Ideal Bose Gas

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1 Introduction

In the canonical ensemble, we write the following partition function of the quantum ideal gas,

$$Z = Z(T,V,N) = \sum_{n_{j\,(}\sum_j n_j = N)} exp\left(-\beta \sum_j \epsilon_j n_j\right) \tag{1}$$

where the problem consists in calculating the sum (which does not factorize) over the occupation numbers with the restriction imposed by the fixed total number of particles. This calculation becomes much simpler if we work in the grand canonical ensemble, owing to the removal of this restriction on fixed number of particles.

In the grand canonical ensemble we have,

$$\begin{aligned} \Xi = \Xi(T,V,\mu) &= \textstyle\sum_{N=0}^{\infty} exp(\beta\mu N)\ Z(T,V,N) \\ &= \textstyle\sum_{N=0}^{\infty} exp(\beta\mu N) \sum_{n_{j\sum_j n_j = N}} exp\left(-\beta \sum_j \epsilon_j n_j\right) \\ &= \textstyle\sum_{N=0}^{\infty} \sum_{n_{j\sum_j n_j = N}} exp[-\beta(\epsilon_1-\mu)n_1 - \beta(\epsilon_2-\mu)n_2 - \beta(\epsilon_3-\mu)n_3 - ...] \end{aligned} \tag{2}$$

As the sum is initially performed over the set of occupation numbers n_1 , n_2,.., with the restriction that $N = n_1 + n_2 + ..$ is fixed, but there is then another sum over all values of N, we obtain the same final result if we sum over the set of occupation numbers without any restriction (which corresponds to a mere rearrangement of the terms of this multiple sum). Hence we have,

$$\begin{aligned} \Xi &= \sum_{n_1,n_2..} exp[-\beta(\epsilon_1-\mu)n_1 - \beta(\epsilon_2-\mu)n_2 - ...] \\ &= \left(\sum_{n_1} exp[-\beta(\epsilon_1-\mu)n_1]\right)\left(\sum_{n_2} exp[-\beta(\epsilon_2-\mu)n_2]\right)... \\ &= \Pi_j \left(\sum_n exp[-\beta(\epsilon_j-\mu)n]\right) \end{aligned} \tag{3}$$

by factorizing. Now to obtain Bose Einstein statistics, the sum over n runs from 0 to ∞. Hence, we get

$$\sum_{n=0}^{\infty} exp[-\beta(\epsilon_j - \mu)n] = \frac{1}{1 - exp[-\beta(\epsilon_j - \mu)]} \tag{4}$$

by using formula for infinite GP series. Taking log on both sides of the above eqn we have,

$$ln\Xi(T, V, \mu) = -\sum_j ln\{1 - exp[-\beta(\epsilon_j - \mu)]\} \tag{5}$$

where the sum is over all single particle states. The expected value $\langle n_j \rangle$ of the occupation number of orbital j is given by the relation $\langle n_j \rangle = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_j} ln\Xi$. Therefore, for Bosons we get the average occupation number i.e. average number of particles filling in a jth energy state is given by

$$\langle n_j \rangle = \frac{1}{exp[\beta(\epsilon_j - \mu)] - 1} \tag{6}$$

This is the Bose-Einstein distribution function.

If the bosons are non-relativistic particles with spin s, then their energy can be expressed as $\epsilon(k) = \frac{\hbar^2 k^2}{2m}$ with $\epsilon(0) = 0$. For discrete quantum states, $\epsilon(0)$ denotes the ground state energy which could be greater than 0. However, the chemical potential must be within the range $-\infty > \mu > \epsilon(0)$. A chemical potential larger than the lowest energy or ground state energy would lead to unphysical occupation number. Note eqn (6): if $\mu > \epsilon(0)$, then $exp[\beta(\epsilon_j - \mu)]$ becomes less than 1 and average occupation number n_j becomes -ve which is impossible. This is special case for bosons only, remember we do not have such scenario for fermions. Try out finding the reason, why did not we have such thing for fermions?

Therefore, the system must have strictly negative chemical potential, $\mu < 0$. At very high temperatures (in the classical limit), it is easy to check that the chemical potential is always negative. In the quantum context, with a fixed number of particles, the chemical potential is still negative, but increases with decreasing temperatures, and may eventually 0 at some point, which gives rise to a peculiar phenomenon known as Bose-Einstein condensation. If we consider the occupation of the lowest energy state, with μ approaching zero from below, viz when $-\beta\mu \ll 1$. Then the ground state occupation number becomes, $n(\epsilon_0 = 0) = \frac{1}{e^{-\beta\mu} - 1} = \frac{1}{1 - \beta\mu + \ldots - 1} \approx -\frac{1}{\beta\mu}$. Now if we consider that the chemical potential is entering from -ve to +ve by crosssing zero, the occupation number of the ground state $n(\epsilon_0 = 0)$ approaches ∞. That means the ground state becomes infinitely occupied. This is not just a mathematical artifact, this has been observed experimentally and this is called Bose Einstein condensation when most of particles occupy the ground state.

2 Density of states

The calculation of density of states is the same as in the case of Fermi system. Students must go through the previous note. We consider a situation when the gas is in a box with volume $V = L_x L_y L_z$ and subject to periodic boundary conditions, as we did in Fermi gas. In the thermodynamic limit ($N \to \infty, V \to \infty$, with $n = N/V =$ const), the sums over wavevector k can be replaced by integrals. However, here we have to be careful when μ happens to approach the value 0. In order to see what kind of trouble we then might get into, let us calculate the ground state occupation. Look at the formula for density of states for the fermionic system,

$$D(\epsilon) = (2s+1)\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int \sqrt{\epsilon}d\epsilon \tag{7}$$

The density of states vanish for ground state energy $\epsilon = 0$ i.e. $lim_{\epsilon\to 0}D(\epsilon) = 0$. This is where we are going to encounter a problem. The ground state has zero weight even if, we have just seen that the ground state is infinitely occupied. Fermionic systems do not encounter this problem due to the Pauli principle, which imposes that the occupation number is either 0 or 1. The way out to solve this problem is that we have to consider the ground state separately.

3 Free bosons in normal region $\mu < 0$

For a strictly negative chemical potential, we can write the logarithm of the grand partition function of the ideal Bose gas as a power series of the fugacity $z = e^{\beta\mu}$. From equation (5) we have,

$$ln\Xi(T,V,z) = -ln(1-z) - \sum_{j\neq 0} ln[1 - zexp(-\beta\epsilon_j)] \tag{8}$$

here the first term is for ground state $\epsilon_0 = 0$ and second term is for higher states. Thus, in the thermodynamic limit, $V \to \infty$ with $z < 1$ we have

$$\frac{1}{V}ln\Xi(T,V,z) \to -(2s+1)\frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \sqrt{\epsilon}ln[1 - zexp(-\beta\epsilon)]d\epsilon \tag{9}$$

where the transformation of the sum into an integral does not present any problems. The first term can be taken as negligible in the $V \to \infty$ with $z < 1$ mentioned above. We recall that the Taylor series expansionof Log term as $ln(1-y) = -\sum \frac{y^n}{n}$ for $|y| < 1$. Therefore we write,

$$\frac{1}{V}ln\Xi(T,V,z) = (2s+1)\frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \sqrt{\epsilon}\left[ze^{-\beta\epsilon} + \frac{1}{2}z^2e^{-2\beta\epsilon} + ..\right]d\epsilon \tag{10}$$

As done previously in case of Ideal Fermi system, we use the integral formula

$$\int_0^\infty x^2 \; ln \; (1 - ze^{-x^2}) \; dx = -\frac{\sqrt{\pi}}{4} \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}} \tag{11}$$

where we define

$$g_{5/2}(z) = -\frac{\sqrt{\pi}}{4} \int_0^\infty x^2 \; ln \; (1 - ze^{-x^2}) \; dx = \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}} \tag{12}$$

Note that $g_{5/2}(z)$ and $f_{5/2}(z)$ (as defined in Ideal Fermi system) differ by a sign $(-1)^{n+1}$ in the summand. We can write in terms of this new notation:

$$\frac{1}{V} ln\Xi(T, V, z) = (2s+1)\frac{1}{\lambda^3} \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}} = (2s+1)\frac{1}{\lambda^3} g_{5/2}(z) \tag{13}$$

where we have defined same dimensionaless variable $\lambda = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$ is the thermal de Broglie wave length. Therefore, total number of particles,

$$N = z\frac{\partial}{\partial z} ln\Xi(T, V, z) = (2s+1)\frac{V}{\lambda^3} g_{3/2}(z) \tag{14}$$

where $g_{3/2}(z) = z\frac{\partial}{\partial z} g_{5/2}(z)$. In a similar way, the total internal energy of the bose system is

$$U = -\frac{\partial}{\partial \beta} ln\Xi = \frac{3(2s+1)V}{\beta\lambda^3} g_{5/2}(z) \tag{15}$$

As an example, let us calculate the specific heat at constant volume per mole, given by

$$c_V(T, V) = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right)_{V,N} = -\frac{k\beta^2}{N}\left(\frac{\partial U}{\partial \beta}\right)_{V,N} \tag{16}$$

To carry out this calculation, we need the function U in terms of β, V, N. However, we just have U as a function of β, V and the fugacity z, but but not N. On the other hand, we know N as a function of β, V, z separately. So we need to make variable transformation i.e. the technique of Jacobian (see any Mathematical Methods book). If we omit the dependence on volume, which is always fixed, we may write,

$$\left(\frac{\partial U}{\partial \beta}\right)_{V,N} = \frac{\partial(U, N)}{\partial(\beta, N)} = \frac{\partial(U, N)}{\partial(\beta, z)}\frac{\partial(\beta, z)}{\partial(\beta, N)} = \left(\frac{\partial U}{\partial \beta}\right)_z - \left(\frac{\partial U}{\partial z}\right)_\beta \frac{\left(\frac{\partial N}{\partial \beta}\right)_z}{\left(\frac{\partial N}{\partial z}\right)_\beta} \tag{17}$$

Using eqn (14) and (15), we are prepared to calculate all of these derivatives. Thus, we have

$$\left(\frac{\partial U}{\partial \beta}\right)_z = -\frac{15(2s+1)V}{4\beta^2\lambda^3} g_{5/2}(z); \quad \left(\frac{\partial U}{\partial z}\right)_\beta = \frac{3(2s+1)V}{2z\beta\lambda^3} g_{3/2}(z) \tag{18}$$

$$\left(\frac{\partial N}{\partial \beta}\right)_z = -\frac{3(2s+1)V}{2\beta\lambda^3} g_{3/2}(z); \quad \left(\frac{\partial N}{\partial z}\right)_\beta = \frac{(2s+1)V}{z\lambda^3} g_{1/2}(z) \tag{19}$$

Hence, the specific heat at constant volume is given by,

$$c_V = \frac{3}{2}k\left(\frac{5}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{3}{2}\frac{g_{3/2}(z)}{g_{1/2}(z)}\right) \tag{20}$$

where eqn (14) is used to eliminate fugacity z. In the classical limit, $g(z) \approx z$. Therefore, $c_V \approx (3/2)k$ as given by theorem of equipartition of energy in classical statistical mechanics.

4 Bose Einstein Condensation

At high temperature, the chemical potential for fermions, bosons and classical particles vary in a similar manner. However, as temperature decreases, chemical potential of fermions and classical particles may enter into positive regions. But chemical potential of bosons can never become positive, as it will lead to unphysical occupation number. So, what happens for bosons is that: at some temperature (say T_0) chemical potential for bosons reaches 0 and continues to become 0 for all temperature $T < T_0$. This is called critical temperature for BE condensation. We now consider such limit of low temperatures and high particle densities (called, quantum limit), where one finds important qualitative differences between bosons, fermions and classical particles. Note eqn (8) from previous section,

$$ln\Xi(T,V,z) = -ln(1-z) - \sum_{j\neq 0} ln[1 - zexp(-\beta\epsilon_j)] \tag{21}$$

We ingored the first term in the high temperature (hence, $\mu < 0$) limit. But now on, we can not simply neglect such term as they are important in low temperature limit where μ gradually becomes -ve to 0. We write the particle density $n = N/V = z\frac{\partial}{\partial z} ln\Xi(T,z)$ as

$$n = \frac{(2s+1)}{V}\frac{z}{1-z} + (2s+1)\frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu} - 1} \tag{22}$$

We can estimate the regular contribution to the particle density for $\mu = 0$ as

$$\lim_{\mu\to 0}\int_0^\infty \frac{A\sqrt{\epsilon}d\epsilon}{e^{\beta(\epsilon-\mu)} - 1} = \frac{A}{\beta^{3/2}}\int_0^\infty \frac{\sqrt{x}dx}{e^x - 1} = \frac{A}{\beta^{3/2}} \tag{23}$$

where we have used the dimensionless variable $x = \beta\epsilon$ and we have used short notation $A = \frac{2s+1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}$. Therefore the expression for particle density becomes,

$$n = 2.61A\,(kT)^{3/2} + \frac{2s+1}{V}\frac{1}{e^{-\beta\mu} - 1} \tag{24}$$

This is a mixed representation where we have taken the limit $\mu \to 0$ for the regular contribution, but not for the occupation of the ground state. A is the same as written above. It is evident that the critical temperature in the large volume limit $V \to \infty$ becomes,

$$2.61 \frac{2}{\sqrt{\pi}} \frac{2s+1}{\lambda^3} \tag{25}$$

where $\lambda = \frac{h}{\sqrt{2\pi m k T_0}}$. Note the first term does not appear as the volume is large. T_0 is the Bose Einstein transition temperature. Below T_0, the gas of free bosons displays some very peculiar features. The Bose-Einstein condensation actually is characterized by divergences in occupation numbers. Some state starts becoming hugely populated at very low temperature and particle density of that state becomes significantly large.