Thermodynamics of quantum 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 earlier, come in useful. The grand potential is defined as

$$\Xi = -k_B T \ \ln Z = \ -P\ V$$

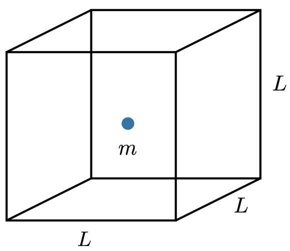
It implies

$$\frac{P\ V}{k_B T} = \ \ln Z = \begin{cases} -\sum_k \ln\left[1 - \ \varsigma\ e^{-\beta\ \epsilon_k}\right] & (\text{Bose} - \text{Einstein}\ ) \\ \sum_k \ln\left[1 + \ \varsigma\ e^{-\beta\ \epsilon_k}\right] & (\text{Fermi} - \text{Dirac}\ ) \end{cases}$$

Where the fugacity $\varsigma = \ e^{\beta \mu}$. Average number of particles in the system in terms of fugacity is given by

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

To proceed any further, we need to know the details of the system, namely the precise form of the single particle energies ϵ_k. Let us consider the case of quantum gas in a cubical box of length L.



The corresponding Schrödinger equation (x component) is

$$\frac{\partial^2 \psi(x)}{\partial x^2} + k^2\ \psi(x) = 0$$

Where $k^2\ = 2\ m\ E\ /\hbar^2$. For a free particle, i.e., in the absence of interaction between the particles, the momentum of the particles is defined as $p = \ \sqrt{2\ m\ E}$. This implies, $p = \hbar\ k$. The general solution of the

$$\psi(x)\ = A\ e^{i\ k\ x} + B\ e^{-i\ k\ x}$$

Where A and B are constants. The derivative of the wave function is

$$\psi'(x)\ = A\ ik\ e^{i\ k\ x} - B\ ik\ e^{-i\ k\ x}$$

Consider the periodic boundary conditions at the channel walls, which represent a macroscopic system. This implies

$$\psi(0)\ = \ \psi(L) \quad ; \quad \psi'(0)\ = \ \psi'(L)$$

These boundary conditions give

$$A + B = A\,e^{i\,k\,L} + B\,e^{-i\,k\,L}$$
$$A - B = A\,e^{i\,k\,L} - B\,e^{-i\,k\,L}$$

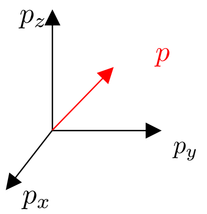
If we add the above two equations, we get $1 = e^{i\,k\,L}$. Note that $e^{i\,k\,L} = \cos(k\,L) + i\sin(k\,L)$. The only solution for this is $k\,L = 2\,n\,\pi$. Since $p = \hbar\,k$, we get the following possible values of momentum

$$p = \hbar\,k = \hbar\,\frac{2\,n\,\pi}{L}$$
$$p_n = \frac{n\,h}{L}$$

This implies, $n = p_n\,L/h$. 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 $p_x\,, p_y\,, p_z$. This implies,

$$\sum_{n_x, n_y, n_z} \rightarrow \frac{V}{h^3} \int_{-\infty}^{\infty} d\,p_x \int_{-\infty}^{\infty} d\,p_y \int_{-\infty}^{\infty} d\,p_z$$

Note that the actual integration is over the position and momentum coordinates in the phase space, same as in the classical case. The contribution from the position coordinates (in 3D) is V, the physical volume of the system.



As the energy of the system does not depend individually on $p_x\,, p_y\,, p_z$ but on ${p_x}^2 + {p_y}^2 + {p_z}^2$, one can use spherical polar coordinates in the momentum space integration.

$$\sum_{n_x, n_y, n_z} \rightarrow \frac{V}{h^3} \int_{0}^{\infty} 4\,\pi\,p^2\;dp$$

For an ideal gas of bosons, the average number of particles can now be written as

$$\langle N \rangle = \frac{4\,\pi\,V}{h^3} \int_0^{\infty} \frac{p^2}{\varsigma^{-1}\,e^{\beta p^2/(2m)} - 1}\,dp$$

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

$$\langle N \rangle = \frac{2\,V}{\sqrt{\pi}\,h^3}\,(2\pi\,m\,k_B T)^{3/2} \int_0^{\infty} \frac{\sqrt{t}}{\varsigma^{-1}\,e^{t} - 1}\,dt$$

Where $\lambda = h/\sqrt{2\pi\, m\, k_B T}$ and the integral is defined as

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

Here, $\Gamma(\nu)$ is the gamma function. Thus, number of particles per unit volume can be written as

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

In the process of approximating the summation over the quantum state by integral over momenta, have inadvertently 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 $\langle n_0 \rangle = \frac{\varsigma}{1-\varsigma}$, which is obtained by putting $k = 0$ and $\epsilon_k = 0$ in

$$\langle n_k \rangle = \frac{1}{\varsigma^{-1}\, e^{\beta \epsilon_k} - 1}$$

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

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

Note that in the above expression $\frac{\langle n_0 \rangle}{V}$ represents the number of particles per unit volume in the ground state and $\frac{g_{3/2}(\varsigma)}{\lambda^3}$ represents the total number of particles per unit volume other than the ground state.

The equation of state for Bosons can now be written as

$$\frac{PV}{k_B T} = -\sum_k \ln\left[1 - \varsigma\, e^{-\beta\, \epsilon_k}\right]$$

$$\frac{PV}{k_B T} = \frac{4\, \pi\, V}{h^3} \int_0^\infty p^2\, \ln\left[1 - \varsigma\, e^{-\beta p^2/(2m)}\right] dp$$

$$\frac{PV}{k_B T} = \frac{2\, V}{\sqrt{\pi}\, h^3} (2\pi\, m\, k_B T)^{3/2} \int_0^\infty \sqrt{t}\, \ln[1 - \varsigma\, e^{-t}]\, dt$$

The integration can be done by parts to obtain

$$\frac{PV}{k_B T} = \frac{2\, V}{\sqrt{\pi}\, h^3} \frac{1}{\lambda^3} \left[\frac{t^{3/2}}{3/2} \ln[1 - \varsigma\, e^{-t}] - \frac{2}{3} \int_0^\infty \frac{t^{3/2}\ \varsigma\, e^{-t}}{1 - \varsigma\, e^{-t}}\, dt \right]$$

$$\frac{P}{k_B T} = \frac{1}{\lambda^3} \frac{1}{\Gamma(5/2)} \int_0^\infty \frac{t^{\frac{5}{2}-1}}{\varsigma^{-1}\, e^t - 1}\, dt$$

$$\frac{P}{k_B T} = \frac{1}{\lambda^3}\, g_{5/2}(\varsigma)$$

Bose-Einstein condensation

The average number of particles of the Bose-gas is

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

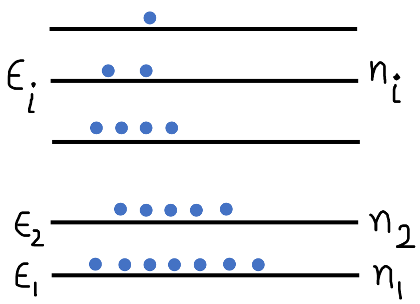
Where $\langle n_0\rangle=\frac{\varsigma}{1-\varsigma}$. In order that $\langle n_0\rangle$ to be positive $0\leq\varsigma<1$. Also, $g_{3/2}(\varsigma)$ is monotonically increasing function of ς. Thus, the maximum value that $g_{3/2}(\varsigma)$ can take is $g_{3/2}(1)$. $\frac{g_{3/2}(\varsigma)}{\lambda^3}$ represents the total number of particles per unit volume other than the ground state. The maximum particles per unit volume that all the excited states can hold is $\frac{g_{3/2}(1)}{\lambda^3}$. If $\frac{\langle N\rangle}{V}<\frac{g_{3/2}(1)}{\lambda^3}$ all the particles can fit in the excited states. However, we 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, $\frac{g_{3/2}(1)}{\lambda^3}$ becomes smaller than $\frac{\langle N\rangle}{V}$ and the excited states can no longer hold all the particles. The excess 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 occupy 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 critical condition

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

Thus, the transition temperature is given by

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

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, the following equation 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



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

The average number of particles of the Bose-gas can be expressed as

$$n = n_0 + \frac{g_{\frac{3}{2}}(\varsigma)}{\lambda^3}$$

$$n_0 = n\left[1 - \frac{g_{\frac{3}{2}}(\varsigma)}{\lambda^3}\right]$$

$$\frac{n}{n_0} = 1 - \frac{g_{\frac{3}{2}}(\varsigma)}{n\,\lambda^3}$$

At the maximum occupancy, i.e., $\varsigma = 1$, the above expression can be expressed as

$$\frac{n}{n_0} = 1 - \frac{{\lambda_c}^3}{\lambda^3}$$

Where ${\lambda_c}^3 = \frac{g_{\frac{3}{2}}(\varsigma=1)}{n}$. In terms of temperature, the above expressions can be written as

$$\frac{n}{n_0} = 1 - \left(\frac{T_c}{T}\right)^{\frac{3}{2}}$$