Physics 127a: Class Notes

Lecture 14: Bose Condensation

Ideal Bose Gas

We consider an gas of ideal, spinless Bosons in three dimensions. The grand potential $\Omega(T, \mu, V)$ is given by

$$\frac{\Omega}{kT} = \frac{V}{\lambda^3} \frac{2}{\pi^{1/2}} \int_0^\infty y^{1/2} \ln(1 - ze^{-y}) \, dy, \tag{1}$$

with $\lambda = h/\sqrt{2\pi mkT}$ and $z = e^{\beta\mu}$ the fugacity. It is convenient to integrate by parts, and write the result in the form

$$\frac{\Omega}{NkT} = -\frac{1}{\rho\lambda^3} \frac{4}{3\pi^{1/2}} \int_0^\infty \frac{y^{3/2}}{z^{-1}e^y - 1} dy. \tag{2}$$

The chemical potential is fixed by the number of particle N in the physical system, or in terms of the density $\rho = N/V$ (see Eq. (25) of lecture 15)

$$\rho\lambda^3 = \frac{2}{\pi^{1/2}} \int_0^\infty \frac{y^{1/2}}{z^{-1}e^y - 1} dy \tag{3}$$

which is to be solved for $z(\rho, T)$.

Equations (2) and (3) completely give the thermodynamics. Remember, for example $\Omega = -PV$ in general, and for a non-relativistic gas the internal energy is $U = \frac{3}{2}PV = -\frac{3}{2}\Omega$. To evaluate the properties we need to look at the properties of the *Bose functions*
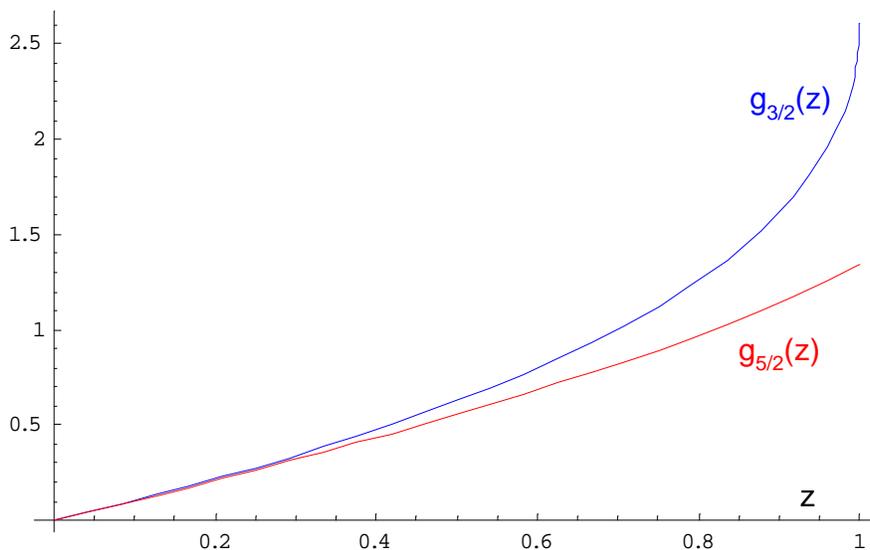
$$g_\nu(z) = \frac{1}{(\nu - 1)!} \int_0^\infty \frac{y^{\nu-1}}{z^{-1}e^y - 1} dy \tag{4}$$

(for half-integral factorials $\frac{1}{2}! = \frac{\sqrt{\pi}}{2}$ and $\frac{3}{2}! = \frac{3}{2} \times \frac{1}{2}!$, etc.). Then we have

$$\rho\lambda^3 = g_{3/2}(z) \tag{5}$$

$$\frac{\Omega}{NkT} = -\frac{g_{5/2}(z)}{g_{3/2}(z)}. \tag{6}$$

Properties of these functions are calculated in the Mathematica file Bose.nb on the website, and also see Appendix D of *Pathria*. The functions are plotted below.

It is often good to look at the *high temperature expansion* first. The physics is easy as $T \to \infty$ (classical, interactions unimportant), and expanding about here can give useful insights.

At high temperatures $\rho\lambda^3 \to 0$, and so $z \to 0$. You can get Mathematica (or Maple, Scientific Word etc.) to expand the Bose functions as a Taylor expansion in z, or you can do it by hand noting that for small z

$$\frac{1}{z^{-1}e^y - 1} = \frac{z^{-y}}{1 - ze^{-y}} = \sum_{n=1}^{\infty}(ze^{-y})^n \tag{7}$$

and

$$\frac{1}{(\nu - 1)!} \int_0^{\infty} y^{\nu-1}e^{-ny} = \frac{1}{n^\nu}. \tag{8}$$

Either way you should find

$$\rho\lambda^3 = z + 2^{-3/2}z^2 + \cdots \tag{9}$$

which can be inverted to give

$$z = \rho\lambda^3 - 2^{-3/2}(\rho\lambda^3)^2 + \cdots . \tag{10}$$

Note that the first term in the series gives the classical (non-degenerate) result for the chemical potential. Similarly

$$-\frac{\Omega}{NkT} = \frac{z + 2^{-5/2}z^2 + \cdots}{z + 2^{-3/2}z^2 + \cdots} \simeq 1 - 2^{-5/2}z + \cdots \simeq 1 - 2^{-5/2}\rho\lambda^3 + \cdots . \tag{11}$$

(Going to this order is pretty easy. To go higher order by hand is a little tedious.) From this we can get the expansion for the equation of state

$$\frac{PV}{NkT} = 1 - 2^{-5/2}\rho\lambda^3 + \cdots . \tag{12}$$

Note this is also a *low density* expansion, and is known as the *virial expansion* (although this is more commonly an expansion in weak interactions rather than weak quantum effects). The specific heat is

$$\frac{C_V}{Nk} = \frac{1}{Nk}\left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{3}{2}\frac{\partial}{\partial T}\left(-\frac{\Omega}{Nk}\right)_{N,V} = \frac{3}{2}\left(1 + 2^{-7/2}\rho\lambda^3 + \cdots\right). \tag{13}$$

You can identify the classical results as the first terms in the expansions. Note the specific heat *rises above* the classical result as the temperature is lowered, even though it must go to zero as $T \to 0$.

Now we look at what happens as the temperature is lowered with fixed density $\rho = N/V$. Lets look at Eq. (3) first. As the temperature is lowered and $\rho\lambda^3$ increases, z must increase so that the right hand side increases. However $z < 1$, otherwise the integral diverges (there would then be some y for which the denominator goes to zero). At $z = 1$ the function $g_{3/2}(z)$ takes on its greatest value, equal to $\zeta(\frac{3}{2}) = 2.6124$ (see Mathematica plots). This is a problem, since the left hand side continues to increase as T is lowered! Thus Eq. (3) *breaks down* for $T < T_c$ given by

$$\rho\lambda^3(T_c) = \zeta(\tfrac{3}{2}). \tag{14}$$

The problem arises because the occupation $N_0 = \langle n_{\mathbf{p}=0}\rangle$ of the $\mathbf{p} = 0$ ($\varepsilon_{\mathbf{p}} = 0$) state diverges as $z \to 1$

$$N_0 = \frac{1}{z^{-1} - 1} \simeq \frac{-kT}{\mu}. \tag{15}$$

Below T_c we must allow for a *macroscopic number* of particles in the zero momentum state, and then *the steps going from a sum over discrete momentum states to an integral over continuous momentum is incorrect*

for this state. The total number of particles $N_{p>0}$ in the $\mathbf{p} \neq 0$ states is still adequately given by the integral expression, though, and so below T_c we have

$$N = N_0 + N_{p>0} \tag{16}$$

with $N_{p>0}$ given by Eq. (3) with $z = 1$ on the right hand side, and $N_{p>0}$ replacing N on the left hand side, so that

$$\frac{N_{p>0}}{V} \lambda^3(T) = \zeta(3/2) \tag{17}$$

which using Eq. (14) can be written

$$\frac{N_{p>0}}{N} = \left(\frac{T}{T_c}\right)^{3/2} \tag{18}$$

and then

$$\frac{N_0}{N} = 1 - \frac{N_{p>0}}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}. \tag{19}$$

Finally this fixes μ through Eq. (15) to be $-kT/N_0$, which is $O(1/N)$ and so zero for thermodynamic purposes..

The grand potential Eq. (2) is now easily evaluated since for $T < T_c$ we have on the right hand side $g_{5/2}(z = 1) = \zeta(5/2) = 1.3415$. Thus using the results for the thermodynamics outlined below Eq. (3):

$$\frac{\Omega}{NkT} = -\frac{1}{\rho\lambda^3} \zeta(5/2) \tag{20}$$

$$U = \frac{3}{2} kT \frac{V}{\lambda^3} \zeta(5/2) \tag{21}$$

$$P = kT \frac{1}{\lambda^3} \zeta(5/2) \tag{22}$$

$$c_V = \frac{C_V}{N} = \frac{15}{4} \frac{V}{N\lambda^3} \zeta(5/2) \propto T^{3/2}. \tag{23}$$

Note the strange results that the internal energy is independent of the number of particles, and the pressure is independent of the volume! The latter means the compressibility is infinite. With a little effort you can also show that the specific heat is continuous at T_c but has a cusp— a discontinuous slope. (This comes from differentiating Eq. (2) w.r.t. T and noting that the temperature derivative of the integral is zero at T_c. which in turn depends on the fact that $g_{3/2}(z)$ approaches its $z \to 1$ limiting value with infinite slope—see the figure.)

Note that the contribution to Ω from the $\mathbf{p} = 0$ state is $kT \ln(1 - z)$ which for $T < T_c$ becomes of order $kT \ln N_0$. Although large, this is not $O(N)$, and so can be ignored in the calculation. Thus Ω is properly given by the integral expression (except, of course, when we calculate N given by $\partial\Omega/\partial\mu$!). Also it can be seen that that the occupation number of the momentum states near zero are $O(N^{2/3})$, which again is large, but negligible compared to the other, $O(N)$ terms, so that corrections to the integral expression from these states is not important.

Real Systems

The Bose-Einstein condensation (BEC) temperature for an ideal Bose gas is from Eq. (14)

$$kT_c \simeq 0.061 \frac{h^2}{m} \left(\frac{N}{V}\right)^{2/3}. \tag{24}$$

There are two strategies that have been successful in observing BEC in the laboratory:

- Density typical of everyday liquids, and then weak interactions so that solidification does not occur, even at low temperatures, and small mass so that the quantum effects are large: liquid He[4] density $1.5 \times 10^{22} \text{cm}^{-3}$ and then T_c should be about 3K.

- Dilute systems (so that the interactions are not so important) at the *very* low temperatures that are attainable by laser cooling (supplemented with other techniques) for atom traps, e.g. 5×10^5 sodium atoms trapped at a density of 10^{14}cm^{-3} at 10^{-6}K.

I will discuss the first case here, and refer you to the 2001 Nobel Prize website for lectures on the second case (see class website for links).

Superfluid He[4]   The condensed phase of the Bose isotope of Helium remains liquid down (it is believed) to the absolute zero of temperature at pressures below 25atmos because of the large zero point energy (small mass) and small attractive energy. At a temperature T_c that is around $2 - 3$K there is a phase transition to a new phase with remarkable superfluid properties. Since the temperature is around where BEC is expected, and the superfluid properties can be understood in terms of BEC (see below) we associate the transition with BEC i.e. a *macroscopic occupation of the zero momentum state*.

The specific heat is rather different than the predictions for the ideal Bose gas, varying as T^3 at low temperatures, and showing a divergence at T_c as

$$C(T) \sim A_\pm \, |T - T_c|^{-\alpha} + C'(T) \tag{25}$$

where $C'(T)$ is a smooth background, the constants $A_\pm$ are for $T \gtrless T_c$, and the exponent α is found to be very small $\alpha \simeq -0.026$. (For a long time the divergence was thought to be logarithmic, i.e. $\ln |T - T_c|$, which would correspond to $\alpha \to 0$.) The shape of $C(T)$ is reminiscent of the greek letter λ, and the transition is sometimes called the *lambda transition*. We will derive the T^3 and will understand the divergence in terms of critical phenomena next term later in the course.

For a review of other neat properties of the superfluid phase, see *States of Matter*, by David Goodstein, §5.4.

Is there BEC? For the ideal Bose gas, the occupation N_0 of the zero momentum state at zero temperature (the ground state) is the total number of particles N. This is certainly not true in He[4], since it is readily shown that this state is not an eigenstate of the interacting Hamiltonian H. In fact operating on this state with the Hamiltonian we get the sum of states with two particles excited from the zero momentum state to states with momentum $\pm \hbar \mathbf{k}$

$$H \, |N, 0, 0, \cdots \rangle = \sum_{\mathbf{k}} C_k \, |N - 2, 0, \cdots, N_{\mathbf{k}} = 1, N_{-\mathbf{k}} = -1, \cdots \rangle. \tag{26}$$

(This is easy to see in the coordinate representation where the ground state is just a constant, and the damaging part of H is the potential

$$V = \frac{1}{2} \sum_{i,j} V(\mathbf{x}_i - \mathbf{x}_j) = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{k}} \tilde{V}_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{x}_i - \mathbf{x}_j)} \tag{27}$$

taking the Fourier transform in the last step.)

However there is evidence that N_0 remains macroscopic, i.e. the *condensate fraction* $f_0 = N_0/N$ is some number between 0 and 1 that remains nonzero as $N \to \infty$. The evidence comes partly from considering the *weakly interacting Bose gas* where $V(r)$ is assumed small, and it can be shown that f_0 is nonzero

$$f_0 = 1 - \frac{8}{3} \left(\frac{N}{V} \frac{a^3}{\pi} \right)^{1/2} \tag{28}$$

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where a is the scattering length $mg/4\pi\hbar^2$ and $g = \int V(r)\, d^3r$ (so weak interactions is small g). In He^4 itself, there is evidence from neutron scattering, and also from numerical Monte Carlo calculations that $f_0 \simeq 0.1$.