The Bose-Einstein Condensate

Under normal conditions, the wave packets that corresponds to individual atoms in a gas are small in size relative to their average spacing. As the temperature is reduced, the average spacing diminishes and ultimately becomes of the same order as the wave packets. If the gas is made of bosons, the particles will all fall into the lowest energy state and their wave packets merge. This is the Bose-Einstein condensate.

In order to be more quantitative, recall the grand-canonical partition function of a ideal (non-interacting) Bose gas:

$$\mathcal{Z} = \prod_{\vec{p}} \frac{1}{1 - z e^{-\beta \varepsilon_{\vec{p}}}} \quad , \quad \varepsilon_{\vec{p}} = \frac{\vec{p}^{\,2}}{2m}$$

where the product is over all modes and $z = e^{\beta\mu}$ is the fugacity. The equations of state are

$$\frac{pV}{k_B T} = \log \mathcal{Z} = - \sum_{\vec{p}} \log(1 - z e^{-\beta \varepsilon_{\vec{p}}})$$

$$N = z \frac{\partial}{\partial z} \log \mathcal{Z} = \sum_{\vec{p}} \frac{z e^{-\beta \varepsilon_{\vec{p}}}}{1 - z e^{-\beta \varepsilon_{\vec{p}}}}$$

Now we would like to let $V \to \infty$ and replace the sum over modes by an integral using

$$\sum_{\vec{p}}' \quad \longrightarrow \quad \frac{V}{h^3} \int d^3\vec{p} \,, \qquad (V \to \infty) .$$

However this prescription is not valid in the case of the Bose gas, because the integrals would diverge at $\vec{p}^{\,2} = 0$ for $z \to 1$. Note that this is not surprising since we expect the particles to condense to the lowest possible state, $\vec{p}^{\,2} = 0$; giving a density $\propto \delta(\vec{p}^{\,2})$. Hence we need to extract the lowest state and write

$$\sum_{\vec{p}}' = \sum_{\vec{p} \neq 0}' + \sum_{\vec{p}=0} \longrightarrow \frac{V}{h^3} \int d^3\vec{p} \; + \sum_{\vec{p}=0}' \qquad (V \to \infty)$$

Doing so we directly obtain the equations of state

$$(\dagger) \quad \frac{P}{k_B T} = -\frac{4\pi}{h^3} \int_0^\infty dp \, p^2 \log\left(1 - z e^{-\beta \frac{p^2}{2m}}\right) - \frac{1}{V} \log(1 - z)$$

$$= \frac{1}{\lambda^3} \, g_{5/2}(z) - \frac{1}{V} \log(1 - z) \,,$$

$$(\ddagger) \quad \frac{1}{v} = \frac{1}{\lambda^3} \, g_{3/2}(z) + \frac{1}{V} \frac{z}{1 - z} \,,$$

λ is the thermal wave length: $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

where $v = \frac{V}{N}$, and $g_s(z) = Li_s(z)$ denotes the polylogarithm

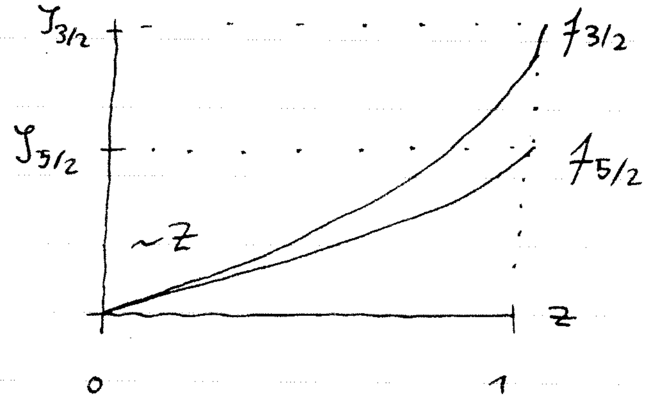
$$g_s(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^s}$$

(This is a generalization of the log since $Li_1(z) = -\log(1-z)$)

The functions $g_{5/2}(z)$ and $g_{3/2}(z)$ are monotonically increasing and we have:

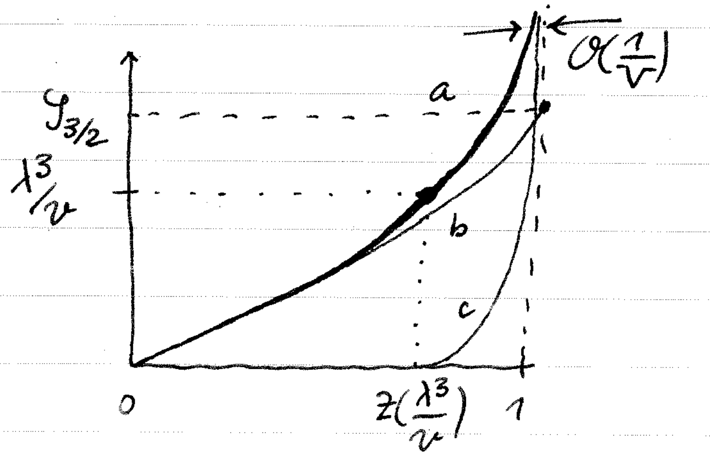
$$g_{5/2}(1) = \zeta_{5/2} = 1.3414\ldots$$

$$g_{3/2}(1) = \zeta_{3/2} = 2.6123\ldots$$



The derivative of $g_{3/2}$ has a pole at $z=1$, but $f_{3/2}$ is finite there. This is a hint that something interesting might happen at $z=1$...

Now we want to obtain z as a function of T and v using the equation of state eq. (‡). We solve graphically (no closed form solution) for $V \gg 1$:

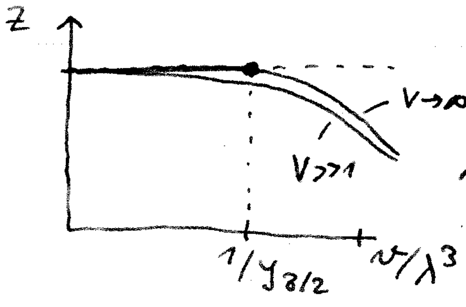


$$a = b + c$$

$$b = g_{3/2}(z), \qquad c = \frac{\lambda^3}{V}\frac{z}{1-z}$$

As we take the limit $V \to \infty$ (for v fixed) we get

$$z = \begin{cases} 1 & \text{if } \frac{\lambda^3}{v} \geq g_{3/2}(1) = \zeta_{3/2} \\ \underbrace{g_{3/2}^{-1}\left(\frac{\lambda^3}{v}\right)}_{\text{numerical method only.}} & \text{if } \frac{\lambda^3}{v} \leq g_{3/2}(1) = \zeta_{3/2} \end{cases}$$



Hence we see that z is discontinuous along the critical line defined by

$$\boxed{\frac{\lambda^3}{v} = g_{3/2}(1)}$$

Interpretation $\lambda^3 \sim v$!

denoting a (first order) phase - transition. When all parameters but one are fixed this defines the critical values

$$\lambda_c^3 = v \cdot g_{3/2}(1) \quad , \quad k_B T_c = \frac{2\pi\hbar^2/m}{[v\, g_{3/2}(1)]^{2/3}} \, , \quad v_c = \frac{\lambda^3}{g_{3/2}(1)} .$$

In terms of T_c and v_c the region of condensation is the region in which $T < T_c$ or $v < v_c$.

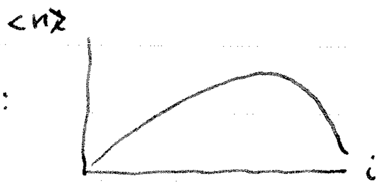
We can now investigate the properties of the Bose - Einstein condensate. First we show that the lowest energy state has a macroscopic occupation :

$$\frac{1}{N}\frac{z}{1-z} = \frac{\langle n_0 \rangle}{N} \overset{(\ddagger)}{=} 1 - \frac{v}{\lambda^3}\, g_{3/2}(z)$$

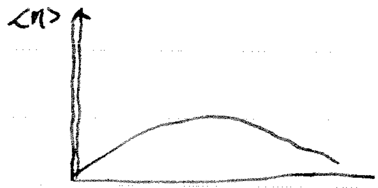
$$= \begin{cases} 0 & \text{if } \frac{\lambda^3}{v} \geq g_{3/2}(1) \\ 1 - \left(\frac{T}{T_c}\right)^{3/2} = 1 - \frac{v}{v_c} \, , & \text{other wise} \end{cases}$$

Hence we see that in the BEC phase a finite fraction of the particles in the system occupy the single level with $\vec{p} = 0$. For $V \to \infty$ this corresponds to a δ function

$N_{tot} = const$:



gas



BEC

At the absolute zero all particles occupy the lowest energy level with $\vec{p} = 0$. For $0 < T < T_c$ the system is in a mixture of the two phases (gaseous & BEC), and for $T > T_c$ only the gaseous phase is present.

We now consider the equation of state ~~for the BEC phase~~. It is given by eq. (+) such that

$$\frac{p}{k_B T} = \begin{cases} \frac{1}{\lambda^3}\, g_{5/2}(z) & v > v_c \\ \frac{1}{\lambda^3}\, g_{5/2}(1) & v < v_c \end{cases}$$

as $V \to \infty$. Using this we can compute the compressibility. Using

$$\frac{\partial v}{\partial z} \overset{(\ddagger)}{=} -\lambda^3 \frac{g'_{3/2}(z)}{\left(g_{3/2}(z)\right)^2}$$

and

$$\frac{\partial p}{\partial v} \overset{(+)}{=} \frac{k_B T}{\lambda^3}\, g'_{5/2}(z)\, \frac{\partial z}{\partial v}$$

such that the compressibility is given by

$$K_T = \frac{1}{v}\frac{\partial v}{\partial p} = \frac{1}{v}\, \frac{\lambda^6}{k_B T \left(g_{3/2}(z)\right)^2} \cdot \frac{g'_{3/2}(z)}{g'_{5/2}(z)} .$$

The compressibility diverges at the phase transition $T \to T_c$, since the derivative $g'_{3/2}(z) \to \infty$ as $z \to 1$. In the BEC phase the pressure p in independent of v and we must have $K_T = \infty$ there. The BEC is actually infinitely compressible, i.e. it does not resist to compression!

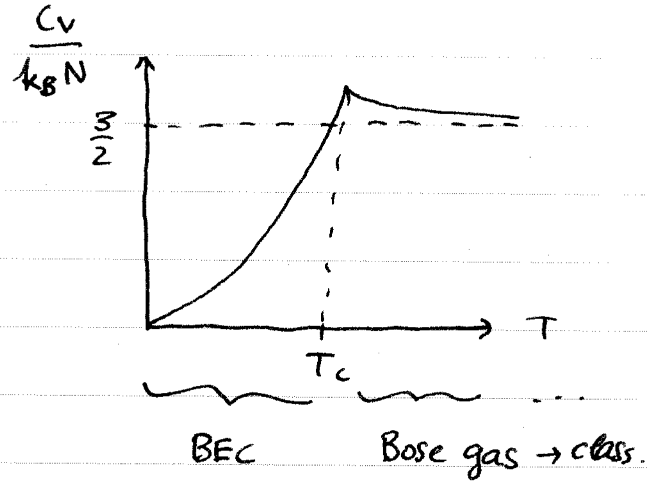
(3.62) in the script.

The heat capacity can be obtained from the internal energy $U = \frac{3}{2} pV = \frac{3}{2} N k_B T v \, g_{5/2}(z) / \lambda^3$:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \begin{cases} N k_B \left(\frac{15 v}{4\lambda^3} g_{5/2}(z) - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} \right), & T > T_c \\ N k_B \left(\frac{15}{4} \frac{g_{5/2}(1)}{g_{3/2}(1)} \right) \left(\frac{T}{T_c} \right)^{3/2}, & T < T_c \end{cases}$$

$$\left(= \frac{\partial U}{\partial z} \frac{\partial z}{\partial T} \right)$$

The heat capacity has a cusp at T_c, typical of first order phase transitions, and reproduce the classical result $C_V = \frac{3}{2} k_B N$ in the high temp. limit.



The entropy can be computed as

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = \left(\frac{\partial pV}{\partial T}\right)_{V,\mu} = \begin{cases} N k_B \left(\frac{5 v}{2\lambda^3} g_{5/2}(z) - \log(z) \right) \\ N k_B \frac{5}{2} \frac{g_{5/2}(1)}{g_{3/2}(1)} \left(\frac{T}{T_c} \right)^{3/2} \end{cases}$$

In accordance with the 3rd law of thermodynamics the entropy and the heat capacity go to zero as $T \to 0$.

The transition line in the p-T diagram is given by the equation (vapor pressure)

$$p_c(T) = \frac{k_B T}{\lambda^3} g_{5/2}(1)$$

$$\propto T^{5/2}$$

such that the Clausius-Clapeyron equation reads

$$\frac{d p_c(T)}{dT} = \frac{5}{2} \frac{k_B\, g_{5/2}(1)}{\lambda^3}$$

$$= \frac{1}{T v_c} \left[\frac{5}{2} k_B T \frac{g_{5/2}(1)}{g_{3/2}(1)} \right] = \frac{L}{T \Delta V}$$

and thus we see that the latent heat per particle must must be

$$L = \frac{g_{5/2}(1)}{g_{3/2}(1)} \cdot \frac{5}{2} k_B T$$

since the BEC phase has specific volume $v = 0$ such that $\Delta v = v_c$. This proves that Bose-Einstein condensation is a first order phase-transition!

<u>Final note</u>: Solving eq. (‡) for z was equivalent to fixing the number of particles N. Actually BEC occurs only if the particle number is conserved. For example: photons do <u>not</u> condense!