Chapter 4

Ideal Systems: Some Examples

In this chapter we consider some examples which visualize the statistical physics approach of chapter 2 to describing many-particle systems. This will also demonstrate characteristic thermodynamical and statistical properties of such systems.

4.1 2-level systems

A 2-level system is a quantum mechanical system whose Hilbert space consists of exactly 2 states, e.g. a spin $\frac{1}{2}$ in a magnetic field $\vec{B} = (0, 0, B)$.

$$H_i = -g\mu_0 \vec{\sigma}_i \cdot \vec{B} = -2\mu_0 \sigma_{z,i} B \tag{4.1}$$

with the Landé factor $g = 2$ and the spin components along the z-axis $s_i = \pm\frac{1}{2}$. We consider a system of $N \gg 1$ such non-interacting spins,

$$H = \sum_{i=1}^{N} H_i \tag{4.2}$$

which has the energy eigenvalues

$$E\left(\{m_i\}\right) = -\sum_{i=1}^{N} 2\mu_0 s_i B, \qquad s_i = \pm\frac{1}{2}. \tag{4.3}$$

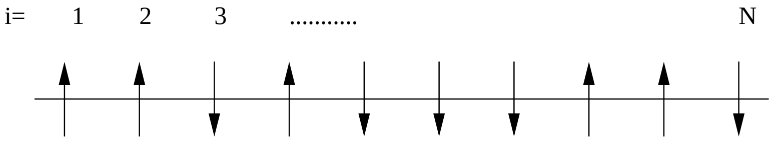

Figure 4.1: System of many independent spins

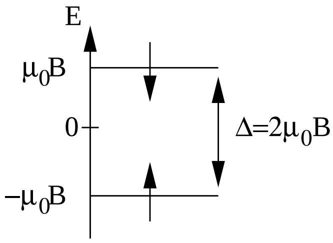

Figure 4.2: Two-level system

The possible energy eigenvalues of the system with N independent spins are

$$\begin{aligned} E_n &= -n\mu_0 B && (4.4)\\ n &= -N, -N+2, \ldots, N && (4.5)\\ n &= n_\uparrow - n_\downarrow && (4.6)\\ &= \text{number of up-spins - number of down-spins} \end{aligned}$$

4.1.1 Microcanonical treatment (isolated system)

The energy has a fixed value. To calculate the equlibrium distribution of the isolated system, the number of microstates with a given energy E_n must be enumerated:

$$\begin{aligned} n_\uparrow + n_\downarrow &= N && (4.7)\\ n_\uparrow - n_\downarrow &= n && (4.8) \end{aligned}$$

For given N, n, there are

$$\begin{aligned} n_\uparrow &= \frac{1}{2}(N+n) \qquad \text{spins } \uparrow && (4.9)\\ n_\downarrow &= \frac{1}{2}(N-n) \qquad \text{spins } \downarrow && (4.10) \end{aligned}$$

Note: $n_\uparrow, n_\downarrow \in \mathbb{N}_0$ for N even or odd.

Thus,

$$\begin{aligned}
\Omega(E_n) \equiv \Omega(N,n) &= \begin{pmatrix} \text{number of possibilities to} \\ \text{select } n_\uparrow = \frac{1}{2}(N+n) \text{ spins } \uparrow \\ \text{from } N \text{ spins without ordering} \end{pmatrix} && (4.11) \\
&= \frac{N\cdot(N-1)\cdot\ldots\cdot(N-n_\uparrow+1)}{n_\uparrow!} && (4.12) \\
&= \frac{N!}{n_\uparrow!(N-n_\uparrow)!} && (4.13) \\
&= \frac{N!}{\left(\frac{N+n}{2}\right)!\left(\frac{N-n}{2}\right)!} && (4.14)
\end{aligned}$$

and

$$W_M(N,n) = \frac{1}{\Omega(N,n)}. \qquad (4.15)$$

The average value of one spin (e.g. s_1) in the system with energy E_n is

$$\langle s_1\rangle = \frac{1}{2}\frac{1}{\Omega(N,n)}\left[N\left(s_1=\frac{1}{2}\right) - N\left(s_1=-\frac{1}{2}\right)\right] \qquad (4.16)$$

with

$$\begin{aligned}
N\left(s_1=\pm\frac{1}{2}\right) &= \text{number of spin configurations with } s_1=\pm\frac{1}{2} && (4.17) \\
&\quad\ \textit{and} \text{ total energy } E_n \\
&= \Omega(N-1, n\mp 1) && (4.18) \\
&= \begin{cases} \frac{(N-1)!}{\left(\frac{N+n-2}{2}\right)!\left(\frac{N-n}{2}\right)!} \\ \frac{(N-1)!}{\left(\frac{N+n}{2}\right)!\left(\frac{N-n-2}{2}\right)!} \end{cases} . && (4.19)
\end{aligned}$$

Thus,

$$\langle s_1\rangle = \frac{1}{2}\frac{1}{N}\left[\frac{(N+n)}{2} - \frac{(N-n)}{2}\right] = \frac{1}{2}\frac{n}{N} = \frac{1}{2}\frac{(n_\uparrow - n_\downarrow)}{(n_\uparrow + n_\downarrow)}. \qquad (4.20)$$

The average fluctuations (variance) about this mean value are

$$\left\langle (s_1 - \langle s_1\rangle)^2\right\rangle = \langle s_1^2\rangle - \langle s_1\rangle^2 = \frac{1}{4}\left(1-\frac{n^2}{N^2}\right), \qquad (4.21)$$

where we have used

$$\langle s_1^2\rangle = \frac{1}{4}\frac{1}{\Omega(N,n)}\left[N\left(s_1=\frac{1}{2}\right)+N\left(s_1=-\frac{1}{2}\right)\right]=\frac{1}{4}. \tag{4.22}$$

The fluctuations never vanish for $N\to\infty$, unless E_n has its maximum absolute value, i.e. all spins point in the same direction, $n=\pm N$. This is clear, because any energy $|E_n|<|E_{\max}|=N\mu_0 B$ can be realized by several spin configurations with $s_1=+\frac{1}{2}$ or $s_1=-\frac{1}{2}$.

Entropy and temperature

The entropy of the microcanonical ensemble is

$$S(E) \quad = \quad k_B \ln\Omega(N,n) \tag{4.23}$$

$$\overset{N!\approx\left(\frac{N}{e}\right)^N}{\approx} \quad -k_B\left[\frac{N+n}{2}\ln\left(\frac{N+n}{2}\right)+\frac{N-n}{2}\ln\left(\frac{N-n}{2}\right)\right]. \tag{4.24}$$

With $E=-n\mu_0 B, n=-N,-N+2,\ldots,N$ as above and $dE\equiv dU=T\,dS$ we can calculate the temperature

$$\frac{1}{T}=\frac{\partial S}{\partial E} \quad = \quad \frac{1}{-\mu_0 B}\frac{\partial S}{\partial n}=\frac{k_B}{2\mu_0 B}\ln\left(\frac{1-\frac{n}{N}}{1+\frac{n}{N}}\right)=\frac{k_B}{\Delta}\ln\left(\frac{1-\frac{2E}{\Delta}}{1+\frac{2E}{\Delta}}\right) \tag{4.25}$$

or

$$E=-N\frac{\Delta}{2}\tanh\left(\frac{\Delta/2}{k_B T}\right). \tag{4.26}$$

Hence we have

$$T\begin{cases} >0 & \text{for}\, E<0\\ <0 & \text{for}\, E>0\end{cases} \tag{4.27}$$

It is a general feature of systems whose energy spectrum is bounded from above, that their entropy is zero both for the minimum and the maximum energy value, since these two microstates are non-degenerate. Therefore, S must have a maximum for an intermediate energy, as shown in figure 22, and $T=\left(\frac{\partial S}{\partial E}\right)^{-1}$ can be >0 or <0.

The physical meaning of negative temperatures will become more evident in the canonical ensemble.

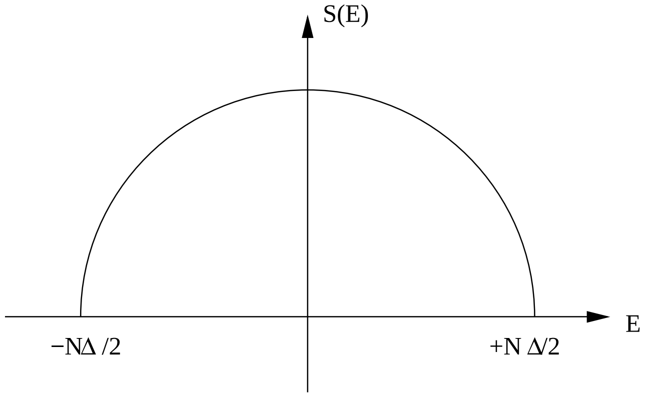

Figure 4.3: Entropy of an ideal spin system in the microcanonical ensemble

We see from the above calculations that for the microcanonical treatment the enumeration of the states $\Omega(N, n)$ is crucial. This can be a cumbersome task, because the counting is constrained by the fact that the energy is fixed, i.e. that $n = n_\uparrow - n_\downarrow$ has a fixed value. Therefore, in most cases it is more efficient to calculate in the canonical ensemble, where the summation in Z_c runs over all microstates, irrespective of their energy.

4.1.2 Canonical treatment and thermodynamic properties of a 2-level system

The canonical partition function is

$$Z_c = \sum_{s_1=\pm\frac{1}{2}} \sum_{s_2=\pm\frac{1}{2}} \dots \sum_{s_N=\pm\frac{1}{2}} e^{-\frac{E(s_1,\dots,s_N)}{k_B T}}, \tag{4.28}$$

where the total energy of the N-spin system is

$$E_n = E(s_1, \dots, s_N) = \sum_{i=1}^{N} E^1(s_i) = \sum_{i=1}^{N} (-2 s_i \mu_0 B). \tag{4.29}$$

$$
\begin{aligned}
Z_c &= \sum_{s_1=\pm\frac{1}{2}} \dots \sum_{s_N=\pm\frac{1}{2}} e^{-\frac{E_1(s_1)}{k_BT}} e^{-\frac{E_1(s_2)}{k_BT}} \dots e^{-\frac{E_1(s_N)}{k_BT}} && (4.30)\\
&= \left(\sum_{s=\pm\frac{1}{2}} e^{-\frac{E_1(s)}{k_BT}} \right)^N = (Z_{c,1})^N , && (4.31)
\end{aligned}
$$

where

$$
Z_{c,1} = \sum_{s=\pm\frac{1}{2}} e^{-\frac{-2s\mu_0 B}{k_BT}} = 2\cosh\left(\frac{\mu_0 B}{k_BT}\right) = 2\cosh\left(\frac{\Delta/2}{k_BT}\right). \tag{4.32}
$$

It is generally true:

Note: For a system of N *independent* subsystems (i.e. not interacting with each other) the canonical partition sum Z_c factorizes into the product of the canonical partition sums of each subsystem, $Z_{c,1}$.

This is because for non-interacting subsystems the total energy is simply the sum of the energies of the subsystems.

The Boltzmann distribution function is then

$$
W_c(n) = \frac{1}{Z_c} e^{-\frac{E_n}{k_BT}} \prod_{i=1}^{N} \frac{1}{Z_{c,1}} e^{\frac{\Delta}{k_BT}s_i} = \prod_{i=1}^{N} W_{c,1}(s_i). \tag{4.33}
$$

The average value of the spin s_i is

$$
\begin{aligned}
\langle s_i \rangle &= \sum_{s_1=\pm\frac{1}{2}} \dots \sum_{s_i=\pm\frac{1}{2}} \dots \sum_{s_N=\pm\frac{1}{2}} s_i W_{c,1}(s_1) \dots W_{c,1}(s_i) \dots W_{c,1}(s_N) && (4.34)\\
&= \sum_{s_i=\pm\frac{1}{2}} s_i W_{c,1}(s_i) && (4.35)\\
&= \frac{1}{Z_{c,1}} \frac{1}{2} \left[e^{\frac{\Delta/2}{k_BT}} - e^{-\frac{\Delta/2}{k_BT}} \right] && (4.36)\\
&= \frac{1}{2} \tanh\left(\frac{\Delta/2}{k_BT}\right). && (4.37)
\end{aligned}
$$

It is seen that the average spin $\langle s_i \rangle$ is independent of the other spins in the canonical ensemble, since the total energy is not fixed.

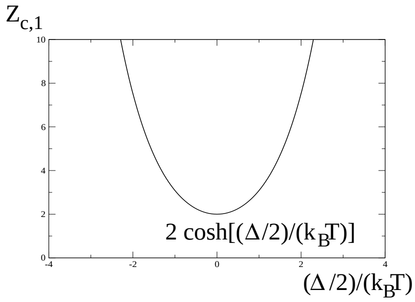

Figure 4.4: Canonical partition sum of a two-level system

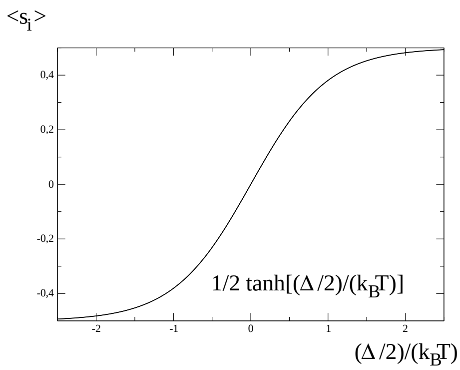

Figure 4.5: Average spin per site

The magnetization of the system is

$$M = Ng\mu_0 \langle s_i \rangle = Ng\mu_0 \frac{1}{2} \tanh\left(\frac{\Delta/2}{k_B T}\right) = N\mu_0 \tanh\left(\frac{\mu_0 B}{k_B T}\right). \tag{4.38}$$

Thermodynamics of spin systems (2-level systems)

The **free energy** can be calculated microscopically from the canonical partition sum:

$$F(T) = -k_B T \ln Z_c = -N k_B T \ln\left(2\cosh\left(\frac{\Delta/2}{k_B T}\right)\right) \tag{4.39}$$

The **entropy** is

$$S(T) = -\frac{\partial F}{\partial T} = N k_B \left[\ln\left(2\cosh\left(\frac{\Delta/2}{k_B T}\right)\right) - \frac{\Delta/2}{k_B T}\tanh\left(\frac{\Delta/2}{k_B T}\right)\right] \tag{4.40}$$

and the **specific heat** for $B = \text{const.}$,

$$C_B(T) = \left(\frac{\delta Q}{\partial T}\right)_B = T\left(\frac{\partial S}{\partial T}\right)_B = Nk_B\left(\frac{\Delta/2}{k_BT}\right)^2 \frac{1}{\cosh^2\left(\frac{\Delta/2}{k_BT}\right)}. \tag{4.41}$$

Discussion of the T-dependence of c_B:

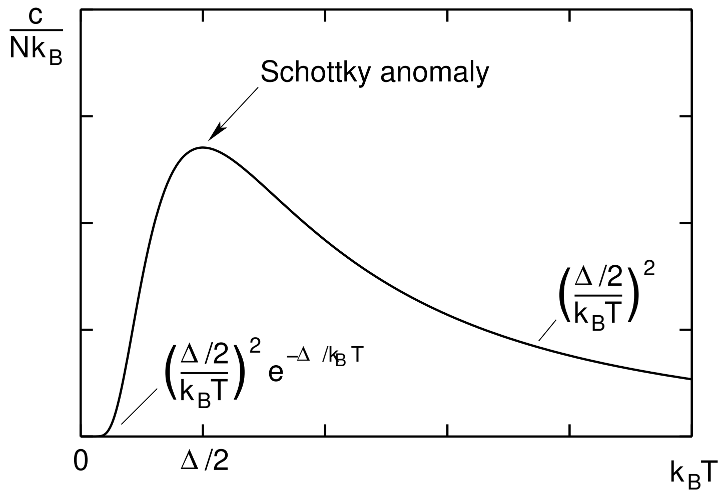

Figure 4.6: Specific heat of an ideal two-level system

(1) For $k_BT \ll \Delta/2, c_B \sim \left(\frac{\Delta/2}{k_BT}\right)^2 e^{-\frac{\Delta}{k_BT}}$ vanishes exponentially in a nonanalytical way (all derivatives are zero). This is typical for systems with an excitation gap Δ between the ground state and the first excited state:
At low T, the occupation of the excited state(s) is exponentially small due to the Boltzmann distribution, making the T-dependence of the internal energy U and of the specific heat $c_B = \left(\frac{\partial U}{\partial T}\right)_B$ exponential.

(2) For $k_BT \gg \Delta/2, c_B \sim \frac{1}{T^2} \xrightarrow{T\to\infty} 0$.
This is typical for systems whose energy spectrum is bounded from above: For $k_BT \gg E_{\max} = \Delta/2$ ground state and excited state(s) are equally occupied, and increasing T does not increase U anymore.$\longrightarrow c_B = \left(\frac{\partial U}{\partial T}\right)_B \to 0$.

(3) From (1) and (2) it follows $c_B(T)$ must have a maximum. This maximum is called *Schottky anomaly* and is characteristic for a discrete 2-level system. It is therefore often used to detect 2-level systems in experiments.

The **internal energy** is calculated from the above expressions as,

$$U = F + TS = -N\mu_0 \tanh\left(\frac{\mu_0 B}{k_B T}\right) = -MB \tag{4.42}$$

or equivalently

$$U = \sum_i (-2\mu_0 B)\langle s_i\rangle = -\underbrace{2N\mu_0\langle s_i\rangle}_{M} B. \tag{4.43}$$

The **magnetization** can also be calculated by thermodynamic derivative:

$$\begin{aligned}
M &= -\left(\frac{\partial F}{\partial B}\right)_T & (4.44)\\
&= -\frac{\partial}{\partial B}\left(k_B T \ln Z_c\right) & (4.45)\\
&= -\frac{\partial}{\partial B}\left(N k_B T \ln Z_{c,1}\right) & (4.46)\\
&= -N k_B T \frac{1}{Z_{c,1}} \frac{\partial Z_{c,1}}{\partial B} & (4.47)\\
&\overset{(*)}{=} 2N\mu_0 \sum_{s=\pm\frac{1}{2}} s\, e^{-\frac{2s\mu_0 B}{k_B T}} & (4.48)\\
&= 2N\mu_0 \langle s\rangle & (4.49)\\
&= N\mu_0 \tanh\left(\frac{\mu_0 B}{k_B T}\right) & (4.50)\\
(*) \qquad Z_{c,1} &= \sum_{s=\pm\frac{1}{2}} e^{-\frac{2s\mu_0 B}{k_B T}}, & (4.51)
\end{aligned}$$

as in the direct calculation, Eqs. (4.34)–(4.38).

This shows how statistical averages are generated by thermodynamic derivatives of F.

The **magnetic susceptibility** χ of a system of *distinguishable* (e.g. localized) spins is

$$\chi = \left(\frac{\partial M}{\partial B}\right)_{S,V,N} = N\,\frac{\mu_0^2}{k_B T}\,\frac{1}{\cosh^2\left(\frac{\mu_0 B}{k_B T}\right)}\ . \tag{4.52}$$

Hence, for vanishing B-field the susceptibility is

$$\chi = \left(\frac{\partial M}{\partial B}\right)_{S,V,N;B=0} = N\ \frac{\mu_0^2}{k_B T}\ . \tag{4.53}$$

This so-called Curie behavior, $\chi_{B=0} \sim 1/T$, is characteristic for localized spins and is used experimentally to detect local magnetic moments in solids, as compared to the $T-independent$ low-temperature susceptibility of the mobile spins of electrons in a metal (see section 5.2.2).

Negative "temperature":
$T < 0$ leads to nondiverging occupation probabilities, if the spectrum is bounded from above, and corresponds to an occupation inversion, as shown in figure 26, i.e. to a nonequilibrium state. In the case $T < 0$, T should, therefore, be understood as a mere parameter to describe a special (non-equilibrium) distribution rather than an actual temperature. The latter is defined only in thermodynamic equilibrium and must be positive semidefinite. The inversion can be realized experimentally by adiabatically (i.e. quickly) inverting the magnetic field $B \to -B$, so that no relaxation of the average occupation numbers $W_C(E)$ is possible:

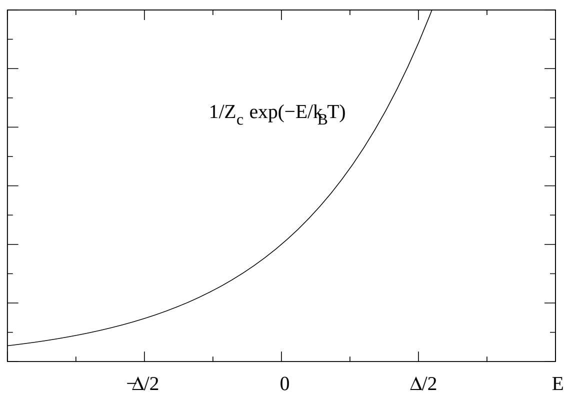

Figure 4.7: Occupation probability for $T < 0$

$$E\left(s_i = +\frac{1}{2}\right) = -\mu_0 B \to +\mu_0 B \tag{4.54}$$

$$E\left(s_i = -\frac{1}{2}\right) = +\mu_0 B \to -\mu_0 B \tag{4.55}$$

Adiabatic demagnetization:
By quickly (adiabatically) reducing the external magnetic field $B \to B' < B$, such that no change of the occupation probabilities $W_C(E)$ occurs during this process, the temperature T is reduced by the factor B'/B. This is because in $W_C(E)$ the quantities B and T appear as the ratio B/T only, and because $W_C(E)$, and hence B/T remains unchanged. This method is called *adiabatic demagnetization*.

The lowest, technically reachable temperatures ($T \approx 1\mu K$) are realized in spin systems by using this method.

4.2 A system of independent harmonic oscillators

We consider a system of N identical, uncoupled harmonic oscillators with eigen-frequency ω:

$$H = \sum_{i=1}^{N} \hbar\omega \left(a_i^\dagger a_i + \frac{1}{2} \right) \tag{4.56}$$

with possible energy eigenvalues of a microstate

$$|n\rangle = |n_1, n_2, \ldots, n_N\rangle \tag{4.57}$$

are

$$E_n = \sum_{i=1}^{N} \hbar\omega \left(n_i + \frac{1}{2} \right) = \sum_{i=1}^{N} E_{n_i}^{(1)}, \tag{4.58}$$

where n_i is the number of excitation quanta ("phonons") of the i-th oscillator, $i = 1, \ldots, N$.
The canonical partition sum factorizes like for any system of non-interacting subsystems:

$$\begin{aligned} Z_c &= Z_{c,1}^N = \left(\sum_{n=0}^{\infty} e^{-\frac{E_{n_i}^{(1)}}{k_B T}} \right)^N & (4.59) \\ &= \left(e^{-\frac{\hbar\omega}{2k_B T}} \frac{1}{1 - e^{-\frac{\hbar\omega}{k_B T}}} \right)^N & (4.60) \\ &= \left(\frac{1}{2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)} \right)^N & (4.61) \end{aligned}$$

It is seen that in the canonical ensemble the summation over all microstates is easily performed, because one can sum over all eigenstates of the individual oscillators independently, without the restriction that the total energy of the N-oscillator system is constant, which would be there in the microcanonical ensemble.

All physical quantities can be computed from Z_c:

- **Internal energy U:**

$$U = \langle E \rangle = \frac{1}{Z_c} \sum_n E_n \, e^{-\frac{E_n}{k_B T}} \tag{4.62}$$

$$= \sum_{\substack{n_i=0 \\ i=1,\ldots,N}}^{\infty} (E_{n_1} + E_{n_2} + \ldots + E_{n_N}) \prod_{j=1}^{N} \frac{e^{-\frac{E^{(1)}_{n_j}}{k_B T}}}{Z_{c,1}} \tag{4.63}$$

$$= N \left(\sum_{n_1=0}^{\infty} E^{(1)}_{n_1} \frac{e^{-\frac{E^{(1)}_{n_1}}{k_B T}}}{Z_{c,1}} \right) = N \left\langle E^{(1)} \right\rangle , \tag{4.64}$$

where the expression in brackets in the last line is the internal energy of a single oscillator. It can be calculated directly from the partition sum as a derivative, as seen from:

$$\left\langle E^{(1)} \right\rangle = -\frac{\partial}{\partial \beta} \ln Z_c^{(1)} \tag{4.65}$$

$$= 2 \sinh \left(\frac{\hbar\omega}{2 k_B T} \right) \frac{\cosh \left(\frac{\hbar\omega}{2 k_B T} \right)}{2 \sinh^2 \left(\frac{\hbar\omega}{2 k_B T} \right)} \frac{\hbar\omega}{2} \tag{4.66}$$

$$\text{with} \quad \beta = \frac{1}{k_B T} \tag{4.67}$$

$$\left\langle E^{(1)} \right\rangle = \frac{\hbar\omega}{2} \coth \left(\frac{\hbar\omega}{2 k_B T} \right) . \tag{4.68}$$

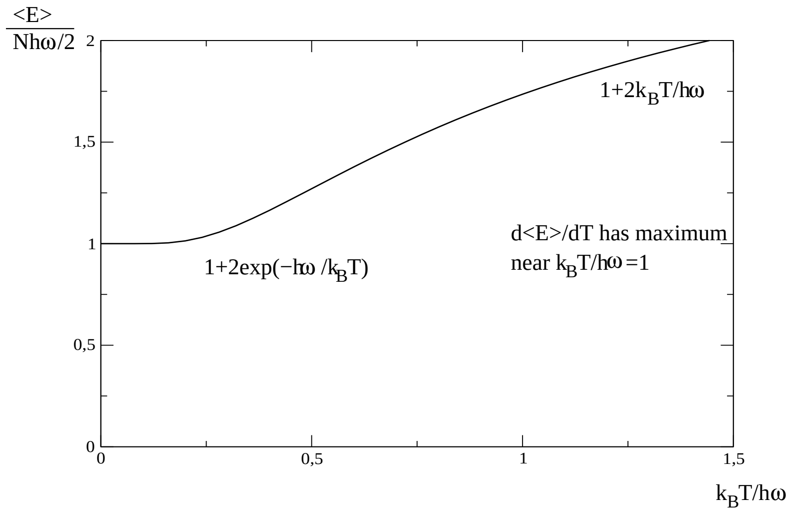

Figure 4.8: Internal energy of a system of N harmonic oscillators

- The internal energy has for $T \to 0$ a finite value $N\frac{\hbar\omega}{2}$ because of the zero-point energy of the harmonic oscillator.
- The T-dependence for $k_BT < \hbar\omega/2$ is *exponential* because there is an excitation gap to the next excited state.
- For $k_BT \gg \hbar\omega/2 \quad \langle E\rangle \sim T$
  This can be understood by calculating the average number of oscillator quanta per oscillator:

$$\langle n\rangle = \sum_{n_1=0}^{\infty} n_1 \frac{e^{-\frac{\hbar\omega\left(n_1+\frac{1}{2}\right)}{k_BT}}}{Z_{c,1}} \tag{4.69}$$

$$= -\frac{\partial}{\partial(\beta\hbar\omega)}\ln Z_{c,1} - \frac{1}{2} \tag{4.70}$$

$$= \frac{1}{2}\left[\coth\left(\frac{\hbar\omega}{2k_BT}\right) - 1\right] \tag{4.71}$$

$$\langle n\rangle = \frac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1} \tag{4.72}$$

Thus,

$$\left\langle E^{(1)}\right\rangle = \hbar\omega\left(\langle n\rangle + \frac{1}{2}\right). \tag{4.73}$$

The average number of quanta at a given temperature T is proportional to T for $k_B t \gg \hbar\omega/2$, where each quantum has a fixed T-independent energy $\hbar\omega$. Hence, $\left\langle E^{(1)}\right\rangle \sim T, k_B T \gg \frac{\hbar\omega}{2}$.

- **Free energy F:**

$$\begin{aligned}
F &= -k_B T \ln Z_c && (4.74)\\
&= -N k_B T \ln Z_{c,1} && (4.75)\\
&= N k_B T \ln\left(2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right) && (4.76)\\
&= N\left[k_B T \ln\left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right) + \frac{\hbar\omega}{2}\right] && (4.77)
\end{aligned}$$

- **Entropy S:**

$$\begin{aligned}
S &= -\frac{\partial F}{\partial T} && (4.78)\\
&= -N k_B\left[\ln\left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right) - \frac{\hbar\omega/k_B T}{e^{\frac{\hbar\omega}{k_B T}} - 1}\right] && (4.79)\\
&= \begin{cases} N k_B \dfrac{\hbar\omega}{k_B T} e^{-\frac{\hbar\omega}{k_B T}}, & k_B T \ll \hbar\omega \\[2ex] N k_B\left(\ln\left(\dfrac{k_B T}{\hbar\omega}\right) + 1\right), & k_B T \gg \hbar\omega \end{cases} && (4.80)
\end{aligned}$$

The internal energy can be calculated from the thermodynamic relation,

$$\begin{aligned}
U &= F + TS && (4.81)\\
&= N\left[\frac{\hbar\omega}{2} + \hbar\omega\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\right] && (4.82)\\
&= N\hbar\omega\left[\langle n\rangle + \frac{1}{2}\right] && (4.83)
\end{aligned}$$

in agreement with the above direct calculation.

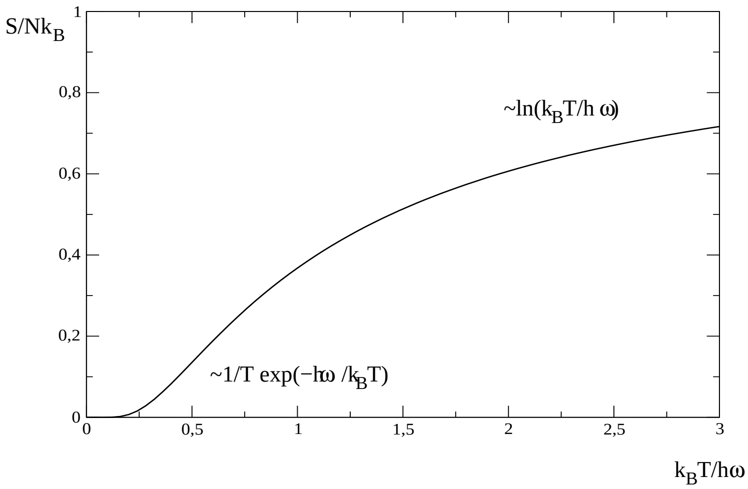

Figure 4.9: Entropy of a system of N independent harmonic oscillators

- **Specific heat:**

$$c = \frac{\partial U}{\partial T} \tag{4.84}$$

$$= N\hbar\omega \frac{\partial \langle n \rangle}{\partial T} \tag{4.85}$$

$$= Nk_B \frac{\left(\frac{\hbar\omega}{2k_BT}\right)^2}{\sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)} \tag{4.86}$$

$$= \begin{cases} Nk_B, & k_BT \gg \hbar\omega \\ Nk_B \left(\frac{\hbar\omega}{2k_BT}\right)^2 e^{-\frac{\hbar\omega}{k_BT}}, & k_BT \ll \hbar\omega \end{cases} \tag{4.87}$$

or equivalently,

$$c = T\frac{\partial S}{\partial T}. \tag{4.88}$$

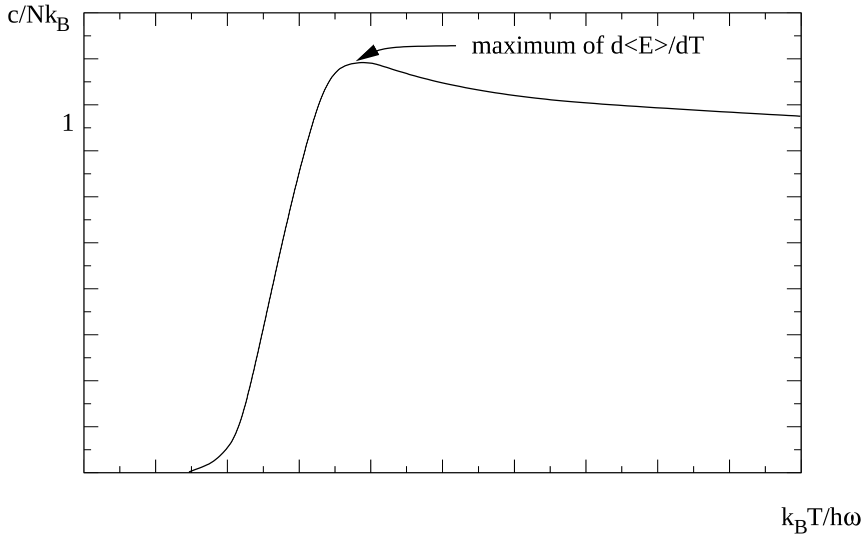

Figure 4.10: Specific heat of a system of N harmonic oscillators

The result for $T \to \infty$ is in agreement with the virial and the equipartition theorems (see Chapter 5.5).

The high-temperature behavior $c(T) = \text{const.}$ is characteristic for systems with a spectrum unbounded from above and is in agreement with the equipartition theorem.

> "In the classical limit $(T, \langle E \rangle \gg \hbar\omega)$ each degree of freedom which appears quadratically in the Hamiltonian, contributes $\frac{1}{2}k_B$ to the specific heat c."

(Here the degrees of freedom are p_i and $x_i, i = 1, \ldots, N$.)

The general equipartition theorem will be discussed later.

From the above calculation one can learn that

- thermodynamic expectation values, like $\langle E \rangle, \langle n \rangle$ etc. can often be calculated directly as derivatives of Z_c with respect to appropriate variables.
- for non-interacting systems which do not share the same volume, derivatives of $\ln Z_c$ wrt. an intensive variable (e.g. T) are extensive, trivially. This will be different for a classical ideal gas.

4.3 The ideal Boltzmann gas and the Gibbs paradox

As the third important example we consider a system of N non-interacting particles in a large cubic box of length L and volume $V = L^d$, where d is the spatial dimension. This example will serve two purposes:

(1) The fact that these particles share the same volume V means that they are indistinguishable in the quantum mechanical sense - in contrast to the spins or harmonic oscillators of the previous sections, which are not mobile and therefore distinguishable. The treatment as distinguishable particles familiar from classical mechanics will lead to an unresolvable inconsistency, which will motivate the treatment as a quantum gas, introducing *quantum statistics*.

(2) By deriving the ideal gas law from a *microscopic* statistical basis, we will be able to make the identification of the Boltzmann constant k_B of statistical physics with the proportionality factor k_B of the gas law.

4.3.1 Statistics of the ideal gas

As usual, we define first the Hamiltonian H, the energy eigenstates $|n\rangle$, and the possible total energy eigenvalues E_n of the N-particle system:

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} = \sum_{i=1}^{N} \frac{1}{2m} \left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2 \right) \tag{4.89}$$

$$\psi_{\vec{k}_i}(\vec{x}_i) = \frac{1}{\sqrt{V}} e^{i\vec{k}_i \vec{x}_i} \tag{4.90}$$

with quantization

$$\vec{k}_i = \frac{2\pi}{L}\left(n_{ix}\widehat{e}_x + n_{iy}\widehat{e}_y + n_{iz}\widehat{e}_z\right) \tag{4.91}$$

$$n_{ix}, n_{iy}, n_{iz} = -\infty, \ldots, \infty \tag{4.92}$$

and in position representation

$$\langle\{\vec{x}\}|n\rangle = \psi_{\vec{k}_1}(\vec{x}_1)\psi_{\vec{k}_2}(\vec{x}_2)\ldots\psi_{\vec{k}_N}(\vec{x}_N) \tag{4.93}$$

$$E_n = \frac{1}{2m}\left(\frac{2\pi\hbar}{L}\right)^2\left[\sum_{i=1}^{N}\left(n_{ix}^2 + n_{iy}^2 + n_{iz}^2\right)\right], \tag{4.94}$$

with

$$\Delta := \frac{2\pi^2\hbar^2}{mL^2} \tag{4.95}$$

Note: This corresponds to the treatment of *classical distinguishable* particles, since in the many-body wave function $\langle\{\vec{x}\}|n\rangle$ the particles are distinguishable, particle 1 (with coordinate $\vec{x}_1$) being in state $\vec{k}_1$, etc. The representation of the states in terms of wave functions is chosen here only make the $\vec{k}$-states discrete and, thus, to make it easy to enumerate the states. Otherwise the treatment is classical.

In the canonical ensemble the partition function factorizes, because the particles and their momentum components are independent,

$$Z_c = (Z_1)^{N\cdot d} \tag{4.96}$$

$$\text{with} \quad Z_1 = \sum_{n=-\infty}^{+\infty} e^{-\frac{2\pi^2\hbar^2}{mL^2k_BT}n^2} = \sum_{n=-\infty}^{+\infty} e^{-\frac{-\lambda_T^2}{L^2}n^2} \tag{4.97}$$

being the canonical partition function per particle and spatial direction. The "thermal de Broglie wavelength" λ_T is defined through the relation

$$k_BT = \frac{1}{2m}\left(\frac{2\pi}{\lambda_T}\hbar\right)^2 \tag{4.98}$$

$$\boxed{\lambda_T = \frac{2\pi\hbar}{\sqrt{2mk_BT}} = \sqrt{\frac{\Delta}{k_BT}}\cdot L} \quad \text{thermal wavelength} \tag{4.99}$$

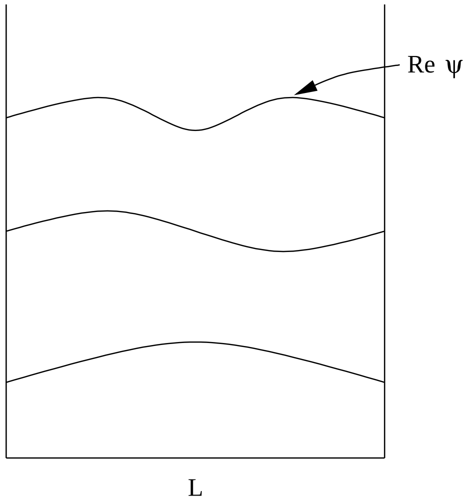

Figure 4.11: Wave functions of free particles in a box of length L

In the thermodynamic limit, $L \gg \lambda_T$, where we must have $T > 0$, the sum in Z_1 can be replaced by an integral and can be evaluated,

$$\lim_{L\to\infty} Z_1 = \int_{-\infty}^{+\infty} dn\, e^{-\left(\frac{\lambda_T}{L}\right)^2 n^2} = \frac{L}{\lambda_T}\sqrt{\pi} \tag{4.100}$$

and

$$\boxed{Z_c = \left(\sqrt{\pi}\frac{L}{\lambda_T}\right)^{Nd}} \tag{4.101}$$

In the limit $T \to 0$ the evaluation as an integral breaks down, and a quantum mechanical treatment in terms of discrete states is required.

The thermodynamic quantities of the ideal Boltzmann gas follow in a straightforward way:

(1) *Free energy:*

$$\begin{aligned} F &= -Nk_BT\ln\left(\sqrt{\pi}^d \frac{V}{\lambda_T^d}\right) && (4.102)\\ &= -\frac{d}{2}Nk_BT\ln\left(\pi\frac{k_BT}{\Delta}\right) && (4.103)\end{aligned}$$

(2) *Entropy:*

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \tag{4.104}$$

$$= \frac{d}{2}Nk_B\ln\left(\pi\frac{k_BT}{\Delta}\right) + \frac{d}{2}Nk_B \tag{4.105}$$

(3) *Internal energy:*

$$\boxed{U = F + TS = \frac{d}{2}Nk_BT} \tag{4.106}$$

(4) *Specific heat:*

$$\boxed{c_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{d}{2}Nk_B} \tag{4.107}$$

equipartition rule (see above)

(5) *Pressure:*

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V} \tag{4.108}$$

$$\boxed{pV = Nk_BT} \quad \text{Ideal gas law} \tag{4.109}$$

Note that the proportionality constant k_B in this equation is the (still arbitrary) Boltzmann constant $k = k_B$ as defined in the context of the statistical entropy. By comparison this statistical law with the thermodynamic definition of the temperature through the gas law (see chapter 1), the value of k_B is now fixed.
(The Maxwell distribution of the velocities in an ideal gas will be computed as an exercise.)

4.3.2 The Gibbs paradox

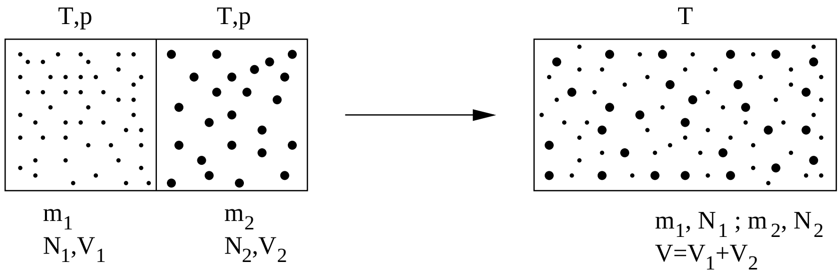

Figure 4.12: Mixing of two gases

We consider two ideal Boltzmann gases $(m_1, N_1, V_1), (m_2, N_2, V_2)$ with particle mass m_1 and m_2, respectively, in volumina V_1 and V_2, separated by a wall, at the same temperature $T = T_1 = T_2$ and pressure $p = p_1 = p_2$. At a time $t = 0$ the wall is removed, and the two gases mix; $T = \text{const.}$.

Before the mixing the total entropy is $(d = 3)$

$$\begin{aligned} S &= S_1 + S_2 && (4.110) \\ &= \frac{3}{2}k_B\left[2N_1 \ln\left(\sqrt{\pi}\frac{V_1^{1/3}}{\lambda_{T_1}}\right) + 2N_2 \ln\left(\sqrt{\pi}\frac{V_2^{1/3}}{\lambda_{T_2}}\right) + N_1 + N_2\right]. && (4.111) \end{aligned}$$

After the mixing the entropy is

$$\begin{aligned} S' &= S'_1 + S'_2 && (4.112) \\ &= \frac{3}{2}k_B\left[2N_1 \ln\left(\sqrt{\pi}\frac{V^{1/3}}{\lambda_{T_1}}\right) + 2N_2 \ln\left(\sqrt{\pi}\frac{V^{1/3}}{\lambda_{T_2}}\right) + N_1 + N_2\right]. && (4.113) \end{aligned}$$

i.e. the entropy changes by

$$\Delta S = S' - S = \frac{3}{2}k_B\left[2N_1 \ln\left(\frac{V_1 + V_2}{V_1}\right)^{1/3} + 2N_2 \ln\left(\frac{V_1 + V_2}{V_2}\right)^{1/3}\right] > 0. \quad (4.114)$$

The increase of entropy is expected, *if the gases are different* $(m_1 \neq m_2)$, because the mixing process is *irreversible* in this case (entropy of mixing).
However, if the two gases consist of the same kind of particles $(m_1 = m_2)$, the mixing process is *reversible*, since it actually constitutes no change of state at

all. Therefore, we must have $\Delta S = 0$ for $m_1 = m_2, T_1 = T_2, p_1 = p_2$. But in our classical treatment the entropy change would still be given by (4.116), $\Delta S > 0$. This is called *Gibbs paradox* of classical statistics. It shows that it is incorrect to consider the identical particles ($m_1 = m_2$) as distinguishable.
The paradox is resolved by quantum statistics:
The states of a many-particle system comprised of particles of the same kind (identical particles) are counted such that the particles are indistinguishable.