Tabish Qureshi

Statistical Mechanics: Lecture 11

Updated June 1, 2020

Thermodynamic Properties of Ideal Gases

We now wish to study the thermodynamic properties of an ideal gas of quantum particles, in grand canonical ensemble. For this purpose, the grand potential that we introduced eralier, come in useful. The grand potential is defined as

$$\Phi(T, V, \mu) = -kT \log \mathcal{Z} = U - TS - \mu N = -PV \tag{1}$$

This single relation can be used to relate various thermodynamic quantities to the grand partition function $\mathcal{Z}$:

$$\begin{aligned} S &= -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} \\ P &= -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} \\ N &= -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \end{aligned} \tag{2}$$

The equation of state can be written, from (1), as

$$\frac{PV}{kT} = \log \mathcal{Z} = \begin{cases} -\sum_j \log(1 - e^{-\beta(\epsilon_j - \mu)}) & \text{(Bose-Einstein)} \\ \sum_j \log\left(1 + e^{-\beta(\epsilon_j - \mu)}\right) & \text{(Fermi-Dirac)} \end{cases} \tag{3}$$

Instead of describing the gas in terms of the chemical potential μ, it is often convenient to describe it in terms of *fugacity* $z \equiv e^{\beta\mu}$. The grand partition function can then be assumed to be a function of z, instead of μ, i.e., $\mathcal{Z}(z, T, V)$. The equation of state then becomes

$$\frac{PV}{kT} = \log \mathcal{Z} = \begin{cases} -\sum_j \log(1 - ze^{-\beta\epsilon_j}) & \text{(Bose-Einstein)} \\ \sum_j \log\left(1 + ze^{-\beta\epsilon_j}\right) & \text{(Fermi-Dirac)} \end{cases} \tag{4}$$

Average number of particles in the system is given by

$$\langle N \rangle = \begin{cases} \sum_k \frac{1}{z^{-1}e^{\beta\epsilon_k} - 1} & \text{(Bose-Einstein)} \\ \sum_k \frac{1}{z^{-1}e^{\beta\epsilon_k} + 1} & \text{(Fermi-Dirac)} \end{cases} \tag{5}$$

To proceed any further, we need to know the details of the system, namely the precise form of the single particle energies ϵ_j. Let us assume that the gas is enclosed in cubical box of length L. The energy of one particle is given by

$$\epsilon_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

The momentum eigenvalue is then given by $p_n = n\pi\hbar/L$, and the energy is given by $\epsilon_n = p_n^2/2m$. Instead of assuming a box with rigid walls, if one applies periodic boundary conditions (which implies that the wavefunction and also its derivative, should match at the two opposite walls), one gets $p_n = n2\pi\hbar/L = nh/L$. [1] Instead of summing over n, one can sum over p_n, as $n = \frac{Lp_n}{h}$. As the particle is confined in a cubical box, there are three quantum numbers n_x, n_y, n_z. As the length of the box becomes very large (macroscopic), the momenta are so closely spaced that they can be assumed to form a continuum. So, in this limit, instead of summing over n_x, n_y, n_z, one can integrate over p_x, p_y, p_z

$$\sum_{n_x,n_y,n_z} \rightarrow \frac{V}{h^3}\int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z$$

As the energy does not depend on p_x, p_y, p_z individually, but only on $p_x^2 + p_y^2 + p_z^2$, one can use spherical

[1] See appendix

polar coordinates in the momentum space integration

$$\sum_{n_x,n_y,n_z} \rightarrow \frac{V}{h^3}\int_0^\infty 4\pi p^2 dp$$

Ideal Bose Gas

Let us first look at the case of an ideal gas of bosons. The average number of particles can now be written as

$$\langle N\rangle = \frac{4\pi V}{h^3}\int_0^\infty \frac{p^2}{z^{-1}e^{\beta p^2/2m}-1}dp \tag{6}$$

Choosing a new variable of integration, $t = \beta p^2/2m$, we get

$$\langle N\rangle = \frac{2V}{\sqrt{\pi}h^3}(2m\pi/\beta)^{3/2}\int_0^\infty \frac{\sqrt{t}}{z^{-1}e^t-1}dt \equiv \frac{V}{\lambda^3}g_{3/2}(\tag{7}$$

where, $\lambda = h/\sqrt{2\pi mkT}$, and

$$g_\nu(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty \frac{t^{\nu-1}}{z^{-1}e^t-1}dt$$

Thus, number of particles per unit volume can be written as

$$\frac{\langle N\rangle}{V} = \frac{1}{\lambda^3}g_{3/2}(z) \tag{8}$$

In the process of approximating the summation over the quantum state by integral over momenta, have inadvertantly assigned weight zero to the lowest ($p = 0$) term. This is clearly wrong, and we would like to separate out the zero energy contribution from the sum. That term is simply $\langle n_0 \rangle = \frac{z}{1-z}$ which is obtained by putting $k = 0$ and $\epsilon_k = 0$ in

$$\langle n_k \rangle = \frac{1}{z^{-1} e^{\beta \epsilon_k} - 1}.$$

Thus, the correct expression for the number of particles per unit volume reads as

$$\boxed{\frac{\langle N \rangle}{V} = \frac{\langle n_0 \rangle}{V} + \frac{1}{\lambda^3} g_{3/2}(z)} \tag{9}$$

The equation of state can now be written as

$$\begin{aligned}
\frac{PV}{kT} &= -\sum_j \log(1 - z e^{-\beta \epsilon_j}) \\
&= \frac{4\pi V}{h^3} \int_0^\infty p^2 \log(1 - z e^{-\beta p^2/2m}) dp \\
&= \frac{2V}{\sqrt{\pi} h^3} (2m\pi/\beta)^{3/2} \int_0^\infty \sqrt{t} \log(1 - z e^{-t}) dt
\end{aligned} \tag{10}$$

The integration can be done by parts to obtain

$$
\begin{aligned}
\frac{P}{kT} =& -\frac{2}{\sqrt{\pi}h^3}(2m\pi/\beta)^{3/2}\int_0^\infty \sqrt{t}\log(1-ze^{-t})dt \\
=& -\frac{2}{\sqrt{\pi}}\frac{1}{\lambda^3}\left[\frac{t^{3/2}}{(3/2)}\log(1-ze^{-t})\Big|_0^\infty\right. \\
& \left. -\frac{2}{3}\int_0^\infty \frac{t^{3/2}ze^{-t}}{1-ze^{-t}}dt\right] \\
=& \frac{1}{\lambda^3}\frac{1}{\Gamma(5/2)}\int_0^\infty \frac{t^{5/2-1}}{z^{-1}e^t-1}dt
\end{aligned}
\tag{11}
$$

Or

$$
\boxed{\frac{P}{kT} = \frac{1}{\lambda^3}g_{5/2}(z)} \tag{12}
$$

Bose-Einstein condensation

Let us look at the average number of particles of the Bose-gas in a bit more detail

$$
\frac{\langle N\rangle}{V} = \frac{\langle n_0\rangle}{V} + \frac{1}{\lambda^3}g_{3/2}(z) \tag{13}
$$

Now in order that $\langle n_0\rangle = \frac{z}{1-z}$ be non-negative, z is constrained to be $0 \leq z \leq 1$. Also $g_{3/2}(z)$ is a monotonically increasing function of z. Thus the maximum value that $g_{3/2}(z)$ can take is $g_{3/2}(1)$. In the above equation, $\frac{1}{\lambda^3} g_{3/2}(z)$ represents the number of particles per unit volume that are present in the energy levels other than the ground state. The maximum particles per unit volume that all the excited states can hold is $\frac{1}{\lambda^3} g_{3/2}(1)$. As long as the total number of particles $\frac{\langle N \rangle}{V}$, is less than $\frac{1}{\lambda^3} g_{3/2}(1)$, all the particles can fit in the excited states. One can see that number of particles that excited states can hold decreases as temperature goes down, because it is proportional to $T^{3/2}$.

As temperature is lowered, eventually $\frac{1}{\lambda^3} g_{3/2}(1)$, becomes smaller than $\frac{\langle N \rangle}{V}$ and the excited states can no longer hold all the particles. The surplus particles are pushed to the ground state. It turns out that at low enough temperature, this phenomenon happens with a spectacular effect. Almost all the particles go en-mass to the ground state. This phenomenon is called *Bose-Einstein condensation*. The temperature, below which the ground state begins to be populated, can be determined from the following condition

$$\frac{\langle N \rangle}{V} = \frac{1}{\lambda^3} g_{3/2}(1) \tag{14}$$

The transition temperature is thus given by

$$\boxed{T_c = \frac{h^2}{2\pi mk}\left(\frac{\langle N\rangle/V}{g_{3/2}(1)}\right)^{2/3}}$$

At temperatures below T_c more and more particles go to lowest energy state. If one keeps the temperature fixed, and decreases to volume to increase the density of the gas, equation (15) can also be interpreted as defining a critical particle-density above which the Bose-Einstein condensation begins. Thus we can write, for the critical particle-density

$$\left(\frac{\langle N\rangle}{V}\right)_c = \frac{1}{\lambda^3} g_{3/2}(1) \tag{15}$$

Appendix: Particle in a box with periodic boundary

For a particle in a box in 1 dimension, the Schrödinger equation is $\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0$, where $k^2 = 2mE/\hbar^2$. You can see that since for a free particle, the momentum is defined as $p = \sqrt{2mE}$, here the momentum values will be given by $\hbar k$. You know that the general solution is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{16}$$

where A and B are unknown constants. The derivative of this function is

$$\psi'(x) = ikAe^{ikx} - ikBe^{-ikx}. \tag{17}$$

If we assume that the box does not have rigid walls, but one end is the same as the other, the $\psi(0)$ should be the same as $\psi(L)$. Also, since it has to be continuous everywhere, it should also satisfy $\psi'(0) = \psi'(L)$. These two conditions give

$$\begin{aligned} A + B &= Ae^{ikL} + Be^{-ikL} \\ A - B &= Ae^{ikL} - Be^{-ikL}. \end{aligned} \tag{18}$$

Adding these two leads us to $1 = e^{ikL}$. The only solution of this is $kL = 2n\pi$. Since $p = \hbar k$, we get the following possible values of momentum:

$$p_n = \hbar k = 2n\pi\hbar/L = nh/L.$$