B Equilibrium Ensembles

4 Microcanonical ensemble (classical)

4.a Description of the ensemble

We consider a classical system with given particle number N in a volume V. The energy of the system be between $E - \Delta$ and E. Further infomation on the system be missing. Due to this missing information we replace the system by an ensemble of constant distribution function ρ_0 within this energy interval (equal partion).
Behind this is the idea, ensemble average equals time average. That is, in the course of a sufficiently long time interval all regions of the energy shell will be transversed by the system so that the average of an observable in time equals the ensemble average. Of course, this had to be proven.
Thus we set

$$\rho(H) = \begin{cases} \rho_0 & E - \Delta < H \le E, \\ 0 & \text{otherwise.} \end{cases} \tag{4.1}$$

This microcanonical ensemble is a stationary ensemble.
The volume of the phase space for the states with energy $H \le E$ amounts to

$$\Phi(E) = \int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\Theta(E - H) \tag{4.2}$$

with the well-known Heaviside step-function

$$\Theta(x) = \begin{cases} 0 & x < 0 \\ 1 & x \ge 0 \end{cases}. \tag{4.3}$$

We have chosen here $\Theta(0) = 1$ somehow arbitrarily, since we wish to include the states with $H = E$. Then we obtain for the constant ρ_0

$$\int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\rho(H) = \rho_0(\Phi(E) - \Phi(E - \Delta)) = 1, \tag{4.4}$$

thus

$$\rho_0 = \frac{1}{\Phi(E) - \Phi(E - \Delta)}. \tag{4.5}$$

If we require precisely $H = E$, then we perform the limit $\Delta \to 0$ and obtain $\rho(H) = c\delta(E - H)$ with

$$\int \mathrm{d}^{3N}x\mathrm{d}^{3N}pc\delta(E - H) = c\int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\frac{\partial\Theta(E - H)}{\partial E} = c\frac{\partial\Phi(E)}{\partial E} = 1, \tag{4.6}$$

thus

$$\rho = \left(\frac{\partial\Phi(E, V)}{\partial E}\right)^{-1} \delta(E - H). \tag{4.7}$$

4.b Monatomic ideal gas

We consider now a monatomic ideal gas. The Hamiltonian consists only of the kinetic energy

$$H = \frac{1}{2m}\sum_{i=1}^{N} p_i^2. \tag{4.8}$$

We obtain for the volume of the phase-space

$$\begin{aligned}
\Phi(E) &= \int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\Theta(E-H) = V^N \int \mathrm{d}^{3N}p\Theta(2mE - \sum_i p_i^2) & (4.9)\\
&= V^N \times \text{volume of the } 3N\text{-dimensional sphere of radius } \sqrt{2mE} & (4.10)\\
&= V^N\Omega_{3N}\int_0^{\sqrt{2mE}} p^{3N-1}\mathrm{d}p = V^N \frac{\Omega_{3N}}{3N}(2mE)^{3N/2}, & (4.11)
\end{aligned}$$

where Ω_{3N} is the full solid angle in $3N$ dimensions, which is equivalent to the surface of the $3N$-dimensional unit sphere, that is of the $3N$-dimensional sphere of radius 1.
This solid angle can be determined by evaluating the following integral in two different ways

$$\begin{aligned}
\int \mathrm{d}^d\alpha \mathrm{e}^{-\alpha_1^2-\ldots-\alpha_d^2} &= \left(\int_{-\infty}^{+\infty}\mathrm{d}\alpha_1\mathrm{e}^{-\alpha_1^2}\right)^d = \pi^{d/2} & (4.12)\\
&= \Omega_d\int_0^\infty \mathrm{e}^{-\alpha^2}\alpha^{d-1}\mathrm{d}\alpha = \frac{\Omega_d}{2}\int_0^\infty \mathrm{e}^{-\alpha^2}\left(\alpha^2\right)^{d/2-1}\mathrm{d}\alpha^2 = \frac{\Omega_d}{2}\left(\frac{d}{2}-1\right)! & (4.13)
\end{aligned}$$

I often write $a!$ ("a factorial") even for non-integer a with the understanding that $a! = \Gamma(a+1)$. Then one obtains

$$\Omega_d = \frac{2\pi^{d/2}}{(\frac{d}{2}-1)!}. \tag{4.14}$$

For $d = 1$ one obtains with $(-\frac{1}{2})! = \Gamma(\frac{1}{2}) = \pi^{1/2}$ the result $\Omega_1 = 2$. This is the number of endpoints of the line from -1 to $+1$. For $d = 2$ one has $0! = \Gamma(1) = 1$ and therefore $\Omega_2 = 2\pi$, the perimeter of the unit circle and for $d = 3$ one obtains $(\frac{1}{2})! = \frac{1}{2}(-\frac{1}{2})! = \pi^{1/2}/2$ and thus the three-dimensional solid angle $\Omega_3 = 4\pi$.
The volume of the phase-space thus obtained

$$\Phi(E) = \frac{V^N(2mE)^{3N/2}\pi^{3N/2}}{(\frac{3N}{2})!} \tag{4.15}$$

increases as function of the energy E extremely rapidly. Thus we have chosen in (4.1) the bounds E and $E-\Delta$ and not $E+\Delta$ and E, since the result depends stronger on the upper then the lower bound. For the same reason one often chooses $\Delta = \infty$ and obtains in this way a result which no longer contains Δ. One says: Nearly the whole volume of the phase-space is in the energy shell.
One may, however, also choose the enrgy shell $H = E$ (4.7), that is $\Delta = 0$. Then we obtain for the normalization constant c

$$\frac{1}{c} = \frac{\partial\Phi(E,V)}{\partial E} = \frac{V^N(2mE)^{3N/2-1}\pi^{3N/2}2m}{(\frac{3N}{2}-1)!.}. \tag{4.16}$$

Upon demand we will choose one or the other possibility.

5 Maxwell distribution and the equation of state of the ideal classical monatomic gas

5.a Maxwell-distribution

We ask now the question: What is the probability $w_{\mathbf{p}_1}(\mathbf{p}_1)\mathrm{d}^3p_1$, to find the atom # 1 in the momentum interval $p_{1x}..p_{1x}+\mathrm{d}p_{1x}$, $p_{1y}..p_{1y}+\mathrm{d}p_{1y}$, $p_{1z}..p_{1z}+\mathrm{d}p_{1z}$? For this purpose we calculate

$$w(\mathbf{p}_1) = \int \rho(p,x)\mathrm{d}^3p_2...\mathrm{d}^3p_N\mathrm{d}^3x_1...\mathrm{d}^3x_N \tag{5.1}$$

with

$$\rho(p,x) = \frac{1}{\frac{\partial\Phi}{\partial E}}\delta(E-H). \tag{5.2}$$

Now we introduce the Hamiltonian function H' and the energy E' for the other $N-1$ atoms

$$H' = \frac{1}{2m}(p_2^2+...p_N^2), \quad E' = E - \frac{1}{2m}p_1^2, \quad E-H = E'-H' \tag{5.3}$$

and obtain

$$\begin{aligned} w(\mathbf{p}_1) &= \frac{1}{\frac{\partial\Phi_N(E)}{\partial E}}\int\delta(E'-H')\mathrm{d}^3p_2...\mathrm{d}^3p_N\mathrm{d}^3x_1...\mathrm{d}^3x_N = \frac{V\frac{\partial\Phi_{N-1}(E')}{\partial E'}}{\frac{\partial\Phi_N(E)}{\partial E}} \\ &= \frac{(\frac{3}{2}N-1)!}{\pi^{3/2}(\frac{3}{2}N-\frac{5}{2})!(2mE)^{3/2}}\left(\frac{E'}{E}\right)^{\frac{3N}{2}-\frac{5}{2}}. \end{aligned} \tag{5.4}$$

For $a \ll \frac{3N}{2}$, $b \ll \frac{3N}{2}$, $1 \ll \frac{3N}{2}$ one has

$$\frac{(\frac{3N}{2}-a)!}{(\frac{3N}{2}-b)!} \approx \frac{(\frac{3N}{2})!}{(\frac{3N}{2})^a}\frac{(\frac{3N}{2})^b}{(\frac{3N}{2})!} = \left(\frac{3N}{2}\right)^{b-a}, \tag{5.5}$$

since in $(\frac{3N}{2}-a)!$ a factors are missing to $(\frac{3N}{2})!$ approximately of size $\frac{3N}{2}$, which is immediately obvious for integer a, but holds true also for non-integer a. This can be derived from the Stirling formula (A.5). Thus one obtains

$$w(\mathbf{p}_1) = \left(\frac{3N}{4\pi mE}\right)^{3/2}\left(1-\frac{p_1^2}{2mE}\right)^{\frac{3N}{2}-\frac{5}{2}}. \tag{5.6}$$

In the average one atom carries the energy $\frac{E}{N}$. Thus one has $p_1^2 = O(\frac{2mE}{N})$. In the limit of large N we may thus use $(1-\frac{a}{N})^{bN} = \exp(-ab)$ and obtain

$$\left(1-\frac{p_1^2}{2mE}\right)^{\frac{3N}{2}-\frac{5}{2}} = \exp(-\frac{3N}{2}\frac{p_1^2}{2mE}), \tag{5.7}$$

where $(...)^{-5/2}$ converges for large N to 1. With the abreviation

$$\beta = \frac{3N}{2E} \tag{5.8}$$

one obtains the Maxwell distribution

$$w(\mathbf{p}_1) = \left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\left(-\beta\frac{p_1^2}{2m}\right). \tag{5.9}$$

From this distribution we may calculate the expectation value of p_{1x}^2

$$\begin{aligned}
\langle p_{1x}^2\rangle &= \int \mathrm{d}^3p_1 p_{1x}^2 w(\mathbf{p}_1) &(5.10)\\
&= \left(\frac{\beta}{2\pi m}\right)^{1/2}\int \mathrm{d}p_{1x}p_{1x}^2\exp(-\beta\frac{p_{1x}^2}{2m})\left(\left(\frac{\beta}{2\pi m}\right)^{1/2}\int \mathrm{d}p_{1y}\exp(-\beta\frac{p_{1y}^2}{2m})\right)^2 &(5.11)\\
&= \frac{m}{\beta}1^2 = \frac{2mE}{3N}. &(5.12)
\end{aligned}$$

5.b Equation of state

In order to determine the pressure P we assume that the gas is enclosed in a box of length l and exerts a force K on the boundary area F at the end of the box. Then the pressure is given by

$$P = \frac{\langle K\rangle}{F}. \quad (5.13)$$

The momentum transfer during time t is given by the force as $\int K\mathrm{d}t = t\langle K\rangle$. If we consider one atom then its momentum transfer per collision is $2p_{1x}$ and the time t, after which the atom hits again the wall is $t = 2lm/p_{1x}$. Then one obtains for the pressure

$$P = N\langle\frac{2p_{1x}}{tF}\rangle = N\langle\frac{2p_{1x}p_{1x}}{2lmF}\rangle = \frac{N}{Vm}\langle p_{1x}^2\rangle = \frac{N}{V}\frac{1}{\beta}, \quad (5.14)$$

that is one obtains the equation of state

$$PV = N\frac{1}{\beta}. \quad (5.15)$$

Comparison with the well-known equation of state

$$PV = Nk_{\mathrm{B}}T \quad (5.16)$$

shows that the quantity β is related to the temperature T by

$$\frac{1}{\beta} = k_{\mathrm{B}}T, \quad (5.17)$$

where $k_{\mathrm{B}} = 1.380\cdot 10^{-16}\mathrm{erg\ K}^{-1}$ is the Boltzmann constant. The equation of state is often given for one mole of a gas. One mole contains $N_{\mathrm{mol}} = 6.025\cdot 10^{23}$ atoms (Loschmidt number). This yields the equation of state

$$PV = RT \quad (5.18)$$

with the gas constant $R = N_{\mathrm{mol}}k_{\mathrm{B}} = 8.316\cdot 10^7\mathrm{erg\ K}^{-1}$. Finally we express the energy as a function of temperature using (5.8)

$$E = \frac{3N}{2\beta} = \frac{3}{2}Nk_{\mathrm{B}}T. \quad (5.19)$$

The Boltzmann constant is a conversion factor between temperature and energy.

6 Microcanonical ensemble (quantummechanical)

6.a Ensemble

As in the classical case the system have fixed volume V and fixed particle number N. The energy be within $E-\Delta$ and E. The ensemble consists of all states in this energy interval with equal probability

$$\rho = \rho_0 \sum_{n|_{E-\Delta<E_n\le E}} |n\rangle\langle n| = \rho_0(\Theta(E-H)-\Theta(E-\Delta-H)), \tag{6.1}$$

where the states $|n\rangle$ are eigenstates of the Hamiltonian $H|n\rangle = E_n|n\rangle$. The number of states with energies E_n up to E be

$$W_N(E) = \mathrm{tr}(\Theta(E-H)) = \sum_n \Theta(E-E_n). \tag{6.2}$$

One obtains from the normalization condition $\mathrm{tr}(\rho)=1$

$$\rho_0 \underbrace{(W_N(E)-W_N(E-\Delta))}_{W} = 1 \tag{6.3}$$

the constant ρ_0

$$\rho_0 = \frac{1}{W}. \tag{6.4}$$

One introduces the entropy for the microcanonical ensemble by

$$W = \mathrm{e}^{S/k_\mathrm{B}}, \quad S = k_\mathrm{B}\ln W. \tag{6.5}$$

This is the relation between entropy and the number of possible states according to Boltzmann, or expressed by ρ_0

$$S = -k_\mathrm{B}\ln\rho_0. \tag{6.6}$$

6.b Example: Free atom in a cuboid

We consider one free particle ($N=1$) in a cuboid with lengths of edges L_1,L_2, and L_3, $0\le x\le L_1$, $0\le y\le L_2$, $0\le z\le L_3$. We consider two boundary conditions:
Boundary condition 1 (RB1) The wave-function vanishes at the boundary (e.g. in an infinitely deep potential. Then the solutions can be written in the form

$$\psi(x,y,z) = \sqrt{\frac{8}{V}}\sin(k_1x)\sin(k_2y)\sin(k_3z), \quad k_\alpha = \frac{\pi n_\alpha}{L_\alpha}, \quad n_\alpha = 1,2,3,... \tag{6.7}$$

Boundary condition 2 (RB2) We assume periodic boundary conditions

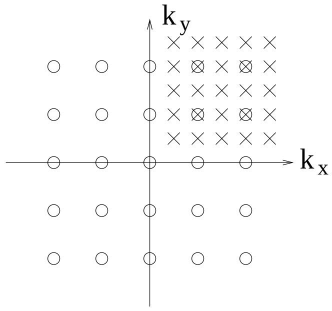
$$\psi(x,y,z) = \psi(x+L_1,y,z) = \psi(x,y+L_2,z) = \psi(x,y,z+L_3). \tag{6.8}$$

Then the solution can be written in the form

$$\psi(x,y,z) = \frac{1}{\sqrt{V}}\,\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}, \quad k_\alpha = \frac{2\pi n_\alpha}{L_\alpha}, \quad n_\alpha = 0,\pm1,\pm2,\pm3,... \tag{6.9}$$

Now we consider the density of states in k-space (momentum space)

Density of states in k-space. Crosses indicate the permitted k-vectors for boundary condition RB1, circles those for RB2.



We obtain for the two boundary conditions

$$\begin{aligned} & \text{(RB1)} && \text{(RB2)} && (6.10)\\ \mathrm{d}W &= \frac{L_1L_2L_3}{\pi^3}\mathrm{d}^3k && \mathrm{d}W = \frac{L_1L_2L_3}{(2\pi)^3}\mathrm{d}^3k && (6.11)\\ &= \frac{V}{\pi^3}\mathrm{d}^3k && = \frac{V}{(2\pi)^3}\mathrm{d}^3k && (6.12)\\ k_1 > 0, k_2 &> 0, k_3 > 0. && && (6.13)\\ \Delta n_\alpha &= \frac{L_\alpha}{\pi}\Delta k_\alpha && \Delta n_\alpha = \frac{L_\alpha}{2\pi}\Delta k_\alpha && (6.14) \end{aligned}$$

Then one obtains for the number $W(E)$ of states up to energy E

$$\left.\begin{array}{ll} \text{(RB1)} & W = \frac{V}{\pi^3}\int \mathrm{d}^3k \\ \text{(RB2)} & W = \frac{V}{(2\pi)^3}\int \mathrm{d}^3k \end{array}\right\} = \frac{V}{(2\pi)^3}\frac{4\pi}{3}\left(\frac{2mE}{\hbar^2}\right)^{3/2} \tag{6.15}$$

For the boundary condition 1 the integral extends over one eighth of a sphere, for the boundary condition 2 over the whole sphere of radius $(2mE/\hbar^2)^{1/2}$. Boundary condition 1 yields standing waves. Contributions with components k_α include those with $-k_\alpha$, so that only $k_\alpha > 0$ has to be considered. Then the states lie doubly dense in all directions in **k**-space in comparison to periodic boundary conditions. In total one obtains the same number $W(E)$ of states. In most cases one works with periodic boundary conditions.

7 Comparison between quantum mechanical and classical behavior

7.a Normalization of Phase-space

For one free particle in a cuboid of volume V we obtained (for $W \gg 1$)

$$W_1^{\rm qu}(E) = \frac{4\pi}{3}\frac{V(2mE)^{3/2}}{h^3}, \quad \Phi_1^{\rm cl}(E) = \frac{4\pi}{3}V(2mE)^{3/2}, \tag{7.1}$$

that is the connection

$$W_1^{\rm qu}(E) = \frac{1}{h^3}\Phi_1^{\rm cl}(E). \tag{7.2}$$

In general there is not such a simple relation between $W_N^{\rm qu}$ and $\Phi_N^{\rm cl}$. There is however the question which relation holds between $W_N^{\rm qu}$ and $\Phi_N^{\rm cl}$, if one is in the limit in which a quantum mechanical system can be described within classical approximation. Is in such a case generally the phase space $\mathrm{d}^3p\,\mathrm{d}^3x$ to be divided by h^3, such that it becomes a dimensionless number?
We consider how dense a complete system of wave-functions is packed in phase space and perform the reflection for one space coordinate x and one momentum coordinate p. The generalzation to $3N$ pairs is obvious. For this purpose we divide x into intervals of length x_0; the nth interval be

$$nx_0 \le x \le (n+1)x_0, \quad n = 0, \pm 1, \pm 2, \pm 3, ... \tag{7.3}$$

A complete orthonormal basis of wave functions in this interval is given by

$$\psi_{n,m}(x) = \frac{1}{\sqrt{x_0}}\left\{ \begin{array}{cl} \mathrm{e}^{\mathrm{i}kx} & \text{in the interval} \\ 0 & \text{elsewhere} \end{array} \right. \tag{7.4}$$

with $kx_0 = 2\pi m$, m integer, that is

$$p = \hbar k = \frac{2\pi\hbar m}{x_0} = p_0 m, \quad p_0 = \frac{h}{x_0}. \tag{7.5}$$

One function requires the space $x_0 p_0 = h$ in (p, x) space. Thus one finds within the phase space Φ approximately Φ/h states. For $3N$ pairs (p, x) one expects $W_N^{\rm cl}(E) = \Phi_N(E)/h^{3N}$, where $W_N^{\rm cl}(E)$ is the number of quantum mechanical states in a quasiclassical approximation.

7.b Undistinguishability of particles

One and the same kind of quantum mechanical particles are undistinguishable. In phase space we distinguish

$$p_1 = p,\ p_2 = p' \text{ and } p_1 = p',\ p_2 = p. \tag{7.6}$$

The states in phase space which transform into each other under permutations are generally quantum mechanical undistinguishable. Thus one has to divide Φ_N by $N!$ in the semi-classical limit

$$W_N^{\rm cl}(E) = \frac{1}{h^{3N}N!}\Phi_N(E). \tag{7.7}$$

7.c Application to the ideal gas

We apply this result to the ideal gas

$$W_N^{\rm cl}(E) = \frac{1}{h^{3N}N!}\Phi_N(E) = \frac{V^N(2mE)^{3N/2}\pi^{3N/2}}{h^{3N}N!(\frac{3N}{2})!} = \frac{1}{\sqrt{6}\pi N}\left(\frac{V(2mE)^{3/2}\pi^{3/2}\mathrm{e}^{5/2}}{h^3 N(\frac{3N}{2})^{3/2}}\right)^N \tag{7.8}$$

and introduce the volume v per atom, the energy ϵ per atom and the thermal de Broglie wave-length λ,

$$v = \frac{V}{N}, \quad \epsilon = \frac{E}{N}, \quad \lambda^2 = \frac{h^2}{\frac{4\pi}{3} m\epsilon} = \frac{h^2}{2\pi m k_{\mathrm{B}} T}. \tag{7.9}$$

The thermal de Broglie wave-length is the quantum mechanical wave-length of a particle of energy $\frac{2\pi}{3}\epsilon = \pi k_{\mathrm{B}} T$. Then W reads

$$W_N^{\mathrm{cl}}(E, V) = \frac{1}{\sqrt{6}\pi N} \left(\frac{v}{\lambda^3} \mathrm{e}^{5/2}\right)^N . \tag{7.10}$$

This is a good approximation for a quantum mechanical gas as long as $v\lambda^{-3}\mathrm{e}^{5/2} \gg 1$ holds, that is for a dilute hot gas. The entropy of this gas reads

$$S_N^{\mathrm{cl}}(E, V) = k_{\mathrm{B}} \ln W_N^{\mathrm{cl}}(E, V) = N k_{\mathrm{B}} \ln\left(\frac{v\mathrm{e}^{5/2}}{\lambda^3}\right) - k_{\mathrm{B}} \ln(\sqrt{6}\pi N), \tag{7.11}$$

where for large systems the last term is negligible in comparison to the predecessing one.

8 Systems in heat (thermal) contact

We consider two systems with particle numbers N_1, N_2 in volumes V_1, V_2 described by Hamiltonians H_1 and H_2, which interact via an interaction H_{12}. The total system is described by

$$H = H_1 + H_2 + H_{1,2}. \tag{8.1}$$

The interaction allows an exchange of energy between the two single systems. We assume however, that the contribution $H_{1,2}$ to the energy of the total system be negligible. The maximum energy of the total system be E and we ask for the number of eigenvalues $E_n \leq E$, and in classical systems for the normalized phase-space of the total system,

$$\text{quantum mechanical} \qquad W(E) = \mathrm{tr}\Theta(E-H) \tag{8.2}$$

$$\text{classical} \qquad W(E) = \frac{1}{N_1!N_2!h^{3N_1+3N_2}} \int \mathrm{d}^{3N_1+3N_2}p\, \mathrm{d}^{3N_1+3N_2}x\, \Theta(E-H). \tag{8.3}$$

We assume in the quasiclassical case, that we can distinguish between the N_1 particles in the volume V_1 and the N_2 particles inside volume V_2. Neglection of $H_{1,2}$ yields

$$\Theta(E-H) = \Theta(E-H_1-H_2) = \int \mathrm{d}E_1 \int \mathrm{d}E_2 \Theta(E-E_1-E_2)\delta(E_1-H_1)\delta(E_2-H_2). \tag{8.4}$$

We obtain in the quantum mechanical case

$$\mathrm{tr}\delta(E_1-H_1)\delta(E_2-H_2) = \mathrm{tr}_1\delta(E_1-H_1)\mathrm{tr}_2\delta(E_2-H_2) = \frac{\partial W_1(E_1)}{\partial E_1}\frac{\partial W_2(E_2)}{\partial E_2}. \tag{8.5}$$

Here tr_1 and tr_2 are the traces in the Hilbert spaces of the subsystems 1 and 2. The derivatives

$$\frac{\partial W_i(E_i)}{\partial E_i} = \omega_i(E_i) \tag{8.6}$$

are the densities of the (N_i-particle) states per energy. This yields

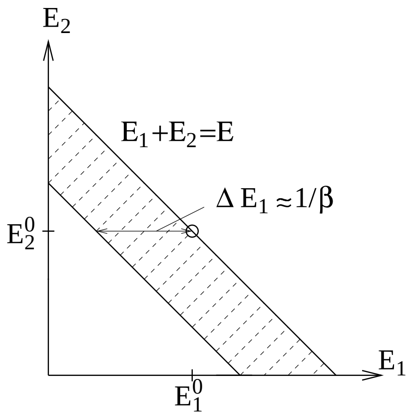
$$W(E) = \int \mathrm{d}E_1 \mathrm{d}E_2 \Theta(E-E_1-E_2)\omega_1(E_1)\omega_2(E_2). \tag{8.7}$$

The same expression is obtained in the classical case with

$$\omega_i(E_i) = \frac{1}{N_i!h^{3N_i}}\frac{\partial \Phi_{N_i}(E_i,V_i)}{\partial E_i}. \tag{8.8}$$

Thus the product $\omega_1(E_1)\omega_2(E_2)$ has to be integrated over all energies $E_1+E_2 \leq E$. Since $W_i(E_i)$ increases rapidly as a function of energy, the same is true for $\omega_i(E_i)$. Thus one expects the maximum of the integrand $\omega_1\omega_2$ at a point, where the sum of both energies has reached its maximum, $E_1^0 + E_2^0 = E$.

The region of integration E_1, E_2. Integration is performed over $E_1+E_2 \leq E$. The main contribution comes from the hatched region.



Then the maximum obeys

$$\frac{\partial}{\partial E_1^0}\left(\omega_1(E_1^0)\omega_2(E-E_1^0)\right)=0, \tag{8.9}$$

that is after division by $\omega_1\omega_2$

$$\frac{\partial \ln\omega_1(E_1^0)}{\partial E_1^0}=\frac{\partial \ln\omega_2(E_2^0)}{\partial E_2^0}=:\beta. \tag{8.10}$$

This is the equilibrium condition for two systems in thermal equilibrium.
Two such systems have the same temperature. We conclude, that β is a function of temperature independent of the system under consideration. For the ideal gas we have already found that $\beta = 1/(k_\mathrm{B}T)$. If we choose as system 2 an ideal gas then we conclude that for an arbitrary system 1 we have $\beta = 1/(k_\mathrm{B}T)$.
In order to estimate the integral for $W(E)$ we integrate $\partial\ln\omega_1/\partial E_1=\beta$ and obtain

$$\omega_1(E_1)=\omega_1(E_1^0)\mathrm{e}^{\beta(E_1-E_1^0)} \tag{8.11}$$

for energies close to E_1^0. A second integration yields

$$W_1(E_1)=\frac{1}{\beta}\omega_1(E_1), \tag{8.12}$$

where no constant of integration has to be added, since $W_1(E_1)\ll W_1(E_1^0)$ for $\beta(E_1^0-E_1)\gg 1$. Then we obtain for $W(E)$

$$W(E)\approx\omega_1(E_1^0)\omega_2(E_2^0)\frac{1}{\beta}\Delta E_1 = W_1(E_1^0)W_2(E_2^0)\beta\Delta E_1, \tag{8.13}$$

where $\Delta E_1/\beta$ is the area of the (E_1,E_2)-plane in which $\omega_1\omega_2$ is of the order of magnitude of the maximum of this function.
Large numbers and extremely large numbers The number of particles N and the entropy in units of the microscopic k_B are for macroscopic systems of the order of the Loschmidt number, thus large numbers of the order of 10^{23} or similarly. The number of quantum states of a macroscopic system is however a number of the order of 10 or e to the power of 10^{23}, thus a number which cannot be expressed by 23 or so digits but by 10^{23} digits. We call such numbers extremely large. The quantities W and ω which we have considered here have this property. Also the partition functions which we will consider later have this property. Similarly as here it will happen, that we have to multiply two quantities of this type and to integrate the product over a variable (here the energy). Then it is sufficient to look for its maximum and to take the corresponding value of the product. More precisely we had to multiply by the width over which the function decays (the ΔE_1 in (8.13)). Normally this factor is small in comparison to the product at its maximum. Since finally nearly always we have to take the logarithm of the integral we can neglect this width. Also this is the reason why we can neglect the last term in (7.11). Sometimes we will need the width in order to determine the fluctuations of the quantity over which we integrated. This can be determined in many cases from the second derivative of the logarithm.

9 Entropy as additive and extensive quantity

9.a Additivity

If a system consists of two systems with volumina V_1 and V_2 and particle numbers N_1 and N_2, then the volume V and the particle number N of the total system are

$$V = V_1 + V_2, \quad N = N_1 + N_2. \tag{9.1}$$

Therefore one calls volume and particle number additive quantities. Momentum, angular momentum, magnetic and electric moment have the same property. It holds for the energy of two non-interacting systems, too. If they interact, then the interaction energy has to be divided appropriately to the two subsystems.
Similarly the same property holds for two non-interacting (weakly interacting) systems, if the single systems are microcanonical systems. If the ensemble of system 1 contains W_1 states $|n\rangle$ and that of system 2 W_2 states $|m\rangle$, then the total system contains $W = W_1 W_2$ states $|n, m\rangle$. Thus the entropy is additive

$$S = k_\mathrm{B} \ln W = k_\mathrm{B} \ln W_1 + k_\mathrm{B} \ln W_2 = S_1 + S_2. \tag{9.2}$$

Note however, that the total ensemble is not microcanonical.
In the preceeding section we considered a macrocanonical system consisting of two subsystems in thermal contact. For this ensemble one obtains from $W = W_1 W_2 \beta \Delta E_1$

$$S = S_1 + S_2 + k_\mathrm{B} \ln(\beta \Delta E_1), \tag{9.3}$$

where S_1 and S_2 are the entropies of the subsystems at defined energies E_1^0 and E_2^0. Since now $S_1 + S_2$ is large for macroscopical systems (see ideal gas) in comparison to $k_\mathrm{B} \ln(\beta\Delta E_1)$, this last term can be neglected.

9.b Entropy as extensive quantity

If we halve the system into two subsystems $V_1 = V_2 = \frac{1}{2}V$, $N_1 = N_2 = \frac{1}{2}N$, then the maximum of $\omega_{N_1}(E_1)\omega_{N_2}(E - E_1 = E_2)$ will normally be found at $E_1^0 = E_2^0 = \frac{1}{2}E$. Then one obtains for the entropy

$$S(E, V, N) = 2S(\frac{E}{2}, \frac{V}{2} \frac{N}{2}). \tag{9.4}$$

The same consideration can be applied for ν equal systems in thermal equilibrium. Then similarly one has

$$S(E, V, N) = \nu S(\frac{E}{\nu}, \frac{V}{\nu}, \frac{N}{\nu}). \tag{9.5}$$

We now choose $\nu = N/N_0$ where N_0 is a fixed particle number large in comparison to one; then one obtains

$$S(E, V, N) = N\sigma(\frac{E}{N}, \frac{V}{N}), \quad \sigma(\frac{E}{N}, \frac{V}{N}) := \frac{1}{N_0} S(N_0 \frac{E}{N}, N_0 \frac{V}{N}, N_0). \tag{9.6}$$

Thus at fixed densities of energy and particles the entropy grows proportional to the number of particles. Such quantities are called extensive. In contrast one calls quantities which stay constant with increasing size of the system at constant quality of the system intensive. Such quantities are for example the densities of energy and particle number, but also temperature and pressure.
Remarks. For gases and fluids one has to allow for the exchange of particles besides energy exchange. This can be done similarly to the enrgy exchange (see section 12.) If the subsystems are small, then the terms $\beta\Delta E$ can become important, which then appear in the $(\nu - 1)$-th power. They can be taken into account without problems.
It is more difficult to estimate the contributions of the interactions $H_{1,2}$ at the boundary surfaces of the partial volumina. We do not consider this. If long-range interactions are present then the situation becomes particularly difficutl. There are proofs, that the entropy of a neutral system consisting of

positive nuclei and negative electrons (fermions!) with Coulomb-interaction is extensive. Compare Thirring, Vorlesungen über Mathematische Physik. Quantenmechanik großer Systeme und Lebowitz and Lieb, Adv. in Math. 9, 316 (1972). The entropy is not extensive in the case of gravitation (stars).

9.c Derivative of the entropy with respect to the energy

We derive a relation between β and the entropy for macroscopic systems. According to section 8 one has

$$\beta = \left.\frac{\partial \ln \omega(E)}{\partial E}\right|_{V,N}, \quad \omega(E) = \beta W(E). \tag{9.7}$$

From this one obtains with $W = \mathrm{e}^{S/k_\mathrm{B}}$

$$\left.\frac{\partial S(E,V,N)}{\partial E}\right|_{V,N} = k_\mathrm{B} \left.\frac{\partial \ln W}{\partial E}\right|_{V,N} = k_\mathrm{B} \left.\frac{\partial \ln \omega}{\partial E}\right|_{V,N} - k_\mathrm{B} \left.\frac{\partial \ln \beta}{\partial E}\right|_{V,N}. \tag{9.8}$$

The last term is of order $1/N$ and thus negligible for large systems. Then one obtains

$$\left.\frac{\partial S(E,V,N)}{\partial E}\right|_{V,N} = k_\mathrm{B}\beta = \frac{1}{T}. \tag{9.9}$$

For constant volume and particle number one obtains for the transition between equilibrium states $\mathrm{d}E = T\mathrm{d}S$, where the energy is transmitted by means of thermal contacts. Thus $T\mathrm{d}S$ is the amount of heat added to the system.

10 Canonical ensemble

10.a Canonical ensemble quantum mechanical

Again we consider two systems in thermal contact and ask for the statistical operator of system 1. One has

$$\rho = \rho_0 \Theta(E - H_1 - H_2) = \rho_0 \sum_{n,m} \Theta(E - E_n - E_m)|n,m\rangle\langle n,m|. \tag{10.1}$$

Here $|n\rangle$ are the energy eigenstates in the subsystem 1 and $|m\rangle$ are the states in the subsystem 2. We calculate the reduced densitiy matrix

$$\rho_1 = \mathrm{tr}_2 \rho = \rho_0 \sum_n \left(\sum_m \Theta(E - E_n - E_m) \right) |n\rangle\langle n| = \rho_0 \sum_n W_2(E - E_n)|n\rangle\langle n|. \tag{10.2}$$

Now we have

$$\ln W_2(E - E_n) = \frac{1}{k_\mathrm{B}} S_2(E - E_n) = \frac{N_2}{k_\mathrm{B}} \sigma_2(\frac{E - E_n}{N_2}, \frac{V_2}{N_2}). \tag{10.3}$$

Here we use, that the entropy is extensive. (comp. section 9). We expand now in E_n

$$\ln W_2(E - E_n) = \frac{N_2}{k_\mathrm{B}} \sigma_2(\frac{E}{N_2}) - \frac{E_n}{k_\mathrm{B}} \frac{\partial \sigma_2}{\partial(E/N_2)} + \frac{E_n^2}{2k_\mathrm{B} N_2} \frac{\partial^2 \sigma_2}{\partial(E/N_2)^2} - ... \tag{10.4}$$

If we keep E/N, V_2/N_2 fixed and consider the limit of large N_2 then we are left with

$$\ln W_2(E - E_n) = \ln W_2(E) - \beta E_n, \tag{10.5}$$

where $\beta = 1/(k_\mathrm{B} T)$ is given by the temperature of the second system, since

$$\frac{\partial \sigma_2}{\partial(E/N_2)} = \frac{\partial S_2}{\partial E} = \frac{1}{T_2}. \tag{10.6}$$

Then one obtains

$$\rho_1 = \frac{1}{Z} \sum_n \mathrm{e}^{-\beta E_n} |n\rangle\langle n| = \frac{1}{Z} \mathrm{e}^{-\beta H_1}. \tag{10.7}$$

In a heat bath (system 2) which is large in comparison to system 1, the system 1 is an ensemble described by $\rho_1 \propto \mathrm{e}^{-\beta H_1}$. This ensemble is called canonical enmsemble. (Now we drop the index 1). The normalization factor

$$Z(\beta, V, N) = \mathrm{tr}\mathrm{e}^{-\beta H} = \sum_n \mathrm{e}^{-\beta E_n} = \int \mathrm{d}E \omega(E, V, N) \mathrm{e}^{-\beta E} \tag{10.8}$$

is called canonical partition function.

10.b Classical case

Corresponding considerations apply to the classical limit. There one obtains

$$\rho_1(p^{(1)}, x^{(1)}) = \int \mathrm{d}^{3N_2} p^{(2)} \mathrm{d}^{3N_2} x^{(2)} \rho_0 \Theta(E - H_1 - H_2) = \rho_0 \Phi_{N_2}^{(2)}(E - H_1) = \rho_0 N_2! h^{3N_2} W^{(2)}(E - H_1) \tag{10.9}$$

and in the limit of a large system 2 (heat reservoir)

$$\rho_1(p^{(1)}, x^{(1)}) \propto \mathrm{e}^{-\beta H_1}. \tag{10.10}$$

If we define (we drop now the index 1) the partition function

$$Z = \frac{1}{h^{3N} N!} \int \mathrm{d}^{3N} p \mathrm{d}^{3N} x \mathrm{e}^{-\beta H}, \tag{10.11}$$

then one obtains

$$\rho(p,x) = \frac{1}{Z\,h^{3N}N!}\mathrm{e}^{-\beta H}. \tag{10.12}$$

For

$$H = \sum_i \frac{p_i^2}{2m} + H_{\mathrm{pot}}(x) \tag{10.13}$$

one can perform the p-integration which yields

$$Z = \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} \int \mathrm{d}^{3N}x \mathrm{e}^{-\beta H_{\mathrm{pot}}(x)} = \frac{1}{N!\lambda^{3N}} \int \mathrm{d}^{3N}x \mathrm{e}^{-\beta H_{\mathrm{pot}}(x)} \tag{10.14}$$

with the thermal de Broglie wave-length (section 7)

$$\lambda = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}}. \tag{10.15}$$

10.c Barometric pressure equation

We consider now a gas, whose atoms are in an external potential $V(\mathbf{x})$, which however, do not interact with each other.

$$H = \sum_i \left(\frac{p_i^2}{2m} + V(x_i)\right). \tag{10.16}$$

In an interaction-free system we have

$$\rho(\mathbf{p}_1, ...\mathbf{p}_N, \mathbf{x}_1, ...\mathbf{x}_N) = \prod_{i=1}^{N} \rho_1(\mathbf{p}_i, \mathbf{x}_i) \tag{10.17}$$

with

$$\rho_1(\mathbf{p},\mathbf{x}) = c\mathrm{e}^{-\beta p^2/(2m) - \beta V(x)}. \tag{10.18}$$

One obtains for the particle density $n(\mathbf{x})$ at point $\mathbf{x}$

$$n(\mathbf{x}) = \sum_i \langle \delta^3(\mathbf{x} - \mathbf{x}_i)\rangle = N \int \mathrm{d}^3 p \rho_1(\mathbf{p},\mathbf{x}) = n_0 \mathrm{e}^{-\beta V(x)} \tag{10.19}$$

with

$$n_0 = \frac{N}{\int \mathrm{d}^3 x \mathrm{e}^{-\beta V(x)}} \tag{10.20}$$

The barometric pressure formula (10.19) can also be derived from mechanical equilibrium. Let us denote the pressure at $\mathbf{x}$ by $P(\mathbf{x})$. The force acting on a particle is $-\operatorname{grad} V(\mathbf{x})$. Thus the average force density is given by $\mathbf{k}(\mathbf{x}) = -n(\mathbf{x}) \operatorname{grad} V(\mathbf{x})$. It must coincide with the gradient of the pressure

$$\operatorname{grad} P(\mathbf{x}) = -n(\mathbf{x}) \operatorname{grad} V(\mathbf{x}). \tag{10.21}$$

On the other hand one has the equation of state $P(\mathbf{x}) = n(\mathbf{x}) k_{\mathrm{B}} T$. Using this expression one obtains

$$\begin{aligned} k_{\mathrm{B}} T \operatorname{grad} n(\mathbf{x}) &= -n(\mathbf{x}) \operatorname{grad} V(\mathbf{x}), & (10.22)\\ k_{\mathrm{B}} T \operatorname{grad} \ln n(\mathbf{x}) &= -\operatorname{grad} V(\mathbf{x}), & (10.23)\\ n(\mathbf{x}) &= n_0 \mathrm{e}^{-\beta V(\mathbf{x})}. & (10.24) \end{aligned}$$

11 Equipartition theorem and virial theorem

11.a Equipartition theorem

We derive the equipartition theorem for classical systems, where we start with the canonical ensemble ($\rho \propto \mathrm{e}^{-\beta H}$). For this purpose we consider

$$\int \mathrm{d}^{3N}p\mathrm{d}^{3N}x \frac{\partial}{\partial p_{i\alpha}}(A(\mathbf{p},\mathbf{x})\rho(\mathbf{p},\mathbf{x})) = \int \mathrm{d}^{3N}p\mathrm{d}^{3N}x \left(\frac{\partial A}{\partial p_{i\alpha}} - \beta A \frac{\partial H}{\partial p_{i\alpha}}\right)\rho = \langle \frac{\partial A}{\partial p_{i\alpha}}\rangle - \beta\langle A\frac{\partial H}{\partial p_{i\alpha}}\rangle = 0. \tag{11.1}$$

The integral vanishes, if $A\rho$ decays sufficiently rapidly as function of $p_{i\alpha}$, since then the integral over $p_{i\alpha}$ vanishes

$$\langle A\frac{\partial H}{\partial p_{i\alpha}}\rangle = k_{\mathrm{B}}T\langle\frac{\partial A}{\partial p_{i\alpha}}\rangle. \tag{11.2}$$

Similarly one shows

$$\langle A\frac{\partial H}{\partial x_{i\alpha}}\rangle = k_{\mathrm{B}}T\langle\frac{\partial A}{\partial x_{i\alpha}}\rangle. \tag{11.3}$$

This yields for example

$$\langle p_{i\alpha}\frac{\partial H}{\partial p_{i\alpha}}\rangle = k_{\mathrm{B}}T, \tag{11.4}$$

$$\langle x_{i\alpha}\frac{\partial H}{\partial x_{i\alpha}}\rangle = k_{\mathrm{B}}T. \tag{11.5}$$

The second relation holds only if the potential experienced by the mass point increases suffiently rapidly. For

$$H = \sum_i \frac{p_i^2}{2m_i} + H_{\mathrm{pot}}(\mathbf{x}) \tag{11.6}$$

one obtains

$$\langle \frac{p_{i\alpha}^2}{m_i}\rangle = k_{\mathrm{B}}T, \tag{11.7}$$

$$\langle x_{i\alpha}\frac{\partial H_{\mathrm{pot}}}{\partial x_{i\alpha}}\rangle = k_{\mathrm{B}}T. \tag{11.8}$$

One obtains for the harmonic oscillator $H_{\mathrm{pot}} = \frac{f}{2}x_\alpha^2$

$$\langle\frac{f}{2}x_\alpha^2\rangle = \frac{1}{2}k_{\mathrm{B}}T. \tag{11.9}$$

A harmonic solid, more precisely for a solid whose atoms are elongated in the average so weakly that it is sufficient to expand the potential up to second order in the elongation $\mathbf{x}$,

$$H_{\mathrm{pot}} = \frac{1}{2}\sum f_{i\alpha,j\beta}x_{i\alpha}x_{j\beta} \tag{11.10}$$

(and which on the other hand is so strongly excited that its quantum mechanical behavior can be neglected) obeys

$$\sum_{i\alpha}\langle x_{i\alpha}\frac{\partial H}{\partial x_{i\alpha}}\rangle = 2\langle H_{\mathrm{pot}}\rangle = 3Nk_{\mathrm{B}}T, \tag{11.11}$$

$$\sum_{i\alpha}\langle p_{i\alpha}\frac{\partial H}{\partial p_{i\alpha}}\rangle = 2\langle H_{\mathrm{kin}}\rangle = 3Nk_{\mathrm{B}}T. \tag{11.12}$$

From these relations one obtains the law of Dulong and Petit

$$\langle H\rangle = 3Nk_{\mathrm{B}}T. \tag{11.13}$$

For real solids there are deviations from this law; at low temperatures the degrees of freedom are frozen in (quantum effects), at high temperatures anharmonicities of the interaction become important.

11.b Virial theorem classical

The potential energy of a gas or a liquid which is confined in a vessel is composed of the interaction energies w between the atoms or molecules and the interaction $W_{\rm a}$ with the wall,

$$H_{\rm pot} = H_{\rm int} + H_{\rm w}, \quad H_{\rm w} = \sum_i W_{\rm a}(\mathbf{x}_i), \quad H_{\rm int} = \frac{1}{2}\sum_{ij} w(\mathbf{x}_i - \mathbf{x}_j). \tag{11.14}$$

We transform now the sum

$$\begin{aligned}
\sum_{i\alpha} x_{i\alpha}\frac{\partial H_{\rm int}}{\partial x_{i\alpha}} &= \frac{1}{2}\sum_{i\alpha,j,k} x_{i\alpha}\frac{\partial w(\mathbf{x}_j-\mathbf{x}_k)}{\partial x_{i\alpha}} \\
&= \frac{1}{2}\sum_{i\alpha,j,k\beta} x_{i\alpha}\frac{\partial w(\mathbf{x}_j-\mathbf{x}_k)}{\partial(x_{j\beta}-x_{k\beta})}\frac{\partial(x_{j\beta}-x_{k\beta})}{\partial x_{i\alpha}} \\
&= \frac{1}{2}\sum_{i\alpha,j,k\beta} x_{i\alpha}\frac{\partial w(\mathbf{x}_j-\mathbf{x}_k)}{\partial(x_{j\beta}-x_{k\beta})}(\delta_{ij}-\delta_{ik})\delta_{\alpha\beta} \\
&= \frac{1}{2}\sum_{j,k}(\mathbf{x}_j-\mathbf{x}_k)\frac{\partial w(\mathbf{x}_j-\mathbf{x}_k)}{\partial(\mathbf{x}_j-\mathbf{x}_k)}.
\end{aligned} \tag{11.15}$$

On the other hand we have

$$\sum_i \langle \mathbf{x}_i \frac{\partial W_{\rm a}}{\partial \mathbf{x}_i}\rangle = \int \mathbf{x}\cdot\mathbf{k}\mathrm{d}^3x = \int \mathbf{x}\cdot P\mathbf{d}f = P\int \operatorname{div}\mathbf{x}\mathrm{d}^3x = 3PV. \tag{11.16}$$

Here $\mathbf{k}$ is the force density (force per volume) acting on the wall. Obviously its range is given by the range of $W_{\rm a}$. We have used Gauss' theorem and $\operatorname{div}\mathbf{x} = 3$. From (11.11), (11.15), and (11.16) one obtains the virial theorem

$$PV = Nk_{\rm B}T - \frac{1}{6}\sum_{ij}\langle \mathbf{x}_{ij}\frac{\partial w}{\partial \mathbf{x}_{ij}}\rangle. \tag{11.17}$$

11.c Virial theorem quantum mechanical

It is not possible to derive an equipartition theorem for quantum mechanical systems as for classical systems. Indeed a commutator of $x_{j\alpha}$ with $A\rho$ is basically the same as a derivative of $A\rho$ with respect to $p_{j\alpha}$. But since the commutator of H with $x_{j\alpha}$ in generally does not commute with H, it is not possible to express the commutator of $x_{j\alpha}$ with $\rho \propto \mathrm{e}^{-\beta H}$ in a simple way.
Instead we consider the commutator of H with $A\rho$, where A is an operator to be choosen. Then one obtains

$$\mathrm{tr}([H, A\rho]) = 0 = \mathrm{tr}([H, A]\rho), \tag{11.18}$$

since $[H,\rho] = 0$. Thus one has

$$\langle [H, A]\rangle = 0. \tag{11.19}$$

With $A = \sum_j \mathbf{x}_j\cdot\mathbf{p}_j$ and the Hamiltonian (11.6) one obtains

$$[H, A] = \sum_{ji\alpha}[\frac{p_{i\alpha}^2}{2m_i}, \mathbf{x}_j]\cdot\mathbf{p}_j + \sum_j \mathbf{x}_j\cdot[H_{\rm pot}(\mathbf{x}), \mathbf{p}_j] = \frac{\hbar}{\mathrm{i}}\sum_{j\alpha}\frac{p_{j\alpha}^2}{m_j} + \mathrm{i}\hbar\sum_i \mathbf{x}_i\cdot\frac{\partial H_{\rm pot}(\mathbf{x})}{\partial \mathbf{x}_i}. \tag{11.20}$$

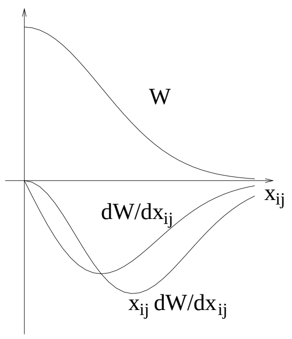
This yields

$$\sum_{i\alpha}\langle x_{i\alpha}\frac{\partial H_{\rm pot}}{\partial x_{i\alpha}}\rangle = 2\langle H_{\rm kin}\rangle. \tag{11.21}$$

Using (11.15), (11.21) one obtains

$$PV = \frac{2}{3}\langle H_{\rm kin}\rangle - \frac{1}{6}\sum_{ij}\langle \mathbf{x}_{ij}\frac{\partial w}{\partial \mathbf{x}_{ij}}\rangle. \tag{11.22}$$

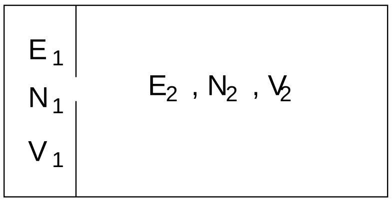
Example: W, $\partial W/\partial x$ and $x\partial W/\partial x$ for a repulsive potential.



12 Systems with exchange of particles: Grandcanonical Ensemble

We divide a microcanonical system into two subsystems with volumes V_1 and V_2. There can be an exchange of both energy and particles between these two subsystems; only an upper limit E for the total energy and a total number N of particles is fixed.

Two subsystems



$$E_1 + E_2 \leq E, \quad N_1 + N_2 = N. \tag{12.1}$$

We treat the subsystems similarly as in the case of heat exchange. The statistical operator of the total system is

$$\rho = \rho_0 \Theta(E - H_1 - H_2)\delta_{N,\hat{N}_1+\hat{N}_2} = \rho_0 \sum_{n,m} \Theta(E - E_n^{(1)} - E_m^{(2)})\delta_{N,N_n^{(1)}+N_m^{(2)}} |n,m\rangle\langle n,m|, \tag{12.2}$$

where $|n,m\rangle$ are the eigenstates of the Hamiltonians and the operators of the particle numbers

$$H_1|n,m\rangle = E_n^{(1)}|n,m\rangle, \quad H_2|n,m\rangle = E_m^{(2)}|n,m\rangle, \quad \hat{N}_1|n,m\rangle = N_n^{(1)}|n,m\rangle, \quad \hat{N}_2|n,m\rangle = N_m^{(2)}|n,m\rangle. \tag{12.3}$$

If we perform the trace over subsystem 2, then there remains the reduced density operator for system 1

$$\rho_1 = \mathrm{tr}_2\rho = \rho_0 \sum_n W^{(2)}(E - E_n^{(1)}, N - N_n^{(1)}, V_2)|n\rangle\langle n|. \tag{12.4}$$

We now transform the logarithm of $W^{(2)}$ similarly as we did before, where we use that the entropy is extensive (9.6),

$$\ln W^{(2)}(E,N,V_2) = \frac{1}{k_\mathrm{B}} S^{(2)}(E,N,V_2) = \frac{1}{k_\mathrm{B}} V_2 \frac{N}{V_2} \sigma(\frac{E/V_2}{N/V_2}, \frac{1}{N/V_2}) = \frac{1}{k_\mathrm{B}} V_2 \tilde{\sigma}(\frac{E}{V_2}, \frac{N}{V_2}). \tag{12.5}$$

Then we may write

$$\ln W^{(2)}(E - E_n^{(1)}, N - N_n^{(1)}, V_2) = \frac{1}{k_\mathrm{B}} V_2 \tilde{\sigma}(\frac{E}{V_2} - \frac{E_n^{(1)}}{V_2}, \frac{N}{V_2} - \frac{N_n^{(1)}}{V_2}). \tag{12.6}$$

Now we keep E/V_2 and N/V_2 constant and let V_2 become very large. Then we obtain

$$\ln W^{(2)}(E - E_n^{(1)}, N - N_n^{(1)}, V_2) = \ln W^{(2)}(E,N,V_2) - E_n^{(1)} \underbrace{\frac{1}{k_\mathrm{B}} \frac{\partial S^{(2)}}{\partial E}}_{\beta} - N_n^{(1)} \underbrace{\frac{1}{k_\mathrm{B}} \frac{\partial S^{(2)}}{\partial N}}_{\alpha} + O(\frac{1}{V_2}), \tag{12.7}$$

from which we conclude in the limit $V_2 \to \infty$

$$\rho_1 = \frac{1}{Y} \sum_n \mathrm{e}^{-\beta E_n^{(1)} - \alpha N_n^{(1)}} |n\rangle\langle n|. \tag{12.8}$$

This ensemble is called grandcanonical ensemble. It contains states of arbitrary particle number $N_n^{(1)}$. Only the two quantities α and β of the reservoir system 2 have an effect on system 1.
For two systems with particle exchange one has similarly as for energy exchange

$$\frac{\partial \ln W^{(1)}}{\partial N^{(1)}} = \frac{\partial \ln W^{(2)}}{\partial N^{(2)}} = \alpha, \tag{12.9}$$

since $W^{(1)}(N^{(1)})W^{(2)}(N^{(2)} = N - N^{(1)})$ has to assume a maximum as function of $N^{(1)}$. Usually one writes $\alpha = -\beta\mu$ and calls μ the chemical potential. In equilibrium one has for heat and particle exchange

$$\beta_1 = \beta_2, \quad \mu_1 = \mu_2. \tag{12.10}$$

As we see for system 2, eq. (12.7) one has

$$\mathrm{d}\ln W = \frac{1}{k_{\mathrm{B}}}\mathrm{d}S = \beta\mathrm{d}E - \beta\mu\mathrm{d}N \tag{12.11}$$

and due to (9.9, 12.9) this holds similarly for system 1. Thus we obtain

$$\mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N \tag{12.12}$$

for fixed volume V.
We may now write the density operator ρ of the grandcanonical ensemble

$$\rho = \frac{1}{Y}\sum_n \mathrm{e}^{-\beta(E_n - \mu N_n)}|n\rangle\langle n| = \frac{1}{Y}\mathrm{e}^{-\beta(H-\mu\hat{N})}. \tag{12.13}$$

The normalization factor Y is the grandcanonical partition function

$$Y(\mu,\beta,V) = \sum_n \mathrm{e}^{-\beta(E_n-\mu N_n)} = \mathrm{tr}\mathrm{e}^{-\beta(H-\mu\hat{N})} = \sum_N Z(N,\beta,V)\mathrm{e}^{\beta\mu N}. \tag{12.14}$$

We have now in the exponent

$$H - \mu\hat{N} = \sum_i \frac{p_i^2}{2m_i} + \sum_i (V_1(r_i) - \mu) + \frac{1}{2}\sum_{i,j} V_2(r_i - r_j). \tag{12.15}$$

As soon as the particle number is variable there is no more an arbitrary additive constant to the one-particle potential V_1. It is now determined by the chemical potential μ. Furthermore we observe in (12.13) that a larger μ favors a larger number of particles. Thus N increases with μ.

13 Pressure and enthalpy

Until now we considered systems in fixed volumina V. Instead we may close the system with a piston, which exerts a pressure P. The area of the piston be F. The pressure can be realized by a mass $m = PF/g$. Then the potential energy of the piston is

$$mgz = PFz = PV. \tag{13.1}$$

The total of the internal energy E of the system and the potential energy of the piston is called enthalpy

$$I = E + PV. \tag{13.2}$$

In a microcanonical ensemble one obtains (classically, similarly for the quantum mechanical case)

$$\tilde{W}_N(I,P) = \frac{1}{h^{3N}N!a} \int \mathrm{d}^{3N}x \mathrm{d}^{3N}p \mathrm{d}z \Theta(I - H(\mathbf{p},\mathbf{x}) - PV(z)), \tag{13.3}$$

where a is a microscopic length, so that $\tilde{W}$ becomes dimensionless. More precisely the kinetic energy of the piston had to be considered, too. Together with the corresponding momentum integration one has to write h instead of a. After the momentum integration one finds, that a is the thermal de-Broglie wavelength of the piston. In practice this factor in front is not important. Now we perform the $\mathbf{x}$ and the $\mathbf{p}$ integrations,

$$\tilde{W}_N(I,P) = \frac{1}{a} \int \mathrm{d}z W_N(I - PV(z), V(Z)). \tag{13.4}$$

We evaluate the integral by looking for the maximum of the integrand

$$\tilde{W}_N(I,P) \approx \max_V W_N(I - PV, V) = W_N(E,V) = \mathrm{e}^{S/k_\mathrm{B}}. \tag{13.5}$$

The equation which determines V reads

$$\frac{\partial W_N(I - PV, V)}{\partial V} = -P\frac{\partial W_N}{\partial E} + \frac{\partial W_N}{\partial V} = \left(-\frac{P}{k_\mathrm{B}}\frac{\partial S}{\partial E} + \frac{1}{k_\mathrm{B}}\frac{\partial S}{\partial V}\right)\mathrm{e}^{S/k_\mathrm{B}}, \tag{13.6}$$

thus we obtain

$$\left.\frac{\partial S}{\partial V}\right|_{N,E} = P \left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{P}{T}. \tag{13.7}$$

14 First law of thermodynamics: Energy conservation

14.a Energy Balance

The first law of thermodynamics deals with the conservation of energy. Its validity follows from the theorem of the conservation of energy in mechanics, electrodynamics and quantum mechanics, generally from the translational invariance of the laws of nature with respect to time; thus it need not to be proven here. Originally it was not clear that heat is a form of energy, too, so that one had different units for mechanical and thermal energy (calories). Here we are left with considering various forms of energy changes. We had derived (12.12), (13.7)

$$\left.\frac{\partial S(E,V,N)}{\partial E}\right|_{V,N} = \frac{1}{T}, \quad \left.\frac{\partial S}{\partial N}\right|_{E,V} = -\frac{\mu}{T}, \quad \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T}. \tag{14.1}$$

Thus we have

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E - \frac{\mu}{T}\mathrm{d}N + \frac{P}{T}\mathrm{d}V \tag{14.2}$$

or solved with respect to $\mathrm{d}E$

$$\mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V. \tag{14.3}$$

Two contributions have a simple meaning: a) If we keep volume and particle number fixed then energy can only be fed in or removed in the form of heat. Denoting the amount of added heat by δQ we find

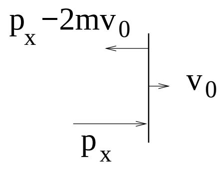
$$\delta Q = T\mathrm{d}S. \tag{14.4}$$

The amount of heat Q is not a state variable; therefore here we do not write $\mathrm{d}Q$, but δQ. If the system is thermally isolated so that it cannot absorb or loose heat and if we carry out mechanical work at the system by compression then the mechanical work delivered is

$$\delta A = -P\mathrm{d}V \tag{14.5}$$

for a slow movement of the piston. Since this is the energy added to the system it follows that the entropy is conserved under this process (adiabatic invariance, conservation of phase-space volume). However, the process has to be performed slowly, so that the system is always in equilibrium. Otherwise the expression for $\mathrm{d}E$ is no longer valid. For a rapid movement of the piston one has $\delta A \neq -P\mathrm{d}V$, since the gas molecules do not trnsfer the momentum $2p_x$ but $2(p_x - mv_x)$ to the piston.

Reflection of a gas molecule at the piston



Finally there is a third contribution

$$\delta_N E = \mu\mathrm{d}N \tag{14.6}$$

by adding $\mathrm{d}N$ particles without any change of entropy and volume. This process is not conspicuous. Instead we derive a relation for μ by adding to the system $\mathrm{d}N$ particles in a volume $\mathrm{d}V$ with energy $\mathrm{d}E$ of same quality, that is at the same temperature, pressure and chemical potential,

$$\mathrm{d}V = \frac{\mathrm{d}N}{N}V, \quad \mathrm{d}E = \frac{\mathrm{d}N}{N}E. \tag{14.7}$$

Since the entropy is extensive one obtains

$$\mathrm{d}S = \frac{\mathrm{d}N}{N}S \tag{14.8}$$

and therefore

$$\mathrm{d}E = \frac{\mathrm{d}N}{N}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V = \frac{\mathrm{d}N}{N}(TS + \mu N - PV), \tag{14.9}$$

that is we obtain the relation

$$E = TS + \mu N - PV \tag{14.10}$$

and thus for μ

$$\mu = \frac{E - TS + PV}{N}. \tag{14.11}$$

Taking the total derivative of (14.10)

$$\mathrm{d}E = T\mathrm{d}S + S\mathrm{d}T + \mu\mathrm{d}N + N\mathrm{d}\mu - P\mathrm{d}V - V\mathrm{d}P \tag{14.12}$$

we obtain with (14.3)

$$S\mathrm{d}T + N\mathrm{d}\mu - V\mathrm{d}P = 0. \tag{14.13}$$

This relation is called Gibbs-Duhem relation.

14.b Enthalpy

Similarly as for the energy we can derive the differential for the enthalpy. From

$$I = E + PV, \quad \mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V \tag{14.14}$$

one obtains

$$\mathrm{d}I = \mathrm{d}E + P\mathrm{d}V + V\mathrm{d}P = T\mathrm{d}S + \mu\mathrm{d}N + V\mathrm{d}P. \tag{14.15}$$

We obtained I by a Legendre transformation from E by replacing the natural variable V by P.

$$\begin{array}{ccc} E & \text{natural variable} & S,N,V \\ I & & S,N,P \end{array} \tag{14.16}$$

For the ideal classical gas we may express the entropy by I, N, P. We use

$$I = E + PV = E + Nk_\mathrm{B}T = \frac{5}{3}E, \quad E = \frac{3}{5}I, \quad PV = \frac{2}{3}E = \frac{2}{5}I, \quad V = \frac{2I}{5P}. \tag{14.17}$$

from which

$$S = k_\mathrm{B}N\ln\left(\frac{VE^{3/2}}{N^{5/2}}\left(\frac{4\pi m}{3h^2}\right)^{3/2}\mathrm{e}^{5/2}\right) \tag{14.18}$$

$$= k_\mathrm{B}N\ln\left(\frac{I^{5/2}}{PN^{5/2}}\left(\frac{4\pi m}{5h^2}\right)^{3/2}\frac{2}{5}\mathrm{e}^{5/2}\right) \tag{14.19}$$

is obtained. If one solves these two relations with respect to E and I, resp., then one obtains these quantities as functions of their natural variables.

15 Partition functions and Potentials

15.a Canonical partition function and free energy

The canonical partition function

$$Z(\beta, N, V) = \mathrm{tr}\mathrm{e}^{-\beta H} = \int \mathrm{d}E\omega(E, N, V)\mathrm{e}^{-\beta E} \tag{15.1}$$

may be approximated by the maximum of the integrand with respect to E

$$Z \approx \max_E(\omega(E, N, V)\mathrm{e}^{-\beta E}) \approx \max_E(W(E, N, V)\mathrm{e}^{-\beta E}), \tag{15.2}$$

where E is determined by

$$\frac{\partial}{\partial E}(W\mathrm{e}^{-\beta E}) = 0. \tag{15.3}$$

Because of $\frac{\partial W}{\partial E} = \beta(E)W$ one obtains

$$\beta(E) - \beta = 0. \tag{15.4}$$

Here $\beta(E)$ is the logarithmic derivative of W (inverse temperature of the system), whereas β in Z is introduced as a parameter (inverse temperature of the reservoir). One calls

$$F(T, N, V) = -k_\mathrm{B}T \ln Z(T, N, V) \tag{15.5}$$

the free energy (Helmholtz free energy). Obviously

$$F = -k_\mathrm{B}T \ln(W\mathrm{e}^{-\beta E}) = -k_\mathrm{B}T \ln W + E = E - TS, \tag{15.6}$$

holds, that is $F = E - TS = \mu N - PV$. From $\mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V$ one obtains

$$\mathrm{d}F(T, N, V) = -S\mathrm{d}T + \mu\mathrm{d}N - P\mathrm{d}V. \tag{15.7}$$

Starting from the definition of Z we consider the derivative $\partial Z/\partial\beta$. From $Z = \sum_n \mathrm{e}^{-\beta E_n}$ one obtains

$$\frac{\partial Z}{\partial \beta} = -\sum_n E_n \mathrm{e}^{-\beta E_n} = -Z\langle H\rangle, \tag{15.8}$$

thus

$$\frac{\partial \ln Z}{\partial \beta} = -\langle H\rangle = -E, \tag{15.9}$$

that is

$$\left.\frac{\partial \ln Z}{\partial T}\right|_{N,V} = \frac{E}{k_\mathrm{B}T^2} = \frac{\partial(-F/k_\mathrm{B}T)}{\partial T}, \tag{15.10}$$

thus

$$E = -k_\mathrm{B}T^2 \frac{\partial(F(T, N, V)/k_\mathrm{B}T)}{\partial T}. \tag{15.11}$$

15.b Canonical partition function and free enthalpy

Analogously to $Z(\beta, V, N)$ we consider $\tilde{Z}(\beta, N, P)$ for a system in thermal contact under pressure P,

$$\tilde{Z}(\beta, N, P) = \frac{1}{a}\int \mathrm{d}z Z(\beta, N, V(z))\mathrm{e}^{-\beta PV(z)}. \tag{15.12}$$

We approximate the integral by the maximum of of the integrand

$$\tilde{Z} \approx \max_V(Z\mathrm{e}^{-\beta PV}) = \max_V(\mathrm{e}^{-\beta F - \beta PV}) \tag{15.13}$$

with V determined by

$$\frac{\partial}{\partial V}(-\beta F - \beta PV)\bigg|_{\beta,N} = \beta(P(V) - P) = 0, \tag{15.14}$$

where $P(V)$ is the pressure of the system, and P the external pressure. We introduce now the free enthalpy (Gibbs' free energy)

$$G = -k_{\mathrm{B}}T \ln \tilde{Z}, \tag{15.15}$$

One obtains for it

$$G = F + PV = I - TS = E - TS + PV = \mu N. \tag{15.16}$$

The relation $G = \mu N$ is called Gibbs-Duhem relation, too. Further one has

$$\mathrm{d}G = -S\mathrm{d}T + \mu \mathrm{d}N + V\mathrm{d}P. \tag{15.17}$$

Taking the derivative of

$$\tilde{Z} = \mathrm{tr}\mathrm{e}^{-\beta(H+P\hat{V})} \tag{15.18}$$

with respect to β and P, one finds that

$$\frac{\partial \ln \tilde{Z}}{\partial \beta}\bigg|_{P,N} = -\langle H + P\hat{V}\rangle = -E - PV = -I \tag{15.19}$$

and

$$\frac{\partial \ln \tilde{Z}}{\partial P}\bigg|_{\beta,N} = -\beta\langle \hat{V}\rangle = -\beta V \tag{15.20}$$

holds.

15.c Grandcanonical partition function and grandcanonical potential

Finally we consider the grandcanonical partition function

$$Y(\beta, \mu, V) = \mathrm{tr}\mathrm{e}^{-\beta(H-\mu\hat{N})} = \sum_N Z(\beta, N, V)\mathrm{e}^{\beta\mu N}. \tag{15.21}$$

If we approximate also here Y by the largest term in the sum, then one obtains

$$Y = \max_N (Z\mathrm{e}^{\beta\mu N}) = \max_N \mathrm{e}^{-\beta F + \beta\mu N} \tag{15.22}$$

with

$$\frac{\partial}{\partial N}(-F + \mu N) = 0. \tag{15.23}$$

To this partition function belongs the grandcanonical potential

$$J = -k_{\mathrm{B}}T \ln Y(\beta, \mu, V). \tag{15.24}$$

One concludes

$$J = F - \mu N = E - TS - \mu N = -PV, \quad \mathrm{d}J = -S\mathrm{d}T - N\mathrm{d}\mu - P\mathrm{d}V. \tag{15.25}$$

15.d Summary of the Potentials

Finally we give a summary of the ensembles and the potentials. Out of each of the three pairs (T, S), (μ, N), and (P, V) we may choose one variable as natural variable. The other ones are obtained as partial derivatives of these variables. However, at least one of the three variables has to be extensive. Thus the combination of the three natural variables T, μ, P is not possible. If one tries to perform the corresponding Legendre-transformation, then one obtains "zero". Indeed any of the three quantities T, μ, P is always determined by the two other ones, whereas the size of the system remains undetermined. The entropy is the natural variable for the first four ensembles. The ensemble is of the form $\Theta(... - H)$, the trace of it (quantum mechanically) is the number W of states, the logarithm thereof is the entropy divided by the Boltzmann constant. However, two of these ensembles are not in use. Temperature is a natural variable of the second four ensembles. They are of the form $\exp(-\beta(H \pm ...))$. Their trace is the partition function, the logarithm thereof multiplied by $-k_B T$ the corresponding potential. The various potentials can be obtained by Legendre transformations from one another. The various numbers of quntummechanical states W which are determined for the first four ensembles of the summary and the partition functions of the other ensembles are obtained by appropriate integration or summation from the W of the microcanonical ensemble.

Übersicht über die Potentiale

Summary of the Potentials

Energie Energy	$E = E$	$= TS + \mu N - PV$	$\mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V$	$\Theta(E - H)$
Enthalpie Enthalpy	$I = E + PV$	$= TS + \mu N$	$\mathrm{d}I = T\mathrm{d}S + \mu\mathrm{d}N + V\mathrm{d}P$	$\Theta(I - H - P\hat{V})$
	$B = E - \mu N$	$= TS - PV$	$\mathrm{d}B = T\mathrm{d}S - N\mathrm{d}\mu - P\mathrm{d}V$	$\Theta(B - H + \mu\hat{N})$
	$C = E - \mu N + PV$	$= TS$	$\mathrm{d}C = T\mathrm{d}S - N\mathrm{d}\mu + V\mathrm{d}P$	$\Theta(C - H + \mu\hat{N} - P\hat{V})$
Freie Energie Helmholtz free energy	$F = E - TS$	$= \mu N - PV$	$\mathrm{d}F = -S\mathrm{d}T + \mu\mathrm{d}N - P\mathrm{d}V$	$\exp(-\beta H)$
Freie Enthalpie Gibbs free energy	$G = E - TS + PV$	$= \mu N$	$\mathrm{d}G = -S\mathrm{d}T + \mu\mathrm{d}N + V\mathrm{d}P$	$\exp(-\beta(H + P\hat{V}))$
Großkanonisches Potential Grandcanonical potential	$J = E - TS - \mu N$	$= -PV$	$\mathrm{d}J = -S\mathrm{d}T - N\mathrm{d}\mu - P\mathrm{d}V$	$\exp(-\beta(H - \mu\hat{N}))$
"Null" "Zero"	$0 = E - TS - \mu N + PV$	$= 0$	$0 = -S\mathrm{d}T - N\mathrm{d}\mu + V\mathrm{d}P$	$\exp(-\beta(H - \mu\hat{N} + P\hat{V}))$