Unit 3-4: Quantum Partition Function for Non-Interacting Particles

We now consider the partition function for a quantum mechanical system of *non-interacting* fermions or bosons – this is the *quantum ideal gas.*

To do this we will use the *occupation number* representation, in which the integer n_i gives how many particles are in the single particle energy eigenstate ϕ_i with single particle energy ϵ_i. The total configuration of the system is given by the set of occupation numbers $\{n_i\}$.

The total energy of the system is then: $\quad E = \sum_i \epsilon_i n_i$ $\hfill$ (3.4.1)

and the total number of particles is: $\quad N = \sum_i n_i$ $\hfill$ (3.4.2)

The canonical partition function for a system of N particles is given by,

$$Q_N(T,V) = \sum_{\substack{\{n_i\} \\ \text{s.t. } \sum_i n_i = N}} e^{-\beta E(\{n_i\})} \;=\; \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) e^{-\beta \sum_i \epsilon_i n_i} \hfill (3.4.3)$$

In the first sum, the sum is restricted to only configurations $\{n_i\}$ that have exactly N particles, $\sum_i n_i = N$. In the second sum, we sum over all possible configurations $\{n_i\}$ and impose the constraint $\sum_i n_i = N$ via a delta function in the summand. Since the argument of this delta function in an integer, this is a Kronecker delta (rather than a Dirac delta), such that $\delta(n) = 1$ when $n = 0$ and $\delta(n) = 0$ when $n \neq 0$.

Factoring the exponential, we can then write,

$$Q_N(T,V) = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \prod_i e^{-\beta \epsilon_i n_i} \hfill (3.4.4)$$

Because of the constraint imposed by the delta function, it is difficult to carry out this summation over the states $\{n_i\}$. We can not sum over the individual n_i independently, because there is a constraint among them, $\sum_i n_i = N$. However we can remove this constraint by going to the *grand canonical ensemble*,

$$\mathcal{L}(T,V,z) = \sum_{N=0}^{\infty} z^N Q_N = \sum_{N=0}^{\infty} \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \prod_i z^{n_i} e^{-\beta \epsilon_i n_i} \hfill (3.4.5)$$

where the fugacity is $z = e^{\beta \mu}$ and we used $z^N = z^{\sum_i n_i} = \prod_i z_i^{n_i}$.

We can now reverse the order of the summations and do the $\displaystyle\sum_{N=0}^{\infty}$ first to eliminate the delta function. We then get,

$$\mathcal{L}(T,V,z) = \sum_{\{n_i\}} \prod_i \left(z e^{-\beta \epsilon_i}\right)^{n_i} \hfill (3.4.6)$$

where the sum over the $\{n_i\}$ is now an unconstrained sum over the individual n_i, corresponding to systems with any number N of particles.

Note: the procedure we used above is analogous to the procedure we used in going from the microcanonical to the canonical ensemble. In the microcanonical ensemble, to find Ω we had to integrate over all of phase space subject to the constraint that the total energy is fixed to be E. This constraint was imposed by the delta function, $\delta(\mathcal{H}[q_i, p_i] - E)$, and this constraint makes the direct calculation of Ω often hard to do. When we took the Laplace transform of Ω to get Q_N in the canonical ensemble, the integral over E removed this delta function constraint and left us with an unconstrained integration over all of phase space. Q_N was thus easier to calculate than Ω. Now we are trying to compute the quantum Q_N, and the constraint to a fixed number of particles N, imposed by the delta function

$\delta(\sum_i n_i - N)$, makes the sum over states in the occupation number representation hard to do. But when we take the Laplace transform of Q_N to get $\mathcal{L}$ in the grand canonical ensemble, the sum over N removes this delta function constraint and leaves us with an unconstrained sum over all sets of occupation numbers $\{n_i\}$. So $\mathcal{L}$ is easier to calculate than is Q_N. Since we know that the grand canonical ensemble is equivalent to the canonical ensemble in the thermodynamic limit (i.e. the two ensembles have all the same thermodynamic properties), we are free to use the grand canonical ensemble to do calculations, even if the true physical system has a fixed number of particles N.

Continuing with our calculation of $\mathcal{L}$,

$$\mathcal{L} = \sum_{\{n_i\}} \prod_i \left(ze^{-\beta\epsilon_i}\right)^{n_i} = \sum_{n_1}\sum_{n_2}\cdots \left(ze^{-\beta\epsilon_1}\right)^{n_1}\left(ze^{-\beta\epsilon_2}\right)^{n_2}\cdots = \left[\sum_{n_1}\left(ze^{-\beta\epsilon_1}\right)^{n_1}\right]\left[\sum_{n_2}\left(ze^{-\beta\epsilon_2}\right)^{n_2}\right]\cdots \quad (3.4.7)$$

$$\mathcal{L} = \prod_i \left[\sum_n \left(ze^{-\beta\epsilon_i}\right)^n\right] \quad (3.4.8)$$

For Fermi-Dirac statistics (i.e. for fermions), $n = 0, 1$ are the only possibilities for the occupation numbers.

$$\Rightarrow \quad \sum_{n=0}^{1}\left(ze^{-\beta\epsilon_i}\right)^n = 1 + ze^{-\beta\epsilon_i} \quad (3.4.9)$$

and so,

$$\boxed{\mathcal{L} = \prod_i \left(1 + ze^{-\beta\epsilon_i}\right) = \prod_i \left(1 + e^{-\beta(\epsilon_i-\mu)}\right) \qquad \text{for FD}} \quad (3.4.10)$$

For Bose-Einstein statistics (i.e. for bosons), $n = 0, 1, 2, \ldots$ can be any integer.

$$\Rightarrow \quad \sum_{n=0}^{\infty}\left(ze^{-\beta\epsilon_i}\right)^n = \frac{1}{1 - ze^{-\beta\epsilon_i}} \qquad \text{assuming } ze^{-\beta\epsilon_i} < 1 \text{ so the geometric series converges} \quad (3.4.11)$$

and so,

$$\boxed{\mathcal{L} = \prod_i \left(\frac{1}{1 - ze^{-\beta\epsilon_i}}\right) = \prod_i \left(\frac{1}{1 - e^{-\beta(\epsilon_i-\mu)}}\right) \qquad \text{for BE}} \quad (3.4.12)$$

Now the grand potential is related to $\mathcal{L}$ by,

$$-\frac{\Phi}{k_B T} = \frac{pV}{k_B T} = \ln\mathcal{L} = \begin{cases} \displaystyle\sum_i \ln\left(1 + e^{-\beta(\epsilon_i-\mu)}\right) & \text{for FD} \\ \displaystyle-\sum_i \ln\left(1 - e^{-\beta(\epsilon_i-\mu)}\right) & \text{for BE} \end{cases} \quad (3.4.13)$$

We can combine the above into a single expression,

$$\boxed{\ln\mathcal{L} = \pm\sum_i \ln\left(1 \pm ze^{-\beta\epsilon_i}\right) = \pm\sum_i \ln\left(1 \pm e^{-\beta(\epsilon_i-\mu)}\right) \quad \text{where} \quad \begin{cases} + \text{ is for FD} \\ - \text{ is for BE} \end{cases}} \quad (3.4.14)$$

We can compare the above result to what one has *classically*. Let us continue to use the occupation number representation where n_i is the number of particles in single particle state i, and $E = \sum_i \epsilon_i n_i$ and $N = \sum_i n_i$. For classical particles, n_i can be any integer.

If the classical particles are *distinguishable*, then for N particles with n_1 in state 1, n_2 in state 2, etc, the number of microscopic states corresponding to a given set of occupation numbers $\{n_i\}$ would be,

$$\frac{N!}{n_1! n_2! \cdots} = \text{number of ways to distribute } N \text{ particles such that } n_i \text{ are in state } i \tag{3.4.15}$$

So we would have,

$$Q_N = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \frac{N!}{n_1! n_2! \cdots} e^{-\beta \sum_i \epsilon_i n_i} \tag{3.4.16}$$

But now we recall Gibb's correction factor $1/N!$ for *indistinguishable* particles, so for the case of indistinguishable particles we get,

$$Q_N = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \frac{1}{n_1! n_2! \cdots} e^{-\beta \sum_i \epsilon_i n_i} = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \prod_i \left[\frac{1}{n_i!} \left(e^{-\beta \epsilon_i}\right)^{n_i}\right] \tag{3.4.17}$$

To evaluate, we now go to the grand canonical ensemble, as we did for the quantum case. Again using $z^N = z^{\sum_i n_i} = \prod_i z^{n_i}$ we have,

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \sum_{N=0}^{\infty} \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \prod_i \left[\frac{z^{n_i} \left(e^{-\beta \epsilon_i}\right)^{n_i}}{n_i!}\right] = \sum_{\{n_i\}} \prod_i \left[\frac{\left(z e^{-\beta \epsilon_i}\right)^{n_i}}{n_i!}\right] \tag{3.4.18}$$

$$= \sum_{n_1} \sum_{n_2} \cdots \frac{\left(z e^{-\beta \epsilon_1}\right)^{n_1}}{n_1!} \frac{\left(z e^{-\beta \epsilon_2}\right)^{n_2}}{n_2!} \cdots = \left[\sum_{n_1} \frac{\left(z e^{-\beta \epsilon_1}\right)^{n_1}}{n_1!}\right] \left[\sum_{n_2} \frac{\left(z e^{-\beta \epsilon_2}\right)^{n_2}}{n_2!}\right] \cdots \tag{3.4.19}$$

$$= \prod_i \left[\sum_{n=0}^{\infty} \frac{\left(z e^{-\beta \epsilon_i}\right)^n}{n!}\right] = \prod_i \exp\left[z e^{-\beta \epsilon_i}\right] = \exp\left[z \sum_i e^{-\beta \epsilon_i}\right] \tag{3.4.20}$$

$$\Rightarrow \quad \mathcal{L} = e^{z Q_1} \qquad \text{where } Q_1 = \sum_i e^{-\beta \epsilon_i} \text{ is the single particle partition function} \tag{3.4.21}$$

and so,

$$\boxed{\ln \mathcal{L} = z Q_1 = z \sum_i e^{-\beta \epsilon_i} = \sum_i e^{-\beta(\epsilon_i - \mu)} \qquad \text{for classical particles}} \tag{3.4.22}$$

Note: the above is just what we found from our earlier classical phase space calculation of $\mathcal{L}$. There we had,

$$\mathcal{L} = \sum_N z^N Q_N = \sum_N z^N \left(\frac{Q_1^N}{N!}\right) = e^{z Q_1} \tag{3.4.23}$$

So we get the same classical result whether we label states the old way, or whether we label them the new way using occupation numbers.

From $\mathcal{L} = e^{z Q_1}$ we then have, as we found before,

$$\left.\begin{array}{l} \dfrac{pV}{k_B T} = \ln \mathcal{L} = z Q_1 \\[2mm] N = z \dfrac{\partial \ln \mathcal{L}}{\partial z} = z Q_1 \end{array}\right\} \quad \Rightarrow \quad \frac{pV}{k_B T} = N \tag{3.4.24}$$

and we get the ideal gas law, independent of what the single particle energy values ϵ_i are.

Note: From the above we see that the state $\{n_1, n_2, \dots\}$ enters the partition function sum with a weight of unity for the quantum calculation, but enters with a weight of $\dfrac{1}{n_1! n_2! \cdots}$ in the classical calculation. Why is this?

The occupation number formulation is inherently designed to treat *indistinguishable* particles, because when we say there are n_i particles in single particle state i, we do no specify which particles these are, only the number. When each particle is in a different single particle state, then $1/(n_1! n_2! \cdots) = 1$, since all the $n_i = 0$ or 1, and $0! = 1! = 1$. So the difference only occurs when more than one particle is in the same single particle state.

For a classical gas described by $6N$ dimensional continuous phase space, two particles being in the same single particle state would mean two particles at the exact same values of $(\mathbf{q}, \mathbf{p})$. When we divide the partition function integration by $1/N!$ to avoid overcounting, this assumes that each particle is at a *different* point $(\mathbf{q}_i, \mathbf{p}_i)$ in phase space. If two particles are at the same $(\mathbf{q}, \mathbf{p})$, then the division by $1/N!$ would be an over-correction of the counting. This because we are correcting for the fact that the state in which particle 1 is at $(\mathbf{q}_1, \mathbf{p}_1)$ and particle 2 is at $(\mathbf{q}_2, \mathbf{p}_2)$ is exactly the same state as when particle 1 is at $(\mathbf{q}_2, \mathbf{p}_2)$ and particle 2 is at $(\mathbf{q}_1, \mathbf{p}_1)$ and we don't want to double count these. However, when both particles 1 and 2 are at the same $(\mathbf{q}, \mathbf{p})$, then there is no double counting.

Classically, the probability that two particles will occur at the exact same $(\mathbf{q}, \mathbf{p})$ in the *continuous* phase space is vanishingly small, since such situations have a vanishing weight when we do the partition function integration over all of phase space, $\int d^3 q_i d^3 p_i$. Therefore we do not have to worry about it – we treat the indistinguishability of the particles by simply dividing the partition function integration by $1/N!$, which is OK *because* essentially each particle is at a *different* $(\mathbf{q}, \mathbf{p})$.

However, when we discretize the single particle states to label them with a discrete index i, then we do have to worry about the situation where more than one particle might be in the same single particle state. To deal with the indistinguishability of the particles in this situation, we need to use the more complicated factor $1/(n_1! n_2! \cdots)$ when we sum over all classical configurations $\{n_i\}$ *in the occupation number representation*. Only by doing this will our classical calculation in the occupation number representation give the same result as our classical calculation in the continuous $6N$ dimensional phase space.