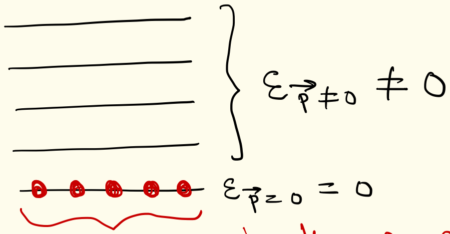
Bose-Einstein Condensation

Consider bosons with single-particle levels $\varepsilon_{\vec{p}} = \frac{\vec{p}^{\,2}}{2m}$. The ground state is clearly obtained by putting all bosons in the single particle level corresponding to $\vec{p} = 0$.



At $T=0$, all bosons in the zero energy single-particle level.

What happens as the temperature becomes non-zero? Does the number of bosons in the ground state continue to scale as N, the total number of bosons?

To answer this, we need to determine the dependence of the chemical potential μ on the temperature T.

First consider $T=0$. Since all particles are in the state $\varepsilon_{\vec{p}=0} = 0$,

$$N = \lim_{\beta \to \infty} \frac{1}{e^{-\beta\mu} - 1}$$

This is a strange looking equation. The RHS is large $\propto N$. For LHS to match up, we must have $e^{-\beta\mu} \approx 1$. More precisely,

$$e^{-\beta\mu} - 1 = \frac{1}{N}$$

$$\Rightarrow \quad \beta\mu = -\log\left[1 + \frac{1}{N}\right] \approx -\frac{1}{N} \quad (N \gg 1)$$

$$\Rightarrow \quad \mu = -\frac{T}{N} \quad \text{as } T \to 0$$

Thus, μ is negative and essentially zero.

What happens at a non-zero T? Denoting the number of bosons in the ground state by N_0, the particle number conservation dictates:

$$N = N_0 + \underbrace{\sum_{\varepsilon_{\vec{p}} \neq 0} n_{\vec{p}}}_{N_{\text{excited}}}$$

Let's determine the second term above:

$$N_{excited} = \frac{V}{(2\pi)^3} \int \frac{d^3 k}{e^{\beta(\hbar^2 k^2/2m - \mu)} - 1}$$

One clearly requires that $\mu < 0$ so that

$$n_{\vec{k}} = \frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} - 1} > 0 \quad \text{for } \vec{k} \approx 0 .$$

Without knowing anything else about μ,

$$N_{excited}(\mu) \leq N_{excited}(\mu = 0)$$

$$= V\, 2\pi \left[\frac{2m}{\hbar^2}\right]^{3/2} T^{3/2} \int_0^\infty \frac{x^{1/2}\, dx}{e^x - 1}$$

The most crucial point is that the integral $\int_0^\infty \frac{x^{1/2}\, dx}{e^x - 1}$ <u>converges</u>. Therefore if

$$\frac{N}{V} \gtrsim 2\pi \left[\frac{2m}{\hbar^2}\right]^{3/2} T^{3/2} \underbrace{\Gamma(3/2)\zeta(3/2)}_{\text{value of the above integral}}$$

then $N_0 \neq 0$ and is proportional to N.
Thus at large densities (i.e. $\rho \gtrsim \left[\frac{2m}{\hbar^2}\right]^{3/2} T^{3/2}$) a macroscopic number of particles continue to occupy the ground state. This is Bose-Einstein condensation.

An aside on integrals of the form

$$\int_0^\infty dx \, \frac{x^n}{e^x - 1} :$$

$$\int_0^\infty dx \, \frac{x^n}{e^x - 1} = \int_0^\infty dx \, \frac{e^{-x} \, x^n}{\left[1 - e^{-x}\right]}$$

$$= \sum_{m=0}^{\infty} \int_0^\infty e^{-x} \, x^n \, e^{-mx} \, dx$$

$$= \sum_{m=0}^{\infty} \int_0^\infty x^n \, e^{-(m+1)x} \, dx$$

$$= \sum_{m=0}^{\infty} \frac{\Gamma(n+1)}{(m+1)^{n+1}}$$

$$= \Gamma(n+1) \, \zeta(n+1)$$

One direct consequence of BEC is that the chemical potential continues to remain zero as long as the above relation between density and temperature is satisfied. This is because to satisfy the equation.

$$N_0 = \underset{\substack{\downarrow \\ \text{fraction of} \\ \text{total particles in} \\ \vec{p}=0 \text{ state}}}{\alpha} N = \frac{1}{e^{-\beta\mu} - 1}$$

one necessarily requires

$$\mu \approx \frac{-T}{\alpha N} = 0 \quad \text{as } N \to \infty$$

for non-zero α.

Clearly, $\frac{N_0}{N} \to 0$ as

$$\frac{N}{V} \to 2\pi \left[\frac{2m}{h^2}\right]^{3/2} T^{3/2} \underset{\sqrt{\pi}/2}{\overset{}{\Gamma(3/2)}} \underset{2.612}{\zeta(3/2)}$$

$$\Gamma(3/2) = \sqrt{\pi}/2, \quad \zeta(3/2) = 2.612$$

Therefore, at the critical temperature T_c,

$$\frac{N}{V} = 2\pi \left[\frac{2m}{h^2}\right]^{3/2} T_c^{3/2} \frac{\sqrt{\pi}}{2}\, 2.612$$

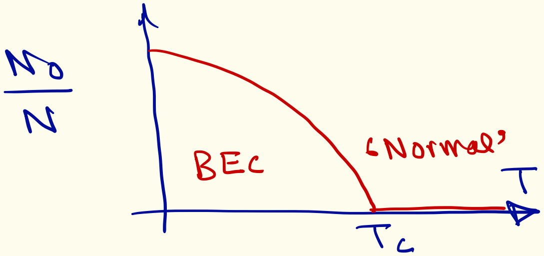
or,

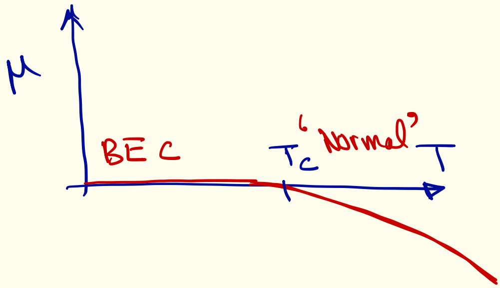
$$\boxed{n \lambda_{T_c}^3 = 2.612}$$

where $\lambda_T = \sqrt{\frac{h^2}{2\pi m T}} = \sqrt{\frac{2\pi}{mT}}$ if we set $\hbar = 1$

Thus, for $T < T_c$, $\mu = 0$ and $\frac{N_0}{N} \neq 0$

while for $T > T_c$, $\mu < 0$ and $\frac{N_0}{N} = 0$





This is an example of a thermodynamic <u>phase transition</u>: thermodynamic quantities such as chemical potential and specific heat are singular functions of the temperature.

Let's calculate properties below T_c and in the vicinity of T_c.

Thermodynamics below T_c (i.e. in the BEC phase):

Since $\mu = 0$ (in the thermodynamic limit) below T_c, the grand partition fn is given by:

$$Q = \prod_{\vec{k}} \left[\frac{1}{1 - e^{-\beta k^2/2m}} \right]$$

$$\Rightarrow \quad -\beta F = -\sum_{\vec{k}} \log \left[1 - e^{-\beta k^2/2m} \right]$$

$$\Rightarrow \quad F = \frac{TV}{8\pi^3} \int_0^\infty 4\pi k^2 \log \left[1 - e^{-\beta k^2/2m} \right] dk$$

Integrating by parts,

$$F = \frac{TV}{2\pi^2} \left\{ \left[\frac{k^3}{3} \log \left[1 - e^{-\beta k^2/2m} \right] \right]_0^\infty \right\} \text{this is zero}$$

$$- \int \frac{k^3 \, e^{-\beta k^2/2m}}{3 \left[1 - e^{-\beta k^2/2m} \right]} \times \frac{+2\beta k}{2m} \, dk \Bigg\}$$

$$= -\frac{V}{6\pi^2 m} \int \frac{k^4 \, dk}{\left[e^{\beta k^2/2m} - 1 \right]}$$

$$= -\frac{V}{6\pi^2 m} \left[\frac{2mT}{2} \right]^{5/2} \int_0^\infty \frac{x^{3/2} \, dx}{e^x - 1} \qquad \left[x = \frac{\beta k^2}{2m} \right]$$

$$= -\frac{cVT}{\lambda_T^3} \quad \text{where } c \text{ is a positive number.}$$

$$\Rightarrow \quad S = -\left.\frac{dF}{dT}\right|_{V,N}$$

$$= \frac{5}{2} c \frac{V}{\lambda^3_T}$$

$$E = F + TS$$

$$= \frac{3}{2} \frac{c V T}{\lambda^3_T} \quad \left(= -\frac{3}{2} F\right)$$

Pressure $P = -\left.\frac{dF}{dV}\right|_N = \frac{cT}{\lambda^3_T} = \frac{2E}{3V}$

$$\Rightarrow \quad \boxed{PV = \frac{2}{3}E}$$

Note that the pressure $P = \frac{cT}{\lambda^3_T}$ is independent of the volume! $\Rightarrow$ compressibility $= -\frac{dV}{dP}$ is infinite.

Specific heat $C_V = \left.\frac{dE}{dT}\right|_V$

$$= \frac{3}{2} \times \frac{5}{2} \frac{cV}{\lambda^3_T} = \frac{15}{4} \frac{cV}{\lambda^3_T}$$

$$\sim T^{3/2}$$

Correlations in the BEC phase :

The Hamiltonian of non-interacting bosons may be written as $H = \sum_p \left[\frac{p^2}{2m} a^+_p a_p\right]$ where a^+_p creates a boson in the single particle level $|\vec{p}\rangle$.

The correlation f^n $\langle a^+(r)\, a(r')\rangle_\beta = \frac{\mathrm{Tr}\, e^{-\beta H} a^+(r)\, a(r')}{\mathrm{Tr}\, e^{-\beta H}}$

is interesting to calculate since it has a definitive signature of the BEC.

Note that $a^+(\vec{r})\,\underset{\text{no particles}}{|0\rangle} = |\vec{r}\rangle = \sum_{\vec{k}} \langle \vec{k}|\vec{r}\rangle |\vec{k}\rangle$

$$= \sum_{\vec{k}} \langle k|\vec{r}\rangle a^+(\vec{k})|0\rangle$$

$$\sum_{\vec{k}} \frac{e^{-i\vec{k}\cdot\vec{r}}}{\sqrt{V}} a^+(\vec{k})|0\rangle$$

$$\Rightarrow a^+(\vec{r}) = \sum_{k} \frac{a^+(\vec{k})\, e^{-i\vec{k}\cdot\vec{r}}}{\sqrt{V}}$$

$$\Rightarrow \langle a^+(\vec{r})\, a(\vec{r}')\rangle_\beta$$

$$= \sum_{\vec{k}\vec{k}'} \frac{\langle a^+(\vec{k})\, a(\vec{k}')\rangle}{V} e^{+i\vec{k}'\cdot\vec{r}' - i\vec{k}\cdot\vec{r}}$$

$$= \underbrace{\frac{1}{(2\pi)^3} \sum_{kk'} \frac{\delta_{kk'}\, e^{+i\vec{k}'\cdot\vec{r}' - i\vec{k}\cdot\vec{r}}}{e^{\beta[k^2/2m]} - 1}}_{\text{contribution from } \vec{k} \neq \vec{0}} + \underbrace{\frac{N_0}{V}}_{\text{Contribution from } \vec{k} = \vec{0}}$$

$$= \frac{N_0}{V} + \frac{1}{(2\pi)^3} \int \frac{d^3k \; e^{i\vec{k}\cdot(\vec{r}\,'-\vec{r})}}{e^{\beta k^2/2m} - 1}$$

When $|r'-r| \gg$ thermal length, most of the contribution comes from $k \ll \sqrt{2mT}$

$\Rightarrow \langle a^+(\vec{r})\, a(\vec{r}\,')\rangle$

$$\simeq \frac{N_0}{V} + \frac{1}{(2\pi)^3} \int \frac{d^3k \; e^{i\vec{k}\cdot(\vec{r}\,'-\vec{r})}\, 2m}{\beta k^2}$$

$$\simeq \frac{N_0}{V} + \frac{2mc}{\beta} \frac{1}{|r'-r|}$$

where $c > 0$ is a constant.

$\Rightarrow \langle a^+(r)\, a(r')\rangle \neq 0$ as $|r'-r| \to \infty$

and the spatial dependence is power-law (and not exponential).

These are signatures of "spontaneous symmetry breaking" which we will discuss in much more detail in the context of Ising models.

Thermodynamics in the vicinity of T_c, just above T_c.

As temperature becomes slightly larger than T_c, chemical potential becomes non-zero. Therefore, μ is a singular f^n of $T-T_c$. To find $\mu(T)$, let's recall the equation for total particle number,

$$\frac{N}{V} = 2\pi\left[\frac{2m}{h^2}\right]^{3/2} T^{3/2}\int_0^\infty \frac{x^{1/2}\,dx}{e^x e^{-\beta\mu} - 1}$$

One finds that (see schematic argument below)

This is exact asymptotically.

$$\int_0^\infty \frac{x^{1/2}\,dx}{e^x e^{-\beta\mu} - 1} = \zeta(3/2)\,\Gamma(3/2) + \Gamma(3/2)\,\Gamma(-1/2)\,(\beta|\mu|)^{1/2} + O(\mu)$$

Thus for small μ, this integral differs from it's $\mu=0$ value by $O(\sqrt{|\mu|})$. Also note that $\Gamma(-1/2) = -2\sqrt{\pi} < 0$

$$\Rightarrow \quad \frac{1}{\lambda_c^{3/2}} = \frac{1}{\lambda^3}\left[1 - c\sqrt{\beta|\mu|}\right]$$

where $c > 0$

$$\Rightarrow \quad |\mu| \sim [T - T_c]^2 / T_c$$

$$\Rightarrow \quad \boxed{\mu \sim -\frac{[T-T_c]^2}{T_c}}$$

Argument for μ dependence of $\displaystyle\int_0^\infty \frac{\sqrt{x}}{e^x e^{-\beta\mu}-1}$

for small μ:

$e^{-\beta\mu} > 1$ Let's denote $e^{-\beta\mu} = e^{\varepsilon}$ ($\varepsilon>0$ and small)

$$\int_0^\infty \frac{\sqrt{x}\,dx}{e^x e^{\varepsilon}-1} = \int_\varepsilon^\infty \frac{\sqrt{x-\varepsilon}\,dx}{e^x-1}$$ (change of variables)

But $$\int_\varepsilon^\infty \frac{\sqrt{x-\varepsilon}\,dx}{e^x-1} = \int_\varepsilon^\infty \frac{\sqrt{x}\left[1-\frac{\varepsilon}{x}\right]^{1/2}dx}{e^x-1}$$

$$= \int_\varepsilon^\infty \frac{\sqrt{x}\left[1-\frac{\varepsilon}{2x}+\cdots\right]dx}{e^x-1}$$

$$= \int_\varepsilon^\infty \frac{\sqrt{x}\,dx}{e^x-1} + O(\varepsilon)$$

Note that the integral multiplying $O(\varepsilon)$ and higher order terms are all convergent due to the limits on integral. (recall $\varepsilon>0$).

$$\Rightarrow \int_0^\infty \frac{\sqrt{x}\,dx}{e^x e^{\varepsilon}-1} - \int_0^\infty \frac{\sqrt{x}\,dx}{e^x-1}$$

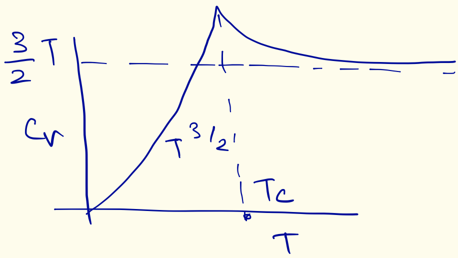
$$= -\int_0^\varepsilon \frac{\sqrt{x}\,dx}{e^x-1} + O(\varepsilon) \simeq -\int_0^\varepsilon \frac{dx}{\sqrt{x}} + O(\varepsilon)$$

Taylor expansion of $\frac{\sqrt{x}}{e^x-1}$.

$$= -2\sqrt{\varepsilon} + O(\varepsilon)$$

$$\Rightarrow \int_0^\infty \frac{\sqrt{x}}{e^x e^{\varepsilon}-1} = \int_0^\infty \frac{\sqrt{x}}{e^x-1} - c\sqrt{\varepsilon} \quad \text{where } c>0.$$

Using T-dependence of μ, one finds a cusp singularity of the specific heat at T_c:



Correlations above T_c:

$$\langle a^+(r)\, a(r')\rangle = \frac{1}{(2\pi)^3}\int \frac{e^{i\vec{k}\cdot(\vec{r}'-\vec{r})}\, d^3k}{e^{\beta k^2/2m}\, e^{-\beta\mu} - 1}$$

Expanding for small $\beta\mu$ and small $\vec{k}$

$$\approx \frac{1}{(2\pi)^3}\int \frac{e^{ik\cdot(\vec{r}'-\vec{r})}\, d^3k}{\left[1+\frac{\beta k^2}{2m}\right]\left[1-\beta\mu\right]-1}$$

$$\approx \frac{1}{(2\pi)^3}\int \frac{e^{ik\cdot(r'-r)}\, d^3k}{\frac{\beta}{2m}\left[k^2 + |\mu|\, 2m\right]}$$

$$\sim \frac{2m}{\beta}\, \frac{e^{-|\vec{r}-\vec{r}'|/\xi}}{|r-r'|} \quad \text{where } \xi \sim \frac{1}{2m|\mu|}$$