<u>pressure</u> – separate out ground state from sum as we saw we needed to do in computing N/V

$$\frac{p}{k_BT} = \frac{1}{V}\ln\mathcal{Z} = -\frac{1}{V}\sum_{\vec{k}} \ln\left(1 - z e^{-\beta\epsilon(\vec{k})}\right)$$

$$\simeq -\frac{1}{V}\ln(1-z) - \frac{4\pi}{(2\pi)^3}\int_0^\infty dk\, k^2 \ln\left(1 - z e^{-\beta\hbar^2k^2/2m}\right)$$

$\uparrow$ $\vec{k}=0$ ground state — $\uparrow$ all other $|\vec{k}|>0$ states

$$= \frac{1}{V}\ln\left(\frac{1}{1-z}\right) + \frac{g_{5/2}(z)}{\lambda^3} \qquad \lambda = \left(\frac{h^2}{2\pi m k_BT}\right)^{1/2}$$

where $g_{5/2}(z) \equiv \dfrac{1}{\Gamma(5/2)}\displaystyle\int_0^\infty dy \frac{y^{3/2}}{z^{-1}e^y - 1}$ as derived when we began our discussion of quantum gases

also recall the number of bosons occupying the ground state is

$$n(0) = \frac{1}{z^{-1}e^{\beta\epsilon(0)} - 1} = \frac{1}{z^{-1}-1} = \frac{z}{1-z}$$

So $\quad n(0)+1 = \dfrac{z}{1-z} + 1 = \dfrac{1}{1-z}$

$$\frac{p}{k_BT} = \frac{\ln(n(0)+1)}{V} + \frac{g_{5/2}(z)}{\lambda^3}$$

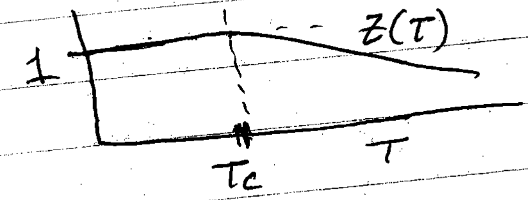
In the thermodynamic limit of $V\to\infty$, the first term always vanishes as $n(0) \leq N = nV$ and $\lim\limits_{V\to\infty}\left[\dfrac{\ln(nV)}{V}\right] = 0$

So the condensate does not contribute to the pressure. This is not surprising as particles in the condensate have $\vec{k}=0$ and hence carry no momentum. In the kinetic theory of gases, one sees that pressure arises from particles with finite momenta $|\vec{p}|>0$ ~~[illegible]~~ hitting the walls of the container

So $\frac{p}{k_B T} = \frac{g_{5/2}(z)}{\lambda^3} = g_{5/2}(z)\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

$p = g_{5/2}(z(T))\left(\frac{2\pi m}{h^2}\right)^{3/2}(k_B T)^{5/2}$ ← equation of state

for a system of fixed density n, z must be chosen to be a function of T that gives the desired density n.

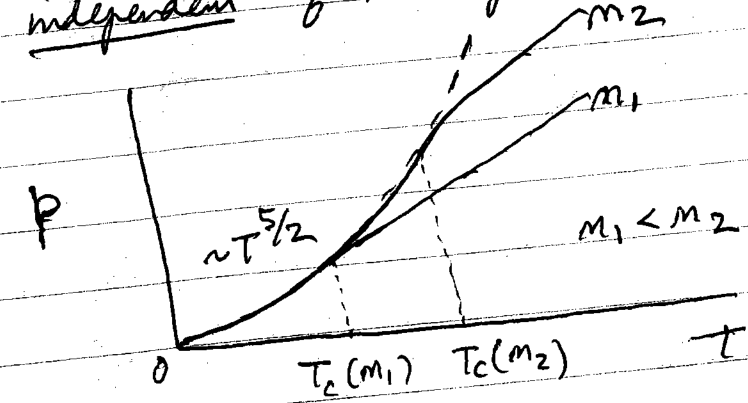


Note $g_{5/2}(z=1) = \zeta(5/2) = 1.342$ is finite

In thermodynamic limit of $V \to \infty$, $z=1$ for $T \leq T_c(n)$ ← critical temperature depends on the system's fixed density

$\Rightarrow p = g_{5/2}(1)\left(\frac{2\pi m}{h^2}\right)^{3/2}(k_B T)^{5/2}$ for $T \leq T_c$

Note: for $T \leq T_c$, the pressure $p \propto T^{5/2}$ is independent of the system density!



p vs T curves at constant density n

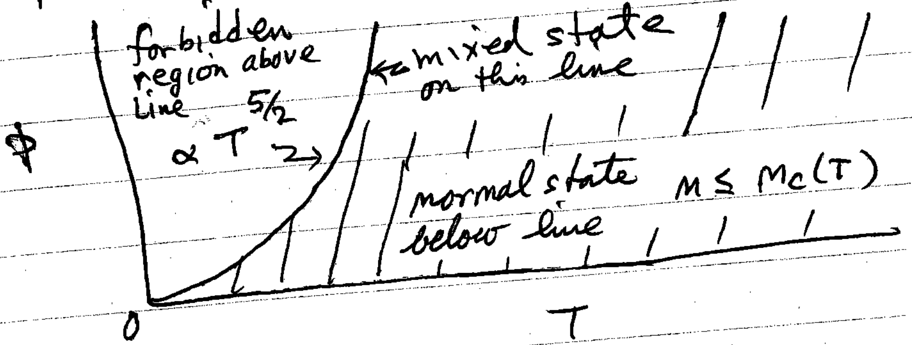
recall $T_c(n) \sim n^{2/3}$

$T_c(n) = \left(\frac{n}{2.16}\right)^{2/3}\frac{h^2}{2\pi m k_B}$

Define $n_c(T) = 2.612\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$ inverse of $T_c(n)$

$n_c(T)$ is the critical density at a given T
— a system with $n \geq n_c(T)$ will be in a bose condensed mixed state at temperature T.

phase diagram in p–T plane



Can also consider the transition in terms of p and $v = \frac{V}{N} = \frac{1}{n}$ for various fixed T.

At the transition $p \propto T_c(n)^{5/2}$, $T_c(n) \propto n^{2/3}$

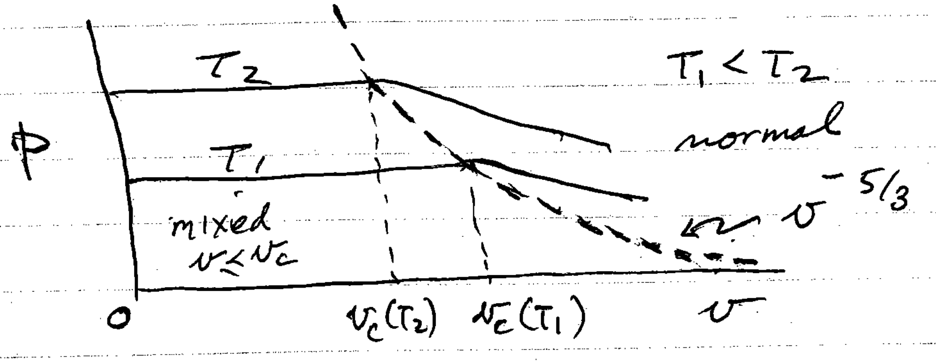
$\Rightarrow$ at the transition $p \propto (n^{2/3})^{5/2} = n^{5/3} = v^{-5/3}$

below the transition p is independent of density and hence independent of v.

For fixed T, the transition occurs when density n exceeds $n_c(T)$, or when v drops below $v_c(T) = \frac{1}{n_c}$

$v_c(T) \sim T^{-3/2}$

curves of p vs v at constant T



Thermodynamic functions

Earlier we found $\frac{E}{V} = \frac{3}{2} p$

$$\Rightarrow \frac{E}{N} = \frac{3}{2} p \frac{V}{N} = \frac{3}{2} p v = \frac{3}{2} \frac{k_B T v}{\lambda^3} g_{5/2}(z)$$

$z = 1$ in mixed state
$z < 1$ in normal state

In above we regard $\frac{E}{N}$ as a function of either v or z. That is we either determine v for a given z, T or we determine z needed for a given v, T (Recall $z = e^{\beta\mu}$, $v = \frac{V}{N}$ and N and μ are conjugate variables)

specific heat

$$\frac{C_V}{N k_B} = \frac{1}{k_B}\left(\frac{\partial (E/N)}{\partial T}\right)_{V,N} = \frac{3}{2} v \left\{ \frac{d}{dT}\left(\frac{T}{\lambda^3}\right) g_{5/2}(z) + \frac{T}{\lambda^3} \frac{\partial g_{5/2}(z)}{\partial z} \frac{dz}{dT} \right.$$

For $T \leq T_c$, $z = 1$ so $\frac{dz}{dT} = 0$ and only 1st term remains

$\frac{T}{\lambda^3} \propto T^{5/2}$ so $\frac{d}{dT}\left(\frac{T}{\lambda^3}\right) = \frac{5}{2}\left(\frac{T}{\lambda^3}\right)\frac{1}{T} = \frac{5}{2}\frac{1}{\lambda^3}$

z=1 here for all $T \leq T_c$

$$\Rightarrow \frac{C_V}{Nk_B} = \frac{3}{2} v \left(\frac{5}{2}\frac{1}{\lambda^3}\right) g_{5/2}(1) = \frac{15}{4} g_{5/2}(1) \frac{v}{\lambda^3}$$

$$= \frac{15}{4} g_{5/2}(1)\, v \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

Note, at T_c, $n = \frac{g_{3/2}(1)}{\lambda_c^3}$, and $v = \frac{1}{n}$

$$\frac{C_V(T_c^-)}{Nk_B} = \frac{15}{4}\frac{g_{5/2}(1)}{g_{3/2}(1)} = \frac{15}{4}\frac{1.341}{2.612} = 1.925$$

this is larger than the classical ideal gas value of $\frac{3}{2}$

So $$\boxed{\frac{C_V}{Nk_B} = 1.925 \left(\frac{T}{T_c}\right)^{3/2} \qquad T \leq T_c}$$

For $T \geq T_c$, z varies with T and we need to evaluate the 2nd term as well

here z depends on T for $T > T_c$

1st term gives $\frac{15}{4} g_{5/2}(z(T)) \frac{v}{\lambda^3}$

2nd term: from Pathria Appendix D Eq(10),

$$z \frac{d}{dz}[g_\nu(z)] = g_{\nu-1}(z)$$

$$\Rightarrow \frac{d g_{5/2}}{dz}\frac{dz}{dT} = g_{3/2}\frac{1}{z}\frac{dz}{dT}$$

To find $\frac{1}{z}\frac{dz}{dT}$ consider our earlier result for the density when $T > T_c$:

$$n = \frac{g_{3/2}(z)}{\lambda^3} \quad \leftarrow \text{determines } z(T) \text{ for fixed } n$$

for n fixed $\Rightarrow$ $0 = \frac{dn}{dT} = \frac{d}{dT}\left(\frac{1}{\lambda^3}\right) g_{3/2} + \frac{1}{\lambda^3}\frac{dg_{3/2}}{dz}\frac{dz}{dT}$

$$0 = \frac{3}{2}\frac{1}{\lambda^3 T} g_{3/2} + \frac{1}{\lambda^3} g_{1/2} \frac{1}{z}\frac{dz}{dT}$$

$$\Rightarrow \frac{1}{z}\frac{dz}{dT} = -\frac{3}{2}\frac{g_{3/2}}{g_{1/2}}\frac{1}{T}$$

$$\frac{C_V}{Nk_B} = \frac{15}{4} g_{5/2}(z)\frac{v}{\lambda^3} + \frac{3}{2} v \frac{T}{\lambda^3} g_{3/2}(z)\left(-\frac{3}{2}\right)\frac{g_{3/2}(z)}{g_{1/2}(z)}\frac{1}{T}$$

use $n = \frac{1}{v} = \frac{g_{3/2}(z)}{\lambda^3} \Rightarrow \frac{v}{\lambda^3} = \frac{1}{g_{3/2}(z)}$

$$\boxed{\frac{C_V}{Nk_B} = \frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)} \qquad T > T_c}$$

Note $g_{1/2}(1) = \sum_{l=1}^{\infty} \frac{1}{l^{1/2}} \to \infty$

So as $T \to T_c^+$ from above, and $z \to 1$

$$\frac{C_V(T_c^+)}{Nk_B} = \frac{15}{4}\frac{g_{5/2}(1)}{g_{3/2}(1)} - \frac{9}{4}\frac{g_{3/2}(1)}{\infty} = \frac{15}{4}\frac{1.341}{2.612} = 1.925$$

$\Rightarrow$ $\boxed{C_V \text{ is continuous at } T_c}$

Finally we want to show that although C_V is continuous at T_c, $\frac{dC_V}{dT}$ is discontinuous

For $T \le T_c$

$$\frac{C_V}{Nk_B} = 1.925\left(\frac{T}{T_c}\right)^{3/2}$$

$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{3}{2}(1.925)\left(\frac{T}{T_c}\right)^{1/2}\frac{1}{T_c} = 2.89\left(\frac{T}{T_c}\right)^{1/2}\frac{1}{T_c}$$

so slope at T_c^- (just below T_c)

is: $$\boxed{\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{2.89}{T_c}, \quad T = T_c^-}$$

For $T > T_c$

$$\frac{C_V}{Nk_B} = \frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}$$

$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{15}{4}\,\frac{g_{3/2}\frac{dg_{5/2}}{dz}\frac{dz}{dT} - g_{5/2}\frac{dg_{3/2}}{dz}\frac{dz}{dT}}{(g_{3/2}(z))^2}$$

$$-\frac{9}{4}\,\frac{g_{1/2}\frac{dg_{3/2}}{dz}\frac{dz}{dT} - g_{3/2}\frac{dg_{1/2}}{dz}\frac{dz}{dT}}{(g_{1/2})^2}$$

$$= \frac{1}{z}\frac{dz}{dT}\left\{\frac{15}{4}\left(\frac{g_{3/2}^2 - g_{5/2}g_{1/2}}{g_{3/2}^2}\right) - \frac{9}{4}\left(\frac{g_{1/2}^2 - g_{3/2}g_{-1/2}}{g_{1/2}^2}\right)\right\}$$

use $\frac{1}{z}\frac{dz}{dT} = -\frac{3}{2}\frac{g_{3/2}}{g_{1/2}}\frac{1}{T}$ as found earlier

$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = -\frac{3}{8T}\frac{g_{3/2}}{g_{1/2}}\left\{15\left(1-\frac{g_{5/2}\,g_{1/2}}{g_{3/2}^2}\right)-9\left(1-\frac{g_{3/2}\,g_{-1/2}}{g_{1/2}^2}\right)\right\}$$

Now as $T \to T_c^+$ from above, $z \to 1$, we have $g_{5/2}(1)$ and $g_{3/2}(1)$ are finite, but $g_{1/2}(1)$ and $g_{-1/2}(1) \longrightarrow \infty$

$\Rightarrow$ at T_c^+

$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{45}{8T_c}\frac{g_{5/2}(1)}{g_{3/2}(1)} - \frac{27}{8T_c}\,g_{3/2}^2(1)\,\frac{g_{-1/2}(1)}{g_{1/2}^3(1)}$$

Now from Pathria Appendix D Eq (8)

$$g_\nu(1) = \lim_{a\to 0}\frac{\Gamma(1-\nu)}{a^{1-\nu}}$$

So
$$\frac{g_{-1/2}(1)}{g_{1/2}^3(1)} = \lim_{a\to 0}\frac{\Gamma(3/2)}{a^{3/2}}\left(\frac{a^{1/2}}{\Gamma(1/2)}\right)^3 = \frac{\Gamma(3/2)}{[\Gamma(1/2)]^3}$$

$$= \frac{\frac{1}{2}\pi^{1/2}}{\pi^{3/2}} = \frac{1}{2\pi} \quad \text{since } \Gamma(\tfrac{1}{2}) = \sqrt{\pi},\ \Gamma(\tfrac{3}{2}) = \tfrac{1}{2}\sqrt{\pi}$$

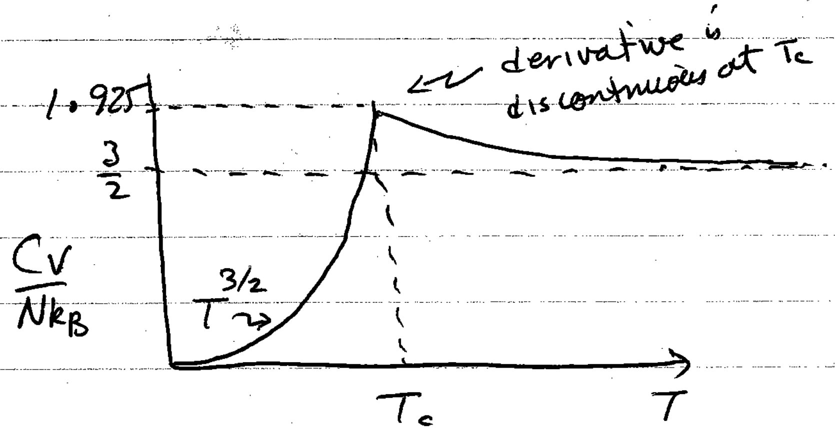
$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{45}{8}\,\frac{1.341}{2.612}\,\frac{1}{T_c} - \frac{27}{8}\,\frac{(2.612)^2}{2\pi}\,\frac{1}{T_c}$$

$$= \frac{2.89}{T_c} - \frac{3.66}{T_c} = -\frac{0.77}{T_c}$$

$$\boxed{\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{-0.77}{T_c}, \quad T = T_c^+}$$

slope of C_V is discontinuous at T_c.

C_V has a cusp at T_c



$\frac{dC_V}{dT} > 0$ for $T = T_c^-$

$\frac{dC_V}{dT} < 0$ for $T = T_c^+$

<u>Entropy</u>

For single species gas we had for Gibbs free energy

$$G = N\mu$$

Also $G = E - TS + pV$ (since G is Legendre transform from E with respect to S and V)

$$\Rightarrow N\mu = E - TS + pV$$

or $$S = \frac{E + pV - N\mu}{T}$$

$$\frac{S}{Nk_B} = \frac{E + pV}{Nk_B T} - \frac{\mu}{k_B T}$$

we had earlier $E = \frac{3}{2} pV \Rightarrow pV = \frac{2}{3} E$

$$\frac{S}{Nk_B} = \frac{5}{3} \frac{E}{N} \frac{1}{k_B T} - \frac{\mu}{k_B T}$$

$$z = e^{\mu/k_BT} \quad , \quad z = 1 \quad \text{for } T < T_c$$

we had earlier $\frac{E}{N} = \frac{3}{2} \frac{k_BT\, v}{\lambda^3} g_{5/2}(z)$

and $n = \frac{1}{v} = \frac{g_{3/2}(z)}{\lambda^3}$ for $T > T_c$

$$\Rightarrow \frac{S}{Nk_B} = \frac{5}{2} \frac{v}{\lambda^3} g_{5/2}(z) - \ln z = \begin{cases} \frac{5}{2} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \ln z &, T > T_c \\ \frac{5}{2} \frac{v}{\lambda^3} g_{5/2}(1) &, T \leq T_c \end{cases}$$

Note: For $T \leq T_c$ we had ~~that the density of the "normal"~~ a density $n_0 = n - \frac{g_{3/2}(1)}{\lambda^3}$ in the condensate, and a density $\frac{g_{3/2}(1)}{\lambda^3} \equiv n_n$ in the "normal" state (ie the density of excited particles)

$\Rightarrow$ for $T \leq T_c$, $\frac{S}{Nk_B} = \frac{5}{2}\left(\frac{n_n}{n}\right) \frac{g_{5/2}(1)}{g_{3/2}(1)} \rightarrow 0$ as $T \to 0$

we can imagine that each normal particle carries entropy $\frac{5}{2} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)}$. The entropy per particle at $T < T_c$ is just the ~~fixed~~ above entropy per "normal" particle times the fraction of normal particles.

$\Rightarrow$ normal particles carry the entropy
condensate has zero entropy

entropy difference per particle between normal state and condensed state is $\frac{\Delta S}{N} = \frac{5}{2} k_B\, g_{5/2}(1) / g_{3/2}(1)$

latent heat of condensation

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

energy released upon converting one normal particle to one condensate particle.

$\Rightarrow$ mixed phase is like coexistence region of a 1st order phase transition (like water $\Leftrightarrow$ ice – need to remove energy to turn water to ice)

$\Rightarrow$ "two fluid" model of mixed region

Bose-Einstein Condensation in laser cooled gases

gases of alkali atoms Li, Na, K, Rb, Cs

- all have a single s-electron in outermost shell.
  - important for efficiency of laser cooling
- use isotopes such that total intrinsic spin of all electrons and nucleons add up to an integer $\hbar$
  $\Rightarrow$ atoms are <u>bosons</u>
- all have a net magnetic moment - used to confine dilute gas of atoms in a "magnetic trap"
- use "laser cooling" to get <u>very</u> low temperatures in low density gases, to try and see BEC

magnetic trap $\rightarrow$ effective harmonic potential for atoms

$$V(r) = \tfrac{1}{2} m\omega_0^2 r^2 \qquad \omega_0 \approx 2\pi \times 100\,Hz$$

1995 - 10^3 atoms with $T_c \sim 100\,nK$

1999 - 10^8 atoms with $T_c \sim \mu K$ gas size ~ many microns

How was BEC in these systems observed?

energy levels of ideal (non-interacting) bosons in harmonic trap

$$\epsilon(n_x, n_y, n_z) = (n_x + n_y + n_z + 3/2)\,\hbar\omega_0$$

n_x, n_y, n_z integer

ground state condensate wavefunction

$$\psi_0(r) \sim e^{-r^2/2a^2} \quad \text{with} \quad a = \left(\frac{\hbar}{m\omega_0}\right)^{1/2}$$

$\Rightarrow$ condensate has spatial extent $\sim a$

The spatial extent of the n^{th} excited energy level is roughly

$$m\omega_0^2 \langle r^2\rangle \sim \epsilon(n) \simeq n\hbar\omega_0$$

$$\Rightarrow \langle r^2\rangle \sim \frac{n\hbar}{m\omega_0} \quad \text{or} \quad \sqrt{\langle r^2\rangle} = \left(\frac{n\hbar}{m\omega_0}\right)^{1/2}$$

For $k_B T \gg \hbar\omega_0$, the atoms are excited up to level $n \sim \dfrac{k_B T}{\hbar\omega_0}$

$\Rightarrow$ spatial extent of the normal component of the gas is

$$R \sim \left(\frac{n\hbar}{m\omega_0}\right)^{1/2} \sim \left(\frac{\hbar k_B T}{\hbar m\omega_0^2}\right)^{1/2} = \left(\frac{k_B T}{m\omega_0^2}\right)^{1/2}$$

$$R \sim a\left(\frac{k_B T}{\hbar\omega_0}\right)^{1/2} \gg a$$

If T_c is the BEC transition temperature, then for $T > T_c$ one sees a more or less uniform cloud of atoms with radius $R \sim a\,(k_BT/\hbar\omega_0)^{1/2} \gg a$. But when one cools to $T < T_c$, one now has a finite fraction of the atoms condensed in the ground state. $\Rightarrow$ superimposed on the atomic cloud of radius R one sees the growth of a sharp peak in density at center of cloud — this peak has a radius $a \ll R$.

To find T_c, (use $z=1$ at $T \leq T_c$)

for $T \leq T_c$

$$n = n_0 + \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \frac{1}{e^{(n_x+n_y+n_z)\hbar\omega_0/k_BT} - 1}$$

$$= n_0 + \left(\frac{k_BT}{\hbar\omega_0}\right)^3 \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz \frac{1}{e^{(x+y+z)} - 1}$$

$$= n_0 + \left(\frac{k_BT}{\hbar\omega_0}\right)^3 \zeta(3)$$

at T_c, $n_0 = 0 \Rightarrow k_BT_c = \hbar\omega_0 \left(\frac{n}{\zeta(3)}\right)^{1/3}$

condensate density $n_0(T) = n\left(1 - \left(\frac{T}{T_c}\right)^3\right)$

different from ideal free gas due to presence of magnetic trapping potential

$$\zeta(3) = 1 + \frac{1}{2^3} + \frac{1}{3^3} + \frac{1}{4^3} + \cdots$$

The existence of Bose Einstein condensation is particular to the dimensionality of the system. To see this, consider a general d-dimensional system. Then

$$\frac{1}{V}\sum_k n(\epsilon(k)) \to \alpha \int dk\, k^{d-1} \frac{1}{z^{-1} e^{\beta \hbar^2 k^2/2m} - 1}$$

is largest when $z \to 1$, so consider this case

$$\alpha \int dk\, k^{d-1} \frac{1}{e^{\beta\hbar^2 k^2/2m} - 1} \qquad \text{let } y = \frac{\beta\hbar^2 k^2}{2m}$$

$$k = \sqrt{\frac{2my}{\beta\hbar^2}}$$

$$\alpha \left(\frac{2m}{\beta\hbar^2}\right)^{d/2} \int_0^\infty dy \frac{y^{\frac{d}{2}-1}}{e^{y}-1} \qquad dk = \sqrt{\frac{2my}{\beta\hbar^2}}\,\frac{dy}{2y}$$

again the most singular part of the integral is as $y \to 0$

for $y^* \ll 1$, $$\int_0^{y^*} dy \frac{y^{\frac{d}{2}-1}}{e^y - 1} \approx \int_0^{y^*} dy \frac{y^{\frac{d}{2}-1}}{y} = \int_0^{y^*} dy\, y^{\frac{d}{2}-2}$$

The integral will converge at its lower limit $y \to 0$ only for $\frac{d}{2} - 2 > -1$ or $d > 2$

For $d \leq 2$, the integral will diverge. Therefore it will always be possible to find a z such that

$$n = \frac{N}{V} = \frac{1}{(2\pi)^d} \int d^d k \frac{1}{z^{-1} e^{\beta\hbar^2 k^2/2m} - 1}$$

$\Rightarrow$ No Bose Einstein Condensation in two dimensions or below!

and so it will never be necessary to have a macroscopic occupation of the ground state, i.e. $n_0 = 0$ for all T. Ground state is macroscopically occupied only at $T=0$

$\Rightarrow$ there is no Bose Einstein condensation in two dimensions or below.

Bose Einstein condensation is often ~~given~~ invoked as the physical mechanism behind the ~~sup~~ phenomenon of superfluidity in ultra cold liquid ^4He. (even though the system of strongly interacting ^4He atoms (which are bosons) are far from being an ideal gas)

Yet superfluidity has been found to exist even in very thin "two dimensional" films of ^4He, where there can be no BE condensation.

Thus to have superfluidity, a BE condensate is not strictly necessary. The borderline dimension $d=2$ where one crosses from no BEC to BEC has sufficiently anomalous behavior to support ~~superconductivity~~ superfluidity.