Ideal Bose Gas

Bose Einstein Condensation

Bose occupation function

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

We had for the density of an ideal (non-interacting) bose gas

$$\frac{N}{V} = \frac{1}{V}\sum_k \frac{1}{z^{-1} e^{\beta\epsilon(k)} - 1} = \frac{1}{(2\pi)^3}\int_0^\infty dk\, 4\pi k^2 \frac{1}{z^{-1} e^{\beta \hbar^2 k^2/2m} - 1}$$

spin zero bosons $g_s = 1$

recall, we need $z \le 1$ for the occupation number at $\epsilon(k=0) = 0$ to remain positive $n(0) \ge 0$

$$n(0) = \frac{1}{z^{-1} - 1} = \frac{z}{1-z} \Rightarrow z \le 1, \quad z = e^{\beta\mu} \Rightarrow \mu \le 0$$

substitute variables $y = \frac{\beta\hbar^2 k^2}{2m} \Rightarrow k = \sqrt{\frac{2my}{\beta\hbar^2}}$

$$dk = \sqrt{\frac{2my}{\beta\hbar^2}}\,\frac{dy}{2y}$$

$$\Rightarrow \frac{N}{V} = \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \frac{4\pi}{(2\pi)^3}\,\frac{1}{2}\int_0^\infty dy\, \frac{y^{1/2}}{z^{-1}e^{y} - 1}$$

$$\frac{N}{V} = \frac{1}{\lambda^3}\, g_{3/2}(z) \quad \text{where } \lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \text{ thermal wavelength}$$

$$g_{3/2}(z) \equiv \frac{2}{\sqrt{\pi}}\int_0^\infty dy\, \frac{y^{1/2}}{z^{-1}e^{y} - 1}$$

Consider the function

$$g_{3/2}(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty dy \, \frac{y^{1/2}}{z^{-1} e^{y} - 1} = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots$$

$g_{3/2}(z)$ is monotonic increasing function of z for $z \leq 1$

as $z \to 1$, $g_{3/2}(z)$ approaches a finite constant

$$g_{3/2}(1) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \cdots \equiv \zeta(3/2) \simeq 2.612$$

↑ Reimann zeta function

We can see that $g_{3/2}(1)$ is finite as follows:

$$g_{3/2}(1) = \frac{2}{\sqrt{\pi}} \int_0^\infty dy \, \frac{y^{1/2}}{e^{y} - 1}$$

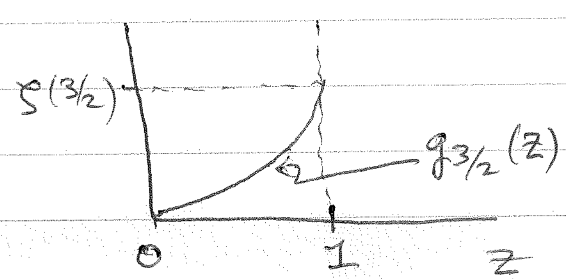
as $y \to \infty$ the integral converges. Integral is largest at small y

(recall small y corresponds to low energy where $n(\epsilon)$ is largest)

For small y we can approx $\frac{1}{e^{y}-1} \simeq \frac{1}{y}$

$$\int_0^{y^*} dy \, \frac{y^{1/2}}{e^{y}-1} \simeq \int_0^{y^*} dy \, \frac{1}{y^{1/2}} = 2 \, y^{1/2} \Big|_0^{y^*}$$

So we see the integral also converges at its lower limit $y \to 0$.



So we conclude

$$n = \frac{N}{V} = \frac{g_{3/2}(z)}{\lambda^3} \leq \frac{g_{3/2}(1)}{\lambda^3} = \frac{2.612}{\lambda^3} = 2.612 \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

But we now have a contradiction!
For a system with fixed density of bosons n, as T decreases we will eventually get to a temperature below which the above inequality is violated!
This temperature is

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

Solution to the paradox:
when we made the approx $\frac{1}{V}\sum_k \rightarrow \frac{1}{(2\pi)^3}\int_0^\infty dk\, 4\pi k^2$

we gave a weight $\frac{4\pi k^2}{(2\pi)^3}$ to states with wavevector $|\vec{k}|$.

This gives zero weight to the state $\vec{k}=0$, ie to the ground state. But as T decreases, more and more bosons will occupy the ground state, as it has the lowest energy. Thus when we approx the sum by an integral, we should treat the ground state separately

$$\frac{1}{V}\sum_k n(\epsilon(k)) \cong \frac{n(0)}{V} + \frac{1}{(2\pi)^3}\int_0^\infty dk\, 4\pi k^2\, n(\epsilon(k))$$

ground state with occupation $n(0)$.
This term is important when $n(0)/V$ stays finite as $V \to \infty$, ie a macroscopic fraction of bosons occupy the ground state

Then we get

$$n = \frac{N}{V} = \frac{n(0)}{V} + \frac{g_{3/2}(z)}{\lambda^3}$$

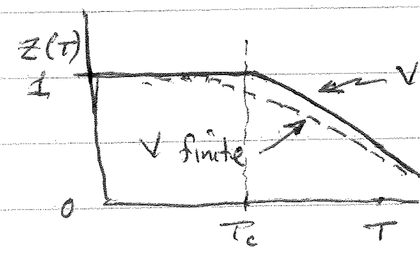
$$n = n_0 + \frac{g_{3/2}(z)}{\lambda^3} \qquad \text{where } n_0 = \frac{n(0)}{V} \text{ density of bosons in ground state}$$

For a system with fixed n, at higher T one can always choose z so that $n = \frac{g_{3/2}(z)}{\lambda^3}$ and $n_0 = 0$.

But when $T < T_c$ it is necessary to have $n_0 > 0$.

Using $n(0) = \frac{z}{1-z}$ we can write above as

$$n = \frac{z}{1-z}\frac{1}{V} + \frac{g_{3/2}(z)}{\lambda^3}$$



For $T > T_c$ we will have a solution to the above for some fixed $z < 1$. In thermodynamic limit $V \to \infty$, the first term will then vanish, ie the density of bosons in the ground state vanishes.

As $T \to T_c$, $z \to 1$ and as $V \to \infty$ the first term $\left(\frac{z}{1-z}\right)\left(\frac{1}{V}\right)$ stays finite to give the additional needed density at $T < T_c$:

$\left(\frac{z}{1-z}\right)$ diverges as $z \to 1$; $\left(\frac{1}{V}\right)$ vanishes as $V \to \infty$

$$\frac{z}{1-z}\frac{1}{V} = n_0 = n - \frac{g_{3/2}(1)}{\lambda^3}$$

T_c defines the Bose-Einstein transition temperature below which the system develops a finite density of particles in the ground state n_0.
n_0 is also called the condensate density.
The particles in the ground state are called the condensate

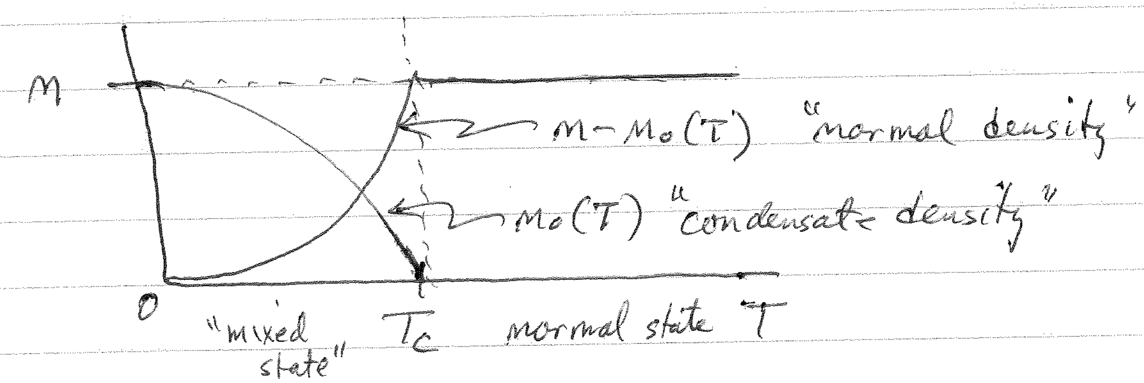
$$\left.\begin{array}{l} z(T) \to 1 \\ \mu(T) \to 0 \end{array}\right\} \text{as } T \to T_c \quad , \quad \left.\begin{array}{l} z(T) = 1 \\ \mu(T) = 0 \end{array}\right\} \text{for } T \leq T_c$$

For $T \leq T_c$

$$n_0(T) = n - \frac{g_{3/2}(1)}{\lambda^3} = n - 2.612 \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

$$\boxed{n_0(T) = n\left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right)}$$

condensate density vanishes continuously as $T \to T_c$ from below



At $T = 0$, all bosons are in condensate
At $T > T_c$, all bosons are in the "normal state"
At $0 < T < T_c$, a macroscopic fraction of bosons are in the condensate, while the remaining fraction are in the normal state – call it the "mixed state"

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

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

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

$\vec{k}=0$ ground state — 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 $g_{5/2}(z) \equiv \frac{1}{\Gamma(5/2)}\int_0^\infty dy\, \frac{y^{3/2}}{z^{-1}e^y - 1}$ 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 $n(0)+1 = \frac{z}{1-z} + 1 = \frac{1}{1-z}$

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

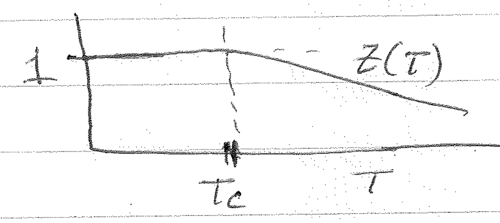
In the thermodynamic limit of $V\to\infty$, the first term always vanishes as $n(0) \leq N = nV$ and $\lim_{V\to\infty}\left[\frac{\ln(nV)}{V}\right] = 0$

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 momentum $|\vec{p}|>0$ hitting the walls of the container

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

$p = g_{5/2}(z(T))\left(\dfrac{2\pi m}{h^2}\right)^{3/2}(k_B T)^{5/2}$ ← 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.



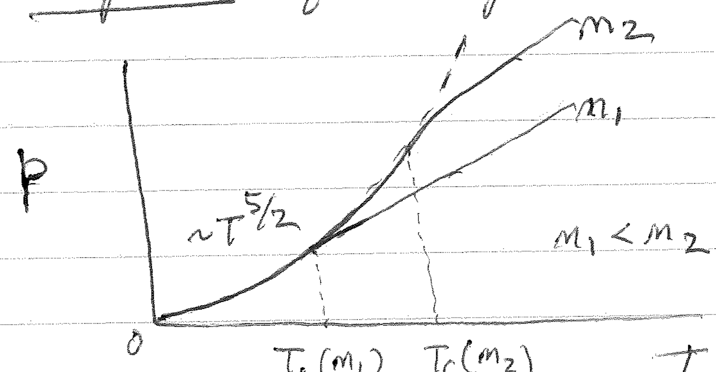
Note $g_{5/2}(z=1) = \zeta(5/2) = 1.342$ is finite

In thermodynamic limit of $V \to \infty$, $z = 1$ for $T \leq T_c(n)$

↑ critical temperature depends on the system's fixed density

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

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



p vs T curves at constant density n

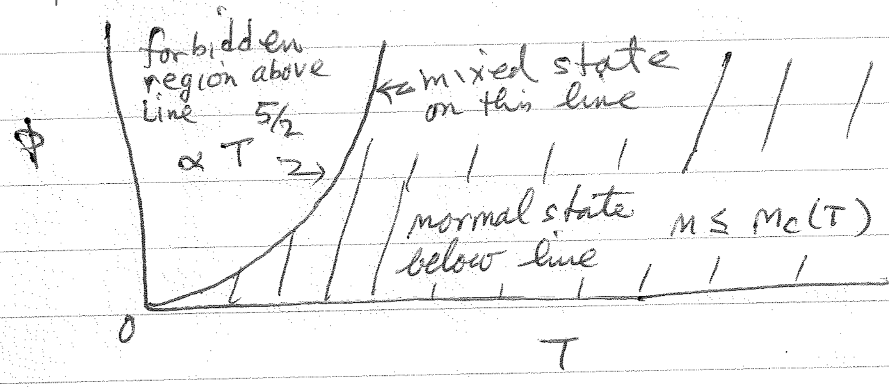
recall $T_c(n) \sim n^{2/3}$

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

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 $n > n_c(T)$ 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 $p \propto T_c(n)^{5/2}$, $T_c(n) \propto n^{2/3}$

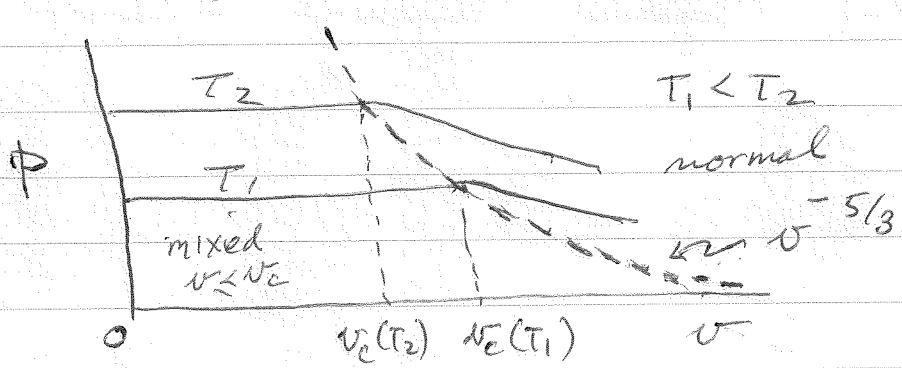
$\Rightarrow$ at the transition $p \propto (n^{2/3})^{5/2} = n^{5/3} = v^{-5/3}$

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 $v_c(T) = \frac{1}{n_c(T)}$

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

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 $T \le T_c$, $z = 1$ 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 $T \le T_c$

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

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

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

For $T \ge T_c$, 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),

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

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

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

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

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

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

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

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

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

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

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

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

$\Rightarrow$ at T_c^+

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

Now from Pathria Appendix D Eq (8)

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

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

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

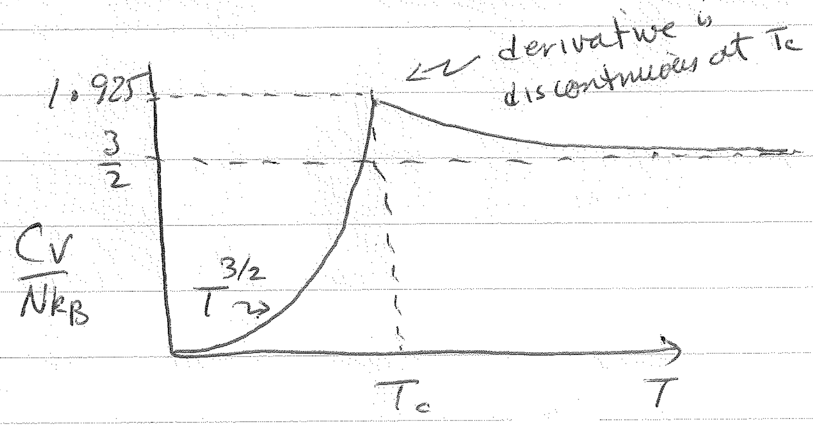
$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{45}{8}\,\frac{1.341}{2.612}\,\frac{1}{T_c} - \frac{27}{8}\,\frac{(2.612)^2}{2\pi}\,\frac{1}{T_c}$$

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

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

slope of C_V is discontinuous at T_c.

C_V has a <u>cusp</u> at T_c



goes to classical $\frac{3}{2}$ as $T \to \infty$

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

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

Entropy

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

$$\frac{S}{Nk_B} = \frac{E + pV}{Nk_BT} - \frac{\mu}{k_BT}$$

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

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

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

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

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

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

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

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

we can imagine that each normal particle carries entropy $\frac{5}{2} k_B \dfrac{g_{5/2}(1)}{g_{3/2}(1)}$. The entropy/per particle at $T < T_c$ is just the ~~[illegible]~~ 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 $\dfrac{\Delta S}{N} = \frac{5}{2} k_B\, g_{5/2}(1)/g_{3/2}(1)$

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