

Bose-Einstein Gases

An amazing thing happens if we consider a gas of non-interacting bosons. For sufficiently low temperatures, essentially all the particles are in the same state (the ground state). This *Bose-Einstein condensation* can occur even when the temperature is high enough that one would naively expect that higher energy states should be well populated. In addition, properties of the gas change when it is in this state, so something like a phase transition occurs.

Note that photons obey Bose statistics so they constitute a non-interacting gas of bosons. We've already calculated their distribution (which has $\mu = 0$). It's just the Planck distribution and this distribution does not have a Bose-Einstein condensation. The difference between photons and the situation we're about to discuss is that there is no fixed number of photons. If a photon gas is cooled, the number of photons per unit volume decreases. This is related to the fact that photons are massless. It's possible to create or destroy a photon of arbitrarily small energy. The gases we'll be considering will contain a fixed number of matter particles. One can't create or destroy these bosons without doing something about the rest mass energy (and perhaps other conserved quantum numbers)!

So let the gas contain N particles. The Bose-Einstein distribution is

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/\tau} - 1},$$

and the sum of this distribution function over all states must add up to N . For convenience, we adjust the energy scale so that the lowest energy state has $\epsilon = 0$.

When $\tau \rightarrow 0$, all the particles must be in the ground state,

$$\begin{aligned} \lim_{\tau \rightarrow 0} \frac{1}{e^{-\mu/\tau} - 1} &= N, \\ \lim_{\tau \rightarrow 0} e^{-\mu/\tau} - 1 &= \frac{1}{N}, \\ \lim_{\tau \rightarrow 0} e^{-\mu/\tau} &= 1 + \frac{1}{N}, \\ \lim_{\tau \rightarrow 0} \left(1 - \frac{\mu}{\tau} + \dots\right) &= 1 + \frac{1}{N}, \\ \lim_{\tau \rightarrow 0} \frac{-\mu}{\tau} &= \frac{1}{N}, \\ \lim_{\tau \rightarrow 0} \mu &= -\frac{\tau}{N}. \end{aligned}$$

Recall that μ must be lower than any accessible energy for the Bose-Einstein distribution and here we have $\mu < 0$ in agreement with this constraint, although it converges to 0 as

$\tau \rightarrow 0$, but this is to be expected as all the particles must pile up in the ground state when $\tau \rightarrow 0$. It's instructive to evaluate μ for a mole of particles at a temperature of 1 K. The result is

$$\mu(1 \text{ K}) = -2.3 \times 10^{-40} \text{ erg}.$$

If we consider a mole of ${}^4\text{He}$ and treat it as an ideal gas with $p = 1 \text{ atm}$ and $T = 1 \text{ K}$, then its volume would be $V = 82 \text{ cm}^3$. This would be equivalent to a cube of side $L = 4.3 \text{ cm}$. Recall that the energies of single particle states in a cube are

$$\epsilon(n_x, n_y, n_z) = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2).$$

The ground state has $n_x = n_y = n_z = 1$ and in the first excited state one of these quantum numbers is 2. Using the L we just calculated and the mass of ${}^4\text{He}$, we find

$$\epsilon(1, 1, 1) = 1.34 \times 10^{-31} \text{ erg}, \quad \epsilon(2, 1, 1) = 2.68 \times 10^{-31} \text{ erg}.$$

Actually, the ground state energy is supposed to be adjusted to 0, so we need to subtract $\epsilon(1, 1, 1)$ from all energies in the problem. Then the ground state energy is 0 and the first excited state energy is

$$\epsilon_1 = 1.34 \times 10^{-31} \text{ erg} = 5.8 \times 10^8 |\mu|,$$

at $T = 1 \text{ K}$. The key point is that even though the energy of the first excited state is incredibly small, and you might think such a small energy can have nothing to do with any macroscopic properties of a system, this energy (or more properly, the difference in energy between the ground state and the first excited state) is almost nine orders of magnitude bigger than μ (at the temperature and density we're considering). Under these conditions, what is the population of the first excited state?

$$\begin{aligned} N_1 &= \frac{1}{e^{(\epsilon_1 - \mu)/\tau} - 1}, \\ &= \frac{1}{e^{-5.8 \times 10^8 \mu/\tau} - 1}, \\ &= \frac{1}{1 - 5.8 \times 10^8 \mu/\tau + \dots - 1}, \\ &= \frac{1}{-5.8 \times 10^8 \mu/\tau}, \\ &= \frac{1}{5.8 \times 10^8 / N}, \\ &= \frac{N}{5.8 \times 10^8}, \end{aligned}$$

so the occupancy of the first excited state is almost 9 orders of magnitude smaller than the occupancy of the ground state. Essentially all the particles are in the ground state even though kT is much larger than the excitation energy!

Now we want to do a proper sum of the occupancy over the energy states. We might try to write

$$N = \int_0^{\infty} f(\epsilon) \mathcal{D}(\epsilon) d\epsilon,$$

where

$$\mathcal{D}(\epsilon) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon},$$

is the same density of states we used for the Fermi-gas except there's a factor of two missing because we're assuming a spin 0 boson gas. (If the spin were different from 0, we would include a factor $2S + 1$ to account for the multiplicity of the spin states.) The expression above has the problem that it fails to count the particles in the ground state. We have had this problem in previous calculations but it never mattered because there were only a few (2 or less) in the ground state and ignoring these particles makes absolutely no difference to any quantity involving the other $\sim 10^{23}$ particles.

However, we are expecting to find many, and in some cases, most of the particles in the ground state. It would not be a good idea to ignore them in the sum! So we write the sum as

$$N = N_0 + \int_0^{\infty} f(\epsilon) \mathcal{D}(\epsilon) d\epsilon,$$

where the first term is the number of particles in the ground state and the second term accounts for all particles in excited states. This term still makes an error in the low energy excited states (since we're integrating rather than summing), but when these states contain a lot of particles, the ground state contains orders of magnitude more, so errors in the occupancies of these states are of no concern. In the case that these states don't contain many particles, it means that the occupancies of all states are small, and again we make no appreciable error if we miss on the occupancies of a few of the low energy excited states.

So, the number of particles in the ground state is

$$N_0 = \frac{1}{e^{-\mu/\tau} - 1},$$

and the number of particles in excited states is

$$\begin{aligned} N_e &= \int_0^{\infty} f(\epsilon) \mathcal{D}(\epsilon) d\epsilon, \\ &= \int_0^{\infty} \frac{1}{e^{(\epsilon - \mu)/\tau} - 1} \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} d\epsilon, \\ &= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\infty} \frac{1}{e^{(\epsilon - \mu)/\tau} - 1} \sqrt{\epsilon} d\epsilon, \end{aligned}$$

$$\begin{aligned}
&= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{1}{e^{\epsilon/\tau} - 1} \sqrt{\epsilon} d\epsilon \quad (\text{since } |\mu|/\tau \ll \epsilon/\tau), \\
&= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \tau^{3/2} \int_0^\infty \frac{1}{e^x - 1} \sqrt{x} dx \quad (x = \epsilon/\tau), \\
&= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \tau^{3/2} \Gamma(3/2) \zeta(3/2), \\
&= 1.306 \sqrt{\pi} \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \tau^{3/2}, \\
&= 2.612V \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2}, \\
&= 2.612V n_Q,
\end{aligned}$$

where n_Q is the quantum concentration again.

The major approximation we made in the above calculation was ignoring the chemical potential. As long as there are an appreciable number of particles in the ground state, then $|\mu|$ must be much smaller than the energy of any excited state and this is a good approximation. With the numerical example we worked out before, $|\mu|$ will be closer to 0 than to the first excited state energy provided the ground state contains about 10^{15} or more particles which means the excited states must contain about $6 \times 10^{23} - 10^{15} = 6 \times 10^{23}$ particles. In other words, our approximation for N_e above should be valid all the way to the point where $N_e = N$. This means that the $N_e \propto \tau^{3/2}$. We define the proportionality constant by defining the *Einstein condensation temperature*, τ_E , such that

$$N_e = N \left(\frac{\tau}{\tau_E} \right)^{3/2},$$

so

$$\tau_E = \frac{2\pi\hbar^2}{m} \left(\frac{N}{2.612V} \right)^{2/3},$$

and we expect the expression for N_e should be valid from $\tau = 0$ up to $\tau = \tau_E$. Then the number in the condensate is

$$N_0 = N \left(1 - \left(\frac{\tau}{\tau_E} \right)^{3/2} \right).$$

Numerically, the Einstein temperature is

$$T_E = \frac{115}{V_m^{2/3} m},$$

where T_E is in Kelvins, V_m is the molar volume in cm^3 and m is the molar weight in grams. For liquid ^4He , with a molar volume of 27.6 cm^3 , this gives $T_E = 3.1 \text{ K}$. There

is actually a transition in liquid helium at about 2.17 K. Below this temperature, liquid ^4He develops a superfluid phase. This phase is most likely a Bose-Einstein condensation, but it is more complicated than the simple theory we have worked out because there are interatomic forces between the helium atoms. We know this because there must be forces that are responsible for the condensation of helium gas to liquid helium at $T = 4.2$ K and one atmosphere.

If you read the articles referenced at the beginning of these notes, you'll see that a major problem faced by the experimenters in creating BE condensates in other systems is getting the atoms cold enough and dense enough to actually form the condensate. In the case of helium, the attractive interactions help to get the density high enough to form the condensate at more accessible temperatures!

Superfluid Helium

As mentioned, the transition of ^4He at 2.17 K at 1 atm is believed to be the condensation of most of the helium atoms into the ground state—a Bose-Einstein condensation. That this does not occur at the calculated temperature of 3.1 K is believed to be due to the fact that there are interactions among helium atoms so that helium cannot really be described as a non-interacting boson gas! Above the transition temperature, helium is referred to as He I and below the transition, it's called He II.

K&K present several reasons why thinking of liquid helium as a non-interacting gas is not totally off the wall. You should read them and also study the phase diagrams for both ^4He and ^3He (K&K figures 7.14 and 7.15).

The fact that something happens at 2.17 K is shown by the heat capacity versus temperature curve (figure 7.12 in K&K) which is similar to the heat capacity curve for a phase transition and also not all that different from the curve you're going to calculate for the Bose-Einstein condensate in the homework problem (despite what the textbook problem actually says about a marked difference in the curves!). In addition to the heat capacity, the mechanical properties of ^4He are markedly different below the transition temperature. The liquid helium becomes a superfluid which means it flows without viscosity (that is, friction).

The existence of a Bose-Einstein condensate does not necessarily imply the existence of superfluidity.

To understand this we need to examine the mechanics of friction on a microscopic level. Without worrying about the details, friction must be caused by molecular collisions which transfer energy from the average motion (represented by the bulk velocity) to the microscopic motion (internal energy).

If our Bose-Einstein condensate were really formed from a gas of non-interacting particles, then it would be possible to excite any molecule in the condensate out of the ground state and into the first excited state simply by providing the requisite energy (and momentum). Previously, we calculated that under typical conditions, the energy difference between the ground state and the first excited state was about 10^{-31} erg, an incredibly small amount of energy that would be very easy to provide given that thermal energies are about 10^{-16} erg.

In order to have superfluid behavior, it must be that there are interactions among the molecules such that it's not possible to excite just one molecule out of the condensate and into the first excited state. A better way to say this is that due to the molecular interactions, the single particle states are not discrete energy states of the superfluid. We need to consider the normal modes of the fluid—the longitudinal oscillations or the sound waves. In particular, we can consider travelling sound waves of wave vector \mathbf{k} and frequency ω . (Rather than the standing waves which carry no net momentum.) A travelling wave carries energy in units of $\hbar\omega$ and momentum in units $\hbar\mathbf{k}$. The number of units is determined by the number of phonons or *quasiparticles* in the wave.

Now imagine an object of mass M moving through a stationary superfluid with velocity \mathbf{V}_i . In order for there to be a force on the object, there must be a momentum transfer to the superfluid. In order to do this, the object must create excitations in the fluid which contain momentum (the quasiparticles in the travelling waves we just discussed). Of course, if quasiparticles already exist, the object could “collide” with a quasiparticle and scatter it to a new state of energy and momentum. (This can also be viewed as the absorption of one quasiparticle and the emission of another.) We will assume that there are not very many existing quasiparticles and consider only the creation (emission) of a quasiparticle.

So, let's consider this emission process. Before the event, the object has velocity \mathbf{V}_i and afterwards it has velocity \mathbf{V}_f . We must conserve both energy and momentum,

$$\frac{1}{2}MV_i^2 = \frac{1}{2}MV_f^2 + \hbar\omega ,$$

and

$$M\mathbf{V}_i = M\mathbf{V}_f + \hbar\mathbf{k} .$$

We can go through some algebra with the goal of solving for $\mathbf{V}_i \cdot \mathbf{k}$. The momentum equation can be rewritten as

$$M\mathbf{V}_i - \hbar\mathbf{k} = M\mathbf{V}_f ,$$

squared and divided by $2M$,

$$\frac{1}{2}MV_i^2 - \hbar\mathbf{V}_i \cdot \mathbf{k} + \frac{1}{2M}\hbar^2k^2 = \frac{1}{2}MV_f^2 .$$

Subtract from the energy equation to get

$$\hbar \mathbf{V}_i \cdot \mathbf{k} = \hbar \omega + \frac{1}{2M} \hbar^2 k^2,$$

or

$$\mathbf{V}_i \cdot \frac{\mathbf{k}}{k} = \frac{\hbar \omega}{\hbar k} + \frac{\hbar k}{2M}.$$

What we really want to do is place a lower limit on the magnitude of V_i . This means we can drop the term containing M on the right hand side. The smallest value will occur when \mathbf{V}_i is parallel to \mathbf{k}/k , the unit vector in the \mathbf{k} direction. This corresponds to emission of the quasiparticle in the forward direction. Thus

$$V_i > \frac{\hbar \omega}{\hbar k}.$$

I've left the \hbar 's there in order to emphasize that the right hand side is the ratio of the energy to the momentum of an excitation,

Suppose the excitations are single particle states with momentum $\hbar \mathbf{k}$ and energy $\hbar^2 k^2 / 2m$. This is the travelling wave analog to the standing wave particle in a box states we've discussed many times. Then the right hand side becomes $\hbar k / 2m$ which goes to zero as $k \rightarrow 0$. Thus, an object moving with an arbitrarily small velocity can produce an excitation and feel a drag force—there is no superfluid in this case. (Note: k must be bigger than $\sim 1/L$, where L is the size of the box containing the superfluid, but as we've already seen the energies corresponding to this k are tiny compared to thermal energies.)

Suppose the excitations are sound waves (as we've been assuming) and the phase velocity is independent of k . Then

$$V_i > \frac{\omega}{k} = v_s,$$

where v_s is the phase velocity of sound in the fluid. This means that if an object flows through the fluid at less than the velocity of sound, the flow is without drag! That is, the fluid is a superfluid.

In fact, the v_s is not independent of k and what sets the limit is the minimum phase velocity of any excitation that can be created by the object moving through the fluid. Figure 7.17 in K&K shows that this minimum is about 5000 cm s^{-1} for the low lying excitations in ^4He . K&K point out that Helium ions have been observed to travel without drag through He II at speeds up to about 5000 cm s^{-1} !

Comment 1: It appears that we've shown that any fluid should be a superfluid as long as we don't move things through it faster than its speed of sound. In our derivation, we made an assumption that doesn't apply in most cases. Can you figure out which assumption it was?

Comment 2: As a general rule, superfluidity or superconductivity requires the condensation of many particles into a single (ground) state and a threshold for creating excitations. The minimum velocity required to create an excitation is the threshold for non-viscous flow.