag{4.4}$$

Now we bring the two systems into “thermal contact”, or more precisely couple the two systems by an interaction V depending on the observables of both systems. The interaction term is assumed to be weak, $V \ll \mathcal{H}_i$, such that it can be neglected as compared to $\mathcal{H}_a$ and $\mathcal{H}_b$. Nevertheless its presence is sufficient to allow energy exchanges between a and b. The term “thermal contact” here also means that V is an interaction which is out of our control and whose detailed form we either do not know since there is no way to determine it experimentally or it is in some sense “complicated enough” to cause “mixing” in the state space of the composite system. We are facing again, the fundamental problem of statistical mechanics, i.e. the ergodicity problem. Again, we assume that the outcome of such an interaction between the subsystems will be that the final state of the composite system is a thermal equilibrium state, whose density matrix we can obtain by the maximum entropy principle. Since in the final equilibrium state we are now left with only *one* constant of motion, the total energy $E = E_a + E_b$ of the combined system, one can introduce a *single* Lagrange multiplier β such that the density operator becomes

$$\rho = \frac{1}{Z} e^{-\beta \mathcal{H}} = \frac{1}{Z_a(\beta) Z_b(\beta)} e^{-\beta(\mathcal{H}_a + \mathcal{H}_b)} \,. \tag{4.5}$$

Note that we have used that V can be neglected with respect to both $\mathcal{H}_a$ and $\mathcal{H}_b$; its only purpose was to bring the two subsystems in the state of thermal equilibrium with each other. In summary, the Lagrangian multiplier β provides a relative temperature scale since thermal equilibrium between two systems is reflected by the equality of this parameter.

This allows us to define the concepts of *thermostats* (or heat reservoir) and *thermometers.* Consider a situation, where the system b is much larger than system a. Let the initial relative temperatures before the two systems are brought into thermal contact be β_a and β_b, respectively. After the systems have been brought into thermal contact the energy variation of the larger system will be of the order of the energy of the smaller system and hence negligible, $E_b/E_a \ll 1$. As a consequence its final value for the relative temperature β'_b will be almost identical to its initial value β_b. Hence the temperature of the small system will become identical to the temperature of the large system, $\beta'_a = \beta_b$. The large system is called a thermostat since it forces it temperature on the small system. The small system is a thermometer since it adjusts its temperature to the temperature of the large system. Upon observing some property of the small system, such as the volume or the resistivity, depending on the energy $\langle E_b \rangle$, one can define a relative tempertaure scale.

The 0^{th} law of thermodynamics, which was formulated above for closed systems can be generalized to open systems. In its above form it deals with the thermal equilibrium between two systems which are allowed to exchange "heat" (non-mechanical energy; see below). Let us now allow for the exchange of some other constant of motion between, e.g. exchange of one or several types α of particles. Then the Lagrangian multipliers $-\lambda_\alpha$ for the conserved quantities N_α play the same role for particle exchange as β plays for energy exchange. By analogy equilibrium between two systems implies that the Lagrange multipliers become equal, $\lambda_\alpha^{(a)} = \lambda_\alpha^{(b)}$. The parameter β, the conjugate of the energy, characterizes the tendency to absorb heat; the variables $-\lambda_\alpha$, the conjugates of the particle numbers N_α of particle type α, characterize the tendency to loose particles. Again, we can introduce the concept of a reservoir and a λ_α-stat.

In summary, equilibrium between two systems a and b, which are allowed to exchange quantities of the constants of motion A_i, are characterized by the equality of the conjugate Lagrangian multipliers,

$$\lambda_i^{(a)} = \lambda_i^{(b)} \; ; \tag{4.6}$$

hence we can use the Lagrangian multipliers to characterize the equilibrium state of a system.

4.1.2 The 1^{st} law of thermodynamics

Before we discuss the formulation of the first law of thermodynamics let us introduce some concepts:

- *Quasi-static process:* A change of the state of the system that takes place so slowly that the system can be considered in thermal equilibrium (with a test system) at each step of the change is called a quasi-static process.

- *Reversible process:* A process is called a reversible process if the initial state can be obtained from the final state following the inverse of each step of the original process.
- *Adiabatic process:* A change of the state that occurs while the system is thermally isolated (i.e. not in contact or equilibrium with any other system) is called a adiabatic process.

In its **thermodynamic formulation** the **first law** (for a gas or a fluid) has the form:

1. *Associated with each system there is a function U of the state of the system, called the internal energy, such that the work done on the system ΔW in going from state (P_i, V_i) to (P_f, V_f) in an adiabtic process is*

   $$\Delta U = U_f - U_i = \Delta W\,, \tag{4.7}$$

   independently of the path joining the initial and the final states. It follows that for a quasi-static process $\int_\Gamma PdV$ is independent of the path Γ.

2. *The quantity of heat ΔQ absorbed by te system in* any *change of the state is defined by*

   $$\Delta Q = \Delta U - \Delta W \tag{4.8}$$

   and for an infinitesimal quasi-static *change*

   $$\delta Q = dU - \delta W = dU + PdV\,, \tag{4.9}$$

   where we have written δQ since the right hand sige is not necessarily an exact differential of some function.

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The **microscopic interpretation** of the first law is quite simple. It is a consequence of the dynamic laws governing the microscopic world; the internal energy

$$U = \langle E \rangle = \mathsf{Tr}\,(\rho\mathcal{H}) \tag{4.10}$$

for an isolated system obeys the following Ehrenfest equation

$$i\hbar\frac{d}{dt}U = \langle[\mathcal{H},\mathcal{H}]\rangle = 0\,. \tag{4.11}$$

If we consider the system under study together with the one's with which it exchanges work and heat as a single isolated system, conservation of the total macroscopic energy of the composite system follows immediately from that of the microscopic energy,

$$\Delta U = \Delta W + \Delta Q\,. \tag{4.12}$$

– figure missing –

Figure 4.1: Illustration of an isolated system composed of the system which we are interested in systems with which it echanges heat and work, respectively.

The intersting questions we can ask and answer now is: "What is heat and what is work in statistical mechanics?" To understand "heat" we consider a non-isolated system which exchanges energy with some other system (see Figure 4.1). To be precise, we again assume that there is a weak (not well known) interaction $V \ll \mathcal{H}$ facilitating this energy exchange. The effect of this weak interaction is that it drives the total system towards a thermal equilibrium state which can be specified by the maximum entropy principle, $\rho \rightarrow \rho + d\rho$. Note that, as a consequence, the approach towards equilibrium is *not* governed by the von Neumann equation! The change in internal energy then equals the heat δQ absorbed by the system,

$$\delta Q = \mathsf{Tr}\left(d\rho\, Q\right) . \tag{4.13}$$

If we now take an ONB $\{|m\rangle\}$ of energy eigenstates, $\mathcal{H}|m\rangle = E_m|m\rangle$, the change in the density operator reads $d\rho = \sum_m dp_m|m\rangle\langle m|$ and hence

$$\delta Q = \sum_m dp_m E_m . \tag{4.14}$$

This allows a statistical interpretation of heat as the gain in internal energy due a redistribution of the probabilities for the energy eigenstates $|m\rangle$; the system "heats up" when the relative probabilities for states with higher energies increase.

To make the concept of "work" precise we consider a set of macroscopic control parameters $\{\xi_\alpha\}$ of the Hamiltonian $\mathcal{H}(\{\xi_\alpha\})$, e.g. the volume V of a gas, which are changed slowly and in a well controlled fashion, $\xi_\alpha(t)$. The resulting change of the Hamiltonian is

$$d\mathcal{H} = \mathcal{H}(\{\xi_\alpha + d\xi_\alpha\}) - \mathcal{H}(\{\xi_\alpha\}) = \sum_\alpha \frac{\partial \mathcal{H}}{\partial \xi_\alpha} d\xi_\alpha . \tag{4.15}$$

Work is defined as $\delta W = d\mathcal{H}$ during such a change in control parameters. According to the Ehrenfest theorem (for an operator with an explicit time dependence) the change in internal energy is

$$\frac{dU}{dt} = \langle \frac{\partial \mathcal{H}}{\partial t} \rangle = \sum_\alpha \langle \frac{\partial \mathcal{H}}{\partial \xi_\alpha} \rangle \frac{d\xi_\alpha}{dt} \equiv \sum_\alpha \langle X_\alpha \rangle \frac{d\xi_\alpha}{dt} \tag{4.16}$$

where we have introduced the generalized forces $X_\alpha = \partial\mathcal{H}/\partial\xi_\alpha$. In summary, we have found

$$dU = \delta W = \sum_\alpha \langle X_\alpha \rangle d\xi_\alpha = \mathsf{Tr}\left(\rho\, d\mathcal{H}\right) . \tag{4.17}$$

We have yet to show that the exchange of work with another system by a controlled change of some control parameters is adiabatic. This follows from

$$dS = -k_{\mathrm{B}}\mathsf{Tr}\left(d\rho(\ln\rho + 1)\right) = -k_{\mathrm{B}}\mathsf{Tr}\left(d\rho\ln\rho\right) \tag{4.18}$$

and the von Neumann equation for the density operator (which is even valid for a Hamiltonian with an explicit time dependence),

$$i\hbar\frac{dS}{dt} = -k_{\mathrm{B}}\mathsf{Tr}\left(i\hbar\frac{d\rho}{dt}\ln\rho\right) = -k_{\mathrm{B}}\mathsf{Tr}\left([\mathcal{H},\rho]\ln\rho\right) = 0\,, \tag{4.19}$$

where in the last step we have used the cyclic invariance of the trace operator.

If a system exchanges energy with other systems in a quasi-static process the change in internal energy is a sum of “heat” and “work”,

$$dU = \mathsf{Tr}\left(d\rho\mathcal{H}\right) + \mathsf{Tr}\left(\rho d\mathcal{H}\right)\,. \tag{4.20}$$

where the heat supplied is uncontrolled and irreversible, whereas the work supplied is controlled, adiabatic and reversible.

4.1.3 The 2^{nd} law of thermodynamics

We again start our discussion with the *thermodynamic formulation*[1]. In doing so we will essentially follow the historic development in terms of Carnot cycles, Kelvin’s statement of the second law, the absolute temperature scale and the entropy. For simplicity, we restrict ourselves to a discussion of gases, whose state can be specified by pressure P, volume V and relative temperature ϑ.

The 1^{st} law of thermodynamics simply states that all processes in nature only involve energy conversion but never any creation or destruction of energy. It puts no constraints on the direction and amount of energy conversion between different energy forms (such as heat and work). This is the domain of the 2^{nd} law. It grew out of trying to understand the efficiencies of heat engines in the early 19th century.

A *heat engine* is an engine that uses heat to produce mechanical work by carrying a working substance through a cyclic process. Of particular importance for the development of thermodynamics are heat engines working between two heat reservoirs (thermostats), a low and a high temperature reservoir at relative temperatures ϑ_1 and ϑ_2, respectively; for an illustration see Figure 4.2a. The performance of a heat engine is measured by its thermal efficiency, which is defined as the ratio of work output to heat input, i.e., $\eta = W/Q_2$, where W is the net work done, and Q_2 is heat transferred from the high temperature reservoir. Due to the first law we have $\Delta U = 0$ since the process is cyclic. This implies $W = \Delta Q = Q_2 - Q_1$ and hence $\eta = 1 - Q_1/Q_2$.

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[1] **Recommended reading:** The Feynman Lectures on Physics, volume I, chapter 44.

– figure missing –

Figure 4.2: a) Illustration of a heat engine working between two heat reservoirs ϑ_1 and ϑ_2. b) Illustration of the Carnot cycle in the PV diagram.

The important contribution of Carnot[2] was to suggest a particular idealized design for a cyclic process such that each step of the process can be considered as *reversible*, i.e. a quasi-static process which can be infinitesimally reversed[3]. As illustrated in Figure 4.2b the *reversible Carnot cycle* consists of two isothermal ($\vartheta = const.$) and two adiabatic ($\delta Q = 0$) processes

1. *Reversible isothermal expansion of the gas at the "hot" temperature,* ϑ_2. During this step, we can picture the expanding gas as causing a frictionless piston to do work on the surroundings. The gas expansion is driven by reversible absorption of heat Q_2 from the high temperature reservoir; the idea is that infinitesimal temperature differences in contrast of finite ones can be reversed.

2. *Reversible adiabatic expansion of the gas.* For this step we assume the piston and cylinder are thermally insulated, so that no heat is gained or lost, $\delta Q = 0$. The gas continues to expand, doing work on the surroundings. The gas expansion causes it to cool to the "cold" temperature, ϑ_1. This idealized frictionless mechanical process is considered to be reversible if done sufficiently slowly.

3. *Reversible isothermal compression of the gas at the "cold" temperature,* ϑ_1. Now the surroundings do work on the gas, causing heat to flow out of the gas to the low temperature reservoir.

4. *Reversible adiabatic compression of the gas.* Once again we assume the piston and cylinder are thermally insulated. During this step, the surroundings do work on the gas, compressing it and causing the temperature to rise to ϑ_2. At this point the gas is in the same state as at the start of step 1.

Our starting point is **Kelvin's statement of the second law**: *No cyclic process exists whose sole effect is to extract heat from a substance and convert it entirely into work. In other words, there can be no perpetuum mobile which converts the whole energy of a body into mechanical work.*

An equivalent **statement of Clausius** reads (see problem sets): *There is no transformation whose sole effect is to extract heat from a colder reservoir and transfer it to a hotter reservoir. In other words "heat flows from hot to cold".*

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[2] In 1824, Carnot published his classic work, *"Reflections on the Motive Power of Heat"*. There he analysed the efficiency of engines in converting heat into work.

[3] Of course, there is nothing like a real reversible process in nature. The Carnot cycle is a (mathematical) idealization.

Using a Carnot cycle Kelvin's statement implies that both Q_1 and Q_2 are positive if the heat engine does the work $W > 0$. This can be seen as follows. Assume that $Q_1 \leq 0$, i.e. the engine takes the heat Q_1 from the low temperature reservoir. Next we bring the two reservoirs into thermal contact. According to the Clausius statement heat will flow from the hotter to the colder reservoir. We stop this process when the amount of heat flow is Q_1 such that heat Q_1 consumed by the heat engine during the cycle is fully given back. The netto effect of this procedure is that heat would be taken up from the hotter reservoir and fully be transformed into work. This contradicts Kelvin's statement. Thus $Q_1 > 0$ and according to the first law $Q_2 = W + Q_1 > 0$.

Next we consider two heat engines and show **Carnot's Fundamental Theorem**: *All reversible heat engines working between two heat reservoirs have the same efficiency, which is larger than for any irreversible engine. In other words, "you can not beat Carnot".*

– figure missing –

Figure 4.3: Two coupled heat engines.

For the proof of this theorem we argue as follows. Consider two heat engines A and A' working between the reservoirs at temperatures ϑ_1 and ϑ_2, where the first engine is a Carnot engine and the second may be any heat engine; see Figure 4.3. According to the first law we have

$$W = Q_2 - Q_1\,, \quad \text{and} \quad W' = Q_2' - Q_1'\,. \tag{4.21}$$

Next we note that the ratio Q_2/Q_2' can be approximated by a rational number N'/N, where N and N' are two natural numbers, to any desired accuracy. Now consider a process with N' cycles of the second engine and N cycles of the reversible Carnot engine working in the reverse direction. Then the total amount of heat taken from the reservoir at temperature ϑ_2 equals zero: $Q_2^{\text{total}} = N'Q_2' - NQ_2 = 0$. According to the first law this implies

$$W^{\text{total}} = -Q_1^{\text{total}} = -(N'Q_1' - NQ_1)\,. \tag{4.22}$$

According to Kelvin's statement the total amount of work must not be positive. Hence $Q_1^{\text{total}} \geq 0$, i.e. $N'Q_1' \geq NQ_1$. Upon eliminating N/N' we find

$$Q_1'/Q_2' \geq \frac{Q_1}{Q_2}\,. \tag{4.23}$$

If both engines are reversible we can reverse the role of engine A and A', implying $Q_1'/Q_2' \leq Q_1/Q_2$. This is consistent with Eq. 4.23 only if

$$Q_1'/Q_2' = \frac{Q_1}{Q_2}\,. \tag{4.24}$$

All of this implies that

$$\eta' = 1 - \frac{Q_1'}{Q_2'} \leq 1 - \frac{Q_1}{Q_2} = \eta_C \tag{4.25}$$

with equality holiding if both engines are reversible Carnot engines.

An obvious corrolary of Carnot's fundamental theorem is that the ratio

$$Q_1/Q_2 = f(\vartheta_1, \vartheta_2) \tag{4.26}$$

is a *universal* function of ϑ_1 and ϑ_2. Now consider two reversible engines A_1 and A_2. The first works between reservoirs ϑ_0 and ϑ_1, absorbing a quantity of heat Q_1 during the first isothermal change and yielding a quantity of heat Q_0 during the second isothermal change. The second cycle operates between temperatures ϑ_0 and ϑ_2 absorbing Q_2 and also yielding Q_0. Note that we can always adjust the relative size of the engines such that both yield the same amount of heat Q_0; otherwise just perform the same construction as above with $Q_0/Q_0' = N'/N$. Then we have for these cycles

$$\begin{aligned} Q_1/Q_0 &= f(\vartheta_1, \vartheta_0) &(4.27)\\ Q_2/Q_0 &= f(\vartheta_2, \vartheta_0)\,. &(4.28) \end{aligned}$$

Combining the two machines by reversing the direction of A_1 results in

$$Q_2/Q_1 = f(\vartheta_2, \vartheta_1)\,. \tag{4.29}$$

Eqs.4.27–4.29 give

$$f(\vartheta_2, \vartheta_1) = \frac{f(\vartheta_2, \vartheta_0)}{f(\vartheta_2, \vartheta_0)} \equiv \frac{\Theta(\vartheta_2)}{\Theta(\vartheta_1)}\,, \tag{4.30}$$

where – since the reference temperature ϑ_0 is arbitrary – we have introduced the universal function Θ. This allows us to define an *absolute temperature* T by

$$T = \alpha\Theta(\vartheta)\,, \tag{4.31}$$

where α is some constant scale factor. This temperature scale is universal and independent of the working substance of the heat engine. It also implies that the Carnot cycle's efficiency reads

$$\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}\,. \tag{4.32}$$

Let us consider now an arbitrary cyclic process, where at each instant the system is at a well defined temperature T. Then one can show the **Clausius theorem**: *For any cycle K*

$$\oint \frac{\delta Q}{T} \leq 0\,, \tag{4.33}$$

where the equal sign holds for a reversible process.

To prove this statement we discretize the cyclic process K into n steps at temperatures $T_1, T_2, \cdots T_n$. Now choose a set of reversible Carnot processes C_i such that the quantities of heat Q_i taken from the heat reservoirs $T_1, T_2, \cdots T_n$ are the same as for the cyclic process K. Let T_0 be the reference (cold) heat reservoir for all the Carnot cycles. Then according to Kelvin's theorem

$$\frac{Q_i}{Q_{i,0}} = \frac{T_i}{T_0}\,. \tag{4.34}$$

If we combine the cyclic process K with the reversed Carnot cycles C_i the heat transfers to the reservoirs T_i cancel out, such that in the combined process the quantity of heat

$$Q_0 = \sum_{i=1}^{n} Q_{i,0} = T_0 \sum_{i=1}^{n} \frac{Q_i}{T_i} \tag{4.35}$$

is supplied by the reference reservoir at temperature T_0. According to Kelvin's theorem this must not be positive such that $Q_0 \leq 0$ and hence assuming $T_0 > 0$

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0\,. \tag{4.36}$$

If we let $n \to \infty$ this proofs the first part of Clausius statement. If K is reversible, we can run it backward and combine it with forward running Carnot machines. This leads to the same set of equations as above with all the signs reversed, such that $\sum_{i=1}^{n}(-Q_i)/T_i \leq 0$. Hence for reversible engines we have

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} = 0\,. \tag{4.37}$$

The Clausius theorem for reversible cycles, $\oint \frac{\delta Q}{T} = 0$, implies that we can define a quantity S such that

$$dS = \frac{\delta Q}{T} \tag{4.38}$$

is an exact differential of the function $S(V,T)$ of the state of the system, called **entropy**. It is clear that S defined in this way is only determined up to an additive constant. In other word, only the difference

$$S(V_f,T_f) - S(V_i,T_i) = \int_\Gamma \frac{\delta Q}{T} \tag{4.39}$$

is defined, for Γ any *reversible* path joining the two states.

As a corollary to Clausius theorem one can show the more general statement

$$\Delta S = S_f - S_i \geq \int_\Gamma \frac{\delta Q}{T} \tag{4.40}$$

which holds for any path Γ from state (V_i,T_i) to state (V_f,T_f) with equality holding if Γ is reversible.

To prove this result, consider the cycle K composed of Γ and the inverse of the reversible path Γ_R joining the states i and f. For the reversible path we have

$$S_f - S_i = \int_{\Gamma_R} \frac{\delta Q}{T} \tag{4.41}$$

Upon combining it with Carnot's theorem for the cycle K gives

$$\oint \frac{\delta Q}{T} = \int_\Gamma \frac{\delta Q}{T} - \oint_{\Gamma_R} \frac{\delta Q}{T} \leq 0 \tag{4.42}$$

and hence proves 4.40.

In summary, the 2^{nd} **law of thermodynamics according to Clausius** can be formulated as:

If a sytem is in thermodynamic equilibrium one can assign to it two quantities, the absolute temperature T and the entropy S, which is a function of the state of the system. In a reversible process during which the system passes at any time through equilibrium states which exchange heat and work with the outside, the change in entropy is given by

$$dS = \frac{\delta Q}{T} \,. \tag{4.43}$$

For any other transformation from some initial to some final equilibrium state the entropy change of the system obeys the inequality

$$\Delta S = S_f - S_i \geq \int_\Gamma \frac{\delta Q}{T} \,, \tag{4.44}$$

where T is the temperature of the source providing the heat δQ to the system under consideration along the path Γ. Hence for irreversible changes of state in a thermally isolated system, the entropy never decreases, $\Delta S \geq 0$.

Note that the system which may pass through any non-equilibrum state may not have a well defined temperature in contrast to the reservoirs at the temperatures T. Also note that in the thermodynamic formulation of the second law both T and S are defined up to a multiplicative constant depending on ones choice of units. In addition, the entropy is only defined up to an additive constant.

After this lengthy detour to the historical formulation of the second law let us come back to *statistical mechanics*. Here things are much simpler. During a quasi-static transformation (say in a canonical ensemble) we can describe the system – according to the maximum entropy principle – at any time by a density operator

$$\rho = \frac{1}{Z(t)} \, e^{-\beta(t)\mathcal{H}(t)} \,, \quad \text{with} \quad Z(t) = \mathsf{Tr}\left(e^{-\beta(t)\mathcal{H}(t)}\right) \,. \tag{4.45}$$

The exchanges of heat and work with the outside are reflected in changes with time in β and $\mathcal{H}$ through the parameters ξ_α. Note that the time evolution of the density operator does not follow the von Neumann equation: the system is, in fact, in thermal contact with a thermostat and we assume that this coupling leads it all times to the state with maximum disorder.

Let us now calculate the entropy change during such a quasi-static process

$$dS = -k_\mathrm{B} \mathsf{Tr}\left(d\rho \ln \rho\right) = k_\mathrm{B} \mathsf{Tr}\left(d\rho (\ln Z + \beta\mathcal{H})\right) = k_\mathrm{B}\beta \mathsf{Tr}\left(d\rho\mathcal{H}\right) \tag{4.46}$$

Upon comparing this with $\delta Q = \mathsf{Tr}\left(d\rho\mathcal{H}\right)$ we find

$$dS = k_\mathrm{B}\beta \, \delta Q \tag{4.47}$$

for all quasi-static changes $d\beta$ and $d\xi_\alpha$. Note that in statistical mechanics β is a universal scale for thermal equilibrium to begin with; there is no need to show that it is system independent. Upon comparing Eq.4.47 with Eq.4.43 we can relate the statistical mechanics scale β with the thermodynamic scale T by

$$\beta = \frac{1}{k_{\mathrm{B}}T}\,, \tag{4.48}$$

and the statistical entropy with the thermodynamic entropy defined in the Clausius theorem apart from an additive constant.

If we now consider an isolated system which undergoes any kind of transformation from one equilibrium to another equilibrium state. Then the statistical entropy on the microscopic scale has to increase simply for statistical reasons, such as badly known couplings between various parts of the system, loss of information to inaccessible degrees of freedom, or increase of microscopic disorder. Now consider an isolated system composed of a subsystem A in contact with heat reservoirs at temperatures T_j. These heat sources are assumed to undergo quasi-static transformations such that they receive the amounts of heat $-\delta Q_j$ and this lead to a entropy change $dS_j = -\delta Q_j/T_j$. Let the entropy change of the subsystem be $S_f - S_i$. Then the total change of entropy of the isolated system has to be positive,

$$S_f - S_i - \sum_j \frac{\delta Q_j}{T_j} \geq 0\,. \tag{4.49}$$

This completes the second law of thermodynamics in its statistical formulation and shows its equivalence to the thermodynamic concepts.

If we want to take for the **unit of the absolute temperature** T the Kelvin, the most commonly used scale in practice, which is defined by putting the temperature at the triple point of water equal to $273.16K$, we must take $k_{\mathrm{B}} = 1.38 \times 10^{-23}\mathrm{JK}^{-1}$. Another choice which follows naturally from statistical physics would be to put $k_{\mathrm{B}} = 1$; the quantity $1/\beta$ then defines the absolute temperature measured in energy units and the entropy S would be dimensionless. In order to remember the magnitude of k_{B} bear in mind that room temperature $T = 300\mathrm{K}$ corresponds to an energy $k_{\mathrm{B}}T = \frac{1}{40}eV$.

4.1.4 The 3rd law of thermodynamics (Nernst's law)

The 3rd law was proposed by Walther Nernst in 1906 on the basis of experimental observations. It expresses the impossibility to reach absolute zero. In analytical form this impossibility is reflected by the fact that at zero temperature the entropy becomes independent of the parameters ξ_α which characterize the equilibrium states of the system: otherwise one could reach the absolute zero by an adiabatic transformation, varying some of the ξ_α.

The thermodynamic entropy was defined apart from an additive constant. The 3rd law shows that this constant is independent of the system; one can therefore choose it in such a way that the *entropy vansihes at absolute zero (Planck).*

In contrast to the thermodynamic entropy, the statistical entropy does *not* contain any arbitrary additive constant. When $T \to 0$, the probabilities

$$p_n = \frac{e^{-\beta E_n}}{\sum_m e^{-\beta E_m}} = \frac{e^{-\beta(E_n - E_0)}}{\sum_m e^{-\beta(E_m - E_0)}} \tag{4.50}$$

tend exponentially to zero for all excited states $|n\rangle$ with energies larger than the ground state E_0. The density operator ρ reduces to the projection onto the ground state, provided it is not degenerate, and this describes a pure state with entropy $S = -k_\mathrm{B} \sum_m p_m \ln p_m$ equal to zero. This is the Third Law of thermodynamics.

In fact, this condition is too restrictive. For large systems such as are considered by thermodynamics, the Third Law means that the entropy per unit volume tends to zero. To derive this from microscopic physics, it is thus sufficient to prove that the entropy is non-extensive in the limit $T \to 0$

$$\lim_{\beta\to\infty} \lim_{V\to\infty} \frac{S}{V} \to 0 \tag{4.51}$$

where the volume V tends to infinity before the temperature tends to zero. At low temperatures the entropy, whether canonical or microcanonical, is of the order of $k_\mathrm{B} \ln W$, where W is the number of eigenstates of $\mathcal{H}$ with energies below $E_0 + \Delta$, the interval Δ remaining finite as $V \to \infty$. This number W represetnts the multiplicity of the ground state E_0 together with the weakly excited states; it depends on the volume of the system. Nernst's law only requires $(\ln W)/V \to 0$; it therefore holds as long as the multiplicity W grows less rapidly than the exponential of the volume. In practice, W is always large, as the ground state of a macroscopic system is always degenerate or nearly degenerate; however, experiments show that in most cases $(\ln W)/V$ tends to zero in the large volume limit, and this explains why the vanishing of S at $T = 0$ has been given the status of a Law.

As a consequence of the fact that the entropy tends to a non-extensive constant as $T \to 0$ it follows that it is impossible to reach absolute zero (see any introductory course on thermodynamics).

4.1.5 Extensivity (or the -1^{st} law of thermodynamics)

Thermodynamics is interested in systems which are, at least locally, homogeneous on a macroscopic scale. The dimension of such systems can be considered as inifinite compared to the distance between the elementary microscopic constituents. Thus we are naturally lead to the limit where the number of microscopic constituents N tends to infinity. In this thermodynamic limit we distinguish between *extensive* and *intensive* variables. Extensive variables, such as the volume V, total internal energy U, entropy S, scale proportional to N. Intensive variables, such as temperature T, chemical potentials μ_α, scale as 1, i.e. are not affected by the system size.

It is actually neither obvious nor true in general that the entropy is an extensive quantity for any arbitrary system. A proof of extensivity is, in general, difficult and appeals to special conditions, which must be satisfied by the interactions between the constituent particles. They must repel each other at small distances in order that matter does not collapse, and they must have not too long range.

In the following we will postulate that *the entropy as a function of the volume V and of the constants of motion such as U and N is a homogeneous function of degree 1*

$$S(xU, xV, xN) = xS(U, V, N)\,. \tag{4.52}$$

This reflects our intuition about nature on our scale, a homogeneous continuum, whose characteristics are not altered upon subdivision, except by scaling of extensive quantities.

In the thermodynamic limit, extensivity of the entropy guarantees that all ensembles are actually equivalent!

4.2 Thermodynamic potentials

4.2.1 Legendre transformation

In the following we will often encounter a situation where we would like to change from one set of variables to another set of variables. This can be accomplished by a Legendre transformation (see also a course on Classical Mechanics).

Consider a function $F(\{x_i\};\{t_\alpha\})$ with partial derivatives given by

$$y_i = \frac{\partial F}{\partial x_i} \tag{4.53}$$

$$u_\alpha = \frac{\partial F}{\partial t_\alpha} \tag{4.54}$$

such that the total differential reads

$$dF = \sum_i y_i dx_i + \sum_\alpha u_\alpha dt_\alpha \tag{4.55}$$

We call y_i and u_α the variables conjugate to x_i and t_α with respect to the function F. We would like to have a function $G(\{y_i\};\{t_\alpha\})$, which depends on the variables y_i instead of x_i. The transformation $F \rightarrow G$ is obtained by the Legendre transform defined as

$$G := F - \sum_i x_i y_i \tag{4.56}$$

With Eq.4.55 this gives

$$dG = -\sum_i x_i dy_i + \sum_\alpha u_\alpha dt_\alpha \tag{4.57}$$

and hence the partial derivatives of G read

$$x_i = -\frac{\partial G}{\partial y_i} \tag{4.58}$$

$$u_\alpha = \frac{\partial G}{\partial t_\alpha} \tag{4.59}$$

Note that the partial derivatives with respect to t_α for F and G mean derivatives where the variables x_i and y_i are kept constant, respectively!

For the new function G the variable conjugate to y_i is $-x_i$; we still have that the variable conjugate to t_α is u_α. With this it is simply to go back to the original function F by another Legendre transform

$$F := G + \sum_i x_i y_i \,. \tag{4.60}$$

Apart from a few signs, the Legendre transform is symmetric!

There are important relations between the second derivatives (see problem sets):

$$\delta_{il} = -G_{ik}F_{kl} \tag{4.61}$$

$$G_i^\alpha = -G_{ik}F_k^\alpha \tag{4.62}$$

$$G^{\alpha\beta} = F^{\alpha\beta} + F_i^\alpha G_{il} F_l^\beta \tag{4.63}$$

where we have used the convention that one has to sum over repeated indices and defined the partial derivatives

$$\begin{aligned} F_{ij} &= \frac{\partial^2 F}{\partial x_i \partial x_j}\,, & G_{ij} &= \frac{\partial^2 G}{\partial y_i \partial y_j} \\ F_i^\alpha &= \frac{\partial^2 F}{\partial x_i \partial t_\alpha}\,, & G_i^\alpha &= \frac{\partial^2 G}{\partial y_i \partial t_\alpha} \\ F^{\alpha\beta} &= \frac{\partial^2 F}{\partial t_\alpha \partial t_\beta}\,, & G^{\alpha\beta} &= \frac{\partial^2 G}{\partial t_\alpha \partial t_\beta} \end{aligned}$$

These relations show that the matrices of the second derivatives of F with respect to the x_i and $-G$ with respect to the y_i are each others' inverse. If the function F is arbitrary, its Legendre transform G is not necessarily single-valued. Nevertheless, if f is *convex* (or *concave*), its matrix of second derivatives with respect to the x_i is positive (or negative), and its Legendre transform is not only *single-valued*, but also *concave* (or *convex*).

4.2.2 The fundamental relation

Given a set of Lagrange multipliers λ_i to fix the constraints $\mathsf{Tr}\,(\rho A_i) = \langle A_i \rangle$ and given a set of control parameters ξ_α for the Hamiltonian $\mathcal{H}(\{\xi_\alpha\})$, the maximum entropy principle of statistical mechanics provides us with the partition sum

$$Z(\{\lambda_i\};\{\xi_\alpha\}) = \mathsf{Tr}\left(e^{-\sum_i \lambda_i A_i}\right)\,, \tag{4.64}$$

where in the following we will take $A_0 = \mathcal{H}$ and $\lambda_0 = \beta$. Whether we treat a extensive parameter like a strictly fixed control parameter or as constrained on average by a Lagrange multiplier is not essential in the thermodynamic limit; it matters for small systems. For instance, we may either include the volume V as an external parameter or fix it on average in the isobaric ensemble.

We have seen in chapter 3 that the entropy can be obtained from the partition sum by a Legendre transform with respect to the Lagrange parameters

$$\frac{S}{k_{\mathrm{B}}} = \ln Z + \sum_i \lambda_i \langle A_i \rangle \tag{4.65}$$

such that $S = S(\{A_i\}; \{\xi_\alpha\})$ and the partial derivatives of S with respect to the constants of motion $\langle A_i \rangle$ are given by

$$k_{\mathrm{B}} \lambda_i = \frac{\partial S}{\partial \langle A_i \rangle} \, . \tag{4.66}$$

We would also like to know the partial derivatives of S with respect to the control parameters ξ_α. Since S/k_{B} is the Legendre transform of $\ln Z$ with respect to the Lagrange parameters but not the control parameters we simply have

$$\frac{\partial S}{\partial \xi_\alpha} = k_{\mathrm{B}} \frac{\partial \ln Z}{\partial \xi_\alpha} = -k_{\mathrm{B}} \beta \langle \frac{\partial \mathcal{H}}{\partial \xi_\alpha} \rangle = -\frac{1}{T} \langle X_\alpha \rangle \tag{4.67}$$

In summary, we have for the total differential of the entropy

$$dS = \frac{1}{T} dU + \sum_{i \geq 1} (k_{\mathrm{B}} \lambda_i) d\langle A_i \rangle - \frac{1}{T} \sum_\alpha \langle X_\alpha \rangle d\xi_\alpha \tag{4.68}$$

For the remainder of this chapter we will restrict ourselves to systems in the thermodynamic limit. Then, we may simply write A_i for $\langle X_i \rangle = \overline{X}_i$ and X_α for $\langle X_\alpha \rangle = \overline{X}_\alpha$; note also that then A_i and X_α are the values of mecroscopic obeservables and no longer operators. Since in the thermodynamic limit it does not matter whether we fix a macroscopic parameter exactly, like the control parameters ξ_α, or on average only, like the constants of motion A_i. Hence the distinction is no longer necessary, and we will simplify notation by denoting all natural variables of the entropy as A_i with

$$\gamma_i = \begin{cases} k_{\mathrm{B}} \lambda_i & \text{for} \quad A_i \\ -\frac{X_\alpha}{T} & \text{for} \quad X_\alpha \end{cases} \tag{4.69}$$

such that

$$dS = \sum_i \gamma_i dA_i = \frac{1}{T} dU + \sum_{i \geq 1} \gamma_i dA_i \tag{4.70}$$

In particular, for a one-component gas we have $S = S(U, V, N)$

$$dS = \frac{1}{T} dU - \frac{\mu}{T} dN + \frac{P}{T} dV \tag{4.71}$$

The manifold $S(U,V,N)$ (or, in general, $S(\{A_i\})$), is known as the *fundamental relation* in thermodynamics since it specifies the thermodynamic properties of a system completely; for an illustration see Fig.4.4.

– figure missing –

Figure 4.4: Illustration of the fundamental relation $S(U,\{A_i\}$.

The **maximum entropy principle** in thermodynamics reduces to:
The equilibrium states of a system are characterized on the macroscopic scale by a set of *extensive variables* A_i and by a function of these variables, the entropy S, which is *continuously differentiable, positive, and additive*: the entropy of a composite system is the sum of those of its parts, the entropy of a homogeneous substance is extensive. In an *isolated composite* system the lifting of some constraints may allow exchange between subsystems, which are reflected in changes in the A_i; the domain $\mathcal{A}$ that is allowed for the A_i variables is restricted by the remaining constraints and by the *conservation laws.* In the final equilibrium state the system reaches, the value of the A_i variables is determined by looking for the *maximum of the entropy in the domain* $\mathcal{A}$.

This maximum entropy principle for *isolated* systems (i.e. $U = constant$) is equivalent to a *minimum energy principle* for *isentropic* systems (i.e. $S = constant$). Indeed, the relation

$$dS = \frac{1}{T} dU + \sum_{i\geq 1} \gamma_i dA_i \tag{4.72}$$

shows that in equilibrium we have $\sum_{i\geq 0} \gamma_i dA_i = 0$ on the domain $\mathcal{A}$. At equilibrium the second differntial

$$\begin{aligned} d^2S &= \frac{1}{T} d^2U + \frac{\partial}{\partial U}\left(\frac{1}{T}\right) dU^2 + 2\sum_{i,j\geq 1} \frac{\partial^2 S}{\partial U \partial A_i} dU dA_i \\ &\quad + \sum_{i\geq 1} \gamma_i d^2 A_i + \sum_{i,j\geq 1} \frac{\partial^2 S}{\partial A_i \partial A_j} dA_i dA_j \end{aligned} \tag{4.73}$$

is negative when $dU = d^2U = 0$ and for variations of A_i in $\mathcal{A}$. As a result d^2U is positive for variations of A_i in $\mathcal{A}$, if $dS = d^2S = dU = 0$; for an illustration see Fig.4.4.

Starting from the fundamental relation for the energy $U = U(S,\{A_i\})$ we can define other thermodynamic potentials using appropriate Legendre transformations. For simplicity we will restrict our discussion to one-component gases described by the extensive variables S, V and N such that for $U = U(S,V,N)$ we have the total differential

$$dU = TdS - PdV + \mu dN \,. \tag{4.74}$$

We start with the **free energy** defined as the Legendre transform of the internal energy with respect to the conjugate pair of variables $(S, T = \partial U/\partial S)$

$$F(T,V,N) := U(T,V,N) - TS \,. \tag{4.75}$$

Then, one finds for the the total differential

$$dF = -SdT - pdV + \mu dN\,. \tag{4.76}$$

The free eneergy can be calculated within the canonical ensemble; in fact we have previously (in the context of statistical mechanics) defined the free energy such that $F = -k_{\mathrm{B}}T\ln Z_C$, where Z_C is the canonical partition sum. This definition is equivalent to the above definition, which can be seen as follows. From

$$\begin{aligned} S &= -k_{\mathrm{B}}\mathsf{Tr}\,(\rho_C \ln \rho_C) = k_{\mathrm{B}}\ln Z_C + k_{\mathrm{B}}\beta\langle\mathcal{H}\rangle \qquad (4.77)\\ &= \frac{1}{T}\,(k_{\mathrm{B}}T\ln Z + U) \end{aligned}$$

we see that

$$F(T,V,N) = U - TS = -k_{\mathrm{B}}T\ln Z_C(\beta,V,N) \tag{4.78}$$

The minimum energy principle at fixed entropy translates into a minimum free energy principle at fixed temperature. This is obvious from the Legendre transform. It can also be illustrated physically upon considering the equilibrium of a system in contact with a thermostat at temperature T. Let

$$S_{\mathrm{tot}} = S + S_{\mathrm{th}} \tag{4.79}$$
$$U_{\mathrm{tot}} = U + U_{\mathrm{th}} \tag{4.80}$$
$$\tag{4.81}$$

be the total entropy and energy, respectively. The maximum entropy principle states that

$$d(S + S_{\mathrm{th}}) \;=\; 0 \tag{4.82}$$
$$d^2(S + S_{\mathrm{th}}) \leq 0 \tag{4.83}$$

i.e. the thermal equilibrium state is at a maximum of the entropy (for an isolated system!). Since the heat exchange with the thermostat is quasi-static and at constant temperature T we have

$$dS_{\mathrm{th}} = \frac{1}{T}dU_{\mathrm{th}} = -\frac{1}{U}dU \tag{4.84}$$

and

$$d^2S_{\mathrm{th}} = -\frac{1}{T}d^2U \tag{4.85}$$

These relations allow us to get rid of the thermostat and write down the conditions of equilibrioum for the system we are interested in:

$$d(S - \frac{1}{T}U) \;=\; 0 \tag{4.86}$$
$$d^2(S - \frac{1}{T}U) \;<\; 0 \tag{4.87}$$

The form $S - U/T$ of the expression, the maximum of which we must find, reflects the tendencies to which the system is subject. The first term expresses thtropy S increases. The second term expresses that this effect is opposed and controlled by the coupling to the thermostat. The latter appears solely through its temperature T. The energy U of the system tends to decrease, as U enters with a minus sign, and this tendency is more strongly, the lower the temperature T of the thermostat, as the coefficient of U is $1/T$.

Hence we can formulate the *principle of minimum free energy*: When a system is maintained at a temperature T and when certain internal exchanges allow the $\{A_i\}$ parameters, other than the total energy U, to change in a domain $\mathcal{A}$, the equilibrium values of these parameters are obtained by looking for the minimum of the free energy F on $\mathcal{A}$ for a given value of T.

We can define other thermodynamic potentials as follows:

Free enthalpy (Gibbs free energy)

$$G(T, P, N) := U - TS + PV \tag{4.88}$$

with

$$dG = -SdT + \mu dN + VdP \tag{4.89}$$

It can be derived from the isobaric-isothermal ensemble such that

$$G = -k_{\mathrm{B}} T \ln Z_p(\beta, P, N) \tag{4.90}$$

$G \rightarrow$ Min at fixed T and P upon variation of the particle number N.

Enthalpy

$$H(S, P, N) := U + PV \tag{4.91}$$

$$dH = TdS + VdP + \mu dN \tag{4.92}$$

Grand canonical potential

$$\Phi(T, V, \mu) := U - TS - \mu N = -k_{\mathrm{B}} T \ln Z_G \tag{4.93}$$

$$d\Phi = -SdT - PdV - Nd\mu \tag{4.94}$$

$\Phi \rightarrow$ Min at fixed T and μ for variation in the volume V.

to be completed

4.3 Thermodynamic Identities

4.3.1 Gibbs-Duhem Relations

Changing the volume V by a factor λ multiplies all extensive variables by the same factor λ, such that the entropy satisfies the identity

$$S(\lambda U, \lambda\{A_i\}) = \lambda S(U, \{A_i\}) \tag{4.95}$$

for an extensive system. Upon differentiating this expression with respect to λ and setting $\lambda = 1$, we get

$$\frac{U}{T} + \sum_{i\geq 1} \gamma_i A_i = S(U, \{A_i\}) \tag{4.96}$$

between the intensive variables T, γ_i, U/S and A_i/S. The differential form of the Gibbs-Duhem relation is derived from Eq.4.96 and using Eq.4.70, which gives

$$Ud(\frac{1}{T}) + \sum_{i\geq 1} A_i d\gamma_i = 0 \tag{4.97}$$

expressing the fact that for fixed $(U, \{A_i\})$ the intensive variables T, γ_i are not independent.

For a one-component gas the Gibbs-Duhem relations reduce to

$$U = TS - PV + \mu N \tag{4.98}$$

$$0 = SdT - VdP + Nd\mu \tag{4.99}$$

As a consequence of the Gibbs-Duhem relation for the energy we can find analogous relations of other thermodynamic potentials. For, example consider the Gibbs free energy

$$G = U - TS + PV \tag{4.100}$$

which upon using Eq.4.98 reduce to

$$G = \mu N \tag{4.101}$$

With

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial N}\right)_{T,P} + \mu \tag{4.102}$$

we see that the chemical potential μ is indpendent of the particle number N, such that we can write

$$\frac{G(T,P,N)}{N} = \mu(T,P) \tag{4.103}$$

i.e. for a homogeneous thermodynamic system at constant temperature and constant pressure the Gibbs free energy per particle is identical to the chemical energy, which is a function of T and P only.

Similarly, one can show that the grand canonical potential for homogeneous systems may be written as

$$\frac{\Phi(T,V,\mu)}{V} = -P(T,\mu) \tag{4.104}$$

4.3.2 Response Coefficients and Maxwell Relations

In many experiments we do not measure the equation of state (i.e. information derived from the first derivatives of the thermodynamic potentials), but second derivatives of some fundamental relation. As an example let us consider the Gibbs free energy $G = G(T, P, N)$ of a one-component gas, where we keep N fixed and vary T and P. Then the total differential reads

$$dG = -SdT + VdP \tag{4.105}$$

i.e.

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_P && (4.106)\\ V &= \left(\frac{\partial G}{\partial P}\right)_T && (4.107)\end{aligned}$$

The second derivatives are

$$\begin{aligned} \frac{\partial^2 G}{\partial T^2} &= -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_p}{T} && (4.108)\\ \frac{\partial^2 G}{\partial T \partial P} &= \left(\frac{\partial V}{\partial T}\right)_P = V\alpha && (4.109)\\ \frac{\partial^2 G}{\partial P^2} &= \left(\frac{\partial V}{\partial P}\right)_T = -V\kappa_T && (4.110)\end{aligned}$$

where we have defined the response functions

$$\begin{aligned} C_p &= T\left(\frac{\partial S}{\partial T}\right)_P \quad \text{(specific heat at constant pressure)} && (4.111)\\ \alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{(thermal expansion coefficient)} && (4.112)\\ \kappa_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{(isothermal compressibility)} && (4.113)\end{aligned}$$

These three response coefficients (for fixed N) form a *complete set* of second derivatives. There are plenty of other response coefficients one can define. But, since one thermodynamic potential (here G) contains the full thermodynamic information, any other second derivative of any other thermodynamic potential can be written in terms of the above three response coefficients. The following of this subsection will provide us with some mathematical tools to rewrite one set of thermodynamic response functions in terms of others.

The first set of helpful identities are the **Maxwell relations**. They are nothing but the simple fact that we can interchange the order in partial derivatives of a function F

$$\frac{\partial^2 F}{\partial x_i \partial x_j} = \frac{\partial^2 F}{\partial x_j \partial x_i} \tag{4.114}$$

applied to the thermodynamic potentials. For simplicity, let's again consider a one-component gas with N fixed. Then we get the following set of relations

$$\text{Internal energy } U: \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{4.115}$$

$$\text{Free energy } F: \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{4.116}$$

$$\text{Free enthalpy } G: \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{4.117}$$

$$\text{Enthalpy } H: \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{4.118}$$

4.3.3 Jacobians and Transfomations

In the previous sections all thermodynamic identities were referring to sets of conjugate variables (γ_i, A_i). Often one would like to calculate derivatives of some macroscopic variable with respect to another arbitrary thermodynamic variable. Such manipulations are best performed by using the concept of Jacobians. If we have a set of n functions $y_1, y_2, \cdots y_n$ of n variables $x_1, x_2, \cdots x_n$, the Jacobian is defined as the determinand of all the partial derivatives

$$\frac{\partial(y_1, y_2, \cdots, y_n)}{\partial(x_1, x_2, \cdots x_n)} \equiv \det \left| \frac{\partial y_i}{\partial x_j} \right| \tag{4.119}$$

For example,

$$\frac{\partial(f, g)}{\partial(u, v)} = \det \begin{vmatrix} \frac{\partial f}{\partial u} & \frac{\partial f}{\partial v} \\ \frac{\partial g}{\partial u} & \frac{\partial g}{\partial v} \end{vmatrix} \tag{4.120}$$

The Jacobians are antisymmetric with respect to the x and y variables. They occur in the calculation of response coefficients through relations like

$$\left(\frac{\partial y}{\partial x_1}\right)_{x_2, \cdots, x_n} = \frac{\partial(y, x_2, \cdots, x_n)}{\partial(x_1, x_2, \cdots, x_n)} \tag{4.121}$$

Under changes of variables, they have simple properties which result from those of determinants, and which are refleczed ub rge important *group laws*

$$\begin{aligned} \frac{\partial(y_1, y_2, \cdots, y_n)}{\partial(x_1, x_2, \cdots x_n)} &= \left(\frac{\partial(x_1, x_2, \cdots x_n)}{\partial(y_1, y_2, \cdots, y_n)}\right)^{-1} \\ &= \frac{\partial(y_1, y_2, \cdots, y_n)}{\partial(z_1, z_2, \cdots, z_n)} \frac{\partial(z_1, z_2, \cdots, z_n)}{\partial(x_1, x_2, \cdots x_n)} = \end{aligned} \tag{4.122}$$

Example:

$$\left(\frac{\partial f}{\partial u}\right)_v = \frac{\partial(f, v)}{\partial(u, v)} = \frac{\partial(f, v)}{\partial(f, u)} \frac{\partial(f, u)}{\partial(u, v)} = \frac{\partial(f, v)}{\partial(f, u)} \left(-\frac{\partial(f, u)}{\partial(v, u)}\right) = -\frac{\left(\frac{\partial f}{\partial v}\right)_u}{\left(\frac{\partial u}{\partial v}\right)_f}$$

4.4 Phase equilibria of one-component systems

In nature we find matter in different phases: gas, liquid, solid, ...

– **to be completed** –

A typical phase diagram for a one-component system whose macroscopic state can be described by (P, V, T) looks like Fig.4.5. The solid lines separate the (P, T)–plane into regions in which a unique phase is the stable thermodynamic state. As the system passes through one of these lines, called *coexistence curves*, a *phase transition* occurs. In Figure 4.5 there are two special points, the *triple point* (P_t, T_t), and the *critical point* (P_c, T_c). At the critical point the properties of the fluid and the vapor phase become identical. We will come back to these special points in later chapters of these lecture notes. Note that the properties of the system vary smoothly along any curve which does not cross a coexistence curve. Thus, it is possible to pass continuously from the vapor to the liquid phase by taking the system to high enough temperatures, increasing the pressure, and then lowering the temperature again. It is not possible to avoid the liquid-solid coexistence curve; this curve extends to $P = \infty$, $T = \infty$ (as far as we know). The analogous phase diagram for a ferromagnetic substance is shown in Figure4.6 in the (H, T) plane with a critical point at $H_c = 0$, T_c.

– **figure missing** –

Figure 4.5: Schematic phase diagram of a simple one component fluid in the (P, T)–plane.

– **figure missing** –

Figure 4.6: Schematic phase diagram for a ferromagnet in the (H, T)-plane.

Let's now consider a system on one of the coexistence lines, say the one between gas and liquid. The coexistence phase may be thought of as two equilibrium systems in contact with each other. Then, we find from the maximum entropy principle for

$$S(U, V, N) = S_g(U_g, V_g, N_g) + S(U_l, V_l, N_l) \tag{4.123}$$

upon allowing the exchange of energy, volume and material that $T_g = T_l$, $P_g = P_l$ and $\mu_g = \mu_l$, respectively. From the Gibbs-Duhem relation we obtain

$$\mu_g(P, T) = \mu_l(P, T) \tag{4.124}$$

i.e. a unique *line* (phase boundary) $P = P(T)$ in the (P, T) diagram. At the triple point we have three phase coexistence, and hence

$$\mu_g(P, T) = \mu_l(P, T) = \mu_s(P, T) \tag{4.125}$$

defines a unique *point* in the (P, T) diagram. Note, that this is why one defines the temperature scale at the triple point.

We now would like to learn something about the *shape* of the coexistence curves. With $dG = -SdT + VdP + \mu dN$ and the Gibbs-Duhem relation $G = \mu N$ we have

$$d\mu = -sdT + vdP \tag{4.126}$$

where $s = S/N$ and $v = v/N$ are entropy and volume per particle. Since the equality Eq.4.124 holds along the entire coexistence curve we have

$$d\mu_f = d\mu_g : \quad -s_f dT + v_f dP = -s_g dT + v_g dP \tag{4.127}$$

This implies that the slope of the coexistence curve is related to the ratio of the entropy and volume differences of the two phases

$$\left(\frac{\partial P}{\partial T}\right)_{\text{co}} = \frac{s_g - s_f}{v_g - v_f} = \frac{\Delta s}{\Delta v} \tag{4.128}$$

We now define the *latent heat* (per particle) as

$$q = T(s_g - s_f) \tag{4.129}$$

such that

$$\left(\frac{\partial P}{\partial T}\right)_{\text{co}} = \frac{q}{T(v_g - v_f)} \tag{4.130}$$

Equation 4.130 is known as the **Clausius-Clapeyron** equation. It is valid on any coexistence curve. For the particular case of a liquid to vapor transition with $v_g \gg v_L$ and $v_g = k_{\text{B}}T/P$ it reduces to

$$\left(\frac{\partial P}{\partial T}\right)_{\text{co}} \approx \frac{q}{k_{\text{B}}T^2} P \tag{4.131}$$

and if $q > 0$ is roughly constant along the coexistence curve we have

$$P(T) \approx P_0 \exp\left[-\frac{q}{k_{\text{B}}T}\right] . \tag{4.132}$$

For a discussion of the van der Waals equation and the Maxwell construction see chapter 5.4 in Schwabl “Statistische Mechanik”

4.5 Chemical equilibria of gas mixtures

One interesting fact about chemical reactions is that they hardly ever go to completion. Consider, for example, the dissociation of water into H^+ and OH^- ions:

$$H_2O \leftrightarrow H^+ + OH^- \tag{4.133}$$

Under ordinary conditions, this reaction tends strongly to go to the left; an ordinary glass of water at equilibrium contains about 500 million water molecules for every pair of H^+ and OH^- ions. Naively, we tend to think of the water molecule as being "more stabe" than the ions. But this can't be the whole story – otherwise there would be no ions in a glass full of water, when in fact there are quadrillions of them. To get the correct physical picture we have to consider the Gibbs free energy $G(T, P, \mu) = U - TS + PV$, which is the proper thermodynamical potential for chemical reactions which usually take place in systems which are in contact with reservoirs at constant temperature and pressure. Chemical equilibrium of a given reaction is acieved when the Gibbs free energy is at a minimum,

$$0 = dG = \sum_i \mu_i dN_i \,, \tag{4.134}$$

where μ_i are the chemical potentials of the molecules participating in the chemical reaction. The changes in the N_i are not independent. In our example an increase of one H^+ is always accompanied by an increase of one OH^- and a decrease of one H_2O. One set of possible changes is

$$dN_{H_2O} = -1 \,, \quad dN_{H^+} = 1 \,, \quad dN_{OH^-} \,. \tag{4.135}$$

Plugging these numbers into equation 4.134 yields

$$\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-} \,. \tag{4.136}$$

In general, we may write a chemical reaction in the form

$$\sum_i \nu_i A_i = 0 \tag{4.137}$$

where A_i are the reacting species and ν_i denote the stochiometric coefficients of the chemical reactions. In our simple example we have $A_i = \{H_2 0, H^+, OH^-\}$ and $\nu_{H_2O} = 1$, $\nu_{H^+} = -1$, and $\nu_{OH^-} = -1$. If we parametrize the reaction by λ, Eq.4.137 requires

$$dN_i = \nu_i \lambda \tag{4.138}$$

and hence

$$\sum_i \mu_i \nu_i = 0 \,, \tag{4.139}$$

as the general condition for chemical equilibrium; it is obtained from the chemical reaction equation 4.137 by simply replacing the chemical symbol of a given species by its chemical potential.

The next step in understanding chemical equilibrium is to write each chemical reaction potential μ_i in terms of the concentration of that species; then one can solve for the equilibrium concentrations. This will depend on the specific conditions under which the chemical reaction takes place. Here we will restrict ourselves to situations where the chemical reaction takes place in a gas mixture or in a dilute solution. Then the chemical potential reads

$$\mu_i = k_{\mathrm{B}}T \ln P_i + \chi_i(T) \tag{4.140}$$

where $P_i = c_i P$ is the partial pressure of the ith component in the gas mixture. Here P is the total pressure of the gas mixture and $c_i = N_i/N$ are the concentrations of the various components of the chemical reaction. The quantity ... **to be completed**

One way to derive Eq.4.140 reads as follows. Starting from the equation of state of an ideal gas $PV = Nk_{\mathrm{B}}T$ and $dF = -SdT - PdV + \mu dN$ we have

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P = -\frac{Nk_{\mathrm{B}}T}{V} \tag{4.141}$$

and hence

$$F(T,V,N) = F(T,V_0,N) - Nk_{\mathrm{B}}T \ln(V/V_0) \tag{4.142}$$

where we have taken as an integration constant the free energy at a reference volume V_0. Since the free energy is an extensive quantity we can write

$$F(T,V,N) = Nf(T, v = V/N) \tag{4.143}$$

with

$$f(T,v) = f(T,v_0) + k_{\mathrm{B}}T \ln v_0/v\,. \tag{4.144}$$

The first term includes the kinetic energy of the center of mass motion and the free energy of inner degrees of freedom such as rotation and vibration. The second term is the entropy of the center of mass motion. If we now consider a mixture of non-interacting ideal gases the free energy simply is the sum of the individual free energies

$$F(T,V,\{N_i\}) = \sum_i F_i(T,V,N_i) = \sum_i N_i \left[f_i(T,v_0) + k_{\mathrm{B}}T \ln(N_i v_0/V)\right] \tag{4.145}$$

This yields for the equation of state of the gas mixture

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,\{N_i\}} = \sum_i \frac{N_i k_{\mathrm{B}}T}{V} \tag{4.146}$$

This suggest to define the partial pressure of component i

$$P_i = \frac{N_i k_{\mathrm{B}}T}{V} = \frac{N_i}{N}\frac{Nk_{\mathrm{B}}T}{V} = c_i P\,, \tag{4.147}$$

where $c_i = N_i/N$ with $N = \sum_i N_i$. The chemical potential then becomes

$$\begin{aligned}\mu_i(T,P,\{c_i\}) &= \frac{\partial F}{\partial N_i} = f_i(T,v_0) + k_{\mathrm{B}}T \ln(N_i v_0/V) + k_{\mathrm{B}}T \\ &= f_i(T,v_0) + k_{\mathrm{B}}T \ln(c_i P v_0/k_{\mathrm{B}}T) + k_{\mathrm{B}}T \\ &\equiv \chi_i(T) + k_{\mathrm{B}}T \ln(c_i P) \end{aligned} \tag{4.148}$$

This allows us now to rewrite the condition for chemical equilibrium in terms of the concentrations as

$$\sum_i \nu_i \chi_i(T) + \sum_i \nu_i k_{\mathrm{B}}T \ln(c_i P) = 0 \tag{4.149}$$

which is equivalent to

$$\prod_i P_i^{\nu_i} = \exp\left[-\sum_i \nu_i \chi_i(T)/k_\mathrm{B}T\right] \equiv K_p(T) \tag{4.150}$$

known as the **law of mass action** ("Massenwirkungsgesetz") by Guldberg and Waage (1864). If instead of the partial pressures P_i we use the concentrations c_i the law of mass action reads

$$\prod_i c_i^{\nu_i} = \exp\left[-\sum_i \nu_i \chi_i(T)/k_\mathrm{B}T\right] P^{-\sum_i \nu_i} \equiv K_c(P,T) \tag{4.151}$$

It is important to note that the constant $K_c(P,T)$ is a function of temperature and pressure only. It does not depend on the initial concentrations of the reacting species. The constant is called the equilibrium constant ("Massenwirkungskonstante"). The dependence of the equilibrium constant on pressure P is completely determined by the factor $P^{-\sum_i \nu_i}$. In order to find the dependence of the equilibrium constant on temperature one needs to specify the function $\chi_i(T)$.

Chapter 5

Ideal Quantum Gases

5.1 Introduction

In this chapter we are going to study ideal quantum gases, i.e. systems of N non-interacting identical particles. A major result of quantum mechanics is that the quantum state describing the N-particle state is *not* simply the product of N single-particle states, but a properly symmetrized or antisymmetrized expression. Among others, this implies that it would be wrong to write the partition sum of a non-interacting quantum system as

$$Z = \frac{1}{N!} Z_1^N \,, \tag{5.1}$$

where Z_1 is the partition sum of one particle. The problem is that the counting factor $N!$, the number of ways of interchangug particles among their various single-particle states, is correct only if the particles are always in *different* states.

To better understand this issue let's consider a very simple example: a system containing two non-interacting particles, either of which can occupy any of five states (see Fig. 5.1). Imagine that all five of these states have zero energy, so every Boltzmann factor equals 1. If the two particles are *distinguishable*, then each has five available single-particle states and the total number of system states is $Z = 5 \times 5 = 25$. If the two particels are *indistinguishable*, Eq. 5.1 would predict $Z = 5^2/2! = 12.5$. But, this can't be right, since Z must (for this system) be an integer.

– figure missing –

Figure 5.1: A simple model of five single-particle states, with two particles that can occupy these states.

So let's count the system states more carefully. Since the particles are indistinguishable, all that matters is the number of particles in any given state. One can therefore represent any system state by a sequence of five integers, each representing the number of particles in a particular state. For instance, 01100 would represent the system state in which the second and third state each contain one particle, while the rest contain none. Here, then, are all the allowed system states:

$$11000 \qquad 01010 \quad 20000 \tag{5.2}$$

$$10100 \qquad 01001 \quad 02000 \tag{5.3}$$

$$10010 \qquad 00110 \quad 00200 \tag{5.4}$$

$$10001 \qquad 00101 \quad 00020 \tag{5.5}$$

$$01100 \qquad 00011 \quad 00002 \tag{5.6}$$

There are 15 system states in all, of which 10 have the two particles in different single-particle states while 5 have the two particles in the same single-particle state. Each of the first 10 system states would actually be *two* different system states if the particles were distinguishable, since then they could be places in either order. These 20 system states, plus the last 5 listed above, make the 25 counted in the previous paragraph. The factor of $1/N!$ in Eq. 5.1 correctly cuts the 20 down to 10, but also incorrectly cuts out half of the last five states; note that in the last five states *both* particles are in the *same* single-particle state.

This simple example illustrates the importance of the correct counting resulting from the fact that identical particles in the same quantum state are indistinguishable. The consequences of this will become evident in the next chapters. Before we go into more mathematical details, let us ask when these quantum effects will really matter. If the number of available single-particle states is much greater than the number of particles, $Z_1 \gg N$, the chance of any of two particles wanting to occupy the same state is negligible. More precisely, only a tiny fraction of all system states have a significant number of states doubly occupied. For an ideal gas, the single-particle partition function is $Z_1 = V/\lambda^3$ with

$$\lambda = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}} \tag{5.7}$$

is the thermal de Broglie wavelength. It is the de Broglie wavelength corresponding to a particle with a kinetic energy proportional to thermal energies, $p^2/2m \sim k_{\mathrm{B}}T$. The condition $Z_1 \gg N$ translates into

$$\lambda^3 \ll \frac{V}{N} = v \tag{5.8}$$

i.e. to the dilute limit where the typical interparticle distance is much larger than the thermal de Broglie wavelength. Quantum effects are expected to become important once the wave packets of the particles overlap, $\lambda \approx v^{1/3}$. The dimensionless ratio λ^3/v will play a key role in what follows.

5.2 Grand canonical partition sum

5.2.1 Single-particle and system states

For an ideal gas (non-interacting particles) the Hamiltonian simply is the sum of the kinetic energies of the individual particles

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} . \tag{5.9}$$

Since the particles are non-interacting we start our considerations with a single particle. Let the particle be confined to a volume $V = L^3$ such that its wave function obeys periodic boundary conditions. Then, the momentum eigenstates $|\mathbf{p}\rangle$ correspond to plane waves

$$\varphi_{\mathbf{p}}(\mathbf{x}) = \langle \mathbf{x}|\mathbf{p}\rangle = \frac{1}{\sqrt{V}}\, e^{i\mathbf{p}\mathbf{x}/\hbar} , \tag{5.10}$$

where the momentum eigenvalues are given by

$$\mathbf{p} = \frac{2\pi\hbar}{L}(\nu_1, \nu_2, \nu_3) \quad \text{with} \quad \nu_i = 0,\, \pm 1,\, \pm 2,\, \cdots \tag{5.11}$$

The energy eigenvalues, also called single-particle energies, read

$$\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m} . \tag{5.12}$$

For particles with spin s we have to add the magnetic quantum numbers m_s to the momentum quantum numbers $\mathbf{p}$ to complete the set of quantum numbers for the single-particle space. Then we have the complete set of quantum numbers $p \equiv (\mathbf{p}, m_s)$ and the corresponding eigenkets $|p\rangle \equiv |\mathbf{p}\rangle|m_s\rangle$. Actually, the following considerations are valid for any set of one-particle energy levels ϵ_p, where p is a complete set of quantum numbers characterizing the single-particle states.

Up to now we have only solved the single-particle problem. From quantum mechanics we know that there are only two sets of N-particle states (system states), which can be constructed from the product of the single-particle states, a fully symmetrized and a fully anti-symmetrized product. They read

$$|p_1, p_2, \cdots, p_N\rangle = \mathcal{N} \sum_{P} (\pm 1)^P |p_1\rangle |p_2\rangle \cdots |p_N\rangle \tag{5.13}$$

where P denotes a permutation of $(1, 2, \cdots, N)$. Particles with fully symmetrized and anti-symmetrized product states are called **bosons** and **fermions**, respectively. The normalization factor reads

$$\mathcal{N} = \begin{cases} \frac{1}{\sqrt{N!}} \frac{1}{\sqrt{n_{p_1}! \, n_{p_2}! \cdots}} & \text{for bosons} \\ \frac{1}{\sqrt{N!}} & \text{for fermions} \end{cases} \tag{5.14}$$

Due to the symmetrization the system state is *completely characterized in terms of the occupation numbers* $\{n_p\}$ *of the single-particle states* $|p\rangle$; the occupation number n_p counts the number of particles in quantum state $|p\rangle$. For bosons the occupations numbers are unrestricted, $n_p = 0, 1, 2, \cdots$, whereas for fermions we have $n_p = 0, 1$ (Pauli exclusion principle). This is the only information we will need in the following to determine the partition sum and the resulting equations of state.

The total particle number N and energy E in terms of the occupation numbers n_p read

$$N = \sum_p n_p \tag{5.15}$$

$$E(\{n_p\}) = \sum_p n_p \epsilon_p \tag{5.16}$$

5.2.2 Partition sum and distribution function

With this we can write for the grand canonical partition sum

$$Z_G = \sum_{N=0}^{\infty} \sum_{\{n_p\}'} \exp\left\{-\beta\left[E(\{n_p\}) - \mu N\right]\right\} , \tag{5.17}$$

where $\{n_p\}'$ indicates that the summation over all sets of occupation numbers has to be such that it obeys the constraint $\sum_p n_p = N$. The latter constraint makes it difficult to calculate the canonical partition sum. The advantage of using the grand canonical ensemble is that we sum over all possible values of the constraint, such that we can write

$$\sum_{N=0}^{\infty} \sum_{\{n_p\}'} \ldots = \sum_{\{n_p\}} \ldots \quad , \tag{5.18}$$

where now the summation over the sets $\{n_p\}$ is unconstrained! With this the partition sum simplifies to

$$\begin{aligned} Z_G &= \sum_{\{n_p\}} \exp\left\{-\beta\left[E(\{n_p\}) - \mu N\right]\right\} \\ &= \sum_{\{n_p\}} \exp\left[-\beta \sum_p (\epsilon_p - \mu) n_p\right] \\ &= \prod_p \sum_{n_p=0}^{\infty} \exp\left[-\beta(\epsilon_p - \mu) n_p\right] \\ &= \prod_p \begin{cases} \sum_{n_p=0}^{\infty} e^{-\beta(\epsilon_p-\mu)n_p} \\ \left[1 + e^{-\beta(\epsilon_p-\mu)}\right] \end{cases} \\ &= \prod_p \begin{cases} \left[1 - e^{-\beta(\epsilon_p-\mu)}\right]^{-1} \\ \left[1 + e^{-\beta(\epsilon_p-\mu)}\right] \end{cases} \quad , \end{aligned} \tag{5.19}$$

where the upper and lower case correspond to bosons and fermions, respectively. For bosons we have used the well known formula for a geometric series, $\sum_{n=0}^{\infty} x^n = 1/(1-x)$. Note that the geometric series converges only if $x < 1$, or equivalently for $\mu < \epsilon_p$ for all quantum numbers p. In other words, for bosons the chemical potential must be less than the ground state energy ϵ_0, which for particles confined to a box of volume V equals to zero. For fermions there is no such constraint on the chemical potential.

From the partition sum we read off the grand canonical potential

$$\Phi = -k_{\mathrm{B}} T \ln Z_G = \pm k_{\mathrm{B}} T \sum_p \ln\left(1 \mp e^{-\beta(\epsilon_p - \mu)}\right) . \tag{5.20}$$

We are now in a position to use the machinery of (statistical) thermodynamics to find the equations of state and any other desired thermodynamic quantity. Since $d\Phi = -SdT - PdV - Nd\mu$ the mean particle number is[1]

$$\begin{aligned} N &= -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -(\pm k_{\mathrm{B}} T) \sum_p \frac{\mp \beta e^{-\beta(\epsilon_p - \mu)}}{1 \mp e^{-\beta(\epsilon_p-\mu)}} \\ &= \sum_p \frac{1}{e^{\beta(\epsilon_p - \mu)} \mp 1} \equiv \sum_p n(\epsilon_p) , \end{aligned} \tag{5.21}$$

where

$$n(\epsilon_p) = \frac{1}{e^{\beta(\epsilon_p-\mu)} \mp 1} \tag{5.22}$$

can be shown[2] to be identical to the average occupation number of state $|p\rangle$, $n(\epsilon_p) = \langle n_p \rangle$. The distribution functions for bosons and fermions are compared with the Boltzmann distribution $e^{-\beta(\epsilon_p-\mu)}$ in Fig. 5.2. The distribution function for fermions

$$n_{\mathrm{FD}}(\epsilon_p) = \frac{1}{e^{\beta(\epsilon_p-\mu)} + 1} \tag{5.23}$$

---

[1] Note that we use N as a symbol for the mean particle number despite the fact that the particle number is not fixed in the grand canonical ensemble. There are fluctuations in the particle number, which oen can calcalate easily.

[2] The corresponding calculation reads as follows

$$\begin{aligned} \langle n_p \rangle &= \mathsf{Tr}\,(\rho_G n_p) \\ &= \sum_{\{n_k\}} n_p \exp\left[-\sum_k \beta(\epsilon_k - \mu) n_k\right] / \sum_{\{n_k\}} \exp\left[-\sum_k \beta(\epsilon_k-\mu) n_k\right] \\ &= \sum_{n_p} n_p \exp\left[-\beta(\epsilon_p - \mu) n_p\right] / \sum_{n_p} \exp\left[-\beta(\epsilon_p-\mu)n_p\right] \\ &= -\frac{\partial}{\partial x} \ln\left(\sum_{n_p} e^{-x n_p}\right)\Bigg|_{x=\beta(\epsilon_p-\mu)} = -\frac{\partial}{\partial x} \ln(1 \mp e^{-\beta(\epsilon_p-\mu)})^{\mp 1} \\ &= \pm \frac{-(\mp) e^{-\beta(\epsilon_p-\mu)}}{1 \mp e^{-\beta(\epsilon_p-\mu)}} = \frac{1}{e^{\beta(\epsilon_p-\mu)} \mp 1} \end{aligned}$$

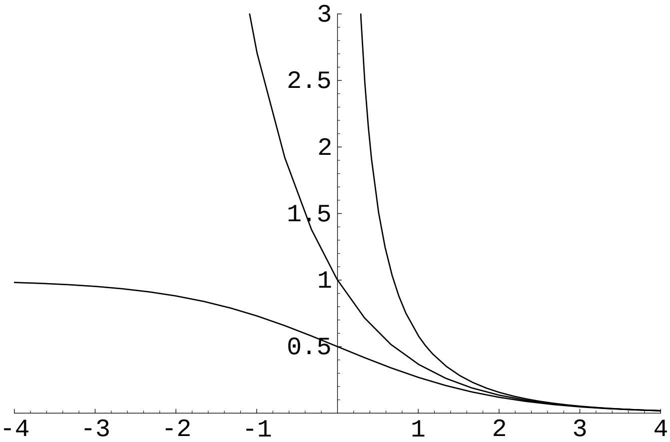

Figure 5.2: Illustration of the Fermi, Boltzmann and Fermi distribution function $n(\epsilon_p) = \langle n_p \rangle$ (from left to right) plotted as a function of $x = (\epsilon_p - \mu)/k_{\mathrm{B}}T$. They all become identical for $\epsilon_p \gg \mu$ but strongly differ for $\epsilon_p \leq \mu$.

is called the **Fermi-Dirac (FD) distribution function**. It goes to zero when $\epsilon_p \gg \mu$, and goes to 1 when $\epsilon_p \ll \mu$. Thus, states with energy much less than the chemical potential μ tend to be occupied, while states with energy much greater than μ tend to be unoccupied. The FD distribution function is 1/2 at $\epsilon_p = \mu$ and falls off from 1 to 0 over a scale proportional to $k_{\mathrm{B}}T$. The distribution function for bosons

$$n_{\mathrm{BE}}(\epsilon_p) = \frac{1}{e^{\beta(\epsilon_p - \mu)} - 1} \tag{5.24}$$

is called the **Bose-Einstein (BE) distribution function**. Like the FD distribution function it goes to zero when $\epsilon_p \gg \mu$. Unlike the FD distribution, however, it goes to infinity as ϵ_p approaches μ from above. It would be negative if ϵ_p could be less than μ. Hence, for bosons, the chemical potential μ must be less than the ground state energy ϵ_0; we have reached the same conclusion above from the convergence properties of the geometric series in the calculation of the partition sum.

We can find the internal energy U by a Legendre transform of the grand canonical potential $U = \Phi + TS + \mu N$, where

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} = -\frac{\partial \beta}{\partial T}\left(\frac{\partial \Phi}{\partial \beta}\right)_{V,\mu} = \frac{1}{k_{\mathrm{B}}T^2}\left(\frac{\partial \Phi}{\partial \beta}\right)_{V,\mu}. \tag{5.25}$$

This gives

$$U = \left(\frac{\partial(\beta\Phi)}{\partial \beta}\right)_{V,\mu} + \mu N\,. \tag{5.26}$$

A simple calculation

$$\begin{aligned} U &= \pm\frac{\partial}{\partial\beta}\sum_p \ln(1\mp e^{-\beta(\epsilon_p-\mu)}) + \mu N \\ &= \pm\sum_p \frac{\pm(\epsilon_p-\mu)e^{-\beta(\epsilon_p-\mu)}}{1\mp e^{-\beta(\epsilon_p-\mu)}} + \mu N \\ &= \sum_p \epsilon_p n(\epsilon_p) - \mu\sum_p n(\epsilon_p) + \mu N \end{aligned}$$

then yields

$$U = \sum_p \epsilon_p n(\epsilon_p) = \sum_p \epsilon_p\langle n_p\rangle\,. \tag{5.27}$$

5.2.3 Large volume limit and equations of state

We have expressed some thermodynamic functions as sums over the single-particle states p, of functions $\varphi(\epsilon_p)$ of the energy eigenvalues ϵ_p. One often has to consider the limit where the extent of the system becomes infinite; the ϵ_p spectrum then becomes a continuum, i.e. so closely space that the sums may be repalced by integrals.

For specificity, let us come back to particles confined to a box of volume $V = L^3$. Then, the sum over the magnetic quantum number m_s simply gives the spin degeneracy factor $g = 2s+1$. As $L \to \infty$ the sum over ν_α becomes an integral $\sum_{\nu_\alpha} \to \int d\nu_\alpha$ such that

$$\sum_{\nu_1,\nu_2,\nu_3} \to \int d^3\nu = \left(\frac{L}{2\pi\hbar}\right)^3 \int d^3p\,, \tag{5.28}$$

where $(2\pi\hbar)^3/V$ is the volume in momentum space occupied by one single-particle state. In summary we have[3]

$$\sum_p \to g\,\frac{V}{(2\pi\hbar)^3}\int d^3p\,. \tag{5.29}$$

Then straightforward calculations yield the results

$$\frac{N}{V} = \frac{1}{v} = \frac{g}{\lambda^3}\begin{cases} g_{3/2}(z) & \text{for bosons} \\ f_{3/2}(z) & \text{for fermions} \end{cases} \tag{5.30}$$

$$\Phi = -PV = -\frac{gV}{\lambda^3}k_{\rm B}T\begin{cases} g_{5/2}(z) & \text{for bosons} \\ f_{5/2}(z) & \text{for fermions} \end{cases} \tag{5.31}$$

---

[3] One gets the same result for particles confined to a box, where the potential is zero inside and infinite outside the box (rigid walls). More generally, one can prove that the result remains valid for a large box of arbitrary shape with arbitrary boundary conditions. This result ensures the existence of the thermodynamic limit for quantum gases without interactions and the extensivity of various thermodynamic quantities. A notable exception - as we will discuss later - are Bose gases at low temperature. In that case the integrand becomes singular as $p \to 0$ and the replacement of the sum by the integral is no longer justified.

where the fugacity $z = e^{\beta\mu}$ and

$$\frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{e^x z^{-1} \mp 1} = \begin{cases} g_\nu(z) \\ f_\nu(z) \end{cases} \tag{5.32}$$

are generalized ζ-functions. $\Gamma(\nu) = \int_0^\infty dt e^{-t} t^{\nu-1}$ is the Gamma-function with the properties $\Gamma(\frac{1}{2}) = \sqrt{\pi}$ and $\Gamma(\nu+1) = \nu\Gamma(\nu)$; see Fig.5.3 for bosons and ?? for fermions.

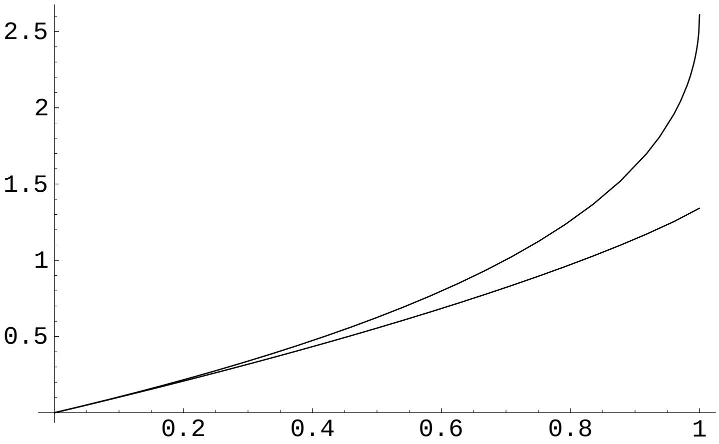

Figure 5.3: The generalized ζ-functions (or polylogarithms) $g_{3/2}(z)$ (top) and $g_{5/2}(z)$ (bottom) as a function of the fugacity $z = e^{\beta\mu}$; in *Mathematica* $g_n(z) = \text{PolyLog}[n, z]$.

Interestingly, one can show that

$$PV = \frac{2}{3} E \tag{5.33}$$

the same relation as for a classical ideal gas.

The details of the calculations for the mean particle number read as follows

$$\begin{aligned}
N &= \sum_p n(\epsilon_p) = g \frac{V}{(2\pi\hbar)^3} \int d^3p\, n(\epsilon_p) \\
&= g \frac{V}{(2\pi\hbar)^3} 4\pi \int dp\, p^2 n(\epsilon_p) \Big|_{\epsilon = p^2/2m} \\
&= g \frac{V}{(2\pi\hbar)^3} \frac{1}{2} 4\pi (2m)^{3/2} \int d\epsilon\, \sqrt{\epsilon} n(\epsilon) \Big|_{x=\beta\epsilon} \\
&= g \frac{V}{(2\pi\hbar)^3} 2\pi (2m)^{3/2} (k_\mathrm{B}T)^{3/2} \int dx\, \sqrt{x} n(x) \\
&= Vg \left(\frac{\sqrt{2\pi m k_\mathrm{B} T}}{h} \right)^{3/2} \frac{2}{\sqrt{\pi}} \int dx\, \sqrt{x} n(x) \\
&= \frac{V}{\lambda^3} \frac{2g}{\sqrt{\pi}} \int_0^\infty dx \frac{\sqrt{x}}{e^x z^{-1} \mp 1} = \frac{g}{\lambda^3} \begin{cases} g_{3/2}(z) & \text{for bosons} \\ f_{3/2}(z) & \text{for fermions} \end{cases}
\end{aligned}$$

and similarly for the grand canonical potential

$$\begin{aligned}
\Phi &= \pm k_{\mathrm{B}}T\sum_p \ln(1 \mp e^{-\beta(\epsilon_p-\mu)}) \\
&= \pm k_{\mathrm{B}}T\frac{gV}{\lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty dx\sqrt{x}\ln(1\mp e^{-x}z)\Big|_{\text{partial integration}} \\
&= \pm k_{\mathrm{B}}T\frac{gV}{\lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty dx(-\frac{2}{3}x^{3/2})\frac{\pm e^{-x}z}{1\mp e^{-x}z} \\
&= -\frac{gV}{\lambda^3}k_{\mathrm{B}}T\frac{4}{3\sqrt{\pi}}\int_0^\infty dx\frac{x^{3/2}}{e^xz^{-1}\mp 1} = -\frac{gV}{\lambda^3}k_{\mathrm{B}}T\begin{cases} g_{5/2}(z) & \text{for bosons} \\ f_{5/2}(z) & \text{for fermions}\end{cases}
\end{aligned}$$

and the energy

$$E = g\frac{V}{(2\pi\hbar)^3}\int d^3p\,\epsilon_p n(\epsilon_p) \tag{5.34}$$

$$= \frac{1}{\lambda^3}\frac{2gV}{\sqrt{\pi}}k_{\mathrm{B}}T\int_0^\infty dx\frac{x^{3/2}}{e^xz^{-1}\mp 1} \tag{5.35}$$

$$= \frac{1}{\lambda^3}\frac{2gV}{\sqrt{\pi}}k_{\mathrm{B}}T\frac{3\sqrt{\pi}}{4}\begin{cases} g_{5/2}(z) & \text{for bosons} \\ f_{5/2}(z) & \text{for fermions}\end{cases} \tag{5.36}$$

$$= -\frac{3}{2}\Phi = \frac{3}{2}PV \tag{5.37}$$

5.3 Classical limit: dilute quantum gases

In this section we are interested in the classical limit, where the thermal de Broglie wavelength is much smaller than the typical interparticle distance

$$\lambda^3 \ll v\,. \tag{5.38}$$

To calculate the correction to the equations of state for an ideal gas we rewrite the generalized ζ-functions as series expansions in the fugacity z:

$$\begin{aligned}
\frac{1}{\Gamma(\nu)}\int_0^\infty dx\frac{x^{\nu-1}}{e^xz^{-1}\mp 1} &= \frac{1}{\Gamma(\nu)}\int_0^\infty dx x^{\nu-1}e^{-x}z\sum_{n=0}^\infty(\pm 1)^n e^{-xn}z^n \\
&= \frac{1}{\Gamma(\nu)}\int_0^\infty dx x^{\nu-1}\sum_{n=0}^\infty(\pm 1)^n e^{-x(n+1)}z^{n+1} \\
&= \frac{1}{\Gamma(\nu)}\int_0^\infty dx x^{\nu-1}\sum_{n=1}^\infty(\pm 1)^{n+1} e^{-xn}z^n \\
&= \frac{1}{\Gamma(\nu)}\sum_{n=1}^\infty(\pm 1)^{n+1}z^n n^{-\nu}\underbrace{\int_0^\infty d(nx)(nx)^{\nu-1}e^{-xn}}_{=\Gamma(\nu)} \\
&= \sum_{n=1}^\infty(\pm 1)^{n+1}\frac{z^n}{n^\nu} = \begin{cases} g_\nu(z) \\ f_\nu(z)\end{cases}\quad .
\end{aligned} \tag{5.39}$$

This implies

$$\frac{1}{v} \approx \frac{g}{\lambda^3}\left[z \pm \frac{1}{2^{3/2}}z^2 + \mathcal{O}(z^3)\right] \tag{5.40}$$

which can be inverted iteratively to give the following series expansion of the fugacity in terms of the small parameter λ^3/v,

$$z = \frac{\lambda^3}{vg} \mp \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{vg} \right)^2 + \mathcal{O} \left(\lambda^3/v \right)^2 . \tag{5.41}$$

Similarly, one finds

$$\begin{aligned} \Phi &= -\frac{gV}{\lambda^3} k_\mathrm{B} T \left(z \pm \frac{1}{2^{5/2}} z^2 + \mathcal{O}(z^3) \right) \\ &= -N k_\mathrm{B} T \left(1 \mp \frac{\lambda^3}{2^{5/2} gv} + \mathcal{O}(\lambda^3/v)^2 \right) \end{aligned} \tag{5.42}$$

and hence the equations of state

$$PV \approx N k_\mathrm{B} T \left(1 \mp \frac{1}{2^{5/2} g} \frac{\lambda^3}{v} \right) . \tag{5.43}$$

and

$$E = \frac{3}{2} PV = \frac{3}{2} N k_\mathrm{B} T \left(1 \mp \frac{1}{2^{5/2} g} \frac{\lambda^3}{v} \right) . \tag{5.44}$$

The additional terms of order $\mathcal{O}(\lambda^3/v)$ are called *exchange corrections*. They are due to the symmetrizations of the system state and their effect on the equations of state for bosons and fermions differ in sign. For bosons in the dilute limit the pressure is reduced as compared to the classical ideal gas expression. This indicates a tendency of bosons to “cluster”. In contrast, the pressure is enhanced for a dilute Fermi gas, indicating a tendency for repulsion which is closely related to the Pauli exclusion principle.

From Eq.5.41 we can also find an approximate expression for the chemical potential

$$\mu = k_\mathrm{B} T \ln z \approx k_\mathrm{B} T \ln \left(\frac{\lambda^3}{gv} \mp \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{gv} \right)^2 \right) \tag{5.45}$$

which is *negative*. Then, the free energy $F = \Phi + \mu N$ is

$$F \approx F_\text{class} \pm N k_\mathrm{B} T \frac{1}{2^{5/2}} \frac{\lambda^3}{gv} \tag{5.46}$$

where

$$F_\text{class} = N k_\mathrm{B} T \left(-1 + \ln \frac{\lambda^3}{gv} \right) \tag{5.47}$$

is the free energy of a classical ideal gas.

5.4 Degenerate Fermi gas

5.4.1 The ground state: Fermi sphere

At absolute zero temperature, $T = 0K$, the Fermi-Dirac distribution function reduces to a step function

$$n(\epsilon_p) = \Theta(\epsilon_F - \epsilon_p) \, , \tag{5.48}$$

where the **Fermi energy** ϵ_F is defined as the value of the chemical potential at absolute zero, $\epsilon_F \equiv \mu(T = 0)$. All single-particle states with energy less than ϵ_F are occupied, while all states with energy greater than ϵ_F are unoccupied (Pauli exclusion principle). When a gas of fermions is so cold that nearly all states below ϵ_F are occupied while nearly all states above ϵ_F are unoccupied it is said to be **degenerate**[4].

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Figure 5.4: At $T = 0K$, the Fermi-Dirac distribution equals 1 for all states p with $\epsilon_p < \epsilon_F$ and equals 0 for all states with $\epsilon_p > \epsilon_F$.

The value of ϵ_F is determined by the total number of fermions present. For particles confined to a volume $V = L^3$ with periodic boundary condition, the allowed momenta are

$$\mathbf{p} = \frac{2\pi\hbar}{L}(\nu_1, \nu_2, \nu_3) \quad \text{with } \nu_i = 0, \pm 1, \cdots \tag{5.49}$$

This is illustrated for a two-dimensional box in Fig.5.5. Each lattice point represents a g-fold degenerate single-particle state with an energy $\epsilon_{\mathbf{p}} = \mathbf{p}^2/2m$. As one adds fermions to the box, they settle into states starting at the origin and gradually working outword. By the time all particles are filled into single-particle states the total number of occupied states is so huge that the occupied region in momentum space is essentially a sphere with radius $p_F = \sqrt{2m\epsilon_F}$, the Fermi momentum.

– figure missing –

Figure 5.5: Illustration of the Fermi sphere for a two-dimensional system. Each dublett of integers (ν_1, ν_2) represents a g-fold degenerate energy level for free fermions. All states up to the Fermi momentum are occupied. This is called the Fermi sphere.

Hence we have

$$N = g \sum_{p \le p_F} 1 = g \frac{V}{(2\pi\hbar)^3} \int d^3p \, \Theta(p_F - p) = g \frac{V}{(2\pi\hbar)^3} \frac{4\pi}{3} p_F^3 \tag{5.50}$$

---

[4] This use of the word degenerate is completely unrelated to its other use to describe a set of quantum states that have the same energy.

such that

$$p_F = \left(\frac{6\pi^2}{g}\right)^{1/3} \hbar n^{1/3} \sim n^{1/3} \tag{5.51}$$

where $n = N/V$. If we reexpress this relation in terms of the de Broglie wavelength $\lambda_F = 2\pi\hbar/p_F$ one finds that it is of the order of the interparticle spacing

$$\lambda_F = 2\pi \left(\frac{6\pi^2}{g}\right)^{-1/3} v^{1/3} \sim v^{1/3} \tag{5.52}$$

The Fermi energy becomes

$$\epsilon_F = \frac{p_F^2}{2m} = \left(\frac{6\pi^2}{g}\right)^{2/3} \frac{\hbar^2}{2m} n^{2/3} \sim n^{2/3} \tag{5.53}$$

Note that this quantity is intensive, since it depends only on the number density of fermions, N/V. As noted above it applies to containers of any shape, although our derivation was for fermions in a cube-shaped box.

One of the most important applications of the physics of a degenerate Fermi gas are conduction electrons in metals[5]. To estimate the Fermi energy in a typical metal we introduce a distance between the fermions as

$$v = \frac{4\pi}{3} r_s^3 , \tag{5.54}$$

set the degeneracy factor to $g = 2$, and introduce the Bohr radius $a_0 = \hbar^2/me^2$. Then the Fermi energy reads

$$\epsilon_F = \frac{e^2}{2a_0} \left(\frac{a_0}{r_s}\right)^2 \left(\frac{9\pi}{4}\right)^{2/3} . \tag{5.55}$$

We can identify $e^2/2a_0$ as the ionization energy for hydrogen ≈ 13.6eV. In a typical metal there is about one conduction electron per atom such that $r_s \approx a_0$ and we can estimate $\epsilon_F \approx 10$eV, which corresponds to a Fermi temperature $T_F = \epsilon_F/k_B \approx 120\,000$ K. At room temperature, $k_B T \approx 1/40$ eV such that $k_B T/\epsilon_F \ll 1$ and a metal at room temperature can be considered as a *low temperature system.* Typical numbers for some metals are: Na ($r_s/a_0 = 3.93$, $\epsilon_F = 3.24$eV), Cu ($r_s/a_0 = 2.67$, $\epsilon_F = 7$eV).

The Fermi energy is the *highest* energy of all the fermions. On average, they will have somewhat less energy, a little more than half ϵ_F. To be more precise we have to evaluate the integral

$$U = \frac{gV}{(2\pi\hbar)^3} \int d^3p \, \epsilon_p n(\epsilon_p) . \tag{5.56}$$

---

[5] It is far from obvious that one can use the physics of an ideal Fermi gas to reach some meaningful conclusion on conduction electrons, which interact both among themselves and with the core electrons by a long-ranged Coulomb interaction. The main reason for the ideal Fermi gas to work so well are screening effects. If you are interested in more details you should consult a text on theoretical solid state physics. Application of Fermi-Dirac statistics to conduction electrons in a metal have been pioneered by Arnold Sommerfeld.

We will use this opportunity to introduce the concept of *density of states*. Since the integrand of Eq.5.56 depends only on $\epsilon_p = \epsilon(|\mathbf{p}|)$, it is convenient to make a change of variables from $|\mathbf{p}|$ to ϵ, and write

$$\begin{aligned} U &= \frac{gV}{(2\pi\hbar)^3}\, 4\pi \int dp\, p^2 \epsilon_p n(\epsilon_p) \\ &= \frac{gV}{(2\pi\hbar)^3}\,\frac{1}{2}\, 4\pi\, (2m)^{3/2} \int d\epsilon\, \sqrt{\epsilon}\, \epsilon\, n(\epsilon) \\ &\equiv \int d\epsilon\, \mathcal{D}(\epsilon)\, \epsilon\, n(\epsilon) \end{aligned} \tag{5.57}$$

where the quantity

$$\mathcal{D}(\epsilon) = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon} = \frac{3N}{2\epsilon_F^{3/2}}\sqrt{\epsilon} \tag{5.58}$$

has a nice interpretation: It is the number of single-particle states per unit energy, or short the **density of states**. The second expression in Eq.5.58 is compact and handy, but perhaps rather confusing since it seems to imply that $\mathcal{D}(\epsilon)$ depends on N, when in fact the N-dependence is cancelled by ϵ_F. The first expression is more explicit and makes clear that the density of states is proportional to the volume V and independent of the particle number N. The most important fact about the density of states is that it grows like $\sqrt{\epsilon}$; see Fig.5.6.

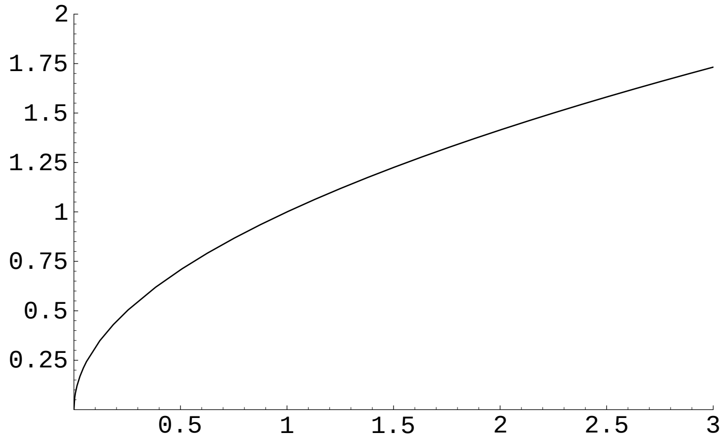

Figure 5.6: Density of states for a system of noninteracting particles in a three-dimensional box.

For the particular case of $T = 0$ K the internal energy becomes

$$U = \frac{3N}{2\epsilon_F^{3/2}} \int_0^{\epsilon_F} d\epsilon\, \epsilon^{3/2} = \frac{3}{5} N\epsilon_F \tag{5.59}$$

With $PV = \frac{2}{3}E$ one finds for the degeneracy pressure

$$P = \frac{2}{5} n\epsilon_F \tag{5.60}$$

It is positive because when you compress a degenerate electron gas, the wavelengths of all the wavefunctions are reduced, hence the energies of all the wavefunctions increase. Degeneracy pressure is what keeps matter from collapsing under the huge electrostatic force that try to pull electrons and protons together. Please note that degeneracy pressure has absolutely nothing to do with the electrostatic repulsion between the electrons (which we have completely ignored); it arises purely by virtue of the exclusion principle. Numerically, the degeneracy pressure comes out to a few billion N/m^2 for a typical metal. But this number is not directly measurable – it is cancelled by the electrostatic forces that hold the electrons in the metal in the first place.

5.4.2 The Sommerfeld expansion

In a next step we would like to understand what happens for small finite temperature. Then the Fermi-Dirac distribution is no longer a step function but smoothens out such that the width of the step is proportional to $k_{\rm B}T$; see Fig.5.7.

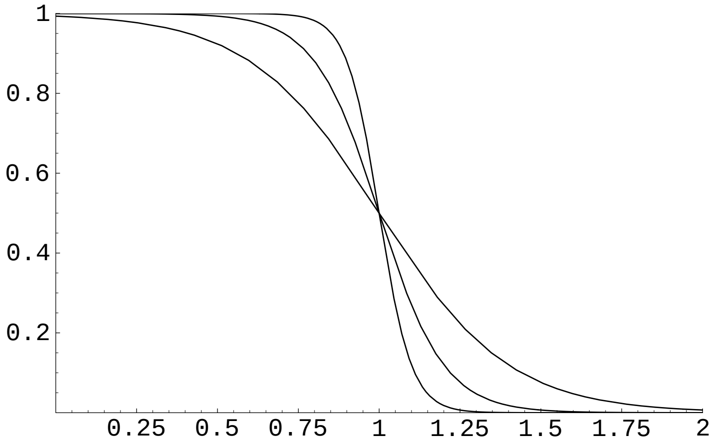

Figure 5.7: Fermi-Dirac distribution function versus ϵ/μ for $T/T_F = 0.05$, 0.1, and 0.2.

We would like to evaluate the expressions for the total particle number and total internal energy

$$N = \int d\epsilon\, \mathcal{D}(\epsilon)\, n(\epsilon) = \frac{3N}{2\epsilon_F^{3/2}} \int d\epsilon\, \sqrt{\epsilon}\, n(\epsilon) \tag{5.61}$$

$$U = \int d\epsilon\, \mathcal{D}(\epsilon)\, \epsilon\, n(\epsilon) = \frac{3N}{2\epsilon_F^{3/2}} \int d\epsilon\, \epsilon^{3/2}\, n(\epsilon) \tag{5.62}$$

This can be done using *Sommerfeld's expansion formula*

$$\begin{aligned} I &= \int_0^\infty d\epsilon\, f(\epsilon) n(\epsilon) \qquad (5.63) \\ &= \int_0^\mu d\epsilon\, f(\epsilon) + \frac{\pi^2}{6}(k_{\rm B}T)^2 f'(\mu) + \frac{7\pi^4}{360}(k_{\rm B}T)^4 f'''(\mu) + \mathcal{O}(k_{\rm B}T)^6 \end{aligned}$$

Sommerfeld's reasoning to derive this series expansion is as follows. Though the integral runs over all positive ϵ, the most interesting region is close to μ, where the Fermi-Dirac distribution falls off steeply (for low enough temperatures such that $T \ll T_F$). So the first trick is to isolate this region

$$I = \int_0^\mu d\epsilon\, f(\epsilon) + \int_0^\infty d\epsilon\, f(\epsilon)\,[n(\epsilon) - \Theta(\mu-\epsilon)]$$

As indicated in Fig.5.8 the difference $\Delta(\epsilon) = n(\epsilon) - \Theta(\mu - \epsilon)$ is anti-symmetric with respect to μ and non-vanishing only in the immediate vicinity of μ. This allows us to extend the integral in the second term towards $-\infty$ with an error which is exponentially small

– figure missing –

Figure 5.8: Illustration of the idea for the Sommerfeld expansion.

$$I \approx \int_0^\mu d\epsilon\, f(\epsilon) + \int_{-\infty}^\infty d\epsilon\, f(\epsilon)\,[n(\epsilon) - \Theta(\mu-\epsilon)]$$

Now we may perform a Taylor expansion of $f(\epsilon)$ around μ

$$\begin{aligned} I &\approx \int_0^\mu d\epsilon\, f(\epsilon) + \int_{-\infty}^\infty d\epsilon \left\{ f(\mu) + f'(\mu)(\epsilon-\mu) + \frac{1}{2}f''(\mu)(\epsilon-\mu)^2 + \cdots \right\} [n(\epsilon) - \Theta(\mu-\epsilon)] \\ &= \int_0^\mu d\epsilon\, f(\epsilon) + (k_\mathrm{B}T)^2 f'(\mu) \underbrace{\int_{-\infty}^\infty dx\, x[n(x) - \Theta(-x)]}_{=2\int_0^\infty dx\, x n(x)} + \frac{2}{3!}(k_\mathrm{B}T)^4 f'''(\mu) \int_0^\infty dx\, x^3 n(x) \end{aligned}$$

where we have substituted $x = \beta(\epsilon - \mu)$ and used that $\Delta(x)$ is anti-symmetric with respect to $x = 0$; for the underbrace in the last line and the third term we have used this anti-symmetry and that $\Theta(-x) = 0$ for $x > 0$. In a last step we use (see my handwritten notes in the supplementary material)

$$\int_0^\infty dx\, \frac{x^{2k-1}}{e^x + 1} = (1 - 2^{1-2k})\,\zeta(2k)\Gamma(2k) \tag{5.64}$$

which finally gives the Sommerfeld expansion Eq.5.63.

From the Sommerfeld expansion we obtain

$$\begin{aligned} 1 &= \frac{3}{2}\epsilon_F^{-3/2} \int_0^\infty d\epsilon\, \sqrt{\epsilon}\, n(\epsilon) \\ &= \frac{3}{2}\epsilon_F^{-3/2} \left(\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 \frac{1}{2}\mu^{-1/2} + \mathcal{O}(k_\mathrm{B}T)^4 \right) \\ &= \left(\frac{\mu}{\epsilon_F}\right)^{3/2} \left(1 + \frac{\pi^2}{6}\left(\frac{k_\mathrm{B}T}{\mu}\right)^2 + \mathcal{O}(k_\mathrm{B}T)^4 \right) \end{aligned} \tag{5.65}$$

such that

$$\mu = \epsilon_F \left(1 - \frac{\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\epsilon_F}\right)^2 + \mathcal{O}(k_\mathrm{B}T)^4 \right) \tag{5.66}$$

The chemical potential gradually decreases as T is raised. The behavior of μ over a wide range of temperature is shown in Fig.5.9; note also the expression for the chemical potential in the classical limit, which is negative.

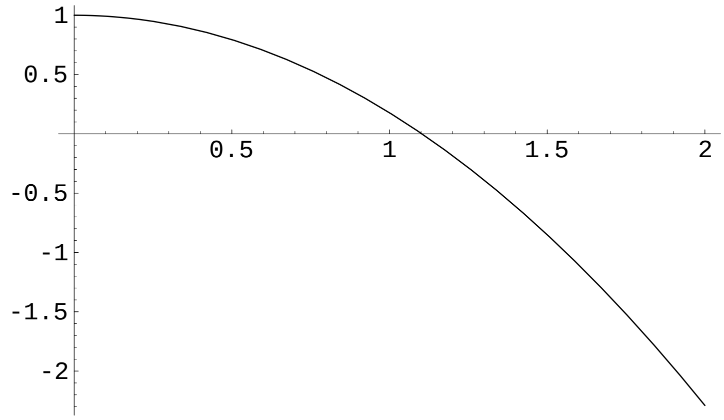

Figure 5.9: Chemical potential μ/ϵ_F of a non-interacting Fermi gas as a function of T/T_F. At low temperatures μ is approximately given by Eq.5.66, while at high temperatures μ becomes negative and approaches the form of an ordinary gas obeying Boltzmann statistics.

Similarly, we get for the total internal energy

$$U = \frac{3}{5} N \epsilon_F \left(1 + \frac{5\pi^2}{12} \left(\frac{k_\mathrm{B} T}{\epsilon_F} \right)^2 + \mathcal{O}(k_\mathrm{B} T)^4 \right) \tag{5.67}$$

which implies for the specific heat to leading order a linear dependence

$$C_V = N k_\mathrm{B} \frac{\pi^2}{2} \frac{T}{T_F} \sim T \tag{5.68}$$

The linear dependence of the specific heat on temperature at low temperatures is indeed observed in metallic systems. For an illustration see Fig.5.10.

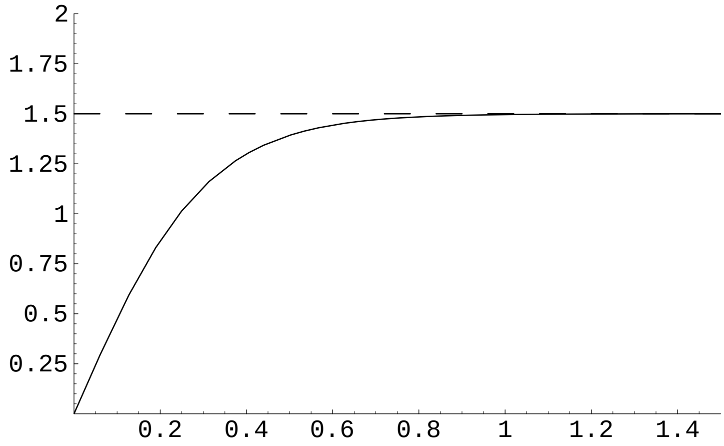

Figure 5.10: Specific heat C_v in units of $N k_\mathrm{B}$ of a non-interacting Fermi gas as a function of T/T_F. At low temperatures C_v grows linear in T and approaches $\frac{3}{2} N k_\mathrm{B}$ at high temperatures.

For the pressure we get

$$P = \frac{2}{5}\epsilon_F n \left(1 + \frac{5\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\epsilon_F}\right)^2 + \mathcal{O}(k_\mathrm{B}T)^4\right) \tag{5.69}$$

and hence for the isothermal compressibility

$$\kappa_T = \frac{3}{2}\frac{v}{\epsilon_F}\left(1 - \frac{\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\epsilon_F}\right)^2 + \mathcal{O}(k_\mathrm{B}T)^4\right) \tag{5.70}$$

Expressions for the specific heat and the isothermal compressibility can also be derived for general density of states. Then one finds

$$C_V = \frac{1}{3}\pi^2\mathcal{D}(\epsilon_F)k_\mathrm{B}^2 T \tag{5.71}$$

$$\kappa_T = \frac{V}{N^2}\mathcal{D}(\epsilon_F) \tag{5.72}$$

5.5 Bose-Einstein condensation

5.5.1 The condensate

We consider a system of N spinless bosons ($g = 1$). Then, the chemical potential μ (a Lagrange multiplier) is determined by the implicit equation $\sum_p n(\epsilon_p) = N$. In section ?? we have replaced the sum over the momenta by an integral and arrived at the implicit equation for the fugacity z

$$n\lambda^3 = g_{3/2}(z)\,. \tag{5.73}$$

We already know the solution of this equation in the classical limit, where μ is large and negative:

$$\mu = k_\mathrm{B}T\ln(gv/\lambda^3) \leq 0\,. \tag{5.74}$$

In the quantum limit as the temperature descends to absolute zero, the system of N bosons settles into its ground state, $\epsilon_0 = 0$. This implies that the estimated occupation number $n(0)$ must approach N as $T \to 0$,

$$\lim_{T\to 0} n(0) = \lim_{T\to 0}\frac{1}{e^{-\mu/k_\mathrm{B}T} - 1} = N\,. \tag{5.75}$$

From this relationship we can asses the behavior of the chemical potential near absolute zero. The inverse fugacity $z^{-1} = e^{-\beta\mu}$ must be extremly close to 1, so that division by the difference between it and 1 yields the large number N. Thus $\mu/k_\mathrm{B}T$ must be small, and we may expand the exponential, writing

$$\frac{1}{1 - \mu/k_\mathrm{B}T - 1} \approx N \tag{5.76}$$

when T is close to zero. Solving this equation for μ yields

$$\mu \approx k_\mathrm{B}T/N\,. \tag{5.77}$$

The resulting temperature dependenc of $\mu(T)$ is shown schematically in Fig.5.11. In summary, for the ideal Bose gas, the allowed range of μ is $-\infty \leq \mu \leq 0$ or equivalently $0 \leq z \leq 1$. This is in sharp contrast to the corresponding range $0 \leq z \leq \infty$ allowed in the case of an ideal Fermi gas. We are interested in the thermodynamic limit as $N \to \infty$. Then there are two possibilities. Either $\mu = 0$ at $T = 0$ K or at some finite $T_c \neq 0$.

– figure missing –

Figure 5.11: The chemical potential μ of an ideal Bose gas plotted as a function of the temperature T.

Let's now study the solution of the implicit equation for the fugacity, Eq. 5.73, which is illustrated in Fig. 5.12. The generalized ζ-function $g_{3/2}(z)$ grows monotonically up to $z = 1$ where

$$g_{3/2}(1) = \sum_{l=1}^{\infty} l^{-3/2} = \zeta(3/2) = 2.612... \tag{5.78}$$

with an infinite slope since

$$z\frac{d}{dz}g_{3/2}(z) = g_{1/2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{\sqrt{l}} \tag{5.79}$$

diverges at $z = 1$. Consider a system with a fixed particle density $n = 1/v$. Then, upon lowering the temperature T, or equivalently increasing the thermal wavelength λ, the fugacity z increases monotonically up to a value $z = 1$ where

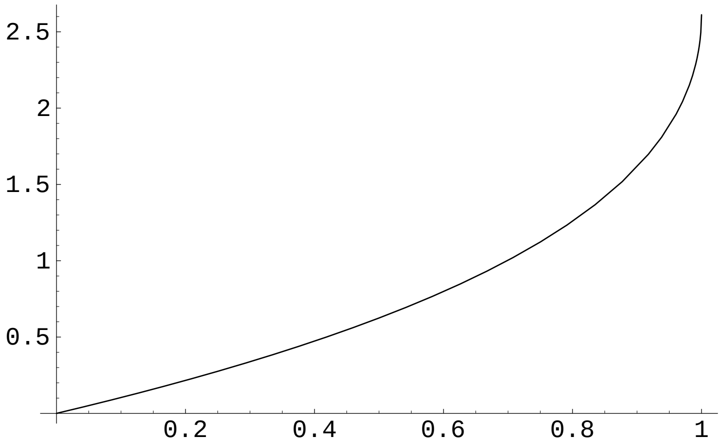

Figure 5.12: Implicit equation $n\lambda^3 = g_{3/2}(z)$ for the fugacity z.

$$n\lambda_c^3 = g_{3/2}(1) = 2.612\ldots\,. \tag{5.80}$$

This defines a (density dependent) critical temperature $T_c(v)$ where the chemical potential becomes identical to zero,

$$k_B T_c(v) = \frac{2\pi\hbar^2}{m} \frac{1}{(2.612\, v)^{2/3}} \,. \tag{5.81}$$

But, what happens for $T < T_c(v)$? Obviously, Eq. 5.73 does *not* have a solution below T_c. So, what went wrong? The failure comes from the fact that we have discarded the weight of the lowest level $\epsilon_0 = 0$ in replacing the sum over the momenta in Eq.?? by an integral. For $n\lambda^3 \to 2.612$ the fugacity approaches $z = 1$. Then the average occupation number $n(0)$ of the ground state $\epsilon = 0$ would diverge

$$\lim_{z\to 1} \frac{1}{z^{-1} - 1} \to \infty \tag{5.82}$$

Hence we should treat the ground state separately

$$\begin{aligned} N &= \sum_p n(\epsilon_p) \\ &= n(0) + \sum_{p\neq 0} n(\epsilon_p) \\ &= \frac{1}{z^{-1}-1} + \frac{V}{(2\pi\hbar)^3} \int d^3p\, n(\epsilon_p) \\ &= \frac{1}{z^{-1}-1} + N\frac{v}{\lambda^3}\, g_{3/2}(z) \end{aligned} \tag{5.83}$$

We are interested in the solution of the latter equation in the (thermodynamic) limit as the particle number N tends to infinity. For temperatures T above the critical temperature T_c the fugacity is less than 1. Then we can neglect the first term on the right hand side and we are back at Eq.5.73. For temperatures below the critical temperature T_c the chemical potential scales as $\mu \sim \mathcal{O}(1/N)$ and hence the fugacity becomes $z = 1 + \mathcal{O}(1/N)$. Then we can not neglect the first term, the occupation number $n(0)$ of the ground state, since it scales with the total particle number N. To leading order in N we may set $z = 1$ in the second term such that we get

$$\begin{aligned} N &= n(0) + N\frac{v}{\lambda^3}\, g_{3/2}(1) \\ &= n(0) + N\left(\frac{T}{T_c}\right)^{3/2} \end{aligned} \tag{5.84}$$

This implies that the average number of bosons in the ground state reads

$$n(0) = N\left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right) \tag{5.85}$$

The fraction of particles in the ground state is called the *condensate fraction* $\nu_0 = n(0)/N$. For fixed density it has the form

$$\nu_0 = \begin{cases} 0 & \text{for } T \geq T_c, \\ 1 - \left(\frac{T}{T_c}\right)^{3/2} & \text{for } T \leq T_c. \end{cases} \tag{5.86}$$

This curious phenomenon of a macroscopically large number of particles accumulating in a single quantum state ($\epsilon_0 = 0$) is generally referred to as *Bose-Einstein condensation.* In a certain sense, this phenomenon is akin to the familiar process of vapor condensing into a liquid state, which takes place in the ordinary physical space. Conceptually, however, the two processes are very different. Firstly, the phenomenon of Bose-Einstein condensation is purely of a quantum origin (occurring even in the absence of any intramolecular forces); secondly, it takes places in momentum space and not in coordinate space.

The condition for Bose-Einstein condensation is

$$n\lambda^3 \geq 2.612... \tag{5.87}$$

or, more explicitely, for a given temperature

$$\frac{N}{V} \geq n_c = \zeta(3/2) \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} (k_\mathrm{B}T)^{3/2}\,, \tag{5.88}$$

and for a given density

$$k_\mathrm{B}T \leq k_\mathrm{B}T_c = \frac{2\pi\hbar^2}{m} \left(\frac{N/V}{\zeta(3/2)}\right)^{2/3} . \tag{5.89}$$

The (T, n) phase diagram is illustrated in Fig. 5.13. Below T_c the system may be looked upon as a mixture of two “phases”:

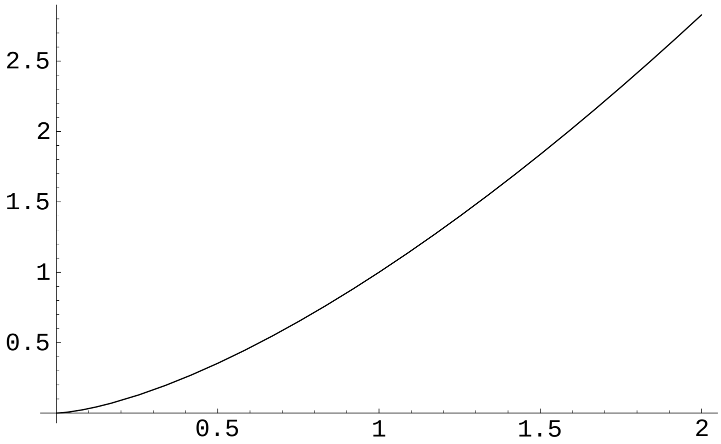

Figure 5.13: Phase diagram for a ideal Bose gas in the (T, n) plane. The line $n/T^{3/2} = \text{const.}$ marks the phase boundary between a gas phase with $\mu < 0$ and a mixed condensed phase with $\mu = 0$, where the ground state $\epsilon_0 = 0$ is occupied by a macroscopic number of particles.

(i) a *normal* phase, consiting of $N_e = N(T/T_c)^{3/2}$ particles distributed over the excited states $\epsilon_p \neq 0$, and

(ii) a *condensed* phase, consisting of $N_0 = N - N_e$ particles accumulated in the ground state $\epsilon_0 = 0$. Figure 5.14 shows the manner in which the complementary fractions N_e/N and N_0/N vary with temperature T.

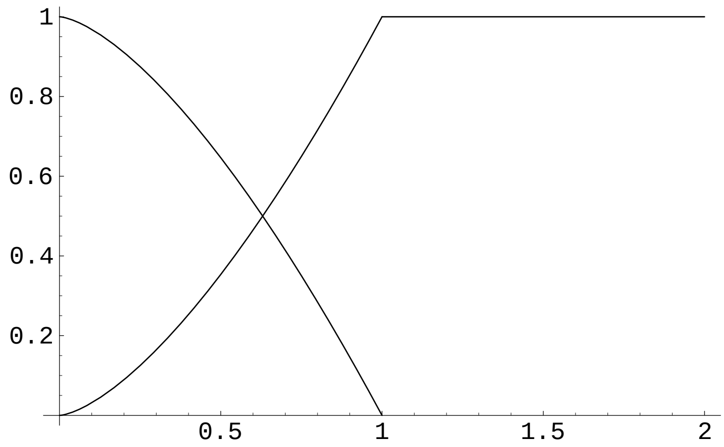

Figure 5.14: Fractions of the normal phase and the condensed phase in an ideal Bose gas as a function of the temperature in units of the critical temperature, T/T_c.

Clearly, the situation is singular at $T = T_c$. For $T \to T_c$ from below the condensate fraction vanishes *linearly*

$$\nu_0 \approx \frac{3}{2}\frac{T_c - T}{T_c} \tag{5.90}$$

5.5.2 Equations of state and phase diagrams

To further analyze the Bose-Einstein condensation we consider the equation of state

$$\frac{P}{k_{\mathrm{B}}T} = \frac{1}{V}\ln Z_G = -\frac{1}{V}\sum_{\mathbf{p}} \ln(1 - ze^{-\beta\epsilon_{\mathbf{p}}}) \tag{5.91}$$

Let us also separate out the ground state. Then

$$\frac{P}{k_{\mathrm{B}}T} = \frac{1}{V}\ln\left(\frac{1}{1-z}\right) + \frac{1}{\lambda^3}\, g_{5/2}(z) \tag{5.92}$$

Since the number of bosons in the ground state is $n(0) = 1/(z^{-1} - 1)$ we have

$$\frac{P}{k_{\mathrm{B}}T} = \frac{\ln\left(n(0)+1\right)}{V} + \frac{1}{\lambda^3}\, g_{5/2}(z) \tag{5.93}$$

In the thermodynamic limit of $V \to \infty$, the first term always vanishes as $n(0) \leq N = nV$ and $\lim_{V\to\infty} \ln(nV)/V = 0$. Hence the condensate does not contribute to the pressure. This is not surprising as particles in the condensate have zero momentum. Thus we have in the thermodynamic limit $V \to \infty$

$$P = \frac{k_{\mathrm{B}}T}{\lambda^3}\, g_{5/2}(z) = \frac{k_{\mathrm{B}}T}{\lambda^3}\begin{cases} g_{5/2}(z) & \text{for} \quad T \geq T_c \\ 1.342 & \text{for} \quad T \leq T_c \end{cases} \tag{5.94}$$

where we have used that below T_c the fugacity $z = 1$ in the thermodynamic limit and $g_{5/2}(1) = \zeta(5/2) = 1.342$. The pressure below T_c vanishes as $T^{5/2}$ and is independent of the density. The pressure-independence is analogous to the behavior of the van der Waals gas in the coexistence region; it is a hallmark of a phase transition. The line $P_c(T) = 1.342\, k_{\mathrm{B}}T/\lambda^3$ marks the critical isochore in the (P, T) phase diagram. On this critical isochore there is phase coexistence between the condensate and the atoms in the excited states (see the discussion above).

Now, we give a detailed examination of the **isochores** in the (P, T) phase diagram, i.e. the variation of the pressure P with the temperature T, keeping the specific volume v fixed. For $T < T_c$, we may set $z = 1$ for the fugacity (see Eq. 5.94) such that the pressure

$$P(T) = \frac{k_{\mathrm{B}}T}{\lambda^3}\,\zeta(5/2) \tag{5.95}$$

is proportional to $T^{5/2}$ and *independent* of the specific volume v – implying infinite compressibility. At the transition point the value of the pressure is

$$P(T_c) = \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} \zeta(5/2)\,(k_{\mathrm{B}}T_c)^{5/2}\,. \tag{5.96}$$

For $T \geq T_c$ it is convenient to rewrite the equation of state as

$$Pv = k_{\mathrm{B}}T\,\frac{g_{5/2}(z)}{g_{3/2}(z)} \tag{5.97}$$

where the fugacity is – as usual – determined by the solution of the implicit equation Eq. 5.73; a special feature of this equation is that the fugacity is a function of T/T_c alone. For small values of the fugacity z, which corresponds to low densities, $g_{5/2}(z) \approx g_{3/2}(z) \approx z$, such that we recover the classical ideal gas law $Pv = k_{\mathrm{B}}T$. In summary, we have

$$\frac{Pv}{k_{\mathrm{B}}T} = \begin{cases} \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}\left(\frac{T}{T_c}\right)^{5/2} & \text{for } T < T_c\,, \\ 1 & \text{for } T \gg T_c, \end{cases} \tag{5.98}$$

and for general values of T we know that the right hand side is a universal function of T/T_c, where the dependence on v is implicit in $T_c(v)$. Then, as illustrated in Fig. 5.15 one may represent all isochores by a single scaling plot.

In view of the direct relationship between the internal energy of the Bose gas and its pressure, see Eq. 5.33, Fig.5.15 depcits equally well the variation of the internal energy U with temperature T at fixed specific volume v. Its slope should, therfore, be a measure of the specific heat $C_v(T)$ of the Bose gas. We readily observe that the specific heat is vanishingly small at low temperatures, rises with T until it reaches a maximum at $T = T_c$; thereafter, it decreases, tending asymptotically to the constant

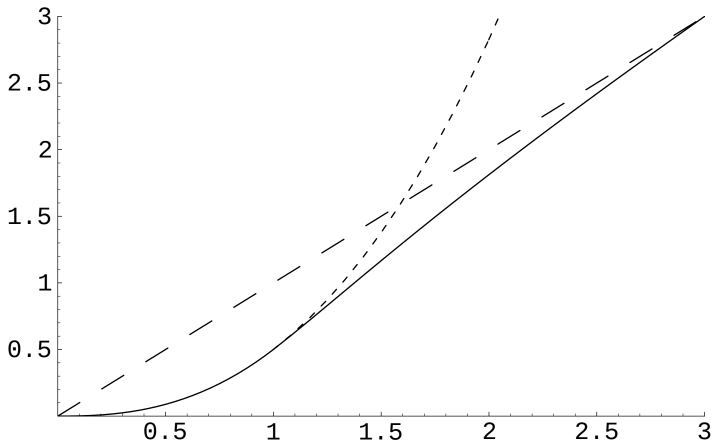

Figure 5.15: Isochores $Pv/k_{\rm B}T_c(v)$ plotted versus $T/T_c(v)$. In this scaling plot all isochores for different v collapse onto one single master curve, sketched as the solid line. Below T_c, the pressure P is independent of v and grows proportional to $T^{5/2}$. Above T_c it asymptotes the classical limit for high temperatures. The classical limit $Pv = k_{\rm B}T$ is indicated by the long dashed line. The short dashed line is the extension of the $P(T)$ curve below T_c to values above T_c. We have added it to guide the eye. But note that there is no physical meaning of this extension.

classical value. Analytically, for $T \leq T_c$, we obtain

$$\begin{aligned} C_v = \left(\frac{\partial E}{\partial T}\right)_v &= \frac{\partial}{\partial T}\left(\frac{3}{2}\,\frac{k_{\rm B}TV}{\lambda^3}\zeta(5/2)\right) \\ &= \frac{3}{2}nk_{\rm B}\,\frac{5}{2}\zeta(5/2)\,\frac{v}{\lambda^3} \\ &= Nk_{\rm B}\frac{15}{5}\,\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}\left(\frac{T}{T_c}\right)^{3/2} \\ &= 1.925Nk_{\rm B}\left(\frac{T}{T_c}\right)^{3/2} \end{aligned} \tag{5.99}$$

The origin of the $T^{3/2}$ behavior is easily understood heuristcally. At $T = 0$ all particles occupy the zero momentum state. At small but finite temperatures there is occupation of states with finite momentum, up to a value of $p_{\rm max}$ such that

$$\frac{\hbar^2 p_{\rm max}^2}{2m} = k_{\rm B}T \tag{5.100}$$

each of these states has an energy proportional to $k_{\rm B}T$. The excitation energy (internal energy) scales then as the phase space volume $Vp_{\rm max}^3$ times the thermal energy $k_{\rm B}T$

$$U \sim Vp_{\rm max}^3 k_{\rm B}T \sim T^{5/2} \tag{5.101}$$

Note that the power of the temperature depends crucially on the dispersion. Here we have $\epsilon_p \sim p^2$ resulting in $C_v \sim T^{3/2}$. If the dispersion would be linear, $\epsilon_p \sim p$, as is the case for long wavelength acoustic phonons (for which $\mu = 0$ for all temperatures), then $C_v \sim T^3$.

Above T_c the calculations are little more cumbersome. We get

$$\begin{aligned}
\frac{C_v}{Nk_\mathrm{B}} &= \frac{3}{2}v\,\frac{\partial}{\partial T}\left(\frac{T}{\lambda^3}g_{5/2}(z)\right)\\
&= \frac{3}{2}v\left[\frac{\partial}{\partial T}\left(\frac{T}{\lambda^3}\right)g_{5/2}(z)+\frac{T}{\lambda^3}\frac{dg_{5/2}(z)}{dz}\,\frac{\partial z}{\partial T}\right]\\
&= \frac{3}{2n}\left[\frac{5}{2}\frac{1}{\lambda^3}g_{5/2}(z)+\frac{T}{\lambda^3}g_{3/2}(z)\,\frac{1}{z}\frac{\partial z}{\partial T}\right]\\
&= \frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)}-\frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}
\end{aligned}$$

In the course of the calculation we have used

$$z\frac{d}{dz}g_\nu(z) = g_{\nu-1}(z) \tag{5.102}$$

and from $n\lambda^3 = g_{3/2}(z)$ we conclude for fixed $v = 1/n$

$$\begin{aligned}
0 = \frac{\partial n}{\partial T} &= g_{3/2}(z)\,\frac{\partial}{\partial T}\frac{1}{\lambda^3}+\frac{1}{\lambda^3}\,\frac{dg_{3/2}(z)}{dz}\,\frac{\partial z}{\partial T}\\
&= \frac{3}{2}\frac{1}{T\lambda^3}g_{3/2}(z)+\frac{1}{\lambda^3}g_{1/2}\frac{1}{z}\frac{\partial z}{\partial T}
\end{aligned}$$

and hence

$$\frac{1}{z}\frac{\partial z}{\partial T} = -\frac{3}{2}\frac{g_{3/2}(z)}{g_{1/2}(z)}\,\frac{1}{T} \tag{5.103}$$

In summary, we have found for the specific heat

$$\frac{C_v}{Nk_\mathrm{B}} = \begin{cases}\frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)}-\frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)} & \text{for } T > T_c,\\ 1.925\,(\frac{T}{T_c})^{3/2} & \text{for } T < T_c,\end{cases} \tag{5.104}$$

Since $\lim_{z\to 1} g_{1/2}(z) = \infty$ we get

$$\lim_{T\to T_c^+}\frac{C_v}{Nk_\mathrm{B}} = \lim_{T\to T_c^-}\frac{C_v}{Nk_\mathrm{B}} = \frac{15}{4}\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} \approx 1.925 > \frac{3}{2} \tag{5.105}$$

such that the specific heat is continuous at T_c. Note also that the value of the specific heat at T_c is larger that the classical value of $3/2Nk_\mathrm{B}$. In contrast, the derivative of the specific heat is discontinuous. We have (the calculations are left as an excercise)

$$\frac{\partial}{\partial T}\frac{C_v}{Nk_\mathrm{B}} = \begin{cases}\frac{2.89}{T_c} & \text{for } T \to T_c^-,\\ -\frac{0.77}{T_c} & \text{for } T \to T_c^+,\end{cases} \tag{5.106}$$

For an illustration of the specific heat see Fig. 5.16.

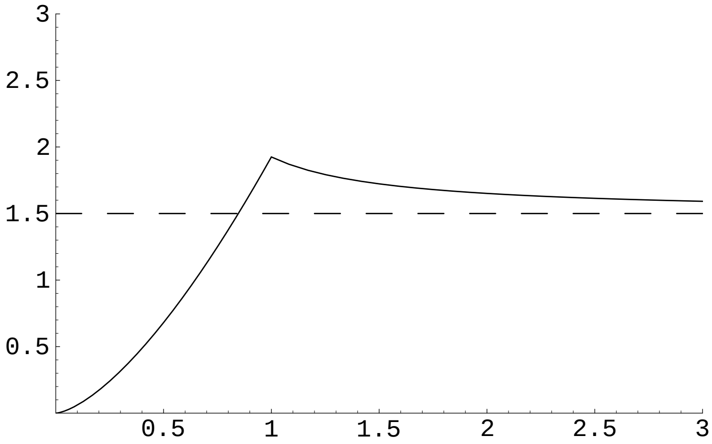

Figure 5.16: The specific heat C_v in units of Nk_B for an ideal Bose gas as a function of T/T_c. At low temperatures the specific heat grows as $T^{3/2}$ and approaches the classical value 3/2. At the critical temperature the specific heat has a "cusp", i.e. it is continuous but its derivative is discontinuous with positive and negative slopes as T_c is approached from below and above, respectively. Note also that the value of the specific heat at the transition temperature is higher that the classical limit!

For the discussion of the *isotherms* in the (P, v) diagram we first determine the phase boundary. This is done by eliminating the temperature from the set of equations

$$P_c(T) = g_{5/2}(1) k_\mathrm{B} T/\lambda^3 \tag{5.107}$$

$$n_c(T) = g_{3/2}(1)/\lambda^3 \tag{5.108}$$

which results in a transition line given by the equation (see Fig. 5.17)

$$P_c v_c^{5/3} = \frac{2\pi\hbar^2}{m} \frac{\zeta(\frac{5}{2})}{(\zeta(\frac{3}{2}))^{5/3}} = \text{const.}. \tag{5.109}$$

Clearly the region to the left of this line belongs to the mixed phase, while the region to the right belongs to the normal phase. In the mixed phase $z = 1$ such that the pressure is constant,

$$P_0 = \frac{k_\mathrm{B} T}{\lambda^3} \zeta(5/2) \tag{5.110}$$

In the normal phase the pressure approaches the ideal gas expression $P = k_\mathrm{B} T/v$ for large v.

The Bose-Einstein condensation is a first order transition with a **latent heat**, which can be calculated using the Clausius-Clapeyron equation. From Eq.5.107 we find for the slope of the critical isochore

$$\frac{dP_c}{dT} = \frac{5}{2} k_\mathrm{B} \frac{g_{5/2}(1)}{\lambda^3} = \frac{5}{2} k_\mathrm{B} \frac{g_{5/2}(1)}{g_{3/2}(1)} n_c \tag{5.111}$$

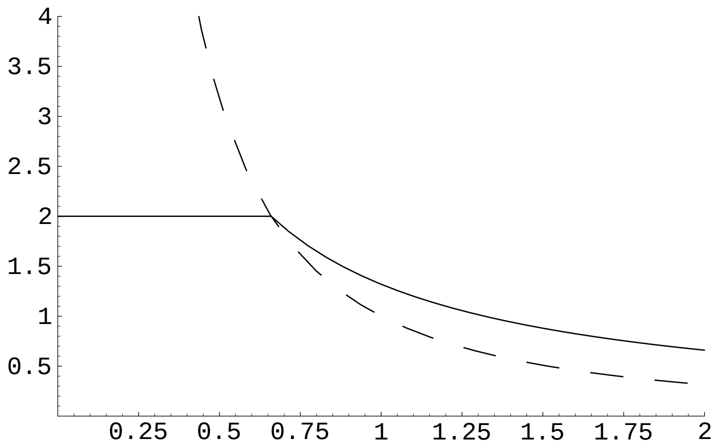

Figure 5.17: The isotherms of the ideal Bose gas. The transition line $Pv^{5/3} = \text{const.}$ (dashed line) separates a mixed phase (left) from the normal phase (right). In the mixed phase the pressure is constant, and decreases monotonically in the normal phase. The solid line is a sketch of an isotherm.

The difference in specific volume between the particles in the condensate and the excited states reads

$$\Delta v = v_c - 0 = \frac{1}{n_c}\,. \tag{5.112}$$

Hence we get from the Clausius-Clapeyron equation $dP_c/dT = \Delta q/T\delta v$ a latent heat per particle

$$\Delta q = \frac{5}{2} k_{\mathrm{B}} T \, \frac{g_{5/2}(1)}{g_{3/2}(1)} \tag{5.113}$$

corresponding to a jump in the entropy.

5.5.3 Experiments on the Bose-Einstein condensation

→ see the supplementary material on the web

5.6 Photons and blackbody radiation

5.6.1 Preliminary Remarks

The blackbody radiation problem was crucial for the discovery of quantum theory. The laws of classical electrodynamics combined with the principles of thermodynamics leads to an infinite energy density independent of temperature. This phenomenon is known as ultra-violet catastrophe since it is the short-wavelengths that contribute more and more to the energy density. Let's sketch the reasoning that leads to these puzzling results.

It is well-known from classical electrodynamics that the dispersion relation for electromagnetic waves in vacuum is given by

$$\omega = ck\,, \qquad k = |\mathbf{k}|\,. \tag{5.114}$$

Here ω is the frequency and $\mathbf{k}$ the wave vector of a plane wave. The speed of light in vacuum, c, connects the latter in a linear fashion, so that one can build wave packets that do not broaden in time, contrary to corresponding ones for massive quantum particles. Since Maxwell's equations are linear the eigenmodes of the electromagnetic field do not interact and are therefor independent. Furthermore the wave equation for, e.g. the electric field, can be transformed into the form of harmonic oscillators

$$\frac{\partial^2}{\partial t^2}\mathbf{E}_{\mathbf{k}}(t) + c^2k^2\mathbf{E}_{\mathbf{k}}(t) = 0\,, \qquad \mathbf{E}_{\mathbf{k}}(t) = \int d^3\mathbf{r}\ \mathbf{E}(\mathbf{r},t)e^{i\mathbf{k}\cdot\mathbf{r}} \tag{5.115}$$

Since the fields $\mathbf{E}, \mathbf{B}$ are transversal $\operatorname{div}\mathbf{E}(\mathbf{r},t) = \operatorname{div}\mathbf{B}(\mathbf{r},t) = 0$ or $\mathbf{k}\cdot\mathbf{E}_{\mathbf{k}}(t) = \mathbf{k}\cdot\mathbf{B}_{\mathbf{k}}(t) = 0$ only two linearly independent orientations of the fields are possible. One can choose, for example, linearly polarized waves or as is usually more convenient in quantum applications circular polarizations as eigenmodes. Then the modes are also eigenfunctions of the spin operator with eigenvalues $\pm\hbar$. The transversality condition rules out the spin projection 0. Since the waves move with the speed of light in all frames of reference, one can convince oneself that this property is Lorentz invariant.

Now consider the electromagnetic radiation to be confined in a cavity of volume $V = L^3$. The (perfect) walls of the container interact with the radiation and the electromagnetic waves will have to be described by an equilibrium ensemble of temperature T. The mean energy $u(\omega, T)$ in each oscillator can depend only on the temperature and the frequency. The total energy per volume is then given by

$$\begin{aligned}
\frac{E}{V} &= 2\times\frac{1}{V}\sum_{\mathbf{k}} u(\omega,T) \\
&= 2\int\frac{d^3\mathbf{k}}{(2\pi)^3}u(\omega,T) \\
&= \frac{1}{\pi^2c^3}\int_0^\infty u(\omega,T)\omega^2 d\omega\,,
\end{aligned} \tag{5.116}$$

where we took care of the two independent polarizations and as in the case of fermions replaced the sum by appropiate integrals. From classical mechanics it is natural to attribute to each oscillator the mean energy of $u_{cl}(\omega,T) = k_BT$. However, the energy density becomes infinite [even the energy density per frequency interval is unbound].

This apparent paradox led Planck in 1900 to an 'Akt der Verzweiflung' and to enter the advent of quantum mechanics. He postulated that the energy of the electromagnetic wave has to come in small quantities called quanta and applied Boltzmann's principle $S = k_B\ln\Gamma$ in a way now known as Bose-Einstein statistics. For a nice presentation of the history of Planck's discovery accessible to physicists see the excellent book of Straumann, *Nichtrelativistische Quantenmechanik* (Springer, 2002). Here we will not follow Planck's reasoning since we already developed all the tools to come to a transparent result. Nevertheless it is worthwile to see that new physics has to be added to the classical picture. Since $u(\omega, T)$ is measured in units of energy as is k_BT, one either concludes that that the energy per oscillator is just a number times k_BT or there must be a new fundamental constant that allows to compare frequencies to energy. Suppose that is possible with some constant $\hbar$, then from dimensional grounds the energy per oscillator can be written as $u(\omega, T) = \hbar\omega\bar{n}(\hbar\omega/k_BT)$ with a new dimensionless universal function $\bar{n}$ of the dimensionless variable $\hbar\omega/k_BT$.

5.6.2 Thermal properties of the photon gas

Photons are non-interacting bosons with a dispersion relation

$$\epsilon_{\mathbf{k}} = \hbar\omega_{\mathbf{k}} = c\hbar k\,, \qquad k = |\mathbf{k}|\,. \tag{5.117}$$

The fact that photons are indeed bosonic in nature is non-trivial and is explained in Quantum Theory II. The conclusion relies on the spin-statistics theorem that asserts that all 'particles' corresponding to half-integer spin are fermionic whereas those to integer ones are bosons. From the quantization of Maxwell's equation one finds that photons are (relativistic) spin 1 particles. Since photons mediate the interaction between charges one finds from the quantum theory of radiation that photons are not strictly non-interacting. A photon can spontaneously create, e.g. an electron-positron pair which couples to other photons. This pair production process cannot satisfy the dispersion relation for electrons and the particles are said to live 'off the momentum shell' and they quickly recombine again to a photon. By drawing an appropiate picture, called Feynman diagram, one can convince oneself that this leads to scattering of photons or in other terms as interaction between the eigenmodes of our cavity. However, the scattering cross section is so small that the time for such photons to come to equilibrium by interacting with each other is much larger than the age of the universe.

The energy for photons is a sum of independent particles

$$\mathcal{H} = \sum_{\lambda\mathbf{k}} \epsilon_{\mathbf{k}} n_{\lambda\mathbf{k}}\,, \qquad n_{\lambda\mathbf{k}} = 0, 1, \ldots, \qquad \lambda = \pm\,. \tag{5.118}$$

Here the degrees of freedom for the two polarizations have been indicated by λ. The energy eigenvalues depend only on the magnitude of the wave vector and the occupation numbers $n_{\lambda\mathbf{k}}$ are unrestriced. Let us make a comment here. From quantum mechanics we would expect a ground state energy of $\hbar\omega_{\mathbf{k}}$ for each oscillator mode. For a finite collection of oscillators this doesn't lead to any problems, since we are free to measure energy differences from this ground state. Here we encounter an infinite number of oscillators which leads to an infinite ground state energy. The conventional wisdom is to argue away these zero-point fluctuations as unobservable and pretend that one can still absorb this quantity by considering only energy differences. A careful study shows that under certain conditions one can design experiments that are sensitive to the change of the ground state energy (Casimir effect).

A special feature occurs that we will encounter for all systems where the particles can be spontaneousley created and don't have to be provided from some heat bath acting as particle source (photons, phonons, magnons, rotons, Bogolons, ...). The number of photons is not fixed. Thus the free energy

$$dF = -SdT - PdV + \mu dN \tag{5.119}$$

will pick the number of photons in such a way to be minimal

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = 0 \tag{5.120}$$

As for the discussion of Fermi gases it is convenient to use the grand canonical ensemble, where the number of particles can fluctuate. Since the chemical potential is zero one finds for the grand canonical potential

$$\Phi = -PV = F - \mu N = F = -k_B T \ln Z_{gr} \,. \tag{5.121}$$

From now on all we have to do is to run the machinery. Then for the grand canonical partition sum is determined by

$$\begin{aligned} Z_{gr} &= Tr \exp(-\beta\mathcal{H}) = \prod_{\lambda\mathbf{k}} \left[\sum_{n_{\lambda\mathbf{k}}=0}^{\infty} \exp\left(-\beta\epsilon_{\mathbf{k}} n_{\lambda\mathbf{k}}\right)\right] && (5.122)\\ &= \prod_{\lambda\mathbf{k}} \left[1 - \exp\left(-\beta\epsilon_{\mathbf{k}}\right)\right]^{-1} && (5.123) \end{aligned}$$

which yields for the free energy (grand canonical potential)

$$\begin{aligned} F &= \beta^{-1} \sum_{\lambda\mathbf{k}} \ln\left[1 - \exp\left(-\beta\epsilon_{\mathbf{k}}\right)\right] && (5.124)\\ &= 2\beta^{-1} \frac{V}{(2\pi)^3} \int d^3\mathbf{k}\ \ln\left[1 - \exp\left(-\beta\epsilon_{\mathbf{k}}\right)\right] && (5.125)\\ &= k_B T \frac{V}{\pi^2} \int_0^{\infty} k^2 dk\ \ln\left[1 - \exp\left(-\epsilon_{\mathbf{k}}/k_B T\right)\right] && (5.126)\\ & && (5.127) \end{aligned}$$

So far the expression is completely general and holds all non-ineracting bosons with vanishing chemical potential. The integral over all wavenumbers can be replaced by a corresponding integral over frequencies

$$\begin{aligned} F &= k_B T \frac{V}{\pi^2 c^3} \int_0^{\infty} \omega^2 d\omega\ \ln\left[1 - \exp\left(-\hbar\omega/k_B T\right)\right] && (5.128)\\ &= \frac{V (k_B T)^4}{\pi^2 \hbar^3 c^3} \int_0^{\infty} x^2 dx\ \ln\left[1 - e^{-x}\right] && (5.129) \end{aligned}$$

The integral over the dimensionless variable $x = \hbar\omega/k_B T$ can be evaluated to

$$\int_0^{\infty} x^2 dx\ \ln\left[1 - e^{-x}\right] = -\frac{\pi^4}{45} \tag{5.130}$$

As final result for the free energy this implies

$$F = -\frac{V(k_B T)^4}{\hbar^3 c^3}\frac{\pi^2}{45} = -\frac{4\sigma}{3c} V T^4 \tag{5.131}$$

with the *Stefan-Boltzmann* constant

$$\sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2} \tag{5.132}$$

This result allows to compute the remaining quantities of interest. For the pressure and entropy one obtains

$$P = -\frac{\Phi}{V} = -\frac{\partial F}{\partial V} = \frac{4\sigma}{3c} T^4 \,, \tag{5.133}$$

$$S = -\frac{\partial F}{\partial T} = \frac{16\sigma}{3c} V T^3 \,. \tag{5.134}$$

Simlarly for the energy and the heat capacity

$$E = F + TS = 4\frac{\sigma}{c} V T^4 = 3PV \,, \tag{5.135}$$

$$C_V = \frac{\partial E}{\partial T} = 16\frac{\sigma}{c} V T^3 \,. \tag{5.136}$$

It is instructive to ask how much each mode or frequency interval contributes to the corresponding quantities. In order to achieve such an interpretation we differentiate the free energy before the integral over all frequencies is performed

$$\begin{aligned} E &= \frac{\partial \beta F}{\partial \beta} = \frac{V}{\pi^2 c^3}\int_0^\infty \omega^2 d\omega \; \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} && (5.137) \\ &= V \int_0^\infty d\omega \; \rho(\omega, T) && (5.138) \end{aligned}$$

Thus for every frequency interval the contribution to the energy density is (Planck distribution)

$$\begin{aligned} \rho(\omega, T) &= \frac{\omega^2}{\pi^2 c^3}\frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} && (5.139) \\ &= \frac{\omega^2}{\pi^2 c^3} u(\omega, T) \,. && (5.140) \end{aligned}$$

In this form one can see that the spectral density is just given by the density of states times the mean energy per quantum oscillator. As a byproduct we derived this mean energy in terms of the now familiar mean occupation number

$$u(\omega, T) = \hbar\omega \bar{n}(\omega, T) \,, \qquad \bar{n}(\omega, T) = \left[\exp\left(\hbar\omega/k_B T\right) - 1\right]^{-1} \,. \tag{5.141}$$

The Planck distribution contains as limiting case the classical law of Rayleigh and Jeans considered in the introductory remarks

$$\rho(\omega, T) = \frac{\omega^2}{\pi^2 c^3} k_B T \,, \qquad \text{for } \hbar\omega \ll k_B T \,, \tag{5.142}$$

as well as the empirical law by Wien

$$\rho(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \hbar\omega e^{-\hbar\omega/k_B T} \,, \qquad \text{for } \hbar\omega \gg k_B T \tag{5.143}$$

Furthermore it gives the microscopic explanation for the scaling of the location of the maximum spectral density as a function of temperature

$$\hbar\omega_{max} = 2.822 k_B T \,, \tag{5.144}$$

which was already discovered by Wien.

To complete the discussion let us derive the total photon number

$$N = \sum_{\lambda \mathbf{k}} \bar{n}(\omega, T) = \frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 d\omega \, \frac{1}{e^{\hbar\omega/k_B T} - 1} \tag{5.145}$$

$$= \frac{2\zeta(3)}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 , \qquad \zeta(3) = \sum_{n=1}^{\infty} \frac{1}{n^3} \approx 1.20206 \tag{5.146}$$

At last we determine the total energy current emitted from a black body at temperature T. From the previous considerations it is clear that the energy current density in the frequency interval $[\omega, \omega + d\omega]$ into the solid angle do is given by

$$c\rho(\omega, T) d\omega \frac{do}{4\pi} \tag{5.147}$$

Then the total energy per time unit and surface area absorbed by a black body is given by

$$J = \int_{hemisphere} \frac{do}{4\pi} \int_0^\infty d\omega \; c\rho(\omega, T) \cos\theta = \sigma T^4 \tag{5.148}$$

The additional cosine in the integral reflects the fact that one has to introduce the projected area to correct for the incident angle of the radiation. In equilibrium this absorbed power of the black body from the thermal radiation is balanced by the emitted power.

5.6.2.1 The Cosmic Microwave Background Radiation

Perhaps the most conclusive (and certainly among the most carefully examined) piece of evidence for the Big Bang is the existence of an isotropic radiation bath that permeates the entire Universe known as the cosmic microwave background (CMB). The word isotropic means the same in all directions; the degree of anisotropy of the CMB is about one part in a thousand. In 1965, two young radio astronomers, Arno Penzias and Robert Wilson, almost accidentally discovered the CMB using a small, well-calibrated horn antenna. It was soon determined that the radiation was diffuse, emanated unifromly from all directions in the sky, and had a temperature of approximately 2.7 Kelvin (ie 2.7 degrees above absolute zero). Initially, they could find no satisfactory explanation for their observations, and considered the possibility that their signal may have been due to some undetermined systematic noise. They even considered the possibility that it was due to 'a white dielectric substance' (ie pigeon droppings) in their horn!

However, it soon came to their attention through Robert Dicke and Jim Peebles of Princeton that this background radiation had in fact been predicted years earlier by George Gamow as a relic of the evolution of the early Universe. This background of microwaves was in fact the cooled remnant of the primeval fireball - an echo of the Big Bang.

If the universe was once very hot and dense, the photons and baryons would have formed a plasma, ie a gas of ionized matter coupled to the radiation through the constant scattering of photons off ions and electrons. As the universe expanded and cooled there came a point when the radiation (photons) decoupled from the matter - this happened about a few hundred thousand years after the Big Bang. That radiation cooled and is now at 2.7 Kelvin. The fact that the spectrum of the radiation is almost exactly that of a 'black body' (a physicists way of describing a perfect radiator) implies that it could not have had its origin through any prosaic means. This has led to the death of the steady state theory for example. In fact the CMB spectrum is a black body to better than 1% accuracy over more than a factor of 1000 in wavelength. This is a much more accurate black body than any we can make in the laboratory!

By the early 1970's it became clear that the CMB sky is hotter in one direction and cooler in the opposite direction, with the temperature difference being a few mK (or about 0.1overall temperature). The pattern of this temperature variation on the sky is known as a 'dipole', and is exactly what is expected if we are moving through the background radiation at high speed in the direction of the hot part. The inference is that our entire local group of galaxies is moving in a particular direction at about 600 km/s. In the direction we are moving the wavelengths of the radiation are squashed together (a blue-shift), making the sky appear hotter there, while in the opposite direction the wavelengths are stretched out (redshift), making the sky appear colder there. When this dipole pattern, due to our motion, is removed, the CMB sky appears incredibly isotropic. Further investigations, including more recent ones by the COBE satellite (eg Smoot et. al.), confirmed the virtual isotropy of the CMB to better than one part in ten-thousand.

5.7 Phonons and the Debye theory of solids

The oscillations of electromagnetic fields and of crystal lattices have much in common. In both cases we are studying the statistical mechanics of quantized vibrations. The quanta of sound are called *phonons*.

5.7.1 The linear chain

To illustrate the quantum mechanics of a crystal lattice we consider a one-dimensional array of particles with a pair interaction potential $v(x)$ such that the Hamiltonian reads

$$\mathcal{H} = T + V = \sum_{j=1}^{n} \frac{1}{2m} p_j^2 + \sum_{j=1}^{N-1} v(x_{j+1} - x_j)\,. \tag{5.149}$$

As illustrated in Fig.5.18 let x_j^0 and $u_j \equiv x_j - x_j^0$ be the equilibrium position and displacement of the jth particle, respectively. The distance between the equilibrium positions, the lattice constant, is $a = x_{j+1}^0 - x_j^0$.

– figure missing –

Figure 5.18: Illustration of a linear chain of N particles interacting via the pair potential $v(x)$.

Upon assuming that the displacements are small we may perform a Taylor expansion of the potential energy V such that

$$V = \sum_{j=1}^{N-1} \left(v(a) + v'(a)(u_{j+1} - u_j) + \frac{1}{2} v''(a)(u_{j+1} - u_j)^2 + \cdots \right) \tag{5.150}$$

The main term in this expansion represents the (minimum) energy of the linear chain when all particles are at rest at their equilibrium positions x_j^0; in the following we denote this energy by the symbol V_0. The next set of terms is identically zero because the potential energy has a minimum at the equilibrium positions x_j^0 and hence its first derivative vanishes.

To leading order (*harmonic approximation*) the Hamiltonian reads

$$\mathcal{H} = \sum_{j=1}^{N} \left(\frac{p_j^2}{2m} + \frac{C}{2}(u_{j+1} - u_j)^2 \right) + V_0(a) \tag{5.151}$$

where we have defined $C := v''(a)$. If we assume periodic boundary conditions, $u_{N+j} = u_j$, the Hamiltonian is invariant with respect to translations of the lattice by multiples of the lattice constant a. This invariance suggest to introduce a linear transformation from the displacement coordinates (u_j, p_j) to normal coordinates (ξ_k, π_k)

$$\xi_k := \frac{1}{\sqrt{N}} \sum_j u_j \, e^{-ikja}\,, \qquad u_j = \frac{1}{\sqrt{N}} \sum_k \xi_k \, e^{ikja} \tag{5.152}$$

$$\pi_k := \frac{1}{\sqrt{N}} \sum_j p_j \, e^{-ikja}\,, \qquad p_j = \frac{1}{\sqrt{N}} \sum_k \pi_k \, e^{ikja} \tag{5.153}$$

Due to the periodic boundary conditions $u_{N+j} = u_j$ we have

$$\exp\left[ikNa\right] = 1 \tag{5.154}$$

such that the mode numbers k may take the N values

$$k = \frac{2\pi}{L} m \quad \text{with} - \frac{N}{2} \leq m \leq \frac{N}{2} \tag{5.155}$$

such that the allowed range of k is $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$. The difference to light waves is that the atomic spacing puts a strict lower limit on the wavelength, $\lambda_{\text{min}} = L/(N/2) = 2a$; it arises when adjacent atoms vibrate in opposite directions. The Hamiltonian in normal modes reads

$$\mathcal{H} = \sum_k \left(\frac{1}{2m} \pi_k^\dagger \pi_k + C(1 - \cos ka) \xi_k^\dagger \xi_k \right) , \tag{5.156}$$

where the hermitean conjugates of the normal modes are $\xi_k^\dagger = \xi_{-k}$ and $\pi_k^\dagger = \pi_{-k}$. The commutation relations for the momenta and displacements $[u_i, p_j] = i\hbar\delta_{ij}$ translate into

$$\left[\xi_k, \pi_{k'}^\dagger\right] = i\hbar\delta_{kk'} \tag{5.157}$$

for the normal modes.

The Hamiltonian Eq.5.156 does not contain any cross terms. It is diagonal in the normal modes with the following characteristic frequencies (see Fig.5.19)

$$\omega_k = \sqrt{\frac{2C}{m}(1 - \cos ka)} = 2\sqrt{\frac{C}{m}} \left| \sin \frac{ka}{2} \right| \tag{5.158}$$

– figure missing –

Figure 5.19: Dispersion of the characteristic frequencies of the normal modes of a linear chain with periodic boundary conditions.

Classically, each of the N normal modes of vibrations corresponds to a wave of distortion of the linear chain, i.e. a (longitudinal) sound wave. Quantum-mechanically, these modes give rise to quanta, called phonons, in much the same way as the vibrational modes of the electromagnetic field give rise to photons. This becomes evident upon rewriting the Hamiltonian in terms of creation and annihilation operators. We define the creation operators[6]

$$a_k := \frac{1}{2\hbar} \left(\xi_k \sqrt{m\omega_k} + i\pi_k \frac{1}{m\omega_k} \right) \tag{5.159}$$

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[6] See a standard textbook on quantum mechanics.

and the annihilation operators $a_k^\dagger$ as hermitean conjugates. They obey the commutation relations

$$[a_k, a_{k'}] = 0\,, \qquad [a_k, a_{k'}^\dagger] = \delta_{kk'} \tag{5.160}$$

and reduce the Hamiltonian to a diagonal form

$$\mathcal{H} = \sum_k \hbar\omega_k(a_k^\dagger a_k + \frac{1}{2}) = \sum_k \hbar\omega_k(n_k + \frac{1}{2}) \tag{5.161}$$

The number operators $n_k = a_k^\dagger a_k$ have the eigenvalues $n_k = 0, 1, 2, \cdots$, which give the number of phonons in each normal mode k.

5.7.2 Hamiltonian of 3D Crystals

One may easily generalize the results of the previous subsection to three-dimensional Bravais lattices. For details see a book on solid state physics, e.g. chapters 22 and 23 in Ashcroft & Mermin.

One again finds, that for an N-ion lattice the Hamiltonian to harmonic order can be written as a sum of $3N$ independent oscillators, whose frequencies are those of the $3N$ classical normal modes

$$\mathcal{H} = \sum_{\mathbf{k},s} \left(n_{\mathbf{k},s} + \frac{1}{2}\right)\omega_{\mathbf{k},s}\,, \tag{5.162}$$

where the sum over s is over all phonon branches. For Bravais lattices with n atoms per unit cell there are 3 acoustic branches, charactericed by linear dependence on k for small k, and $3(n-1)$ optical branches, which are usually quite flat if the intrscellular interactions are much stronger than those between the cells; see also a textbook on solid state physics for sketches of dispersion curves for $\omega_{\mathbf{k},s}$, e.g. Fig.22.14 in Ashcroft & Mermin.

For simplicity we will consider Bravais lattices with a single atom per unit cell. Then there are only three acoustic branches with linear dispersions at small wave vectors, one longitudinal and two degenerate transverse branches,

$$\omega_{\mathbf{k},l} = c_l k\,, \tag{5.163}$$

$$\omega_{\mathbf{k},t} = c_t k \quad \text{(two-fold degenerate).} \tag{5.164}$$

A key quantity for the following analysis is the *density of states* defined as

$$g(\omega) = \frac{1}{3N}\sum_{\mathbf{k},s} \delta(\omega - \omega_{\mathbf{k},s}) \tag{5.165}$$

The prefactor $1/3N$ in the density of states is chosen such that $g(\omega)$ is normalized when integrated over all frequencies $\int d\omega g(\omega) = 1$. We are interested in the behavior of the density of states at low frequencies ω corresponding to small wave vectors k. Then we may write

$$\begin{aligned} g(\omega) &= \frac{1}{3N}\sum_{\mathbf{k}}\left[\delta(\omega-\omega_{\mathbf{k},l})+2\delta(\omega-\omega_{\mathbf{k},t})\right] \\ &= \frac{1}{3N}\,4\pi\,\frac{V}{(2\pi)^3}\int_0^\infty dk k^2\,\left[\delta(\omega-c_l k)+2\delta(\omega-c_t k)\right] \\ &= \frac{V}{N}\,\frac{\omega^2}{6\pi^2}\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\sim\omega^2 \end{aligned} \qquad (5.166)$$

The key feature of the density of states is that it grows like ω^2 for small frequencies ω. This is the same behavior as for photons! This allows us to calculate the thermodynamic properties at low temperatures, where only low energy photons are excited. We find [7]

$$\begin{aligned} U &= \sum_{\mathbf{k},s}\hbar\omega_{\mathbf{k},s}(n_{\mathbf{k},s}+\frac{1}{2}) \\ &= E_0+3N\frac{V}{N}\,\frac{1}{6\pi^2}\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\int_0^\infty d\omega\frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1} \\ &= E_0+3N\frac{V}{N}\,\frac{1}{6\pi^2}\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\frac{1}{\hbar^3\beta^4}\underbrace{\int_0^\infty dx\frac{x^3}{e^x-1}}_{=3\pi^4/45} \\ &= E_0+\frac{V\pi^2}{30\hbar^3}\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)(k_{\mathrm{B}}T)^4 \end{aligned} \qquad (5.167)$$

where $E_0=\frac{1}{2}\sum_{\mathbf{k},s}\omega_{\mathbf{k},s}$ is the zero point energy of the phonons. We had already anticipated the T^4 depedence of the internal energy from heuristic scaling arguments in section 5.5.

For *high temperature* we may approximate the Bose-Einstein distribution function by $1/(e^{\beta\hbar\omega})\approx k_{\mathrm{B}}T/\hbar\omega$ such that the internal energy simply becomes

$$U=E_0+3N\int d\omega g(\omega)\hbar\omega\frac{k_{\mathrm{B}}T}{\hbar\omega}=E_0+3Nk_{\mathrm{B}}T \qquad (5.168)$$

as expected from the equipartition theorem from classical statistical mechanics.

In summary, we have for the specific heat

$$C_v=\begin{cases}\sim T^3 & \text{for low temperatures (Debye law)}\\ 3Nk_{\mathrm{B}} & \text{for high temperatures (Dulong-Petit law)}\end{cases} \qquad (5.169)$$

...

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[7] At low temperatures $\beta\hbar\omega_{max}\ll 1$ one is allowed to replace the density of states by the low energy expression $g(\omega)\sim\omega^2$ since only small values of $\hbar\omega$ give a significant contribution to the integral. Contributions from high energy modes (at the zone boundary) are cut off by the Bose-Einstein distribution.

Debye proposed the approximation where the low-energy density of states Eq.5.166 is extended up to the maximum value ω_D chosen such that $\int_0^{\omega_D} d\omega g(\omega) = 1$. Then we have

$$g(\omega) = \frac{3\omega^2}{\omega_D^3}\theta(\omega_D - \omega) \tag{5.170}$$

with

$$\omega_D = \frac{V}{N}\frac{1}{18\pi^2}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right) \tag{5.171}$$

and the internal energy reads

$$U = E_0 + 3Nk_\mathrm{B}T\, D\left(\frac{\hbar\omega}{k_\mathrm{B}T}\right) \tag{5.172}$$

with the Debye function

$$\begin{aligned} D(x) &= \frac{3}{x^2}\int_0^x dy \frac{y^3}{e^y - 1} \\ &= \begin{cases} 1 - \frac{3}{8}x + \frac{1}{20}x^2 + \cdots & \text{for } x \ll 1, \\ \frac{\pi^4}{5x^3} + \mathcal{O}(e^{-x}) & \text{for } x \gg 1, \end{cases} \end{aligned} \tag{5.173}$$

The Debye frequency also defines a Debye temperature

$$k_\mathrm{B}\Theta_D = \hbar\omega_D \tag{5.174}$$

The phonon contribution to the specific is then given by

$$\begin{aligned} \frac{C_v}{Nk_\mathrm{B}} &= \frac{9T^3}{\Theta_D^3}\int_0^{\Theta_D/T} dy \frac{y^4}{(e^y - 1)^2} \\ &= 3\left(4D(x) - \frac{3x}{e^x - 1}\right) \\ &= \begin{cases} 3\left[1 - \frac{1}{20}(\frac{\Theta_D}{T})^2\right] & \text{for } T \gg \Theta_D, \\ \frac{12\pi^4}{5}(\frac{T}{\Theta_D})^3 + \mathcal{O}(e^{-\Theta_D/T}) & \text{for } T \ll \Theta_D. \end{cases} \end{aligned} \tag{5.175}$$

with $x = \Theta_D/T$, a plot of which is given in Fig. 5.20. At low temperatures the specific heat vanishes like T^3, verifying the third law of thermodynamics. When the temperature is much greater than the Debye temperature the lattive behaves classically, as indicated by the fact that $C_v = 3Nk_\mathrm{B}$. For most solids the Debye temperature is of the order of 220 K. This is why the Dulong-Petit law $C_v = 3Nk_\mathrm{B}$ holds at room temperatures. At extremels high temperatures the model of noninteracting phonons breaks down because the lattice eventually melts.

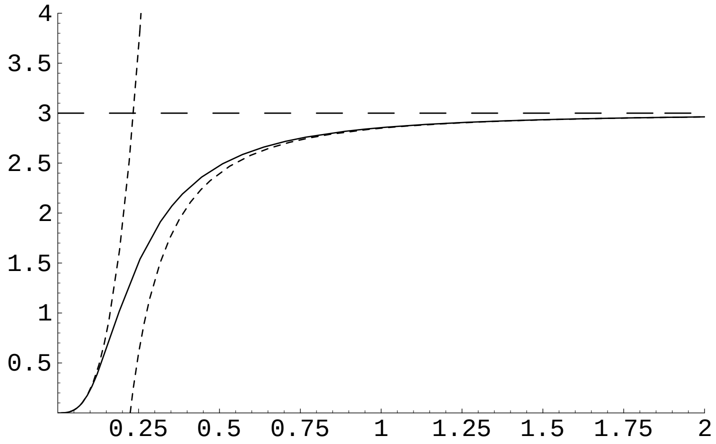

Figure 5.20: Specific heat in units of $Nk_{\rm B}$ as a function of T/T_D in the Debye approximation. The long dashed line is the classical result, and the short dashed lines are the approximate expression for low and high temperatures.