Unit 2-11: Factorization of the Canonical Partition Function for Non-Interacting Particles

Consider a system of N identical *non-interacting* particles. Let $\mathbf{q}_i$ be the three spatial coordinates of particle i, and $\mathbf{p}_i$ are the corresponding momenta. The Hamiltonian $\mathcal{H}$ of the system is then the sum of uncoupled one-particle Hamiltonians $\mathcal{H}^{(1)}$,

$$\mathcal{H}[\{\mathbf{q}_i, \mathbf{p}_i\}] = \sum_{i=1}^{N} \mathcal{H}^{(1)}(\mathbf{q}_i, \mathbf{p}_i) \tag{2.11.1}$$

$\mathcal{H}^{(1)}(\mathbf{q}_i, \mathbf{p}_i)$ depends *only* on the degrees of freedom of particle i.

We can then write for the N-particle canonical partition function,

$$Q_N(T,V) = \frac{1}{N!\,h^{3N}} \left(\prod_{i=1}^{N} \int d\mathbf{q}_i d\mathbf{p}_i \right) \mathrm{e}^{-\beta\mathcal{H}} = \frac{1}{N!\,h^{3N}} \left(\prod_{i=1}^{N} \int d\mathbf{q}_i d\mathbf{p}_i \right) \mathrm{e}^{-\beta \sum_j \mathcal{H}^{(1)}(\mathbf{q}_j, \mathbf{p}_j)} \tag{2.11.2}$$

$$= \frac{1}{N!} \prod_{i=1}^{N} \left(\frac{1}{h^3} \int d\mathbf{q}_i d\mathbf{p}_i \, \mathrm{e}^{-\beta\mathcal{H}^{(1)}(\mathbf{q}_i, \mathbf{p}_i)} \right) \tag{2.11.3}$$

If we define the one-particle partition function,

$$Q_1(T,V) = \frac{1}{h^3} \int d\mathbf{q}_i d\mathbf{p}_i \, \mathrm{e}^{-\beta\mathcal{H}^{(1)}(\mathbf{q}_i, \mathbf{p}_i)} \tag{2.11.4}$$

then the N-particle partition function is,

$$\boxed{Q_N = \frac{1}{N!} (Q_1)^N} \qquad \text{for identical } \textit{non-interacting} \text{ particles} \tag{2.11.5}$$

and the Helmholtz free energy is then,

$$A = -k_B T \ln Q_N = -k_B T \Big[N \ln Q_1 - \ln N! \Big] = -k_B T \Big[N \ln Q_1 - N \ln N + N \Big] \quad \text{using Stirling's formula} \tag{2.11.6}$$

$$= -k_B T N \left(1 + \ln \left[\frac{Q_1}{N} \right] \right) \qquad \text{for identical } \textit{non-interacting} \text{ particles} \tag{2.11.7}$$

The Ideal Gas

Let us now apply the above to the ideal gas of point particles. Here,

$$\mathcal{H}^{(1)}(\mathbf{q}, \mathbf{p}) = \frac{p^2}{2m} \qquad p^2 = |\mathbf{p}|^2 \tag{2.11.8}$$

The momenta can go from $-\infty$ to $+\infty$, while the spatial coordinates are confined to a box of volume V. We then have for the one-particle partition function,

$$Q_1 = \frac{1}{h^3} \int_V d^3q \int_{-\infty}^{\infty} d^3p \; \mathrm{e}^{-\beta p^2/2m} = \frac{V}{h^3} \int_{-\infty}^{\infty} d^3p \; \mathrm{e}^{-\beta p^2/2m} = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \tag{2.11.9}$$

The last step follows from the (by now hopefully familiar) result, $\int_{-\infty}^{\infty} dx\, \mathrm{e}^{-x^2/2\sigma} = \sqrt{2\pi\sigma^2}$. Here $\sigma^2 = m/\beta$, and there are three integrals, one each for p_x, p_y and p_z, hence the factor $(2\pi m/\beta)^{3/2}$.

Thus we have for the one-particle and the N-particle partition functions,

$$Q_1 = \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \qquad \Rightarrow \qquad Q_N = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \left(2\pi m k_B T\right)^{3N/2} \tag{2.11.10}$$

The Helmholtz free energy is then given by Eq. (2.11.7),

$$A(T,V,N) = -k_B T N\left(1 + \ln\left[\frac{Q_1}{N}\right]\right) = -k_B T N\left(1 + \ln\left[\frac{V}{h^3 N}\left(2\pi m k_B T\right)^{3/2}\right]\right) \tag{2.11.11}$$

We can now compute the average energy. From Eq. (2.8.20), and using $\beta = 1/k_B T$, we have,

$$\langle E\rangle = -\left(\frac{\partial(-\beta A)}{\partial\beta}\right)_{V,N} = -\frac{\partial}{\partial\beta}\left(N + N\ln\left[\frac{V}{h^3 N}\left(2\pi m k_B T\right)^{3/2}\right]\right) \tag{2.11.12}$$

$$= -\frac{\partial}{\partial\beta}\left(N\ln\beta^{-3/2} + N\ln\left[\text{stuff independent of }\beta\right]\right) \tag{2.11.13}$$

$$= \frac{3}{2}N\left(\frac{1}{\beta}\right) = \frac{3}{2}N k_B T \qquad \text{and we regain the familiar result} \tag{2.11.14}$$

We can now compute the entropy.

$$S(T,V,N) = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = k_B N\left(1 + \ln\left[\frac{V}{h^3 N}\left(2\pi m k_B T\right)^{3/2}\right]\right) + \frac{3}{2}k_B T N\left(\frac{1}{T}\right) \tag{2.11.15}$$

$$= \frac{5}{2}k_B N + k_B N\ln\left[\frac{V}{h^3 N}\left(2\pi m k_B T\right)^{3/2}\right] \tag{2.11.16}$$

Substitute in $k_B T = \dfrac{2}{3}\dfrac{E}{N}$ to get,

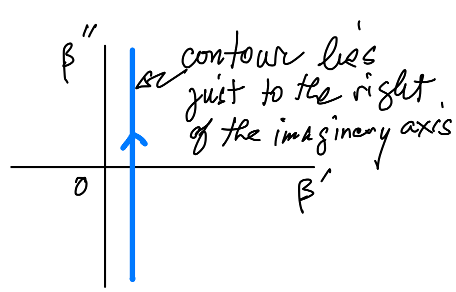
$$S(E,V,N) = \frac{5}{2}k_B N + k_B N\ln\left[\frac{V}{h^3 N}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] \tag{2.11.17}$$

and we have recovered the Sackur-Tetrode equation of Eq. (2.74). I hope you are convinced that this derivation, using the canonical ensemble, is simpler than our previous derivation of S from the microcanonical $\Omega(E,V,N)$.

It is perhaps worth mentioning (although I have never used this) that since Q_N is the Laplace transform of Ω, then Ω is the inverse Laplace transform of Q_N. Formally, we have,

$$Q_N(\beta) = \int \frac{dE}{\Delta E}\,\Omega(E)\,\mathrm{e}^{-\beta E} \tag{2.11.18}$$

So we can say that $Q_N(\beta)$ is the Laplace transform of $\dfrac{\Omega(E)}{\Delta E}$ (I will only write the variable E, and not also V and N, because it is E that is the transform variable).



Therefore $\dfrac{\Omega(E)}{\Delta E}$ is the inverse Laplace transform of $Q_N(\beta)$,

$$\frac{\Omega(E)}{\Delta E} = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} d\beta\; Q_N(\beta)\,\mathrm{e}^{-\beta E} = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\beta''\; Q_N(\beta' + i\beta'')\,\mathrm{e}^{i(\beta'+i\beta'')} \tag{2.11.19}$$

where $\beta' = \mathrm{Re}[\beta] = 0^+$ and the contour of integration is in the complex β plane as shown in the sketch.

Maxwell Velocity Distribution Revisited

In Notes 2-8 we wrote Eq. (2.8.13) for the density matrix for the canonical ensemble,

$$\rho(\{\mathbf{q}_i,\mathbf{p}_i\}) = \frac{\mathrm{e}^{-\mathcal{H}[\{\mathbf{q}_i,\mathbf{p}_i\}]/k_BT}}{\displaystyle\int d^3q_j d^3p_j\,\mathrm{e}^{-\mathcal{H}[\{\mathbf{q}_j,\mathbf{p}_j\}]/k_BT}} \qquad (2.11.20)$$

with the normalization that $\int d^3q_j d^3p_j\,\rho(\{\mathbf{q}_j,\mathbf{p}_j\}) = 1$. In our present notation, $\mathbf{q}_i$ gives the three spatial coordinates of particle i, and $\mathbf{p}_i$ are the corresponding momenta. The density matrix $\rho(\{\mathbf{q}_i,\mathbf{p}_i\})$ is the probability density, per unit volume of phase space, that the system will be found in the state at $\{\mathbf{q}_i,\mathbf{p}_i\}$.

If we want the probability density $\mathcal{P}(\mathbf{p}_k)$ that one particular particle k will have momentum $\mathbf{p}_k$, we should integrate the probability density $\rho(\{\mathbf{q}_i,\mathbf{p}_i\})$ over all degrees of freedom *except* for $\mathbf{p}_k$.

$$\mathcal{P}(\mathbf{p}_k) = \frac{\displaystyle\prod_i{}' \int d^3q_i \int d^3p_i\,\mathrm{e}^{-\beta\mathcal{H}[\{\mathbf{q}_i,\mathbf{p}_i\}]}}{\displaystyle\prod_j \int d^3q_j \int d^3p_j\,\mathrm{e}^{-\beta\mathcal{H}[\{\mathbf{q}_j,\mathbf{p}_j\}]}} \qquad (2.11.21)$$

where $\displaystyle\prod_i{}'$ is a product over all degrees of freedom *except* $\mathbf{p}_k$.

For a general Hamiltonian, with interactions between the degrees of freedom, the above integrations can be difficult to do. But for non-interacting particles, where the degrees of freedom of one particle are uncoupled from those of the other particles, these integrals are easy!

When

$$\mathcal{H}[\{\mathbf{q}_i\mathbf{p}_i\}] = \sum_i \mathcal{H}^{(1)}(\mathbf{q}_i,\mathbf{p}_i) \qquad (2.11.22)$$

then one has,

$$\mathrm{e}^{-\beta\mathcal{H}[\{\mathbf{q}_i,\mathbf{p}_i\}]} = \mathrm{e}^{-\beta\sum_i \mathcal{H}^{(1)}(\mathbf{q}_i,\mathbf{p}_i)} = \prod_i \mathrm{e}^{-\beta\mathcal{H}^{(1)}(\mathbf{q}_i\mathbf{p}_i)} \qquad (2.11.23)$$

and the probability distribution $\mathcal{P}(\mathbf{p}_k)$ becomes

$$\mathcal{P}(\mathbf{p}_k) = \frac{\displaystyle\int d^3q_k\,\mathrm{e}^{-\beta\mathcal{H}^{(1)}(\mathbf{q}_k\mathbf{p}_k)} \prod_{i\neq k}\int d^3q_i d^3p_i\,\mathrm{e}^{-\beta\mathcal{H}^{(1)}(\mathbf{q}_i,\mathbf{p}_i)}}{\displaystyle\prod_i \int d^3q_i d^3p_i\,\mathrm{e}^{-\beta\mathcal{H}^{(1)}(\mathbf{q}_i,\mathbf{p}_i)}} \qquad (2.11.24)$$

$$= \frac{\displaystyle\int d^3q_k\,\mathrm{e}^{-\beta\mathcal{H}^{(1)}(\mathbf{q}_k\mathbf{p}_k)}}{\displaystyle\int d^3q_k \int d^3p_k\,\mathrm{e}^{-\beta\mathcal{H}^{(1)}(\mathbf{q}_k\mathbf{p}_k)}} \qquad (2.11.25)$$

where all the terms for particles $i \neq k$ in the numerator are exactly cancelled out by the corresponding terms in the denominator.

For the ideal gas, $\mathcal{H}^{(1)}(\mathbf{q},\mathbf{p}) = p^2/2m$ is independent of $\mathbf{q}$. Hence the integrals on $\mathbf{q}_k$ in the numerator and the denominator of the above each give a factor of the volume V, and then cancel. We are left with,

$$\mathcal{P}(\mathbf{p}_k) = \frac{\mathrm{e}^{-\beta p_k^2/2m}}{\displaystyle\int d^3p_k\,\mathrm{e}^{-\beta p_k^2/2m}} = \frac{\mathrm{e}^{-p_k^2/2mk_BT}}{(2\pi m k_BT)^{3/2}} \qquad (2.11.26)$$

Setting $\mathbf{p}_k = m\mathbf{v}_k$, with $\mathbf{v}_k$ the velocity of particle k, and using $\mathcal{P}(\mathbf{v})d^3v = \mathcal{P}(\mathbf{p})d^3p \quad \Rightarrow \quad \mathcal{P}(\mathbf{v}) = m^3\mathcal{P}(\mathbf{p})$, we then get for the distribution of the velocity $\mathbf{v}$ of particle k,

$$\mathcal{P}(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \mathrm{e}^{-mv^2/2k_B T} \tag{2.11.27}$$

which is just the Maxwell velocity distribution we found from kinetic theory in Notes 2-1.

An important reminder!

1) In the Maxwell probability distribution we have $\mathcal{P}(\mathbf{v}) \propto \mathrm{e}^{-\beta m v^2/2m} = \mathrm{e}^{-\beta\epsilon_{\mathrm{kin}}}$

Here $\mathcal{P}(\mathbf{v})$ is the probability density for a property of a *single particle*, and the Boltzmann factor that appears involves the energy of that single particle, in this case its kinetic energy $\epsilon_{\mathrm{kin}} = p^2/2m$. This result holds rigorously only in the limit of *non-interacting* particles.

2) In the canonical ensemble we have that the probability for the system to be in a particular state i with total energy E_i is $\mathcal{P}_i \propto \mathrm{e}^{-\beta E_i}$.

Here $\mathcal{P}_i$ is the probability for the entire system to be found in state i (for a classical system of particles, state i would correspond to some position $\{q_i, p_i\}$ in $6N$-dimensional phase space), and the Boltzmann factor that appears involves the *total* energy E_i of the entire system, and i specifies the canonical coordinates of *all* particles (not just a particular particle). This result holds generally for any type of system, no matter what are the interactions among the degrees of freedom.