A. Schekochihin
Stat. Phys. Lectures
Oxford HT-2013

§18. Degenerate Bose gas.

18.1 Bose-Einstein Condensation

Recall that for bosons,

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1} \qquad (1)$$

and multiple particles are welcome to occupy the same state!

Eq. (1) requires $\mu < \varepsilon_i$ for all single-particle states i, otherwise we get an unphysical situation $\bar{n}_i < 0$.

Therefore $\mu < \min(\varepsilon_i) = \underset{\text{lowest state}}{\varepsilon_0} = 0$

(Let's consider here just the cases when this is true (for ideal gas, $\varepsilon = \frac{\hbar^2 k^2}{2m} = 0$ for $k=0$) but can generalise to $\varepsilon_0 \neq 0$ (easy; applies, e.g. to magnetised Bose gas — see PS-8))

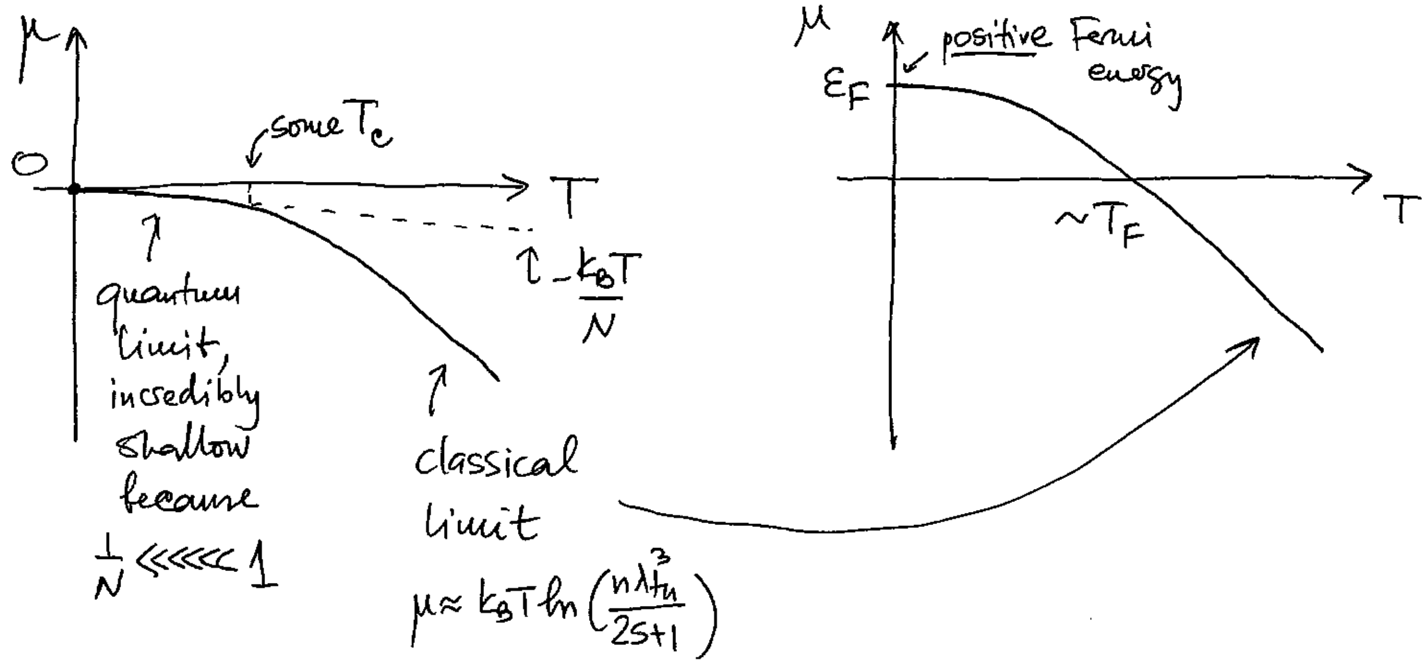
Clearly, as $T \to 0$ ($\beta \to \infty$), the lower the energy the larger the occupation # and so at $T = +0$, we expect them all to be in the ground state:

$$\bar{n}_0 = \frac{1}{e^{-\beta\mu}-1} \to N \text{ as } \beta \to \infty \qquad (2)$$

$$\Downarrow$$

$$\mu(T \to +0) \approx -k_B T \ln\left(1+\frac{1}{N}\right) \approx -\frac{k_B T}{N} \to 0 \text{ from below} \qquad (3)$$

Thus, for Boze gas, Cf., for Fermi gas (p. 189)



Thus, at low temperatures, the lowest-energy state becomes <u>macroscopically occupied</u>:

$\bar{n}_0(T=0) = N$ and clearly, $\bar{n}_0 \sim$ some significant fraction of N for T just above zero.

How does that square with our previous calculations <u>in the continuous limit</u>? We had [eq. (27), p. 175]:

$$\underbrace{\sum_i}_{\text{sum over states}} = \int_0^\infty d\varepsilon\, g(\varepsilon), \quad g(\varepsilon) = \frac{2(2S+1)}{\sqrt{\pi}} \frac{V}{\lambda_{th}^3} \sqrt{\varepsilon}\, \beta^{3/2} \qquad (4)$$

Thus, the $\varepsilon = 0$ state gave us a vanishing contribution to the integral

But clearly, the continuous approximation of $\sum_i$ was only justified provided the # of particles in each particular discrete state was small compared to the total # of particles N!

As we have just seen, this is patently wrong at low enough T, so we must adjust our theory. But in order to adjust it, let us see how, mathematically speaking, it breaks down as $T \to 0$:

[and break down it must, otherwise we'd be in trouble, with spurious results emerging!]

Recall that the first step in any treatment of a quantum gas is to calculate $\mu(n,T)$ from [eq. (28) p. 175]:

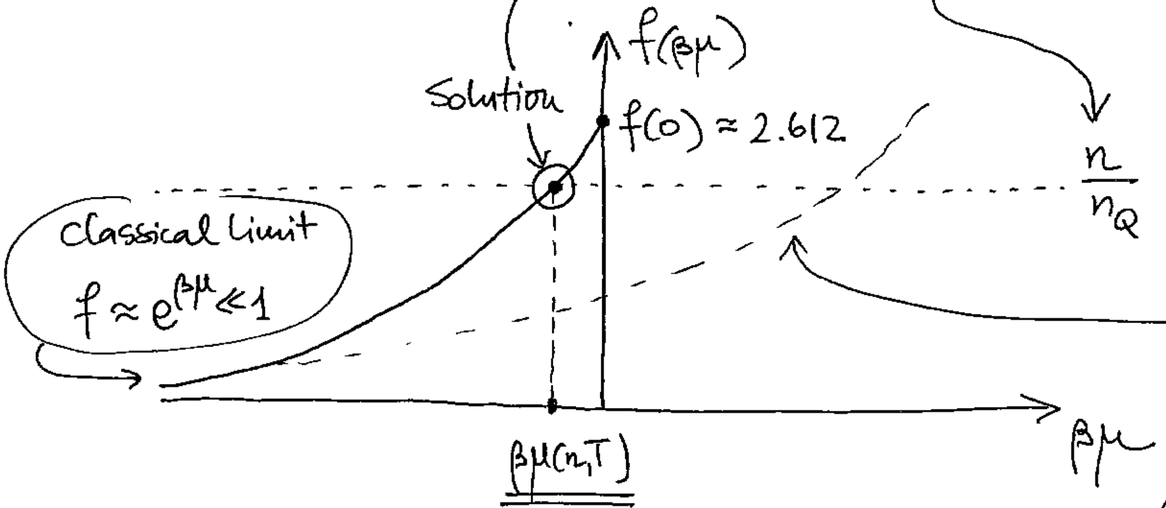
$$N = (2S+1)\frac{V}{\lambda_{th}^3}\underbrace{\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{dx\sqrt{x}}{e^{x-\beta\mu}-1}}_{f(\beta\mu)} \qquad (5)$$

$\uparrow$ bosons!

Thus, ~~the~~ $\mu(n,T)$ is the solution of the transcendental equation

$$\lambda_{th} = \hbar\sqrt{\frac{2\pi}{mk_BT}}$$

$$f(\beta\mu) = \frac{n\lambda_{th}^3}{2S+1} \equiv \frac{n}{n_Q} \propto \frac{n}{T^{3/2}} \quad (6)$$



cf. Fermi gases: as $\beta \to \infty$, $f(\beta\mu) \approx \frac{2}{\sqrt{\pi}}\int_0^{x_F} dx\sqrt{x} = \frac{4}{3\sqrt{\pi}}(\beta\mu)^{3/2}$ [with $\oplus$ in denominator]

Unlike for Fermi gases, for which a solution always exists, for Bose gases, $f(\beta\mu)$ tends to a finite upper limit: $f(0) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{dx\sqrt{x}}{e^x-1} = \zeta(\frac{3}{2}) \approx 2.612$ (7)

"Riemann zeta function"

Thus, if $\frac{n}{n_Q} > f(0)$, there is no longer a solution to eq.(6)! This happens at $T=T_c$ s.t.

$$\frac{n}{n_Q} = \frac{n\lambda_{th}^3}{2S+1} = f(0) \approx 2.612$$

and so
$$\boxed{T_c = \frac{2\pi\hbar^2}{mk_B}\left[\frac{n}{2.612(2S+1)}\right]^{2/3}} \qquad (8)$$

For $T>T_c$, all is well and we can always find $\mu(n,T) \to -0$ as $T \to T_c+0$

For $T<T_c$, we can just set $\mu=0$
[from (3), we know it's a tiny bit below 0, but that is basically 0 in thermodynamic limit $N\to\infty$]

– but this means that now eq. (5) no longer determines μ but rather the # of particles in the excited states ($\varepsilon \neq 0$):

$$N_{exc.} = (2S+1)\frac{V}{\lambda_{th}^3}\underbrace{f(0)}_{=2.612} < N$$

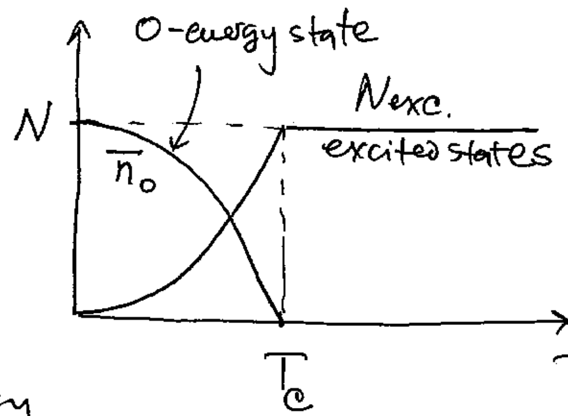
Equivalently,

$$\boxed{\frac{N_{exc.}}{N} = \frac{2.612\,(2S+1)}{n\lambda_{th}^3} = \left(\frac{T}{T_c}\right)^{3/2}}, \qquad (9)$$

for $T<T_c$

Whence the occupation # of the 0-energy state is

$$\boxed{\bar{n}_0 = N\left[1-\left(\frac{T}{T_c}\right)^{3/2}\right]} \qquad (10)$$



This phenomenon of a macroscopic # of particles collecting in the lowest-energy state is called Bose-Einstein condensation (in $\vec{k}$ space!)

When the condensate is present ($T<T_c$), Bose gas behaves as a system whose # of particles is not conserved at all because particles can always leave the excited population (N_{exc}) and drop into the condensate ($\bar{n}_0$) – c.f. photon gas (also $\mu=0$).

Cornell, Wieman & Ketterle got the 2001 Nobel Prize for the first experimental observation of Bose condensation.

Expectedly, $T_c \sim \dfrac{\hbar^2 n^{2/3}}{m k_B} \sim T_{deg} \sim$ a few K under normal conditions

(degeneration temperature (see §16.7))

(≈ 3 K for ^{4}He)

Note. You might wonder whether the lowest-energy state really is so special – might some energy levels above it also be macroscopically occupied? Let us estimate whether they are.

The occupation # of the lowest non-zero level:

$$\overline{n}_1 = \frac{1}{e^{\beta(\varepsilon_1 - \mu)} - 1}, \qquad (11)$$

where $\varepsilon_1 = \frac{\hbar^2 k_{min}^2}{2m}$, $k_{min} = \frac{2\pi}{\underset{\uparrow\ \text{size of the box}}{L}} = \frac{2\pi}{V^{1/3}}$ (smallest possible $k \neq 0$)

$$\Downarrow$$

$$\varepsilon_1 = \frac{2\pi^2\hbar^2}{mV^{2/3}} = \frac{2\pi^2\hbar^2 n^{2/3}}{m}\frac{1}{N^{2/3}} \sim \frac{k_B T_c}{N^{2/3}}$$

$$1 \gg \beta\varepsilon_1 \sim \frac{T_c}{T}\frac{1}{N^{2/3}} \gg \beta\mu \sim -\frac{1}{N} \quad [\text{see eq. (3)}]$$

Thus,
$$\overline{n}_1 \sim \frac{1}{e^{\beta\varepsilon_1} - 1} \sim \frac{T}{T_c} N^{2/3} \qquad (12)$$

This is very large, but in general still much smaller than either $\overline{n}_0$ or N_{exc} (Both $\sim N$):

$$\frac{\overline{n}_1}{\overline{n}_0} \sim \frac{\overline{n}_1}{N_{exc}} \sim \frac{1}{N^{1/3}} \lll 1 \text{ in the thermodynamic limit.}$$

Thus, it was ok to only worry specially about $\overline{n}_0$ – occupation #'s of all individual excited states are $\ll$ the total N.

18.2 Thermodynamics of degenerate Bose gas

Our usual routine:

1) Energy [eq.(30) p.176]: since the condensate is in the 0-energy state, it does not contribute to mean energy, so we need not worry about $\bar{n}_0$ and so, just from the excited states,

$$U = N k_B T \underbrace{\left(\frac{n_Q}{n}\right)}_{=\frac{1}{2.612}\left(\frac{T}{T_c}\right)^{3/2}\ \text{[eq.(8)]}} \underbrace{\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{dx\, x^{3/2}}{e^{x-\beta\mu}-1}}_{\text{for } T<T_c:\ \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{dx\,x^{3/2}}{e^x-1} = \frac{3}{2}\overbrace{\zeta\left(\frac{5}{2}\right)}^{=1.341}}$$

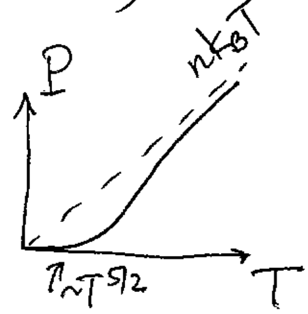
$$\approx \frac{3}{2}\cdot\frac{1.341}{2.612}\left(\frac{T}{T_c}\right)^{3/2} N k_B T$$

or

$$\boxed{U \simeq 0.77\, N k_B T_c \left(\frac{T}{T_c}\right)^{5/2}} \qquad (13)$$

$$\Downarrow$$

2) Grand potential $\Phi = -\frac{2}{3}U = -PV$



$$\Downarrow$$

Equ of state

$$\boxed{\begin{aligned} P &= \frac{2}{3}\cdot 0.77\, n k_B T_c \left(\frac{T}{T_c}\right)^{5/2} \\ &\simeq 0.085\,(2S+1)\frac{m^{3/2}(k_BT)^{5/2}}{\hbar^3} \end{aligned}} \qquad (14)$$

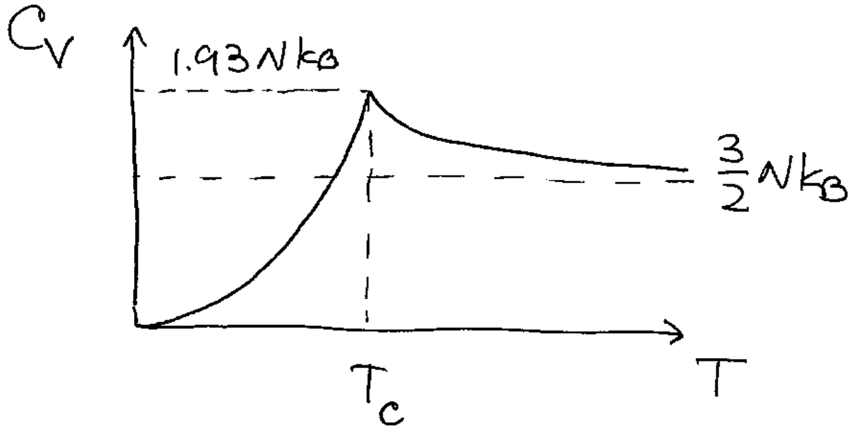
use eq.(8) (NB: $T_c \propto n^{2/3}$)

Thus pressure (and energy density) is independent of either volume or the density of particles — this is because the # of particles with non-zero energy is not conserved, so P is a function only of T (just like for photon gas)

3) Heat capacity:

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{5}{2}\frac{U}{T} \approx 1.93\, N k_B \left(\frac{T}{T_c}\right)^{3/2}} \qquad (15)$$

Note that $1.93 > \frac{3}{2}$, so C_V at $T = T_c$ is larger than it is in the classical limit ($\frac{3}{2} N k_B$)



At $T = T_c$, C_V has a maximum and a discontinuous derivative. The jump in the derivative can be calculated by expanding around $T = T_c$.
This is done in, e.g., Landau & Lifshitz §62.

The answer is

$$\left.\begin{aligned}\left(\frac{\partial C_V}{\partial T}\right)_{T=T_c-0} &\approx 2.89\,\frac{Nk_B}{T_c}\\ \left(\frac{\partial C_V}{\partial T}\right)_{T=T_c+0} &\approx -0.77\,\frac{Nk_B}{T_c}\end{aligned}\right\}\quad(16)$$

[3rd-order phase transition]

Such is the weird and wonderful quantum world. You'll learn more about it in the 3rd year and also in some homework problems that accompany these lectures.

Enjoy!