Chapter 8
Canonical Ensemble (E,V,N)

5. Canonical Partition Function

We rewrite the **distribution function** (7) of the canonical ensemble as

$$\rho(q,p)=\frac{e^{-\beta H(q,p)}}{\int d^{3N}q\,d^{3N}p\quad e^{-\beta H(q,p)}} \qquad (10)$$

For one particle and one dimension $\rho(x,p_x)=\frac{e^{-\beta H(x,p_x)}}{\int dx\,dp_x\quad e^{-\beta H(x,p_x)}}$

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.

Example: Consider a particle that is confined to the region $x \ge 0$ by a potential which is proportional to x as $u(x) = V_0 x$

Find the expectation value of position of the particle at equilibrium temperature T is

Solution: The canonical partition function $\rho = \dfrac{e^{-\frac{p^2}{2mk_BT}-\frac{V_0x}{k_BT}}}{\iint e^{-\frac{p^2}{2mk_BT}}dp \cdot e^{-\frac{V_0x}{k_BT}}dx}$; $\langle x \rangle = \int x\rho(x)\,dx\,dp_x$

The Partition function $Z = \dfrac{1}{h}\int e^{-\frac{p^2}{2mk_BT}}dp\int e^{-\frac{V_0x}{k_BT}}dx$

$$\Rightarrow \langle x \rangle = \int x\rho\, dp\; dx = \frac{\iint xe^{-\frac{p^2}{2mk_BT}}dp \cdot e^{-\frac{V_0x}{k_BT}}dx}{\iint e^{-\frac{p^2}{2mk_BT}}dp \cdot e^{-\frac{V_0x}{k_BT}}dx} = \frac{\int_0^\infty xe^{-\frac{V_0x}{k_BT}}dx}{\int_0^\infty e^{-\frac{V_0x}{k_BT}}dx} = \frac{\left(\frac{k_BT}{V_0}\right)^2\int_0^\infty te^{-t}dt}{\left(\frac{k_BT}{V_0}\right)\int_0^\infty e^{-t}dt} = \frac{k_BT}{V_0}$$

Partition function: The canonical partition function ("kanonische Zustandssumme") Z_n is defined as

$$\boxed{Z_n = \int \frac{d^{3N}q\; d^{3N}p}{h^{3N}N!}\; e^{-\beta H(q,p)}} \qquad (11)$$

For one particle and one dimension.

$$\boxed{Z_1 = \int \frac{dx\; dp_x}{h}\; e^{-\beta H}}$$

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:

$$\frac{\Gamma(E)}{\Gamma_0} = \frac{1}{h^{3N}N!}\int_{E<H(q,p)<E+\Delta} d^{3N}q\; d^{3N}p$$

$$= \int \frac{d^{3N}q\; d^{3N}p}{h^{3N}N!}\left[u(E+\Delta-H)-u(E-H)\right]$$

$$\boxed{\frac{\Gamma(E)}{\Gamma_0} = \int \frac{dq\; dp}{h^3}\left[u(E+\Delta-H)-u(E-H)\right] \quad \text{For one Particle.}}$$

where u is the unit 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

$$\boxed{F = -k_B T \ln Z_n, \qquad Z_n = e^{-\beta F}}$$

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

Proof. In order to proof (11) we perform the differentiation

$$\frac{\partial}{\partial\beta}\ln Z_n = \frac{1}{Z_n}\frac{\partial Z_N}{\partial\beta} = \left[\frac{\partial}{\partial\beta}\int\frac{dqdp}{h^{3N}N!}e^{-\beta H}\right]\Big/\left[\int\frac{dqdp}{h^{3N}N!}e^{-\beta H}\right]$$

$$= \frac{\int dqdp\,(-H)\,e^{-\beta H}}{\int dqdp\, e^{-\beta H}} = -\langle H\rangle = -U$$

where we have used the shortcut $dqdp = d^{3N}q d^{3N}p$ and that $\langle H\rangle = E = U$ is the internal energy. We know $U = \partial(\beta F)/\partial\beta$, we find that

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

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.