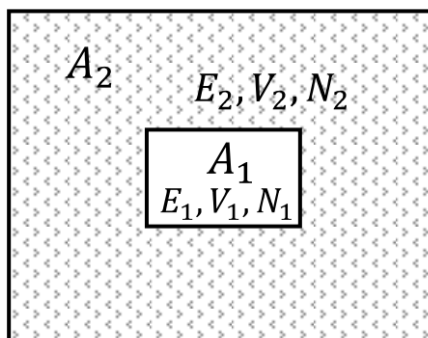# Chapter 9

Canonical ensemble

9.1 System in contact with a heat reservoir

We consider a small system A_1 characterized by E_1, V_1 and N_1 in thermal interaction with a heat reservoir A_2 characterized by E_2, V_2 and N_1 in thermal interaction such that $A_1 \ll A_2$, A_1 has hence fewer degrees of freedom than A_2.

$$
\begin{array}{llll}
E_2 & \gg & E_1 & \qquad N_1 & = & \text{const.} \\
N_2 & \gg & N_1 & \qquad N_2 & = & \text{const.}
\end{array}
$$

with

$$E_1 + E_2 = E = \text{const.}$$

Both systems are in thermal equilibrium at temperature T. The wall between them allows interchange of heat but not of particles. The system A_1 may be any relatively small macroscopic system such as, for instance, a bottle of water in a lake, while the lake acts as the heat reservoir A_2.

Distribution of energy states	The question we want to answer is the following:
	"Under equilibrium conditions, what is the probability of finding the small system A_1 in any particular microstate α of energy E_α? In other words, what is the distribution function $\rho = \rho(E_\alpha)$ of the system A_1?"

We note that the energy E_1 is not fixed, only the total energy $E = E_1 + E_2$ of the combined system.

Hamilton function. The Hamilton function of the combined system A is

$$H(q, p) = H_1(q(1), p(1)) + H_2(q(2), p(2)) ,$$

were we have used the notation

$$q = (q(1), q(2)), \qquad p = (p(1), p(2)) .$$

Microcanonical ensemble of the combined system. Since the combined system A is isolated, the distribution function in the combined phase space is given by the micro-canonical distribution function $\rho(q, p)$,

$$\rho(q, p) = \frac{\delta\left(E - H(q, p)\right)}{\int dq \, dp \, \delta\left(E - H(q, p)\right)}, \qquad \int dq \, dp \, \delta(E - H) = \Omega(E) , \qquad (9.1)$$

where $\Omega(E)$ is the density of phase space (8.4).

Tracing out $A2$. It is not the distribution function $\rho(q, p) = \rho(q(1), p(1), q(2), p(2))$ of the total system A that we are interested in, but in the distribution function $\rho_1(q(1), p(1))$ of the small system A_1. One hence needs to trace out A_2:*

$$
\begin{aligned}
\rho_1(q(1), p(1)) &\equiv \int dq(2) \, dp(2) \, \rho(q(1), p(1), q(2), p(2)) \\
&= \frac{\int dq(2) \, dp(2) \, \delta(E - H_1 - H_2)}{\Omega(E)} \\
&\equiv \frac{\Omega_2(E - H_1)}{\Omega(E)} .
\end{aligned}
\qquad (9.2)
$$

where $\Omega_2(E_2) = \Omega(E - H_1)$ is the phase space density of A_2.

Small E_1 expansion. Now, we make use of the fact that A_1 is a much smaller system than A_2 and therefore the energy E_1 given by H_1 is much smaller than the energy of the combined system:

$$E_1 \ll E .$$

In this case, we can approximate (9.2) by expanding the slowly varying logarithm of $\Omega_2(E_2) = \Omega_2(E - H_1)$ around the $E_2 = E$ as

$$\ln \Omega_2(E_2) = \ln \Omega_2(E - H_1) \simeq \ln \Omega_2(E) - \left[\frac{\partial \ln \Omega_2}{\partial E_2}\right]_{E_2 = E} H_1 + \dots \qquad (9.3)$$

and neglect the higher-order terms since $H_1 = E_1 \ll E$.

Derivatives of the entropy. Using (8.14), namely that

$$S = k_B \ln \left(\frac{\Gamma(E, V, N)}{\Gamma_0}\right) = k_B \ln \left(\frac{\Omega(E)\Delta}{\Gamma_0}\right) , \qquad (9.4)$$

where Δ is the width of the energy shell, we find that derivatives of the entropy like

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k_B \frac{\partial \ln \Omega(E)}{\partial E} \qquad (9.5)$$

---

*A *marginal* distribution function $p(x) = \int p(x, y) dy$ in generically obtained by tracing out other variables from a joint distribution function $p(x, y)$.

can be taken with respect to the logarithm of the phase space density $\Omega(E)$.

Boltzmann factor. Using (9.5) for the larger system A_2 we may rewrite (9.3) as

$$
\begin{aligned}
\Omega_2(E - H_1) &= \exp\left[\ln\Omega_2(E) - \left.\frac{\partial \ln\Omega_2(E_2)}{\partial E_2}\right|_{E_2=E} H_1 + \ldots\right] \\
&= \Omega_2(E)\exp\left[-\frac{H_1}{k_B T_2}\right] .
\end{aligned}
$$

The temperature T_2 of the heat reservoir A_2 by whatever small amount of energy the large system A_2 gives to the small system A_1. Both systems are thermally coupled, such that $T_1 = T_2 = T$. We hence find with (9.2)

$$
\rho_1(q(1), p(1)) = \frac{\Omega_2(E)}{\Omega(E)} e^{-\frac{H_1}{k_B T}} \propto e^{-\frac{H_1}{k_B T}} . \tag{9.6}
$$

The factor $\exp[-H_1/(k_B T)]$ is called the *Boltzmann factor*.

Distribution function of the canonical ensemble. The prefactor $\Omega_2(E)/\Omega(E)$ in (9.6) is independent of H_1. We may hence obtain the the normalization of ρ_1 alternatively by integrating over the phase space of A_1:

$$
\rho_1(q(1), p(1)) = \frac{e^{-\beta H_1(q(1), p(1))}}{\int dq(1)\, dp(1)\, e^{-\beta H_1(q(1), p(1))}} , \qquad \beta = \frac{1}{k_B T} . \tag{9.7}
$$

9.1.1 Boltzmann factor

The probability P_α of finding the system A_1 (which is in thermal equilibrium with the heat reservoir A_2) in a microstate α with energy E_α is given by

$$
P_\alpha = \frac{e^{-\beta E_\alpha}}{\sum_\alpha e^{-\beta E_\alpha}} \tag{9.8}
$$
Boltzmann distribution

when rewriting (9.7) in terms of P_α.

– The number of states $\Omega_2(E_2) = \Omega_2(E - H_1)$ accessible to the reservoir is a rapidly increasing function of its energy.

– The number of states $\Omega_2(E_2) = \Omega_2(E - H_1)$ accessible to the reservoir decreases therefore rapidly with increasing $E_1 = E - E_2$. The probability of finding states with large E_1 is accordingly also rapidly decreasing.

The exponential dependence of P_α on E_α in equation (9.8) expresses this fact in mathematical terms.

Example. Suppose a certain number of states accessible to A_1 and A_2 for various values of their respective energies, as given in the figure, and that the total energy of the combined system is 1007.

- Let A_1 be in a state α with energy 6. E_2 is then in one of the $3 \cdot 10^5$ states with energy 1001.

- If A_1 is in a state γ with energy 7, the reservoir must be in one of the $1 \cdot 10^5$ states with energy 1000.
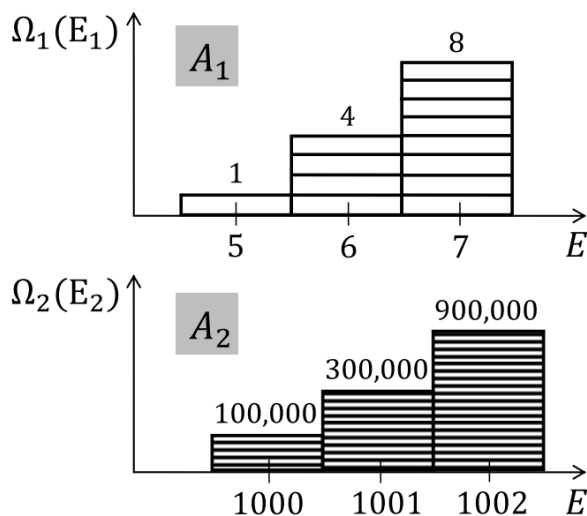
The number of realizations of states with $E_1 = 6$ the ensemble contains is hence much higher than the number of realization of state with $E_1 = 7$.

Canonical ensemble. An ensemble in contact with a heat reservoir at temperature T is called a *canonical ensemble*, with the Boltzmann factor $\exp(-\beta E_\alpha)$ describing the canonical distribution (9.8).

Energy distribution function. The Boltzmann distribution (9.8) provides the probability P_α to find an individual microstates α. There are in general many microstates in a given energy, for which

$$P(E) = \sum_{E < E_\alpha < E+\Delta} P_\alpha \propto \Omega(E)\, e^{-\beta E} , \quad (9.9)$$
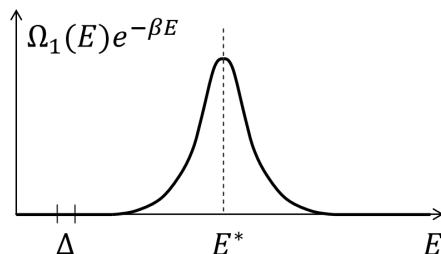
is the corresponding *energy distribution function*. $\Omega(E) = \Omega_1(E)$ is, as usual, the density of phase space.

- $P(E)$ is rapidly decreasing for *increasing* energies due to the Boltzmann factor $\exp(-\beta E_\alpha)$.

- $P(E)$ is rapidly decreasing for *decreasing* energies due to the decreasing phase space density $\Omega(E)$.

The energy density is therefore sharply peaked. We will discuss the the width of the peak, viz the energy fluctuations, more in detail in Sect. 9.6.

9.2 Canonical partition function

We rewrite the distribution function (9.7) of the canonical ensemble as

$$\rho(q,p) \;=\; \frac{e^{-\beta H(q,p)}}{\int d^{3N}q\, d^{3N}p\, e^{-\beta H(q,p)}} \;,$$

where we dropped all the indices "1" for simplicity, though in fact we are still describing the properties of a "small" system (which is nevertheless macroscopically big) in thermal equilibrium with a heat reservoir.

Partition function. The *canonical partition function* ("kanonische Zustandssumme") Z_N is defined as

$$\boxed{Z_N \;=\; \int \frac{d^{3N}q\, d^{3N}p}{h^{3N} N!} e^{-\beta H(q,p)}} \;. \tag{9.10}$$

It is proportional to the canonical distribution function $\rho(q,p)$, but with a different normalization, and analogous to the microcanonical space volume $\Gamma(E)$ in units of Γ_0:

$$
\begin{aligned}
\frac{\Gamma(E)}{\Gamma_0} \;&=\; \frac{1}{h^{3N} N!} \int_{E < H(q,p) < E+\Delta} d^{3N}q\, d^{3N}p \\
&=\; \int \frac{d^{3N}q\, d^{3N}p}{h^{3N} N!} \big(\Theta(E + \Delta - H) - \Theta(E - H)\big) \;,
\end{aligned}
$$

where Θ is the step function.

Free energy. We will show that it is possible to obtain all thermodynamic observables by differentiating the partition function Z_N. We will prove in particular that

$$\boxed{F(T,V,N) \;=\; -k_B T \ln Z_N(T)} \;, \qquad Z_N \;=\; e^{-\beta F(T,V,N)} \;, \tag{9.11}$$

where $F(T,V,N)$ is the Helmholtz free energy.

Proof. In order to proof (9.11) we perform the differentiation

$$
\begin{aligned}
\frac{\partial}{\partial \beta} \ln Z_N \;&=\; \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \\
&=\; \left[\frac{\partial}{\partial \beta} \int \frac{dq\, dp}{h^{3N} N!} e^{-\beta H} \right] \Big/ \left[\int \frac{dq\, dp}{h^{3N} N!} e^{-\beta H} \right] \\
&=\; \frac{\int dq\, dp\, (-H)\, e^{-\beta H}}{\int dq\, dp\, e^{-\beta H}} \\
&=\; -\langle H \rangle \;=\; -U \;.
\end{aligned}
$$

where we have used the shortcut $dq\, dp = d^{3N}q\, d^{3N}p$ and that $\langle H \rangle = E = U$ is the internal energy.

With (5.13), namely that $U = \partial(\beta F)/\partial\beta$, we find that

$$-\frac{\partial}{\partial\beta}\ln Z_N \;=\; U \;=\; \frac{\partial}{\partial\beta}(\beta F), \qquad \ln Z_N \;=\; -\beta F, \qquad \boxed{Z_N = e^{-\beta F}}\;,$$

which is what we wanted to prove.

Integration constant. Above derivation allows to identify $\ln Z_N = -\beta F$ only up to an integration constant (or, equivalently, Z_N only up to a multiplicative factor). Setting this constant to zero results in the correct result for the ideal gas, as we will show lateron in Sect. 9.5.

Thermodynamic properties. Once the partition function Z_N and the free energy $F(T,V,N) = -k_B T \ln Z_N(T,V,N)$ are calculated, one obtains the pressure P, the entropy S and the chemical potential μ as usual via

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \qquad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

Specific heat. The specific heat C_V is given in particular by

$$\frac{C_V}{T} \;=\; \left(\frac{\partial S}{\partial T}\right)_V \;=\; -\frac{\partial^2 F}{\partial T^2} \;=\; \frac{\partial^2}{\partial T^2}\left(k_B T \ln Z_N\right), \tag{9.12}$$

where we have used $F = -k_B T \ln Z_N$.

9.3   Canonical vs. microcanonical ensemble

We have seen that the calculations in the microcanonical and canonical ensembles reduce to a phase space integration and a calculation of a thermodynamic potential:

	Microcanonical ensemble	Canonical ensemble
Phase space integration	Density of states: $\Omega_N(E) = \int d^{3N}q\, d^{3N}p\, \delta(E-H)$	Partition function: $Z_N(T) = \displaystyle\int \frac{d^{3N}q\, d^{3N}p}{h^{3N}N!}e^{-\beta H(q,p)}$
Thermodynamic potential	$S(E,V,N) = k_B \ln\left(\dfrac{\Omega_N(E)\Delta}{h^{3N}N!}\right)$	$F(T,V,N) = -k_B T \ln Z_N(T)$

Laplace transforms. The relation between the density of states $\Omega_N(E)$ and the partition function $Z_N(T)$ can be defined as a Laplace transformation in the following way. We use the definition (9.1) of the density of states $\Omega(E)$,

$$\int dq\, dp\, \delta(E-H) = \Omega(E), \qquad H = H(q,p)\,,$$

in order to obtain

$$\boxed{\int_0^\infty \frac{dE\, e^{-\beta E}}{h^{3N} N!} \Omega_N(E)} = \int d^{3N} q\, d^{3N} p \int_0^\infty \frac{dE\, e^{-\beta E}}{h^{3N} N!} \delta(E - H)$$

$$= \int \frac{d^{3N} q\, d^{3N} p}{h^{3N} N!} e^{-\beta H(q,p)} = \boxed{Z_N(T)} . \qquad (9.13)$$

We have thus shown that $Z_N(T)$ is the Laplace transform[†] of $\Omega_N(E)$.

Additive Hamilton functions. In both the microcanonical and in the canonical ensemble we have to perform an integration which is usually difficult. When the Hamilton function is additive, $H = \sum_i H_i$, the integration in the canonical ensemble can be factorized, which is *not* the case for the microcanonical ensemble. Therefore, it is usually easier to calculate in the canonical ensemble than in the microcanonical ensemble.

9.4 Additivity of $F(T, V, N)$

An important property of the free energy is that it has to be *additive*.

Non-interacting systems. Let us consider two systems in thermal equilibrium. Neglecting the interaction among the systems, the total Hamilton function can be written as a sum of the Hamiltonians of the individual systems,

$$H = H_1 + H_2, \qquad N = N_1 + N_2 .$$
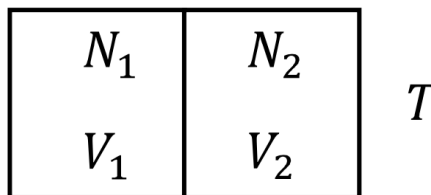
Multiplication of partition functions. The partition function of the total system is

$$Z_N(T, V) = \frac{1}{h^{3N} N_1! N_2!} \int d^{3N} q\, d^{3N} p\, e^{-\beta(H_1 + H_2)} ,$$

where have made use of the fact that there is not exchange of particles between the two systems. The factor in the denominator is therefore proportional to $N_1! N_2!$ and NOT to $N!$. It then follows that the partition function factorizes,

$$Z_N(T, V) = \frac{1}{h^{3N_1} N_1!} \int d^{3N_1} q\, d^{3N_1} p\, e^{-\beta H_1(q_1, p_1)}$$

$$\times \frac{1}{h^{3N_2} N_2!} \int d^{3N_2} q\, d^{3N_2} p\, e^{-\beta H_2(q_2, p_2)}$$

$$= Z_{N_1}(T, V_1)\, Z_{N_2}(T, V_2) ,$$

and that the free energy $F = -k_B T \ln Z_N$ is additive:

$$F(T, V, N) = F_1(T, V_1, N_1) + F_2(T, V_2, N_2) .$$

[†] The Laplace transform $F(s)$ of a function $f(t)$ is defined as $F(s) = \int_0^\infty f(t) \exp(-st) dt$.

Convolution of densities of states. That the overall partition function factorizes follows also from the fact that the density of states $\Omega(E)$ of the combined system,

$$
\begin{aligned}
\Omega(E) &= \int d^{3N}q \, d^{3N}p \, \delta(E - H_1 - H_2) \\
&= \int d^{3N_1}q \, d^{3N_1}p \, d^{3N_2}q \, d^{3N_2}p \int dE_2 \, \delta(E - H_1 - E_2) \, \delta(E_2 - H_2) \\
&= \int dE_2 \, \Omega_1(E - E_2) \, \Omega_2(E_2) \, ,
\end{aligned}
$$

is given by the *(convolution)* of the density of states $\Omega_i(E_i)$ of the individual systems. Using the representation (9.13) for the partition function we obtain[‡]

$$
\begin{aligned}
Z_N &= \int \frac{dE \, e^{-\beta E}}{h^{3N} N_1! N_2} \Omega(E) \\
&= \int \frac{dE \, e^{-\beta(E_1 + E_2)}}{h^{3N} N_1! N_2!} \int dE_2 \, \underbrace{\Omega_1(E - E_2)}_{\Omega_1(E_1)} \, \Omega_2(E_2) \, .
\end{aligned}
$$

A change of the integration variable from dE to dE_1 then leads again to

$$
Z_N(T, V) = Z_{N_1}(T, V_1) \, Z_{N_2}(T, V_2) \, . \tag{9.14}
$$

Note that this relation is only valid if $H = H_1 + H_2$ and $H_{12} = 0$.

9.5   Ideal gas in the canonical ensemble

We consider now the ideal gas in the canonical ensemble, for which the Hamilton function,

$$
H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}, \qquad Z_N(T, V) = \int \frac{d^{3N}q \, d^{3N}p}{h^{3N} N!} e^{-\beta \sum_{i=1}^{N} \vec{p}_i^2/(2m)} \, , \tag{9.15}
$$

contains just the kinetic energy.

Factorization. The integral leading to Z_N factorizes in (9.15):

$$
\begin{aligned}
Z_N(T, V) &= \frac{V^N}{N!} \left(\int_{-\infty}^{+\infty} \frac{dp}{h} e^{-\beta \frac{p^2}{2m}} \right)^{3N} \\
&= \frac{V^N}{N!} \left(\int_{-\infty}^{+\infty} \frac{\sqrt{2k_B T m}}{h} e^{-x^2} dx \right)^{3N} \, , \tag{9.16}
\end{aligned}
$$

where we have used the variable substitution

$$
x^2 = \frac{p^2}{2k_B T m}, \qquad dx = \frac{dp}{\sqrt{2k_B T m}}, \qquad \int_{-\infty}^{+\infty} dx \, e^{-x^2} = \sqrt{\pi} \, . \tag{9.17}
$$

[‡] Note that a variable transfomation $(E, E_2) \to (E_1, E_2)$ with a Jacobian determinant, $\int dE \, dE_2 = \int dE_1 \, dE_2 \, |J|$, where J is the respective Jacobian.

Thermal wavelength. Evaluating (9.16) explicitly with the help of (9.17) we get

$$Z_N(T,V) = \frac{V^N}{N!}\left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^{3N} \equiv \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N , \qquad (9.18)$$

where we have defined the *thermal wavelength* λ_T as

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} .$$

For air (actually nitrogen, N_2, with $m = 4.65 \cdot 10^{-26}$ kg) at $T = 298$ K, the thermal wavelength is 0.19 A°, which is actually smaller than the Bohr radius. Quantum mechanical effects start to play a role only once λ_T becomes larger than the typical interparticle separation.

Thermal momentum. Heisenberg's uncertainty principle $\Delta x \cdot \Delta p \sim h$ allows to define a *thermal momentum* p_T as

$$p_T = \frac{h}{\lambda_T} = \sqrt{2\pi m k_B T}, \qquad \frac{p_T^2}{2m} = \pi k_B T = \frac{2\pi}{3} E_{kin}, \qquad E_{kin} = \frac{3}{2} k_B T ,$$

where we have used (3.5) for the average energy E_{kin} per particle. The thermal momentum p_T is hence of the same order of magnitude as the average momentum $\bar{p}$ of the gas, as defined by $E_{kin} = \bar{p}^2/(2m)$, but not identical.

Free energy. From (9.18) we obtain (with $\log N! \approx N \log N - N$)

$$\begin{aligned}
F(T,V,N) &= -k_B T \ln\left(\frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N\right) \\
&= -k_B T\left(\ln\frac{1}{N!} + \ln\left(\frac{V}{\lambda_T^3}\right)^N\right) \\
&= -k_B T\left(-N\ln N + N + N\ln\frac{V}{\lambda_T^3}\right) \qquad (9.19)
\end{aligned}$$

and hence

$$F(T,V,N) = -Nk_B T\left\{\ln\left(\frac{V}{N\lambda_T^3}\right) + 1\right\}$$

for the free energy of the ideal gas.

Entropy. Using

$$\frac{\partial \lambda_T}{\partial T} = \frac{-\lambda_T}{2T}, \qquad \frac{\partial}{\partial T}\ln\left(\frac{V}{N\lambda_T^3}\right) = -3\frac{\partial \ln \lambda_T}{\partial T} = \frac{3}{2T}$$

we then have

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B\left[\ln\left(\frac{V}{N\lambda_T^3}\right) + 1\right] + Nk_B T\left[\frac{3}{2T}\right] ,$$

which results in the *Sackur-Tetrode equation*

$$S = \boxed{Nk_B \left\{ \ln \frac{V}{N\lambda_T^3} + \frac{5}{2} \right\}} . \tag{9.20}$$

Comparing (9.20) with (8.25), namely with the microcanonical Sackur-Tetrode equation

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

one finds that they coincide when $E/N = 3k_B T/2$.

Chemical potential. The chemical potential μ is

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \left[\ln \frac{V}{N\lambda_T^3} + 1 \right] + N k_B T \left[\frac{V}{N\lambda_T^3} \cdot \frac{\lambda_T^3}{V} \right]$$

$$= \boxed{-k_B T \ln \left(\frac{V}{N\lambda_T^3} \right)} .$$

The previous expressions were much simpler obtained than when calculated in the microcanonical ensemble.

Equivalence of ensembles. In the thermodynamic limit the *average value* of an observable is in general *independent* of the ensemble (microcanonical or canonical).

$$N \to \infty, \qquad V \to \infty, \qquad \frac{N}{V} = \text{const.}$$

is taken. One therefore usually chooses the ensemble that is easier to work with.

Fluctuations of observables. Fluctuations of observables, $\langle A^2 \rangle - \langle A \rangle^2$, may however be ensemble dependent! An example for an observable for which this is the case is the energy, which is constant, by definition, in the microcanonical ensemble, but distributed according to (9.9) in the canonical ensemble.

9.6   Energy fluctuations

We evaluated the representation (9.12) for the specific heat in a first step:

$$\frac{C_V}{T} = \frac{\partial^2}{\partial T^2} \left[k_B T \ln Z_n \right]$$

$$= \frac{\partial}{\partial T} \left[k_B \ln Z_n + \frac{k_B T}{Z_N} \frac{\partial Z_n}{\partial \beta} \frac{\partial \beta}{\partial T} \right] \qquad \frac{\partial \beta}{\partial T} = \frac{-1}{k_B T^2}$$

$$= \frac{\partial}{\partial T} \left[k_B \ln Z_n - \frac{1}{T Z_N} \frac{\partial Z_n}{\partial \beta} \right] .$$

Second derivatives. The remaining derivative with respect to the temperature T are

$$\frac{\partial}{\partial T} k_B \ln Z_n = \frac{-1}{T^2 Z_N} \frac{\partial Z_n}{\partial \beta}$$

$$\frac{\partial}{\partial T} \frac{-1}{T Z_N} \frac{\partial Z_n}{\partial \beta} = \frac{1}{T^2 Z_N} \frac{\partial Z_n}{\partial \beta} + \left[\frac{1}{T Z_N^2} \left(\frac{\partial Z_n}{\partial \beta} \right)^2 - \frac{1}{T Z_N} \frac{\partial^2 Z_n}{\partial \beta^2} \right] \frac{-1}{k_B T^2} \; .$$

With the first two terms canceling each other We find

$$C_V = \frac{1}{k_b T^2} \left[\frac{1}{Z_N} \frac{\partial^2 Z_n}{\partial \beta^2} - \left(\frac{1}{Z_N} \frac{\partial Z_n}{\partial \beta} \right)^2 \right] \tag{9.21}$$

for the specific heat C_v as a functions of derivatives of the partition function Z_N.

Derivatives of the partition function. The definition (9.10) for the partition function corresponds to

$$\frac{1}{Z_N} \frac{\partial Z_n}{\partial \beta} = -\frac{\int \frac{d^{3N} q \, d^{3N} p}{h^{3N} N!} H \, e^{-\beta H(q,p)}}{\int \frac{d^{3N} q \, d^{3N} p}{h^{3N} N!} e^{-\beta H(q,p)}}, \qquad Z_N = \int \frac{d^{3N} q \, d^{3N} p}{h^{3N} N!} e^{-\beta H(q,p)} \; ,$$

viz to

$$\frac{1}{Z_N} \frac{\partial Z_n}{\partial \beta} = -\langle E \rangle, \qquad \frac{1}{Z_N} \frac{\partial^2 Z_n}{\partial \beta^2} = \langle E^2 \rangle \; . \tag{9.22}$$

Specific heat. Our results (9.21) and (9.22) lead to the fundamental relation

$$C_V = \frac{1}{k_b T^2} \left[\langle E^2 \rangle - \langle E \rangle^2 \right] \tag{9.23}$$

between the specific heat C_V and the fluctuations $\langle E^2 \rangle - \langle E \rangle^2$ of the energy.

– Both the specific heat $C_V \sim N$ and the right-hand side of (9.23) are extensive. The later as a result of the central limit theorem discussed in Sect. 8.6, which states that the variance of independent processes are additive.

– The specific heat describes the energy exchange between the system and an heat reservoir. It hence makes that sense that C_V is proportional to the size of the energy fluctuations.

Relative energy fluctuations. The relative energy fluctuations,

$$\frac{\sqrt{\langle E^2 \rangle - \langle E \rangle^2}}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \tag{9.24}$$

vanish in the thermodynamic limit $N \to \infty$.

– The scaling relation (9.24) if a direct consequence of (9.23) and of the fact that both C_V and the internal energy $U = \langle E \rangle$ are extensive.

– Eq. (9.24) is consistent with the demand that the canonical the microcanonical ensembles are equivalent in the thermodynamic limit $N \to \infty$. Energy fluctuations are absent in the microcanonical ensemble.

9.7   Paramagnetism

We consider a system with N magnetic atoms per unit volume placed in an external magnetic field $\mathcal{H}$. Each atom has an intrinsic magnetic moment $\mu = 2\mu_0 s$ with spin $s = 1/2$.

Energy states. In a quantum-mechanical description, the magnetic moments of the atoms can point either parallel or anti-parallel to the magnetic field.

state	alignment	moment	energy	probability
$(+)$	parallel to $\mathcal{H}$	$+\mu$	$-\mu\mathcal{H}$	$P_+ = c\, e^{-\beta\varepsilon_+} = c\, e^{+\beta\mu\mathcal{H}}$
$(-)$	anti-parallel to $\mathcal{H}$	$-\mu$	$+\mu\mathcal{H}$	$P_- = c\, e^{-\beta\varepsilon_-} = c\, e^{-\beta\mu\mathcal{H}}$

We assume here that the atoms interact weakly. One can therefore a single atom as a small system and the rest of the atoms as a reservoir in the terms of a canonical ensemble.

Mean magnetic moment. We want to analyze the mean magnetic moment $\langle \mu_{\mathcal{H}} \rangle$ per atom as a function of the temperature T:

$$\langle \mu_{\mathcal{H}} \rangle = \frac{\mu\, e^{\beta\mu\mathcal{H}} - \mu\, e^{-\beta\mu\mathcal{H}}}{e^{\beta\mu\mathcal{H}} + e^{-\beta\mu\mathcal{H}}}, \qquad \boxed{\langle \mu_{\mathcal{H}} \rangle = \mu \tanh \frac{\mu\mathcal{H}}{k_B T}}\,,$$

where we used that

$$\tanh y = \frac{e^y - e^{-y}}{e^y + e^{-y}}, \qquad y = \beta\mu\mathcal{H} = \frac{\mu\mathcal{H}}{k_B T}\,.$$

Magnetization. We define the *magnetization*, i.e. the mean magnetic moment per unit volume, as

$$\langle M \rangle = N \langle \mu_{\mathcal{H}} \rangle$$

and analyze its behavior in the limit of high- and of low temperatures.

High-temperature expansion. Large temperatures correspond to $y \ll 1$ and hence to

$$e^y = 1 + y + \dots, \qquad e^{-y} = 1 - y + \dots\,.$$

Then,

$$\tanh y = \frac{(1 + y + \dots) - (1 - y + \dots)}{2} \approx y\,,$$

so that

$$\boxed{\langle \mu_{\mathcal{H}} \rangle = \frac{\mu^2 \mathcal{H}}{k_B T}}\,.$$

Curie Law. For the magnetic susceptibility χ, defined as $\langle M \rangle = \chi \mathcal{H}$, we then have

$$\boxed{\chi = \frac{N\mu^2}{k_B T}} \; .$$

At temperatures high compared to the magnetic energies, $\chi \propto T^{-1}$ which is known as the *Curie law.*

Low-temperature expansion. Low temperatures correspond to $y \gg 1$,

$$e^y \gg e^{-y}, \qquad \tanh y \approx 1 \; ,$$

and hence

$$\langle \mu_{\mathcal{H}} \rangle = \mu, \qquad \langle M \rangle = N\mu \; .$$

The magnetization saturates at the maximal value at low temperatures independent of $\mathcal{H}$.