Unit 3-5: Average Occupation Numbers and Comparison of Quantum and Classical Ideal Gases

Average Occupation Numbers

To recap from the previous section, for identical *non-interacting* particles, we have for the quantum grand canonical partition function,

$$\ln \mathcal{L} = \pm \sum_i \ln\left(1 \pm z\mathrm{e}^{-\beta\epsilon_i}\right) = \pm \sum_i \ln\left(1 \pm \mathrm{e}^{-\beta(\epsilon_i - \mu)}\right) \qquad \text{where + is for FD and } - \text{ is for BE} \tag{3.5.1}$$

[Note: in some of our earlier formulas, it was + for BE and − for FD; in the above equation it is the other way around. So always be careful you know which is which!]

and for classical particles we had,

$$\ln \mathcal{L} = zQ_1 = z\sum_i \mathrm{e}^{-\beta\epsilon_i} = \sum_i \mathrm{e}^{-\beta(\epsilon_i - \mu)} \tag{3.5.2}$$

Note, the classical result of Eq. (3.5.2) is just equal to the quantum result of Eq. (3.5.1) in the limit $z \to 0$. This is because $\ln(1+\delta) \approx \delta$ for small δ.

Quantum Average Occupation Numbers

Now, we had from Eqs. (3.1.28) and (3.1.30) of Notes 3-1, that,

$$\langle E \rangle = -\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,z}, \qquad \langle N \rangle = z\left(\frac{\partial \ln \mathcal{L}}{\partial z}\right)_{T,V} \tag{3.5.3}$$

Applying to the quantum $\mathcal{L}$ we get,

$$\langle N \rangle = \pm z \sum_i \frac{\pm \mathrm{e}^{-\beta\epsilon_i}}{1 \pm z\mathrm{e}^{-\beta\epsilon_i}} = \sum_i \frac{z\mathrm{e}^{-\beta\epsilon_i}}{1 \pm z\mathrm{e}^{-\beta\epsilon_i}} \tag{3.5.4}$$

$$\boxed{\langle N \rangle = \sum_i \left(\frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon_i} \pm 1}\right) = \sum_i \left(\frac{1}{\mathrm{e}^{\beta(\epsilon - \mu)} \pm 1}\right) \qquad + \text{ for FD}, - \text{ for BE}} \tag{3.5.5}$$

and,

$$\langle E \rangle = \mp \sum_i \frac{\mp z\epsilon_i \mathrm{e}^{-\beta\epsilon_i}}{1 \pm z\mathrm{e}^{-\beta\epsilon_i}} = \sum_i \frac{z\epsilon_i \mathrm{e}^{-\beta\epsilon_i}}{1 \pm z\mathrm{e}^{-\beta\epsilon_i}} \tag{3.5.6}$$

$$\boxed{\langle E \rangle = \sum_i \left(\frac{\epsilon_i}{z^{-1}\mathrm{e}^{\beta\epsilon_i} \pm 1}\right) = \sum_i \left(\frac{\epsilon_i}{\mathrm{e}^{\beta(\epsilon_i - \mu)} \pm 1}\right) \qquad + \text{ for FD}, - \text{ for BE}} \tag{3.5.7}$$

Now, since,

$$N = \sum_i n_i, \quad \text{we also have} \quad \langle N \rangle = \sum_i \langle n_i \rangle \tag{3.5.8}$$

and since

$$E = \sum_i \epsilon_i n_i, \qquad \text{we also have} \quad \langle E \rangle = \sum_i \epsilon_i \langle n_i \rangle. \tag{3.5.9}$$

Comparing with Eqs. (3.5.5) and (3.5.7) we conclude,

$$\boxed{\langle n_i \rangle = \frac{1}{\mathrm{e}^{\beta(\epsilon_i - \mu)} \pm 1} \qquad + \text{ for FD, } - \text{ for BE}} \tag{3.5.10}$$

Classical Average Occupation Numbers

Using the classical $\mathcal{L}$ of Eq. (3.5.2) we have,

$$\langle N \rangle = z \frac{\partial}{\partial z} \left(\sum_i z \mathrm{e}^{-\beta \epsilon_i} \right) = z \sum_i \mathrm{e}^{-\beta \epsilon_i} = z Q_1 \tag{3.5.11}$$

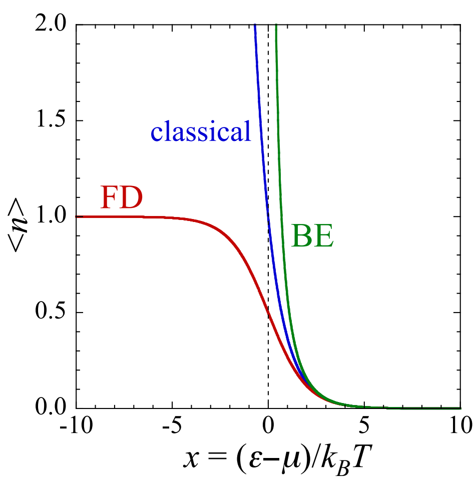
and

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \left(\sum_i z \mathrm{e}^{-\beta \epsilon_i} \right) = \sum_i \epsilon_i z \mathrm{e}^{-\beta \epsilon_i} \tag{3.5.12}$$

which leads to the conclusion,

$$\boxed{\langle n_i \rangle = z \mathrm{e}^{-\beta \epsilon_i} = \mathrm{e}^{-\beta(\epsilon_i - \mu)} \qquad \text{for classical particles}} \tag{3.5.13}$$

We plot these different $\langle n \rangle$ below.



With $x \equiv (\epsilon - \mu)/k_B T$, we see that:

(1) For BE, $\langle n \rangle$ diverges as $x \to 0$, i.e. when $\mu \to \epsilon$.

(2) For FD, $\langle n \rangle \to \begin{cases} 1 & \text{for } x \ll 0, \text{ i.e. } \epsilon \ll \mu \\ 0 & \text{for } x \gg 0, \text{ i.e. } \epsilon \gg \mu \end{cases}$.

(3) All expressions behave as $\langle n \rangle \sim \mathrm{e}^{-x}$ at large x.

(4) For FD, $\langle n \rangle$ goes from 1 to 0 over an interval of $\Delta x \sim O(1)$, i.e. $|\epsilon - \mu| \sim k_B T$.

Comparison of the Classical and Quantum Ideal Gas

Classical phase space approach

We had,

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \sum_{N=0}^{\infty} \frac{[z Q_1]^N}{N!} = \mathrm{e}^{z Q_1} \quad \Rightarrow \quad \ln \mathcal{L} = z Q_1 \tag{3.5.14}$$

where Q_1 is the single particle partition function for a free point particle,

$$Q_1 = \frac{1}{h^3} \int d^3 r \int d^3 p \, \mathrm{e}^{-\beta p^2/2m} = \frac{V}{h^3} (2\pi m k_B T)^{3/2} = \frac{V}{\lambda^3} \qquad \text{with } \lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \tag{3.5.15}$$

λ is the thermal wavelength. In the classical calculation, h was an arbitrary phase space constant.

Quantum sum over quantized energy levels in the classical limit

We now compare the above classical calculation to what we get using the occupation number formulation, in which one sums over the single particle energy levels ϵ_i. Since we want to compare to the classical limit, we will use the expression of Eq. (3.5.2) which we get as the $z \ll 1$ limit of the quantum result of Eq. (3.5.1).

$$\ln \mathcal{L} = zQ_1 = z\sum_i \mathrm{e}^{-\beta\epsilon_i} \tag{3.5.16}$$

Now, however, instead of integrating over continuous phase space to compute Q_1, we will sum over the quantized energy levels of a quantum mechanical particle in a box of volume $N = L^3$.

Taking periodic boundary conditions, the eigenstates of the particle in a box are given by $\phi_{\mathbf{k}}(\mathbf{r}) = \dfrac{1}{\sqrt{V}}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}$, with $k_\alpha = (2\pi/L)n_\alpha$, with n_α integer and $\alpha = x, y, z$, as discussed in Notes 3-3. The momentum of the state is $\mathbf{p} = \hbar\mathbf{k}$ and the energy is $\epsilon_{\mathbf{k}} = \dfrac{\hbar^2k^2}{2m}$. We then have,

$$Q_1 = \sum_{\mathbf{k}} \mathrm{e}^{-\beta\epsilon_{\mathbf{k}}} = \sum_{\mathbf{k}} \mathrm{e}^{-\beta\hbar^2k^2/2m} \tag{3.5.17}$$

The spacing between the allowed values of k_α is $\Delta k = 2\pi/L$, so we can write,

$$Q_1 = \frac{1}{(\Delta k)^3}\sum_{\mathbf{k}}(\Delta k)^3\mathrm{e}^{-\beta\hbar^2k^2/2m} \approx \frac{V}{(2\pi)^3}\int d^3k\, \mathrm{e}^{-\beta\hbar^2k^2/2m} \tag{3.5.18}$$

The approximation of the sum by the integral becomes exact in the thermodynamic limit $V \to \infty$, where $\Delta k \to 0$.

We can now do the Gaussian integration over $\mathbf{k}$ to get,

$$Q_1 = \frac{V}{(2\pi)^3}\left(\frac{2\pi m}{\beta\hbar^2}\right)^{3/2} = V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2} = \frac{V}{\lambda^3} \tag{3.5.19}$$

with,

$$\lambda = \left(\frac{h^2}{2\pi mk_BT}\right)^{1/2} \qquad \text{the thermal wavelength} \tag{3.5.20}$$

This is exactly the same result for Q_1 as in the classical phase space calculation of Eq.(3.5.15), *provided* we take the classically arbitrary phase space constant h to be *Planck's constant*.

Thus if we want the quantum mechanical calculation to agree with the classical calculation, in the classical limit, the phase space constant h must be taken to be Planck's constant.

Validity of the classical limit

We saw that the log of the quantum partition functions $\ln\mathcal{L}$ (for FD or BE) of Eq. (3.5.1) agree with the classical result of Eq. (3.5.2) in the limit $z \ll 1$. We now will see what is the physical meaning of this condition.

Classically:

$$N = z\left(\frac{\partial \ln\mathcal{L}}{\partial z}\right)_{T,V} = z\frac{\partial}{\partial z}(zQ_1) = zQ_1 \tag{3.5.21}$$

So,

$$z = \frac{N}{Q_1} = \frac{N}{V}\lambda^3 = n\lambda^3 \quad \text{where } n = N/V \text{ is the density of particles} \tag{3.5.22}$$

Define $n \equiv 1/\ell^3$, where ℓ is roughly the average spacing between the particles. Then,

$$z = \left(\frac{\lambda}{\ell}\right)^3, \quad \text{and} \quad z \ll 1 \quad \Rightarrow \quad \lambda \ll \ell \tag{3.5.23}$$

With h as Planck's constant, we saw in Notes 3-3 that the thermal wavelength λ is just the de Broglie wavelength of a typical particle taken from a classical Maxwell velocity distribution at temperature T.

$\Rightarrow$ Quantum effects can be ignored, and classical results will give a good approximation whenever $\lambda \ll \ell$, i.e. when the quantum de Broglie wavelength of a typical particle is much less than the average spacing between the particles.

Since $\lambda \sim 1/\sqrt{T}$, as T decreases λ increases. For a gas of fixed density $n = 1/\ell^3$, quantum effects therefore become more important as T *decreases.* At a fixed T, quantum effects become more important as the density n increases (so ℓ decreases).

$\Rightarrow$ The classical limit is a high temperature, low density, limit.