

I.17. Classical and Quantum Statistics

Classical statistics:

For a system of N particles in thermal equilibrium with a thermal reservoir at temperature T , the probability $d\mathcal{P}$ of a phase space element

$$d\tau = d^{3N}q d^{3N}p \quad (1.532)$$

being occupied is

$$d\mathcal{P} \propto d\tau e^{-H/k_B T} \quad (1.533)$$

where $e^{-H/k_B T}$ is the Boltzmann factor and

$$k_B = 1.3806221(59) \times 10^{-16} \text{ erg/K} \quad (1.534)$$

is the Boltzmann constant.

In quantum mechanics, each state occupies a phase space volume of size $h = 2\pi\hbar$ for each degree of freedom. The number of states in $d\tau$ is therefore given by

$$d\mathcal{N} = \frac{d\tau}{h^{3N}} = \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N}}$$

The classical partition function is defined as

$$Z_{\text{cl}}(T) = \int d\tau e^{-H/k_B T} \quad (1.535)$$

so that (1.533) becomes

$$d\mathcal{P} = \frac{1}{Z_{\text{cl}}} d\tau e^{-H/k_B T} \quad (1.535a)$$

with

$$\int d\mathcal{P} = 1 \quad (1.535b)$$

which is a necessary condition for $d\mathcal{P}$ to be a probability.

I.17.1. Canonical Ensemble

The quantum partition function is defined as

$$Z(T) = \text{Tr} e^{-\hat{H}/k_B T} \quad (1.536)$$

where Tr means taking the trace.

For a time-independent system,

$$\hat{H} = H(\hat{\mathbf{x}}, \hat{\mathbf{p}})$$

where $\mathbf{x} = (x_1, \dots, x_{3N})$ and $\mathbf{p} = (p_1, \dots, p_{3N})$. Note that Cartesian coordinates are used to avoid any quantization problem.

The Boltzmann factor is derived by considering an ensemble (or collection) of identical systems with fixed number of particles in contact with a thermal reservoir. This is referred to as a canonical ensemble.

Owing to the similarity between the Boltzmann factor $e^{-\hat{H}/k_B T}$ and the evolution operator $e^{-i\hat{H}t/\hbar}$, we define a quantum partition function as

$$Z_{\text{QM}}(t_b - t_a) = \text{Tr} \hat{U}(t_b, t_a) = \text{Tr} e^{-i(t_b - t_a)\hat{H}/\hbar} \quad (1.537)$$

where \hat{H} is time-independent. Hence,

$$Z(T) = Z_{\text{QM}}\left(-\frac{i\hbar}{k_B T}\right) = Z_{\text{QM}}(-i\hbar\beta) \quad (1.538)$$

where $\beta = \frac{1}{k_B T}$.

1.17.2. Grand-Canonical Ensemble

For a system in contact with both a thermal and a particle reservoir, the corresponding ensemble and partition function are called **grand canonical**.

$$Z_G(T, \mu) = \text{Tr} e^{-(\hat{H} - \mu \hat{N})/k_B T} \quad (1.539)$$

where \hat{N} is the **particle number operator** and μ is the **chemical potential**. Furthermore

$$\hat{H}_G = \hat{H} - \mu \hat{N} \quad (1.540)$$

is called the **grand canonical Hamiltonian**.

The **Helmholtz free energy** (or simply, the **free energy**) F is defined as

$$e^{-F/k_B T} = \text{Tr} e^{-\hat{H}/k_B T} = Z$$

so that

$$F(T) = -k_B T \ln Z(T) \quad (1.541)$$

Similarly, the **grand potential** F_G is

$$e^{-F_G/k_B T} = \text{Tr} e^{-\hat{H}_G/k_B T}$$

so that

$$F_G(T, \mu) = -k_B T \ln Z_G(T, \mu) \quad (1.542)$$

The **internal energy** E is just the average energy given by

$$E = \langle \hat{H} \rangle = \frac{1}{Z(T)} \text{Tr} \left(\hat{H} e^{-\hat{H}/k_B T} \right) \quad (1.543)$$

In general, the (classical) thermodynamic function corresponding to the quantum operator \hat{O} is the average

$$\langle \hat{O} \rangle = \frac{1}{Z(T)} \text{Tr} \left(\hat{O} e^{-\hat{H}/k_B T} \right) \quad (1.543a)$$

Using

$$\frac{\partial}{\partial T} e^{-\hat{H}/k_B T} = -\frac{1}{k_B T^2} \hat{H} e^{-\hat{H}/k_B T}$$

(1.543) can also be written as

$$E = \frac{k_B T^2}{Z} \frac{\partial Z}{\partial T} = k_B T^2 \frac{\partial \ln Z}{\partial T} \quad (1.544)$$

Using (1.541), we get the thermodynamic relation

$$E = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) = \left(1 - T \frac{\partial}{\partial T} \right) F \quad (1.545)$$

For the grand canonical ensemble, Z is replaced by Z_G so that the average particle number is given by

$$N = \langle \hat{N} \rangle = \frac{1}{Z_G(T)} \text{Tr} \left(\hat{N} e^{-\hat{H}_G/k_B T} \right) \quad (1.546)$$

Using

$$\frac{\partial}{\partial \mu} e^{-(\hat{H} - \mu \hat{N})/k_B T} = \frac{1}{k_B T} \hat{N} e^{-(\hat{H} - \mu \hat{N})/k_B T}$$

we have

$$N = \frac{k_B T}{Z_G} \frac{\partial Z_G}{\partial \mu} = k_B T \frac{\partial \ln Z_G}{\partial \mu} \quad (1.547)$$

Using (1.542), we get the thermodynamic relation

$$N = - \frac{\partial F_G}{\partial \mu} \quad (1.548)$$

Analogous to (1.543),

$$E = \langle \hat{H} \rangle = \frac{1}{Z_G(T)} \text{Tr} \left(\hat{H} e^{-\hat{H}_G / k_B T} \right) \quad (1.549)$$

Using

$$\frac{\partial}{\partial T} e^{-(\hat{H} - \mu \hat{N}) / k_B T} = \frac{1}{k_B T^2} (\hat{H} - \mu \hat{N}) e^{-\hat{H}_G / k_B T}$$

we have

$$\begin{aligned} E - \mu N &= \frac{k_B T^2}{Z_G} \frac{\partial Z_G}{\partial T} = k_B T^2 \frac{\partial \ln Z_G}{\partial \mu} \\ &= \left(1 - T \frac{\partial}{\partial T} \right) F_G \end{aligned} \quad (1.550)$$

For a system of N free particles, the number of states up to energy E is

$$\mathcal{N}(E) = \sum_{\mathbf{p}_i} \theta \left(E - \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2M} \right) \quad (1.551)$$

where θ is the step function.

If the particles are confined within a large box of volume L^3 , then \mathbf{p}_i becomes quasi-continuous and

$$\mathcal{N}(E) = \left(\frac{L}{2\pi\hbar} \right)^{3N} \int \prod_{i=1}^N d^3 p_i \theta \left(E - \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2M} \right) \quad (1.552)$$

The integral in (1.552) is simply the volume Ω_{3N} of a 3 N -D sphere of radius $p = \sqrt{2ME}$.

Let S_D be the surface area of a D -D sphere of radius 1. We have

$$\begin{aligned} S_D &= \int d^D x \delta(r-1) & r^2 &= \sum_{i=1}^D x_i^2 \\ &= \int d^D x \, 2 \delta(r^2-1) \\ &= \int d^D x \int_{-\infty}^{\infty} \frac{dk}{\pi} e^{ik(r^2-1)} \\ &= \int_{-\infty}^{\infty} \frac{dk}{\pi} e^{-ik} \int d^D x e^{ikr^2} \\ &= \int_{-\infty}^{\infty} \frac{dk}{\pi} e^{-ik} \left(\int_{-\infty}^{\infty} dx e^{ikx^2} \right)^D \\ &= \int_{-\infty}^{\infty} \frac{dk}{\pi} e^{-ik} \left(\frac{\pi}{-ik} \right)^{D/2} \\ &= \pi^{-1+D/2} \int_{-\infty}^{\infty} dk \frac{e^{-ik}}{(-ik)^{D/2}} \\ &= \frac{2\pi^{D/2}}{\Gamma(D/2)} \end{aligned} \quad (1.557)$$

where Gradshteyn & Ryzhik, Formula 3.382.7 was used.

A less involved way to do so is as follows

$$\begin{aligned} \int_{-\infty}^{\infty} d^D x e^{-\sum_{i=1}^D x_i^2} &= \pi^{D/2} \\ &= S_D \int_0^{\infty} dr r r^{D-1} e^{-r^2} = \frac{S_D}{2} \Gamma\left(\frac{D}{2}\right) \end{aligned}$$

Solving for S_D then gives (1.557).

The volume of a D -D sphere of radius r is therefore

$$\Omega_D(r) = S_D \int_0^r dr r r^{D-1} = \frac{2 \pi^{D/2}}{D \Gamma(D/2)} r^D = \frac{\pi^{D/2}}{\Gamma\left(\frac{D}{2} + 1\right)} r^D \quad (1.554)$$

(1.552) thus becomes

$$\begin{aligned} \mathcal{N}(E) &= \left(\frac{L}{2 \pi \hbar}\right)^{3N} \Omega_{3N}\left(\sqrt{2ME}\right) \\ &= \left(\frac{L}{2 \pi \hbar}\right)^{3N} \frac{(2 \pi ME)^{3N/2}}{\Gamma\left(\frac{3}{2}N + 1\right)} \end{aligned} \quad (1.553)$$

The **density of states** (per energy) is therefore

$$\begin{aligned} \rho(E) &\equiv \frac{\partial \mathcal{N}}{\partial E} \\ &= \left(\frac{L}{2 \pi \hbar}\right)^{3N} 2 \pi M \frac{(2 \pi ME)^{3N/2-1}}{\Gamma\left(\frac{3}{2}N\right)} \end{aligned} \quad (1.558)$$

Given a complete set of states $|a\rangle$,

$$\text{Tr } \hat{O} = \sum_a \langle a | \hat{O} | a \rangle \quad (1.558a)$$

Let $|E_n\rangle$ be the eigenstates of \hat{H} , (1.536) becomes

$$\begin{aligned} Z(T) &= \sum_n \langle E_n | e^{-\hat{H}/k_B T} | E_n \rangle = \sum_n e^{-E_n/k_B T} \\ &= \int dE \rho(E) e^{-E/k_B T} \end{aligned} \quad (1.558b)$$

where

$$\rho(E) = \sum_n \delta(E - E_n) \quad (1.558c)$$

is just another expression of the **density of states** defined in (1.558).

Following (1.533), we expect

$$N \propto \int dE \rho(E) e^{-E/k_B T} \quad (1.558d)$$

For large N , $\rho(E)$ and $e^{-E/k_B T}$ increases and decreases sharply, respectively, as E increases. This means $\rho(E) e^{-E/k_B T}$ is sharply peaked. For free particles,

$$\begin{aligned} \rho(E) e^{-E/k_B T} &\propto E^{3N/2-1} e^{-E/k_B T} \\ &\approx \exp\left(\frac{3}{2} N \ln E - \frac{E}{k_B T}\right) \end{aligned} \quad (1.559)$$

$$\rightarrow \frac{\partial}{\partial E} (\rho(E) e^{-E/k_B T}) \propto \left(\frac{3N}{2E} - \frac{1}{k_B T}\right) \exp\left(\frac{3}{2} N \ln E - \frac{E}{k_B T}\right)$$

The maximum of $\rho(E) e^{-E/k_B T}$ is therefore at

$$E(T) \approx \frac{3}{2} N k_B T \quad (1.560)$$

The width of the peak is found by expanding (1.559) in $\delta E = E - E(T)$. Using

$$\begin{aligned} \ln [E(T) + \delta E] &= \ln E(T) \ln \left[1 + \frac{\delta E}{E(T)} \right] \\ &= \ln E(T) + \frac{\delta E}{E(T)} - \frac{1}{2} \frac{(\delta E)^2}{E(T)^2} + \dots \end{aligned}$$

(1.559) becomes

$$\begin{aligned} &\exp \left\{ \frac{3}{2} N \left[\ln E(T) + \frac{\delta E}{E(T)} - \frac{1}{2} \frac{(\delta E)^2}{E(T)^2} + \dots \right] - \frac{E(T) + \delta E}{k_B T} \right\} \\ &= \exp \left(\frac{3}{2} N \ln E(T) - \frac{E(T)}{k_B T} - \frac{3}{4} N \frac{(\delta E)^2}{E(T)^2} + \dots \right) \quad (1.561) \end{aligned}$$

$\rho(E) e^{-E/k_B T}$ is therefore a Gaussian in the variable δE with standard deviation

$$\sigma = \frac{E(T)}{\sqrt{3N/2}} \quad (1.561a)$$

Since N is large, we can replace the Gaussian with a δ -function so that

$$\rho(E) e^{-E/k_B T} = N(T) \delta[E - E(T)] e^{-E(T)/k_B T} \quad (1.562)$$

where $N(T)$ is some proportionality constant.

According to (1.558a),

$$N = N(T) e^{-E(T)/k_B T}$$

so that $N(T) \geq N$ is roughly the number of states over which the N particles are distributed at temperature T . This allows the definition of the **entropy** as

$$S(T) = k_B \ln N(T) \quad (1.563)$$

where the proportionality constant is named k_B as a tribute to Boltzmann.

Using (1.563) to write (1.562) as

$$\rho(E) e^{-E/k_B T} = e^{S(T)/k_B} \delta[E - E(T)] e^{-E(T)/k_B T} \quad (1.563a)$$

(1.563b) then becomes

$$Z(T) = e^{-[E(T) - T S(T)]/k_B T} \quad (1.564)$$

Comparing with (1.541) gives the familiar thermodynamic relation

$$F(T) = E(T) - T S(T) \quad (1.565)$$

Comparison with (1.545) gives

$$S(T) = - \frac{\partial F(T)}{\partial T} \quad (1.566)$$

For grand-canonical ensembles, (1.558b) is replaced by

$$Z_G(T, \mu) = \int dE dn \rho(E, n) e^{-(E - \mu n)/k_B T} \quad (1.567)$$

where

$$\rho(E, n) e^{-(E - \mu n)/k_B T} \quad (1.568)$$

now strongly peaks at $E = E(T, \mu)$ and $n = N(T, \mu)$.

The analog of (1.563a) can be written down by inspection:

$$\begin{aligned} \rho(E, n) e^{-(E - \mu n)/k_B T} &\approx \delta[E - E(T)] \delta[n - N(T, \mu)] \\ &\times e^{S(T)/k_B} e^{-[E(T, \mu) - \mu N(T, \mu)]/k_B T} \quad (1.569) \end{aligned}$$

(1.567) then gives

$$Z_G(T, \mu) = e^{-[E(T, \mu) - \mu N(T, \mu) - T S(T, \mu)] / k_B T} \quad (1.570)$$

(1.542) thus becomes another well-known thermodynamic relation

$$F_G(T, \mu) = E(T, \mu) - \mu N(T, \mu) - T S(T, \mu) \quad (1.571)$$

Comparison with (1.550) gives

$$S(T, \mu) = -\frac{\partial F_G(T, \mu)}{\partial T} \quad (1.572)$$

For completeness, we rewrite (1.548) as

$$N(T, \mu) = \frac{\partial F_G(T, \mu)}{\partial \mu} \quad (1.572a)$$

Consider a system of volume V . In the canonical ensemble, the independent thermodynamic variables are (T, N, V) . In the grand canonical ensemble, they are (T, μ, V) . In dealing with relations between thermodynamic functions, we should therefore write $F(T, N, V)$ and $F_G(T, \mu, V)$.

Since a thermodynamic potential such as F_G is necessarily extensive, it can be written as

$$F_G = f V \quad (1.572b)$$

where f is an intensive variable. Hence,

$$f = \frac{\partial F_G}{\partial V}$$

On the other hand, $\frac{\partial F_G}{\partial V}$ is the intensive variable conjugate to V . Indeed,

$$\frac{\partial F_G}{\partial V} = -p \quad (1.572c)$$

where p is the **pressure**.

Therefore, (1.572b) becomes another well-known relation

$$F_G = -p V \quad (1.573)$$

Combining eqs (1.572 a,b,c), we have

$$d F_G(T, \mu, V) = -S d T - N d \mu - p d V \quad (1.574)$$

Inserting (1.573) into (1.571) gives the **Euler's equation**,

$$E = T S + \mu N - p V \quad (1.575)$$

(1.566) indicates that E is the Legendre transform of F ,

$$\begin{aligned} E(S, N, V) &= F(T, N, V) - T \frac{\partial F}{\partial T} \\ &= F + S T \end{aligned}$$

(1.575) becomes

$$F = \mu N - p V \quad (1.576)$$