Notes for Lecture 14

Bose gas, and Bose-Einstein condensation

In the last lecture, we learned that the electron gas in normal metals is very energetic and exerts a very high pressure even at $T = 0$. In fact, at room temperature, the pressure and the hardness exhibited by a piece of metal is, to an excellent approximation, the properties of the $T = 0$ electron gas in the metal. They are manifestly quantum phenomena, originating from the Pauli exclusion principle of electrons.

Now, how about bosons? As one might expect, they are quite the opposite. Instead of having an enormous amount of energy and pressure at zero temperature, they have zero energy and zero pressure[1]. This leads to very interesting issues unique to a Bose gas system, the Bose-Einstein condensation, which we will explore in this lecture.

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[1] Those students who have followed the discussions so far carefully will immediately note that photons, a prime example of bosons, *do* have infinite energy and infinite pressure at zero temperature. Here, we are focusing on massive bosons at low temperature/energy.

14.1 Bose gas

14.1.1 General setup

Let us recall, from Eqs. 12.30,12.31, (with $\eta = 1$)

$$N = \int d\varepsilon\, D(\varepsilon) \frac{1}{z^{-1}\, e^{\beta\varepsilon} - 1} \qquad \text{but, see below} \tag{14.1}$$

$$E = \int d\varepsilon\, D(\varepsilon) \frac{\varepsilon}{z^{-1}\, e^{\beta\varepsilon} - 1} \tag{14.2}$$

where $z \equiv \exp(\beta\mu)$. Also, note that we will be considering a spin 0 particle (e.g., ^{4}He). So we shall put the non-orbital degeneracy $g = 1$. For the results below, however, it is easy to put back the non-orbital degeneracy later on: simply multiply g to the function $g_m(z)$, which will be defined shortly below. Also, we shall confine ourselves to the non-relativistic particles. I.e., the dispersion relation of the form $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$ will be assumed. Finally, we will also assume that the spatial dimension is 3. Then,

$$PV = \frac{2}{3} E \tag{14.3}$$

However, generalizing calculations below to other dispersions and to other spatial dimensions should not be viewed as posing any fundamental difficulty.

With the dispersion and the dimensionality thus assumed, we recall the handy *operator identity*, Eq. 12.50,

$$\frac{1}{V} \int_0^\infty d\varepsilon D(\varepsilon) [\ \cdot\ ] = \frac{1}{\lambda^3 \left(\frac{1}{2}\right)!} \int_0^\infty dx x^{1/2} [\ \cdot\ ] \qquad x \equiv \beta\varepsilon \tag{14.4}$$

where $[\ \cdot\ ]$ means an arbitrary integrand that this operator acts on. Using this identity, the above expressions for N and E can be written as

$$n = \frac{N}{V} = \frac{1}{\lambda^3 \left(\frac{1}{2}\right)!} \int_0^\infty dx \frac{x^{1/2}}{z^{-1}\, e^x - 1}, \qquad \text{but, see below} \tag{14.5}$$

$$\frac{E}{V} = \frac{k_B T}{\lambda^3 \left(\frac{1}{2}\right)!} \int_0^\infty dx \frac{x^{3/2}}{z^{-1}\, e^x - 1}. \tag{14.6}$$

Now, we define the following function $g_m(z)$

$$g_m(z) = \frac{1}{(m-1)!} \int_0^\infty dx \frac{x^{m-1}}{z^{-1} e^x - 1} \tag{14.7}$$

Note that

$$\frac{1}{z^{-1}e^{x}-1}=\frac{ze^{-x}}{1-ze^{-x}}=\sum_{n=1}^{\infty}z^{n}e^{-nx}.$$

And so,

$$g_m(z)=\sum_{n=1}^{\infty}\frac{z^n}{(m-1)!}\int_0^{\infty}dx x^{m-1}e^{-nx}.$$

By changing the variable to $y = nx$, it is seen that the integral is $(m-1)!\,n^{-m}$. Therefore, we get the following simple result

$$\begin{aligned}
g_m(z) &= \sum_{n=1}^{\infty}\frac{z^n}{n^m} && && (14.8)\\
g_m(z=1) &= \zeta(m) && \text{Riemann zeta function} && (14.9)\\
\frac{dg_m(z)}{dz} &= \frac{g_{m-1}}{z} && && (14.10)\\
g_m(z=0) &= 0 \quad \text{and} \quad \frac{dg_m(z>0)}{dz}>0 && \text{mononotic for } z\geq 0 && (14.11)\\
g_m(z) &= \text{well defined (convergent)} && \text{for any } m \text{ and } 0\leq z<1 && (14.12)
\end{aligned}$$

For the last fact, one can use the convergence test (e.g., the ratio test) of the series. It can be noted that the Riemann zeta function diverges if $m \leq 1$. From the recursion relation, Eq. 14.10, then, one sees that the function $g_m(z)$ is *not* a nice function around $z = 1$. A derivative will diverge (eventually), and thus g_m is not analytic around $z = 1$. Now, in terms of g_m's we get from the above two equations for $n, E/V$ and from Eq. 14.3,

$$\begin{aligned}
n &= \frac{1}{\lambda^3}g_{3/2}(z) && \text{but, see below} && (14.13)\\
\frac{E}{V} &= \frac{3k_BT}{2\lambda^3}g_{5/2}(z) && && (14.14)\\
P &= \frac{k_BT}{\lambda^3}g_{5/2}(z) && && (14.15)
\end{aligned}$$

14.1.2 Chemical potential

Here, we will use the equation for N (Eq. 14.13) to try solving for the chemical potential, as usual.

First of all, though, let us note the following simple fact about the chemical potential (and thus the fugacity) in the case of the boson gas. Since the Bose-Einstein occupation number[2] $n(\varepsilon) = 1/(e^{\beta(\varepsilon-\mu)} - 1)$ must be non-negative for any ε, and since $\varepsilon \geq 0$ for the current case, it follows that at any temperature

$$\mu \leq 0 \qquad \text{Bose gas} \tag{14.16}$$

This is *much* different from the fermion case, where μ at $T = 0$ is a very large positive number. Of course, as the temperature is raised, or the volume is expanded, the chemical potential for boson or fermion must tend to its classical value—a large negative value (Eq. 8.8). We will see shortly that in the case of the Bose gas

$$\mu \to 0^- \qquad \text{as } T \to 0^+. \tag{14.17}$$

In any case, the non-positive chemical potential means that the fugacity is limited to

$$0 \leq z \leq 1. \tag{14.18}$$

As we saw above (Eq. 14.11), the function $g_m(z)$ is zero at $z = 0$ and monotonically increases as z increases from zero. If $m \leq 2$, then g_m has a divergent derivative at $z = 1$, while its value at $z = 1$ is finite if $m > 1$. Such is the case for $g_{3/2}(z)$. From Eq. 14.13, we can see, then, that

$$n = \frac{g_{3/2}(z)}{\lambda^3} \leq \frac{g_{3/2}(1)}{\lambda^3} = \frac{\zeta(3/2)}{\lambda^3} \approx \frac{2.612}{\lambda^3} \qquad \text{but, see below} \tag{14.19}$$

This is a curious inequality! And it turns out to be *incorrect*! This is the reason for the "but, see below" tags in the equations for N or n. That this must be incorrect is seen by noting that $\lambda = h/\sqrt{2\pi m k_B T}$. So, as $T \to 0$, the right hand side vanishes as $T^{3/2}$. This means that $n \to 0$ as $T \to 0$! This is clearly absurd as the (massive) particles cannot just disappear, simply because the temperature is lowered. Where did things go wrong? This is a subtle and important question. The answer is easy to find, if one considers the case when $T = 0^+$. Physically, what would happen? At zero temperature, the system will seek out the minimum energy state, and that is simply all particles occupying the lowest possible energy state, i.e. the zero energy state. Let us see that the fugacity must be in this case.

$$\begin{aligned} N &= \sum_i \frac{1}{z^{-1}e^{\beta\varepsilon_i} - 1} && \text{at any } T && (14.20) \\ &\to \frac{1}{z^{-1} - 1}. && \text{as } T \to 0^+ && (14.21) \end{aligned}$$

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[2] You may note that the symbol n is used for at least three different things in this lecture note. The Bose-Einstein occupation number, the number density (N/V), and the dummy index for integer. As explained in Section 12.1.3, $n(\varepsilon)$ or $f_{BE}(\varepsilon)$ is the standard notation for the Bose-Einstein occupation number. In this lecture note, only the Bose-Einstein occupation number is used with an argument, as in $n(\varepsilon)$ or $n(0)$. This is how you can distinguish it from other n symbols.

Therefore,

$$z \to \frac{1}{1+N^{-1}} \approx 1 - \frac{1}{N}, \qquad \text{as } T \to 0^+ \qquad (14.22)$$

$$\mu \to -\frac{k_B T}{N}. \qquad \text{as } T \to 0^+ \qquad (14.23)$$

This is the proof of Eq. 14.17. The point here is that the zero energy occupancy $n(\varepsilon = 0) = 1/(z^{-1} - 1)$ becomes macroscopically large at low temperatures[3]. However, this singular value at $\varepsilon = 0$ is completely ignored, when the formula for N as a sum, Eq. 14.20, is converted to the formula for N as an integral, Eq. 14.1!

14.1.3 Fixing the N, n formulae

Fortunately, it is easy to fix this problem. All we need to do is to separately include $n(\varepsilon = 0)$, for N, or $n(\varepsilon = 0)/V$, for $n = N/V$, in all equations tagged "but, see below." In other words, all equations tagged "but, see below" must be interpreted as representing only one-particle excited states, $\varepsilon > 0$, excluding the one-particle ground state, $\varepsilon = 0$. In particular, let us fix Eq. 14.13

$$n = \frac{g_{3/2}(z)}{\lambda^3} + \frac{1}{V}\frac{z}{1-z}. \qquad (14.24)$$

A better form of this equation is

$$n\lambda^3 = g_{3/2}(z) + \frac{n\lambda^3}{N}\frac{z}{1-z}. \qquad (14.25)$$

One reason that this new form is better is that it can be seen to consist of three parameters, $N, n\lambda^3, z$. Since N is a constant, this equation is an implicit equation to solve for z (and thus the chemical potential) given a value of $n\lambda^3$. This is what we set out to do in the previous section! Due to the non-analyticity of $g_{3/2}(z)$, this equation must be solved numerically in general. However, we can already learn generic behaviors by graphing the above equation.

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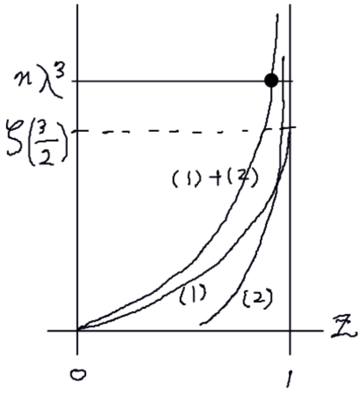
[3] You might worry whether only the zero energy matters here. Only it matters. You can show that for any non-zero energy value the occupancy cannot be macroscopic, i.e. $n(\varepsilon > 0)/N \to 0$ as $N \to \infty$. This is left for your exercise.



As this figure shows, the solution (filled circle) for z can be obtained by the intersection of the horizontal line $n\lambda^3$ and the sum of two curves (1) $g_{3/2}(z)$ and (2) $\frac{n\lambda^3}{N}\frac{z}{1-z}$. It is also clear from this figure that (1) + (2) is a *strictly increasing* function, and so as $n\lambda^3$ increases, z will increase[4]. We can summarize our finding as follows.

As $n\lambda^3$ increases, z increases strictly. z goes monotonically from 0 ($\mu = -\infty$) to 1 ($\mu = 0$) as $n\lambda^3$ goes from 0 (classical limit) to ∞ (quantum limit: low T or high n).

An important thing to note in the above figure is that the graph (2) is highly exaggerated, unless $n(\varepsilon = 0)/N = z/(N(1-z)) \to$ finite.

14.1.4 The BEC condition

The Bose-Einstein condensation refers to the macroscopic occupation of the zero energy level. The bosons that occupy the zero energy level are called collectively a Bose-Einstein condensate (BEC). That is, when a BEC forms

$$\frac{n(\varepsilon = 0)}{N} = \text{finite}. \tag{14.26}$$

When does this transition into the BEC start? Roughly speaking, it is when the excited states cannot hold all the particles any more. Here, we shall state the answers first, before proving all points in the next section.

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[4] Here is a more formal way to argue this point, if necessary. Consider scaling up $n\lambda^3 \to An\lambda^3$ with $A > 1$. Then, the horizontal line scales up by A, and so does part (2). But, part (1) remains constant. Since both (1) and (2) are positive, it follows that (1) + (2) $\to$ (1) + A(2) $<$ A((1) + (2)).

The phase boundary between the BEC phase and the "normal" phase is marked by the following condition.

$$n\lambda^3 = g_{3/2}(1) = \zeta(3/2) \approx 2.612. \tag{14.27}$$

This condition can be interpreted as the condition that the maximum number of particles stored in excited states is equal to N. However, this condition needs some more explanation, since the condition that the excited states can hold all particles is $n\lambda^3 = g_{3/2}(z)$, strictly speaking (Eq. 14.25). How is it that z can be replaced by 1 here? Before explaining this, we summarize other crucial facts related to it.

$$n\lambda^3 = g_{3/2}(1) + n\lambda^3 \frac{n(0)}{N} \qquad n\lambda^3 \geq \zeta(3/2) \quad \text{(BEC phase)} \tag{14.28}$$

$$n\lambda^3 = g_{3/2}(z) \qquad n\lambda^3 \leq \zeta(3/2) \quad \text{(normal phase)} \tag{14.29}$$

The first equation says that *in the BEC phase the fugacity is pinned at 1, i.e., the chemical potential is pinned at 0*, since it is the same equation as the more general equation, Eq. 14.25, except that z is set at 1. So far, we have proved $z = 1$ only for zero temperature. What we are saying now is that this is so throughout the BEC phase[5]. The second equation says in the normal phase we can ignore the $\frac{n(0)}{N}$ term completely, since it is vanishingly small. *Now, the chemical potential is not pinned. If $n\lambda^3$ is given, then μ must be calculated by solving this equation, $n\lambda^3 = g_{3/2}(z)$.* This can be done only numerically, but we already know that μ (or z) must keep on decreasing, as $n\lambda^3$ is reduced.

In the next section, we prove all of these facts[6].

14.1.5 Proof of the BEC transition

Now that we have spelled out our facts in the previous section, it is on our shoulder to prove them. If we prove these two points, then we will have proven all the facts

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[5] However, note the following point. Since z must keep increasing as $n\lambda^3$ increases, as we just showed in the previous section, it must increase minutely but steadily as $n\lambda^3$ increases from $\zeta(3/2)$ to ∞, while staying close to 1 all the while.

[6] While proving these facts is undoubtedly very important, knowing these facts very well would often seem more urgent in many situations.

summarized above.

Point *a*) The BEC condition marks a true phase transition. One way to show it is that an "order parameter" turns on in the BEC phase, and is zero in the normal phase. Here, we shall assume that the **order parameter** is

$$\frac{n(0)}{N} \quad \text{(condensate fraction)}$$

and we will prove that $\frac{n(0)}{N}$ does indeed have the correct behavior. We will have some more to say about the nature of the order parameter in the next lecture, as it will turn out that $\frac{n(0)}{N}$ is only part of the order parameter.

Point *b*) In the BEC phase, z gets pinned at 1.

Before we prove these points, note the following three facts.

1. $\frac{n(0)}{N} \to 1$ as $n\lambda^3 \to \infty$.
2. $z \to 1 - \frac{1}{N}$ as $n\lambda^3 \to \infty$.
3. z is a strictly increasing function of $n\lambda^3$ (as we have proved in Section 14.1.3), and, therefore, so is $n(0) = \frac{1}{z^{-1}-1}$.

Facts 1 and 2 are the generalization of Eq. 14.22, to the high density case, as well as low temperature case. In the high density case, the energy level spacing becomes infinite, and so only the lowest energy level is occupied. Fact 3 along with facts 2,3 mean that, if we prove that $\frac{n(0)}{N} = 0$ but $n(0) \gg 1$ (so that $z \approx 1$) for $n\lambda^3 \approx \zeta(3/2)$, then we have proven everything—both points *a*) and *b*) above! So, the gist of the BEC *phase transition* physics really comes down to the following fact.

$$\boxed{1 \ll n(0) \ll N \text{ at, and near, the phase boundary } (n\lambda^3 \approx \zeta(3/2)).}$$

We prove this by the method of contradiction. Suppose that this conclusion was not true. This would be the case, if $n(0) \sim 1$ or $n(0) \sim N$ at the phase boundary.

The $n(0) \sim 1$ case. We shall assume that $n(0) \lesssim 10$, to be slightly more conservative[7]. Then, it means that $1 - z \geq O(0.1)$, since $n(0) = 10$ means $z \approx 0.9$ and $n(0) = 0$ means $z = 0$ (the end of the classical limit). Since $g_{3/2}(0.9) = 1.6$ is already different by $O(1)$ from $g_{3/2}(1) = \zeta(3/2) = 2.6$, we see that $n\lambda^3 - g_{3/2}(z) \approx g_{3/2}(1) - g_{3/2}(z) = O(1)$, if $n(0) \lesssim 10$. Then, considering the general equation, Eq. 14.25, we have $O(1) = n\lambda^3 n(0)/N$, which is absurd, since $n(0)/N = 0$ for this small $n(0)$ and $n\lambda^3 \approx 2.6$ by assumption.

The $n(0) \sim N$ case. This means that $n(0) = \frac{N}{\alpha}$ where[8] $1 < \alpha \lesssim 10$. Then, we must have $z = 1 - \frac{\alpha}{N}$. But again, this is absurd from the point of view of the general equation: $n\lambda^3 - g_{3/2}(z) = n\lambda^3 n(0)/N$. The left hand side of this equation is basically zero at the phase boundary, since $n\lambda^3 = g_{3/2}(1) = g_{3/2}(z)$, if $z = 1 - \frac{\alpha}{N}$, while the right hand side of this equation is given by $n\lambda^3\alpha \geq O(0.1)$.

14.1.6 T_c, v_c, $n(0)$

Now that we have proved the presence of the BEC transition, and the phase boundary formula, it is time to be quantitative.

If n is held constant, then Eq. 14.27 defines T_c, **the Bose-Einstein condensation transition temperature**, as

$$T_c = \frac{h^2}{2\pi m k_B} \left(\frac{n}{\zeta(3/2)} \right)^{2/3}. \tag{14.30}$$

In this case, the BEC sets in at $T \leq T_c$. If the temperature is held constant, and the volume (or equivalently the density) is varied, then the above equation defines **the transition volume per particle** ($v \equiv 1/n$)

$$v_c = \frac{\lambda^3}{\zeta(3/2)}. \tag{14.31}$$

such that the BEC sets in at $v \leq v_c$.

In the condensed regime ($n\lambda^3 \geq \zeta(3/2)$), we can calculate the **condensate frac-**

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[7] The number 10 here, is not that particularly important. Any "ordinary scale" such as 1000 or 10000 will do just as well.

[8] Exactly the same comment applies to this number 10 as that in the previous footnote.

tion as follows.

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\begin{aligned}
\frac{n(0)}{N} &= 1 - \frac{g_{3/2}(1)}{n\lambda^3} && \text{Eq. 14.28} \qquad (14.32)\\
&= 1 - \left(\frac{T}{T_c}\right)^{3/2} && \text{Eq. 14.30} \qquad (14.33)\\
&= 1 - \frac{v}{v_c}. && \text{Eq. 14.31} \qquad (14.34)
\end{aligned}
$$

So, this gives a quantitative picture of how the order parameter turns on at the transition temperature (volume) and saturates as the temperature (volume) is lowered. As $n(0)$ is a strictly increasing function of $n\lambda^3$, it must stay at 0 in the normal phase ($T > T_c$ or $v > v_c$).