Statistical Physics
Section 5: Bose-Einstein Condensation

In this section we discuss the thermodynamic properties of the Ideal Bose Gas. We consider the case of spinless Bosons so there is no spin factor in the density of states of section 4.

5. 1. Fixing the chemical potential

In order to fix the chemical potential $\mu$ we should choose it so that

$$N = \sum_j n_j = \int_0^\infty f_-(\epsilon, \mu) g(\epsilon) d\epsilon$$

(1)

where $f_-$ is the Bose-Einstein distribution and $g(\epsilon)$ is the density of states.

Using the Bose-Einstein function from section 4

$$f_- = \frac{1}{\exp[\beta(\epsilon_j - \mu)] - 1}$$

and

$$g(\epsilon) = AV \epsilon^{1/2}$$

we obtain from (1) an equation for the density $\rho$, defined as

$$\rho = \frac{N}{V},$$

(2)

which we think of as giving $\rho$ as a function of $\mu$:

$$\rho(\mu) = A \frac{\int_0^\infty \epsilon^{1/2} \exp[\beta(\epsilon - \mu)]}{\exp[\beta(\epsilon - \mu)] - 1} d\epsilon.$$  

(3)

We note that:

- $\rho$ is an increasing function of $\mu$. This can be seen directly from (3).
- The maximum allowed value is $\mu = 0$. To see this we can go back to section 4 where we evaluated

$$Z_j = \sum_{n=0}^\infty \exp[\beta n(\mu - \epsilon_j)]$$

as a geometric series which to converge requires

$$\exp[\beta(\mu - \epsilon_j)] < 1.$$  

In the following we take the ground state energy as

$$\epsilon_0 = 0$$

therefore we must have

$$\mu < 0.$$  

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5. 2. Paradox

Suppose we hold $T$ constant, and increase the density $\rho$ by adding particles to the system from a particle reservoir. For the density to increase, we must correspondingly raise the value of $\mu$.

However, we now find a paradox. If we choose the maximum possible value of $\mu$ (zero) in Eq.3, we obtain

$$\rho = A(kT)^{3/2} \int \frac{x^{1/2}}{e^x - 1} dx \quad (4)$$

Note how we have changed integration variable to $x = \beta \epsilon$ thus rendering the integral over $x$ dimensionless i.e. just a number which happens to be 2.61.... Then condition (4) becomes

$$\rho = \rho_C = \frac{(2mkT/\hbar^2)^{3/2}}{4\pi^2} \times 2.61 \quad (5)$$

Apparently then, our attempt to pack more particles into the system fails at this point: the chemical potential is the maximum possible, but the density $\rho = N/V$ of particles is finite, and stuck at $\rho_C$.

But what if we have an assembly with density greater than $\rho_C$....

**Question:** Where have all the Bosons gone?....

5. 3. Resolution

**Answer:** .... into the ground state

The source of the paradox lies in equation (1) with our replacement of the sum over discrete states with an integral over the density of states $g(\epsilon)$. We noted before in Section 4 that this might possibly be dangerous for low energy states. Therefore, the resolution of the paradox is to be more careful with the low lying states.

Let us separate off the ground state $\epsilon_0 = 0$ and continue to use an integral for the rest.

Accordingly, we should write

$$\rho = \rho_0 + \rho_+ = \frac{1}{V} \frac{1}{e^{-\beta \mu} - 1} + A \int_0^\infty \frac{e^{1/2} d\epsilon}{e^{\beta(\epsilon-\mu)} - 1} \quad (6)$$

where the first term counts the density of particles $n_0/V$ in the ground state, and the second handles all the rest i.e. $\rho_+$ gives the density over all other states than the ground state.

Note that if $\mu$ is close to zero

$$\exp -\beta \mu \simeq 1 - \beta \mu \quad (7)$$

and the first term in (6) can become arbitrarily large (remember $\mu$ is negative):

$$\rho_0 \simeq \frac{k_B T}{-\mu V} \quad (8)$$

while simultaneously (as shown above) the second term approaches a finite limit

$$\rho_+ = \rho_C \quad (9)$$
If this happens the ground state may accommodate a finite fraction of the total particles present. Thus, the number of particles in the ground state is macroscopic and from (6) the fraction of particles in the ground state is

$$\rho_0 = \rho - \rho_C$$  \hspace{1cm} (10)

Therefore the ground state contains the ‘excess density’ in the condensed phase. The particles in the ground state are called the Bose condensate.

**Summary** if we increase the density $\rho = \frac{N}{V}$ at fixed temperature $T$, there is no condensation until $\rho = \rho_C$. For larger $\rho > \rho_C$ the system encounters the fixed “ceiling” $\rho_C(T)$ on the density of “normal” particles, so the remainder must be accommodated as a Bose condensate of density $\rho - \rho_C$.

![Figure 1: Plot of $\rho_0$ and $\rho_+$ as a function of the assembly density $\rho$](image)

It is interesting to note that we can write the critical density (5) as

$$\rho_C = 2.61 \frac{2}{\pi^{1/2}} \frac{1}{\lambda_T^3}$$  \hspace{1cm} (11)

where $\lambda_T$ is the de Broglie wavelength of the particle given by

$$\lambda_T = \left( \frac{2\pi \hbar^2}{MkT} \right)^{1/2}$$  \hspace{1cm} (12)

The prefactor, here $(2\pi)^{1/2}$, may vary from textbook to textbook but it is the combination $\hbar/(MkT)^{1/2}$ which is important. The condensation transition appears in the regime where the interparticle spacing $(V/N)^{1/3} = 1/\rho^{1/3}$ is comparable to the de Broglie wavelength.

Going back to (8) and looking more carefully at the limit $\mu \to 0$ we have

$$\mu = -\frac{k_B T}{V[\rho - \rho_C(T)]} = O(1/N)$$  \hspace{1cm} (13)

Thus strictly it is only in the thermodynamic limit $N, V \to \infty$ that $\mu = 0$.

**N.B.** The maximum allowed value of $\mu$ is determined by the ground state energy which we were free to choose to be zero. This is because we have an arbitrary constant associated with the energy. That is, the energy levels are given by

$$\epsilon = \frac{\hbar^2 \pi^2}{2ML^2} \left[ n_x^2 + n_y^2 + n_z^2 \right] + \text{Constant}$$  \hspace{1cm} (14)
The ground state has \( n_x = n_y = n_z = 1 \) therefore we have chosen the constant to be \(-3\hbar^2\pi^2/2ML^2\). A first excited state (e.g. \( n_x = 2, n_y = n_z = 1 \)) has energy

\[
\epsilon_1 = \frac{3\hbar^2\pi^2}{2ML^2}
\]  

(15)

This is useful in tutorial question 3.5 where we show that in the condensed phase, although the number of particles in the first excited state is large it is not macroscopic i.e. the number \( \bar{n}_1 \sim N^{2/3} \). Therefore we are safe to just separate off the ground state in (6).

5. 4. Phase transition as a function of T

Viewed differently, we can choose some fixed density \( \rho \), and vary the temperature. We expect that at low temperatures we should enter the quantum regime and see the condensation transition. Then we can use condition (5) to define a critical temperature \( T_C(\rho) \) via

\[
\rho = \rho_0 \left( \frac{T}{T_C} \right)^{3/2} + A(kT)^{3/2} 
\]

(16)

Taken by itself, this would imply that, at fixed density, it was impossible to cool the system to below \( T_C \). [Work this idea through if you are unsure.] The resolution is again that: there is no condensate for \( T \geq T_C \), whereas below this temperature we have to separate off the ground state

\[
\rho = \rho_0(T) + A(kT)^{3/2} \times 2.61
\]

(17)

\[
\rho = \rho_0(T) + \rho \left( \frac{T}{T_C} \right)^{3/2}
\]

(18)

where we have used (16) to eliminate the nasty constants in favour of \( T_C \). Therefore the density of particles in the ground state is given by

\[
\rho_0(T) = \rho \left[ 1 - \left( \frac{T}{T_C} \right)^{3/2} \right] \quad \text{for} \quad T < T_C
\]

(19)

Figure 2: Plot of \( \rho_0 \) as a function temperature for fixed assembly density \( \rho \). Note the sharp change in behaviour at \( T_C \)
We now consider the energy in the system. Since the condensed particles have zero energy, we can always write

\[ E = \int g(\epsilon) \epsilon f_(\epsilon, \mu) d\epsilon = AV \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon-\mu)} - 1} \tag{20} \]

Below the transition temperature, we can set \( \mu \simeq 0 \). Setting also \( x = \beta \epsilon \) we find

\[ E = \frac{V(2m/h^2)^{3/2}(kT)^{5/2}}{4\pi^2} \int_0^\infty \frac{x^{3/2} dx}{e^x - 1} = 0.77NkT^{5/2} / T_C^{3/2} \tag{21} \]

where 0.77 comes from the values for the dimensionless integrals

The resulting heat capacity is

\[ C_V = 1.93Nk(T/T_C)^{3/2} \quad T \leq T_C \tag{22} \]

Above the transition temperature, \( \mu \) is varying, so the functional form of \( C_V \) will be different. To calculate the new functional form of \( C_V \) for a fixed density, we must first find \( \mu(N, T) \) from

\[ N = \int g(\epsilon) f(\epsilon, \mu) d\epsilon \tag{23} \]

and then put this into

\[ E = \int g(\epsilon) \epsilon f(\epsilon, \mu) d\epsilon \tag{24} \]

This can be done numerically (with ease) or using transcendental functions (with difficulty). However, for \( T \) large we know that we should recover the classical limit which by the equipartition theorem should yield \( C_V = \frac{3}{2}NkT \). The result for \( C_V \) looks like:

\[ \text{Figure 3: Plot of } C_V \text{ as a function of } T. \text{ Note the cusp at the phase transition point } T_c. \text{ This is an example of a singularity.} \]

**Characteristics of Phase Transition**

- The phase transition is signalled by a sudden change in the functional form of the thermodynamic properties i.e. there are *singularities*. These are manifested by strange behaviour of response function e.g. here, the cusp in the heat capacity. In other kinds of phase transition \( C_V \) may diverge.
• We need to take the thermodynamic limit

\[ \lim_{N,V \rightarrow \infty} \quad \text{at fixed} \quad \rho = \frac{N}{V} \]

(25)

to see true singularities and a true phase transition.

• Bose condensation is an example of a quantum phase transition i.e. phase transitions are often generated by certain interactions becoming important, but here there are no interactions! Instead the transition is a result of indistinguishability at the quantum level.

Bose condensation is at first unintuitive to most physicists. To get a better idea why it happens, consider the following toy model:

A Bose system with just two energy levels, zero and \( \epsilon \). At zero temperature, all \( N \) particles (let us think of being in the canonical ensemble) are in the ground state condensate. What happens if we raise \( T \) a little?

First the consider the case of distinguishable particles: the energy cost for promoting a single particle to the excited state is \( \epsilon \) whereas the entropy gain will be \( k \ln N \) since there are \( N \) ways of choosing the particle. Therefore, if \( N \) is large, entropy wins out over energy and many particles will move in to the excited state (in fact we expect a finite fraction of \( T \) is finite).

However for indistinguishable particles promoting a single particle produces produces no entropy gain! This is because the state with one particle in the excited state and \( N-1 \) in the ground state is a single microstate for indistinguishable particles. Therefore the particles will remain in the ground state!

Actually this example is a bit too simplistic as it is not possible to have just two available states for indistinguishable (non-localised) particles. Nevertheless, it illustrates the fact that thermal excitation of the particles up from the condensate is strongly suppressed by indistinguishability effects. Since most of our intuition comes from handling macroscopic, distinguishable particles, it is not too surprising that it leads us astray where Bose condensation is concerned.

5. 5. Experimental Verification

Bose first established Bose statistics in 1924 and calculated the Planck distribution for photons (which are not conserved). In the same year Einstein studied the case of Bose particles which are conserved and predicted the condensation transition.

However for many years there was no really direct experimental evidence

The traditional candidate was liquid Helium \(^4\)He at low \( T \). This system exhibits something close to a Bose condensation: the transition to a superfluid state at an observed temperature \( T_C = 2.17\text{K} \). This compares well with a theoretical prediction of \( T_C = 3.13\text{K} \) based on the Bose gas. However, the details are different, because the interaction potential \( U \) is fairly strong, not negligible as assumed here. For example, the superfluid (condensate) has a density uniform through space, rather than concentrated at the middle of the box. (If
you think about it, that’s what’s implied by having a finite fraction of the particles in the single-particle ground state.)

Recently however, using special cooling techniques, researchers have been able to cool an atomic gas of Rubidium atoms in a magnetic trap (“box”) to unbelievably low (nanoKelvin) temperatures. Bose condensation is observed – and (amazingly) in this case the condensate particles really do pile up in the middle of the box! See e.g. Physics World, March 97 issue. The first condensate was produced in Rubidium-87 in 1995 and the Nobel prize swiftly followed in 2001.

The main techniques in the cooling involve:

1. Dilution refrigerators which can cool to mK. These are basically fridges with coolant which is a mixture of $^4\text{He}^3\text{He}$

2. Laser cooling which can cool to $\mu\text{K}$. The idea is basically to fire photons off the atoms to slow them down. The fast atoms are selected by the Doppler effect. The Nobel prize was awarded for the development of laser cooling in 1997.

3. Finally to get down to nanoK magnetic traps are employed and fast particles are ‘evaporated’ from the trap. BEC in an harmonic potential is explored in Tutorial 3.6

see the ‘BEC homepage’ http://www.colorado.edu/physics/2000/bec for a gentle intro.