Thermodynamics

1 Microcanonical ensemble

Consider an isolated system with energy E and N particles in a box of volume V. Because the volume is finite, the energy levels are quantized, i.e. they are discrete. However, if V is large, the level spacing is very small, usually much smaller than the resolution with which the energy of the system can be measured. These states, the eigenstates of the Hamiltonian are called *microstates*. The discrete microstates are numbered by n and the energy of a microstate is denoted by E_n.

One defines a *macrostate* as a state defined by the parameters N, V, α and having an energy in the small interval $E \leq E_n \leq E + \delta E$. Here α denotes additional parameters needed to specify the system. This could be e.g. the total spin of the system. In equilibrium the system is fully specified by (E, N, V); additonal parameters are needed to specify non-equilibrium macrostates. Since the level spacing is small, there are very many microstates in the energy range between E and $E + \delta E$. For a large volume and a suitably chosen δE the results depend only very weakly on δE.

We denote by $Z(E, N, V; \alpha)$ the number of microstates that comprise the macrostate defined by $E, N, V; \alpha$. We call $Z(E, N, V; \alpha)$ the microcanonical partition function or the statistical weight of the macrostate. The partition function of the equailibrium state is denoted by $Z(E, N, V)$.

Thermodynamics is built on the following basic postulates:

1 *In an isolated system all microstates compatible with the constraints of the system (E, N, V) are equally likely to occur, i.e. they have equal a priori probabilities.*

2 *The equilibrium state corrsponds to that value of α for which $Z(E, N, V; \alpha)$ attains its maximum value keeping E, N, V fixed.*

It follows from postulate 1 that the probability to be in a microstate n is

$$p_n = 1/Z(E_n, N, V), \tag{1}$$

while the probability to be in a macrostate defined by α is proportional to the number of microstates that comprise the macrostate

$$p(E,N,V;\alpha) = \frac{Z(E,N,V;\alpha)}{Z(E,N,V)}. \tag{2}$$

As an example consider a system consisting of N spin-$\frac{1}{2}$ particles. We assume that the spins are located on a lattice and neglect all interactions between them, since we only want to illustrate the problem of counting states. We also assume that there is no external magnetic field. Since each spin can point up or down there are 2^N possible states. These are the microstates. Since there are no interactions and no magnetic field, all microstates have the same energy E_0. We define a macrostate by the energy between E and $E+\delta E$ and the number of up spins n. Here n corresponds to the parameter α above.

For $n=N$ all spins are pointing up. Clearly there is only one microstate of this kind. Correspondingly, for $n=N-1$, all spins except one are pointing up. Since there are N ways to pick the down spin, there are N independent microstates correpsonding to this value of n. For $n=N-2$ again, there ar $N(N-1)/2$ microstates. In general the corresponding partition function is given by the binomial coefficients

$$Z(n) = \binom{N}{n} = \frac{N!}{n!(N-n)!}. \tag{3}$$

The sum over all n yields $\sum_n Z(n) = 2^N$. In fig. 1 the binomial distribution is show for $N=100$. The maximum probability is reached for $n=N/2$, i.e., in the equilibrium system, the number of up- and down-spins are the same; the system is unpolarized. Note the logarithmic scale. Already for 100 particles the number of microstates for the equilibrium distribution is huge, $\sim 10^{29}$! This is comparable to the total number of microstates $2^{100} \sim 10^{30}$.

In the first part of the lectures we discussed the phase space integrals, and also defined the non-invariant phase space integral

$$Z(E,N,V) = \frac{d\mathcal{N}}{dE} = \frac{V^N}{N!}\int \frac{d^3p_1\cdots d^3p_N}{(2\pi\hbar)^{3N}}\delta(E-\sum_i \varepsilon_i). \tag{4}$$

This function is just the number of microstates with energy E and particle number N, i.e., it is the microcanonical partition function for a system of non-interacting particles.

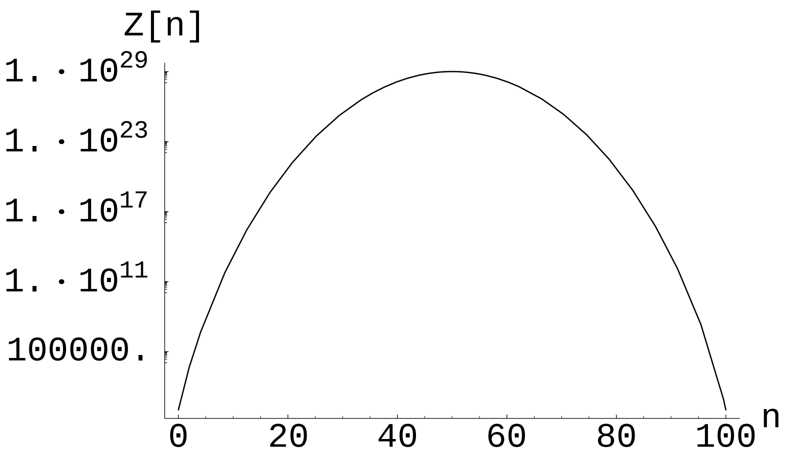

Figure 1: The binomial distribution (3) for $N = 100$.

Now we are ready to define the entropy

$$S(E, N, V; \alpha) = k_B \ln Z(E, N, V; \alpha) \tag{5}$$

Consider two systems 1 and 2, with partition functions Z_1 and Z_2. When the two systems are combined, one obtains a system with $Z = Z_1 Z_2$ microstates, since any microstate of 1 can be combined with any microstate of 2. Hence the entropy of the combined system is $S = S_1 + S_2$, i.e. the entropy defined in this way is an extensive quantity.

The second postulate above can now be reformulated for the entropy:
In an isolated system out of equilibrium the entropy increases and attains its maximum value in the equilibrium state.
This is the second law of thermodynamics!

We can now define an absolute temperature by means of

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V} . \tag{6}$$

Also the pressure and the chemical potential can be obtained from the entropy:

$$P = T \left.\frac{\partial S}{\partial V}\right|_{E,N} \tag{7}$$

and

$$\mu = -T \left.\frac{\partial S}{\partial N}\right|_{E,V} \tag{8}$$

These results can be summarized in the differential

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \tag{9}$$

Let us discuss a simple example, where the microcanonical partition function can be evaluated. Consider a gas of N non/interacting, non/relativistic particles. The partition function is the non/invariant phase space distribution (4). Using scaling arguments, one finds that $Z(E, N, V) = AE^{3N/2-1} \simeq AE^{3N/2}$, where a is a constant independent of E and the approximate equality holds for large N. Now, using (5) and (6) one finds the well-known relation $E/N = 3T/2$

2 Canonical ensemble

In this section we briefly discuss the canonical ensemble, which is sometimes also called Gibb's ensemble. Consider a system in contact with a heat bath. This means that energy can be exchanged between the system and the heat bath. Thus, the energy of the system is not constant; the system is not isolated. Since only energy can be exchanged and not particles, the particle number is still constant.

If the heat bath is very large, the fluctuations of its energy are small compared to its total energy. This means that the temperature is constant. Thus, when one changes from the microcanonical description to the canonical one, the extensive variable $E =$ const. is replaced by the intensive one $T =$ const..

After some standard manipulations which can be found in any good textbook on thermodynamics, one finds the probability that the system is in a microstate n

$$p_n = \text{const.} e^{-\beta E_n}, \tag{10}$$

where $\beta = 1/(k_B T)$. The constant is determined by the normalization condition $\sum_n p_n = 1$, which yields

$$p_n = \frac{1}{Z(T, N, V)}\ e^{-\beta E_n} \tag{11}$$

where

$$Z(T, N, V) = \sum_n e^{-\beta E_n}. \tag{12}$$

This is the canonical partition function. Note that for a given system (N and V fixed) the probability that a microstate is occupied depends only on its energy! The dependence of Z on N and V is lodged in the energy eigenvalues E_n.

There may be several microstates with the same energy. Then we can rewrite the sum over states into a sum over energy eigenvalues

$$Z(T,N,V) = \sum_{E_n} e^{-\beta E_n} g(E_n,N,V), \tag{13}$$

where $g(E_n,N,V)$ is the degeneracy of the eigenvalue E_n. The probability for an eigenvalue E_n to be occupied is

$$p(E_n) = \frac{1}{Z(T,N,V)}\, g(E_n,N,V)\, e^{-\beta E_n}. \tag{14}$$

Often the level spacing is so small that one can approximate the sum over the levels with an integral over a continuous distribution

$$Z(T,N,V) = \int f(E,N,V)\; e^{-\beta E}\, dE \tag{15}$$

where

$$f(E,N,V) = \frac{1}{\Delta E} \sum_{n;E\le E_n\le E+\Delta E} = \frac{1}{\Delta E} \sum_{E_n;E\le E_n\le E+\Delta E} g(E_n) \tag{16}$$

is the density of states. Note that the microcanonical partition function is proportional to the density of states $Z(E,N,V) = f(E,N,V)\,\delta E$.

The average energy of the system is given by

$$\langle E\rangle = \sum_n p_n E_n = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z}\sum_n E_n\, e^{-\beta E_n}. \tag{17}$$

It is interesting to estimate how large the fluctuations in the energy are. One finds

$$\begin{aligned} \langle(\Delta E)^2\rangle &= \langle(E-\langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 \\ &= \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial\langle E\rangle}{\partial\beta} = k_B T^2 C, \end{aligned} \tag{18}$$

where $C = \partial\langle E\rangle/\partial T$ is the heat capacity of the system, which is proportional to the number of particles N. Since the energy $\langle E\rangle$ is also proportional to N

$$\frac{(\langle(\Delta E)^2\rangle)^{1/2}}{\langle E\rangle} = \frac{(k_B T^2 C)^{1/2}}{\langle E\rangle} \propto \frac{1}{\sqrt{N}}. \tag{19}$$

Thus, the fluctuations of the energy are small provided the system is large enough.

In the canonical ensemble the logarithm of the partition sum yields

$$k_B \ln Z(T,N,V) = S - \frac{\langle E\rangle}{T}. \tag{20}$$

A convenient quantity for doing calculations in this ensemble is Helmholtz free energy

$$F(T,N,V) = \langle E\rangle - TS. \tag{21}$$

The derivatives of the free energy yields

$$\begin{aligned} S &= -\left.\frac{\partial F}{\partial T}\right|_{V,N} \\ P &= -\left.\frac{\partial F}{\partial V}\right|_{T,N} \\ \mu &= \left.\frac{\partial F}{\partial N}\right|_{T,V}, \end{aligned} \tag{22}$$

or in compact form

$$dF = -SdT - PdV + \mu dN \tag{23}$$

The canonical partition function for a free, gas of indistinguishable classical particles is given by

$$Z^{Cl}(T,N,V) = \frac{1}{N!}\left(\sum_{\ell} e^{-\beta\varepsilon_\ell}\right)^N. \tag{24}$$

Similarly for a free Fermi=Dirac and Bose-Einstein gas

$$Z^{FD}(T,N,V) = \sum_{\ell_1<\ell_2<\cdots<\ell_N} e^{-\beta(\varepsilon_{\ell_1}+\varepsilon_{\ell_2}+\cdots+\varepsilon_{\ell_N})} \tag{25}$$

and

$$Z^{BE}(T,N,V) = \sum_{\ell_1\le\ell_2\le\cdots\le\ell_N} e^{-\beta(\varepsilon_{\ell_1}+\varepsilon_{\ell_2}+\cdots+\varepsilon_{\ell_N})} \tag{26}$$

respectively. Note that the form of the probability distribution in the canonical ensemble (11) has nothing to do with with the Maxwell-Boltzmann distribution. Equation (11) is the probability distribution for the whole system, and is the same for any statistics, while the Maxwell-Boltzmann distribution yields the single-particle distribution.

Properties,natural state variables	density operator partition sum	- thermodynamic potential - Differential form - Equilibrium condition
Isolated System E, N, V micro canonical ens.	$\hat{\rho}_M = \frac{1}{Z_M}\delta_{\Delta E}(E-\hat{H})$ $Z_M = \delta_{\Delta E}(E-\hat{H})$ $\mathcal{Z} = \lim\limits_{\Delta E\to 0}\frac{1}{\Delta E}Z_M = \delta(E-\hat{H})$	Entropy : $S(E,\Delta E,N,V) = \ln\left(Z_M(E,\Delta E,N,V)\right)$ $dS = \frac{1}{T}(dE - \mu dN + p\,dV)$ Equilibrium correspond to **maximization** of entropy.
Energy exchange β, N, V canonical ens.	$\hat{\rho}_C = \frac{1}{Z_C}e^{-\beta\hat{H}}$ $Z_C = e^{-\beta\hat{H}}$	Free Energy : $F = -T\,\ln(Z_c(\beta,N,V)) = E - T\,S$ $dF = -S\,dT + \mu\,dN - p\,dV$ Equilibrium correspond to **minimization** of free energy.
Energy & particle exchange β, μ, V grand-canonical ens.	$\hat{\rho}_G = \frac{1}{Z_G}e^{-\beta(\hat{H}-\mu\hat{N})}$ $Z_C = e^{-\beta(\hat{H}-\mu\hat{N})}$	Grand potential : $\Omega = -T\,\ln(Z_G(\beta,\mu,V)) = E - T\,S - \mu\,N$ For homogeneous systems $\Omega = -p\,dV$ $d\Omega = -S\,dT + N\,d\mu - p\,dV$ Equilibrium correspond to **minimization** of grand potential.

4 Two systems in contact : Principle of maximum of total entropy !

The system 1 is characterized by $\hat{H}_1$ and the system 2 by $\hat{H}_2$. We neglect the interaction potential $\hat{V}_{12}$ between the two systems.

$$\begin{aligned} Z_{tot} &= Z_1 \times Z_2 \ , \\ S_{tot} &= S_1 + S_2 \ . \end{aligned}$$

The energy exchange

$$E_0 = E_1 + E_2 = const. \ ,$$

thus

$$\begin{aligned} \frac{\partial S_{tot}}{\partial E_0} &= \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \ , \\ &= \beta - \beta \ , \\ &= 0 \ , \end{aligned}$$

$\Rightarrow \hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$: canonical ensemble

In the case of particle exchange.

$$\begin{aligned} N_0 &= N_1 + N_2 = const. \ , \\ \frac{\partial S_{tot}}{\partial N_0} &= \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} \ , \\ &= \beta\mu - \beta\mu \ , \\ &= 0 \ , \end{aligned}$$

$\Rightarrow \hat{\rho} = \frac{1}{Z} e^{-\beta(\hat{H} - \mu\hat{N})}$: grand canonical ensemble

5 Ideal quantum gases

	Fermi-Dirac	Bose-Einstein	Classical
Occupations:	$b_k = 1, 2$	$b_k = 1, 2, 3, \ldots, \infty$	$\langle b_k \rangle \ll 1$
$Z(E, N, V)$	-	-	$AE^{3N/2-1}$
$Z(T, N, V)$	$\sum\limits_{k_1 < k_2 < \cdots < k_N} e^{-\beta(\epsilon_{k_1}+\cdots+\epsilon_{k_1})}$	$\sum\limits_{k_1 \leq k_2 \leq \cdots \leq k_N} e^{-\beta(\epsilon_{k_1}+\cdots+\epsilon_{k_1})}$	$\frac{1}{N!}\left(\sum\limits_k e^{-\beta\epsilon_k}\right)^N$
$Z(T, \mu, V)$	$\prod\limits_{k=1}^{\infty}\left(1 + e^{-\beta(\epsilon_k-\mu)}\right)$	$\prod\limits_{k=1}^{\infty}\left(1 - e^{-\beta(\epsilon_k-\mu)}\right)^{-1}$	$\exp\left(\sum\limits_{k=1}^{\infty} e^{-\beta(\epsilon_k-\mu)}\right)$
$\ln Z(T, \mu, V)$	$\sum\limits_{k=1}^{\infty}\ln\left(1 + e^{-\beta(\epsilon_k-\mu)}\right)$	$-\sum\limits_{k=1}^{\infty}\ln\left(1 - e^{-\beta(\epsilon_k-\mu)}\right)$	$\sum\limits_{k=1}^{\infty} e^{-\beta(\epsilon_k-\mu)}$
av. occupation $f_k = \langle b_k \rangle$	$\frac{1}{e^{\beta(\epsilon_k+\mu)}+1}$	$\frac{1}{e^{\beta(\epsilon_k-\mu)}-1}$	$e^{-\beta(\epsilon_k-\mu)}$
Entropy	$S = -\sum\limits_{k=1}^{\infty}[f_k \ln f_k + (1-f_k)\ln(1-f_k)]$	$S = -\sum\limits_{k=1}^{\infty}[f_k \ln f_k - (1+f_k)\ln(1+f_k)]$	$S = -\sum\limits_{k=1}^{\infty} f_k \ln f_k$

6 Hard Core Equation of State

6.1 Semi-classical partition sum with excluded volume

Spatial part (ignoring overcounting of multi-particle overlaps):

$$Z_V(N) = \frac{V(V-V_{Ex})(V-2V_{Ex})\cdots(V-(N-1)V_{Ex})}{N!} = \binom{V/V_{Ex}}{N} V_{Ex}^N \tag{27}$$

$$\text{with} \quad V_{Ex} = \frac{4\pi}{3}(2R)^3 \tag{28}$$

Momentum part:

$$Z_P(\beta, N) = \int \frac{{}^3k_1}{(2\pi)^3}\cdots\frac{{}^3k_N}{(2\pi)^3}\exp\left[-\sum_i \beta E(k_i)\right] = (Z_P(\beta))^N \tag{29}$$

$$\text{with} \quad Z_P(\beta) = \int \frac{{}^3k}{(2\pi)^3}\exp[-\beta E(k)]$$

$$Z_P(\beta, \mu) = Z_P(\beta)\exp(\beta\mu) \tag{30}$$

Log of grand canonical partition sum:

$$
\begin{aligned}
\ln Z(T,\mu) &= \ln\left\{\sum_N Z_V(N) Z_P(\beta,N)\exp(\beta\mu N)\right\} && (31)\\
&= \ln\left\{\sum_N \binom{V/V_{Ex}}{N}\left[V_{Ex}Z_P(\beta,\mu)\right]^N\right\} && (32)\\
&= \ln\left\{\left[1+V_{Ex}Z_P(\beta,\mu)\right]^{(V/V_{Ex})}\right\} && (33)\\
&= \frac{V}{V_{Ex}}\ln\left\{1+V_{Ex}\int\frac{{}^3k}{(2\pi)^3}\exp[-\beta(E(k)-\mu)]\right\} && (34)
\end{aligned}
$$

Particle number and pressure:

$$
\begin{aligned}
N=\langle N\rangle &= \frac{\partial}{\beta\partial\mu}\ln Z(\beta,\mu)=\frac{VZ_P(\beta,\mu)}{1+V_{Ex}Z_P(\beta,\mu)} && (35)\\
&\Rightarrow \quad Z_P(\beta,\mu)=\frac{N}{V-NV_{Ex}} && (36)\\
p &= \frac{T}{V}\ln Z(\beta,\mu)=\frac{T}{V_{Ex}}\ln\left[1+V_{Ex}Z_P(\beta,\mu)\right] && (37)\\
&= \frac{T}{V_{Ex}}\ln\left[\frac{V}{V-NV_{Ex}}\right] && (38)\\
&= \frac{TN}{V}\left(1+\frac{1}{2}\frac{NV_{Ex}}{V}+\frac{1}{3}\left(\frac{NV_{Ex}}{V}\right)^2+\cdots\right) && (39)
\end{aligned}
$$