\[ \frac{P}{k_B T} = \frac{1}{V} \ln Z = -\frac{1}{V} \sum_k \ln \left( 1 - z e^{-\beta E_k} \right) \]
\[ \leq -\frac{1}{V} \ln (1 - z) - \frac{4\pi}{(2\pi)^3} \int_0^\infty dk \, k^2 \ln (1 - z e^{-\beta k^2/2m}) \]

where \( k = 0 \) ground state  
all other \( 1 \leq k > 0 \) states

\[ = \frac{1}{V} \ln \left( \frac{1}{1 - z} \right) + \frac{g_{5/2}(z)}{a^3} \]

\[ \beta = \left( \frac{k_B T}{2\pi m} \right)^{1/2} \]

where \( g_{5/2}(z) = \frac{1}{\Gamma(5/2)} \int_0^\infty dy \, y^{3/2} e^{-y} \]

as derived when we began our discussion of quantum gases.

Also recall the number of bosons occupying the ground state is

\[ n(0) = \frac{1}{z^{-1} e^{\beta E(0)} - 1} = \frac{1}{z^{-1} - 1} = \frac{z}{1 - z} \]

So \( n(0) + 1 = \frac{z}{1 - z} + 1 = \frac{1}{1 - z} \)

\[ \frac{P}{k_B T} = \frac{\ln (n(0) + 1)}{V} + \frac{g_{5/2}(z)}{a^3} \]

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

So the condensate does not contribute to the pressure.

This is not surprising as particles in the condensate have \( k = 0 \) and hence carry no momentum. In the kinetic theory of gases, one sees that pressure arises from particles with finite momentum \( |p| > 0 \) hitting the walls of the container.
So \[ \frac{\phi}{k_B T} = \frac{g_{5/2}(z)}{2^5} = g_{5/2}(z) \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \]

\[ \phi = g_{5/2}\left(\frac{z(\tau)}{\tau}\right) \left( \frac{2\pi m}{\hbar^2} \right)^{3/2} (k_B T)^{5/2} \quad \text{equation of state} \]

for a system of fixed density \( \rho \), \( z \) must be chosen to be a function of \( T \) that gives the desired density \( \rho \).

Note: \( g_{5/2}(z=1) = \xi(5/2) = 1.342 \)

is finite

In the thermodynamic limit \( V \to \infty \), \( Z = 1 \) for \( T \leq T_c(\rho) \)

\[ \Rightarrow \phi = g_{5/2}(1) \left( \frac{2\pi m}{\hbar^2} \right)^{3/2} (k_B T)^{5/2} \quad \text{for } T \leq T_c \]

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

\[ p \text{ vs } T \text{ curves at constant density } \rho \]

Recall \( T_c(\rho) \sim \rho^{2/3} \)

\[ T_c(\rho) = \left( \frac{\rho}{2.16} \right)^{2/3} \frac{\hbar^2}{2\pi m k_B} \]
Define \( M_c(T) = 2.612 \left( \frac{2\pi m k_B T}{a^2} \right)^{3/2} \) inverse of \( T_c(m) \)

\( M_c(T) \) is the critical density at a given \( T \)

- A system with \( m > M_c(T) \) will be in a base condensed mixed state at temperature \( T \).

Phase diagram in \( \phi - T \) plane

\[
\begin{align*}
\phi & \quad \text{forbidden region above line} \quad 5/2 \quad \alpha \quad T \quad 2 \quad \text{mixed state on the line} \\
\phi & \quad \text{normal state below line} \quad M \leq M_c(T) \\
T & \quad \text{below line}
\end{align*}
\]

Can also consider the transition in terms of \( \phi \) and \( \nu = \frac{V}{N} = \frac{1}{m} \) for various fixed \( T \).

At the transition \( \phi \propto T_c(m)^{5/2} \Rightarrow T_c(m) \propto m^{-2/3} \)

\[
\Rightarrow \text{at the transition} \; \phi \propto (m^{5/3})^{5/2} = m^{5/3} = N^{-5/3}
\]

below the transition \( \phi \) is independent of density and hence independent of \( \nu \).

For fixed \( T \), the transition occurs when density \( m \) exceeds \( M_c(T) \), or when \( \nu \) drops below \( \nu_c(T) = \frac{1}{M_c(T)} \)

\( \nu_c(T) \propto T^{-3/2} \)
\[
\frac{c_v}{N} = \frac{1}{2} \left( \frac{2}{3} \right) \left( \frac{E}{N} \right) = \frac{3}{2} \frac{T}{2} \left( \frac{e}{k} \right) = \frac{3}{2} \frac{k_B T}{N} \frac{e}{k} \frac{1}{N}
\]

**Thermodynamic Functions**

E(k) = E = \frac{3}{2} p V = \frac{3}{2} p u = \frac{3}{2} k_B T - \frac{g_z}{z} (e)

\[
N = N' = \frac{z}{z}
\]

\[
E = \frac{3}{2} p V = \frac{3}{2} p u = \frac{3}{2} k_B T - \frac{g_z}{z} (e)
\]

**Elastic we found**

\[
E = \frac{3}{2} p
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For $T \leq T_c$, $z = 1$ so $\frac{dz}{dT} = 0$ and only 1st term remains

\[ \frac{T}{\lambda^3} \times T^{5/2} \quad \text{so} \quad \frac{d}{dT} \left( \frac{T}{\lambda^3} \right) = \frac{5}{2} \left( \frac{T}{\lambda^3} \right) \frac{1}{T} = \frac{5}{2} \frac{1}{\lambda^3} \]

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

\[ \Rightarrow \frac{C_v}{Nk_B} = \frac{3}{2} \nu \left( \frac{5}{2} \frac{1}{\lambda^3} \right) g_{\frac{3}{2}}(1) = \frac{15}{4} \frac{g_{\frac{3}{2}}(1)}{\lambda^3} \nu \]

\[ = \frac{15}{4} \frac{g_{\frac{3}{2}}(1)}{\lambda^3} \nu \left( \frac{2\pi \hbar k_B T}{\lambda^2} \right)^{3/2} \]

Note, at $T_c$, $m = \frac{g_{\frac{3}{2}}(1)}{\lambda^c}$, and $\nu = \frac{1}{m}$

\[ \frac{C_v(T_c)}{Nk_B} = \frac{15}{4} \frac{g_{\frac{3}{2}}(1)}{g_{3/2}(1)} = \frac{15}{4} \frac{1.341}{2.612} = 1.925 \]

the classical ideal gas value $\approx 0.3^2$

So

\[ \frac{C_v}{Nk_B} = 1.925 \left( \frac{T}{T_c} \right)^{3/2} \quad T \leq T_c \]

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

1st term stays

\[ \frac{15}{4} \frac{g_{\frac{3}{2}}(z)}{\lambda^3} \nu \]

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

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

\[ \Rightarrow \frac{d g_{\frac{3}{2}}}{dz} \frac{dz}{dT} = g_{3/2} \frac{1}{z} \frac{dz}{dT} \]
To find $\frac{1}{2} \frac{d^2z}{dT^2}$ consider our earlier result for the density when $T > T_c$:

$$n = \frac{g_{3/2}(z)}{a^3}$$

determines $z(T)$ for fixed $n$.

for $n$ fixed $\Rightarrow$ 

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

$$0 = \frac{3}{2} \frac{1}{a^3} \frac{dz}{dT} g_{3/2} + \frac{1}{a^3} \frac{1}{8} \frac{dz}{dT}$$

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

$$C_v = \frac{15}{4} g_{5/2}(z) \frac{V}{a^3} - \frac{3}{2} \frac{V}{a^3} g_{3/2}(z) \left( -\frac{3}{2} \right) \frac{g_{3/2}(z)}{g_{1/2}(z)} \frac{1}{T}$$

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

$$C_v = \frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{5/2}(z)}{g_{1/2}(z)} \quad T > T_c$$

Note $g_{1/2}(1) = \frac{6}{\epsilon^2} \left( \frac{1}{1/2} \right) \Rightarrow \infty$

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

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

$
\Rightarrow C_v$ 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 $T \leq T_c$

\[ C_V = \frac{1.925}{N k_B} \left( \frac{T}{T_c} \right)^{3/2} \]

\[ \frac{d}{dT} \left( \frac{C_V}{N k_B} \right) = \frac{3}{2} \left( 1.925 \right) \left( \frac{T}{T_c} \right)^{3/2} \frac{1}{T_c} = 2.89 \left( \frac{T}{T_c} \right)^{3/2} \frac{1}{T_c} \]

so slope at $T_c^-$ (just below $T_c$)

\[ \frac{d}{dT} \left( \frac{C_V}{N k_B} \right) = \frac{2.89}{T_c} \quad T = T_c^- \]

For $T > T_c$

\[ C_V = \frac{15}{4} \frac{g_{3/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} \]

\[ \frac{d}{dT} \left( \frac{C_V}{N k_B} \right) = \frac{15}{4} \frac{g_{3/2} \frac{d g_{3/2}}{dz} \frac{dz}{dT} - g_{3/2} \frac{d g_{3/2}}{dz} \frac{dz}{dT}}{(g_{3/2}(z))^2} \]

\[ - \frac{9}{4} \frac{g_{1/2} \frac{d g_{1/2}}{dz} \frac{dz}{dT} - g_{3/2} \frac{d g_{3/2}}{dz} \frac{dz}{dT}}{(g_{1/2}(z))^2} \]

\[ = \frac{1}{2} \frac{d z}{dT} \left\{ \frac{2}{9} \left( \frac{g_{3/2} - g_{3/2} g_{1/2}}{g_{3/2}} \right) - \frac{9}{4} \left( \frac{g_{1/2} - g_{3/2} g_{1/2}}{g_{1/2}} \right) \right\} \]

Use \[ \frac{1}{2} \frac{dz}{dT} = - \frac{3}{2} \frac{g_{3/2}}{g_{1/2}} \frac{1}{T} \quad \text{as found earlier} \]
\[
\frac{d}{dT} \left( \frac{C_V}{Nk_B} \right) = -\frac{3}{8T} \frac{g_3^{1/2}}{g^1} \left\{ 15 \left( 1 - \frac{g_5^{1/2}}{g^{3/2}} \right) - 9 \left( 1 - \frac{g_3^{3/2}}{g^{3/2}} \right) \right\}
\]

Now as \( T \to T_c^+ \) from above, \( z \to 1 \), we have \( g_5^{1/2} \) and \( g_3^{3/2} \) are finite, but \( g_3^{3/2} \) and \( g_3^{1/2} \) \( \to \infty \)

\( \Rightarrow at \ T_c^+ \)

\[
\frac{d}{dT} \left( \frac{C_V}{Nk_B} \right) = \frac{45}{8T_c} \frac{g_5^{1/2}(1)}{g_3^{3/2}(1)} - \frac{27}{8T_c} \frac{g_3^{3/2}(1)}{g_3^{1/2}(1)}
\]

Now from Pathria Appendix D Eq (8)

\[
q_v(1) = \lim_{a \to 0} \frac{P(1-y)}{a^{1-y}}
\]

So \( \frac{g_3^{1/2}(1)}{g_3^{3/2}(1)} = \lim_{a \to 0} \frac{T(3/2)}{a^{3/2}} \left( \frac{a^{1/2}}{P(1/2)} \right)^3 = \frac{P(3/2)}{[P(1/2)]^3}
\]

\[
= \frac{1}{\pi^{1/2}} = \frac{1}{2\pi} \quad \text{since} \quad P(1/2) = \sqrt{\pi} \quad P(3/2) = \frac{1}{2} \sqrt{\pi}
\]

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

\[
= \frac{2.59}{T_c} - \frac{3.60}{T_c} = -0.77
\]

\[
\frac{d}{dT} \left( \frac{C_V}{Nk_B} \right) = -0.77 \left( \frac{T}{T_c} \right) + \frac{1}{T_c}
\]

Slope of \( C_V \) is discontinuous at \( T_c \).
**Entropy**

For single species gas we had for Gibbs free energy

\[ G = N \mu \]

Also \[ G = E - TS + pV \] (since \( G \) is Legendre transform of \( E \) 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 \[ E = \frac{3}{2} pV \] \( \Rightarrow \) \( pV = \frac{2}{3} E \)

\[ \frac{S}{Nk_B} = \frac{5}{3} \frac{E}{N} \frac{1}{k_B T} - \frac{\mu}{k_B T} \]
\[ Z = e^{\frac{M}{k_B T}}, \quad Z = 1 \text{ for } T < T_c \]

we had earlier \[ \frac{E}{N} = \frac{3}{2} k_B T \frac{v}{\lambda^3} g_{3/2}(z) \]

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

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

Note: For \( T \leq T_c \) we had that the density of the condensed part is a density \( m_0 = m - \frac{g_{3/2}(1)}{\lambda^3} \) in the condensate, and a density \( \frac{g_{3/2}(1)}{\lambda^3} \) in the normal state (i.e., the density of excited particles) \( \frac{m}{\lambda^3} \equiv m_n \)

\[ \Rightarrow \text{for } T \leq T_c, \quad \frac{S}{Nk_B} = \frac{5}{2} \left( \frac{m_n}{m} \right) \frac{g_{5/2}(1)}{g_{3/2}(1)} \rightarrow 0 \text{ as } T \rightarrow 0 \]

We can imagine that each normal particle carries entropy \( \frac{5}{2} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} \) per particle.

The entropy at \( T < T_c \) is just the total entropy per normal particle times the fraction of normal particles.

\[ \Rightarrow \text{normal particles carry the entropy condensate has zero entropy} \]

Entropy difference per particle between normal state and condensed state is \( \frac{dS}{\lambda} = \frac{5}{2} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} \)
latent heat of condensation

\[ L = T \Delta S = \frac{5}{3} k_B T \frac{\theta}{9 \beta} (1) \]

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

⇒ mixed phase is like coexistence region of a 1st order phase transition (like water ↔ ice) – need to remove energy to turn water to ice.

⇒ "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 5-electron in outermost shell
- Important for trapping in laser cooling
- Use isotopes such that total intrinsic spin of all electrons and nucleons add up to an integer \( n \)
  \( \Rightarrow \) atoms are bosons

- All have a net magnetic moment - used to confine dilute gas of atoms in a "magnetic trap"
- Use "laser cooling" to get very low temperatures in low density gases, to try and see BEC

Magnetic trap \( \Rightarrow \) effective harmonic potential for atoms

\[
V(r) = \frac{1}{2} m \omega_0^2 r^2 \quad \omega_0 \approx 2 \pi \times 10^3 \text{ Hz}
\]

1995 - 10^3 atoms with \( T_c \approx 100 \text{ nK} \)
1999 - 10^8 atoms with \( T_c \approx \mu \text{ K} \)

Gas size - many nucleons

How was BEC in these systems observed?

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

\[
E(n_x, n_y, n_z) = (n_x + n_y + n_z + 3/2) \hbar \omega_0
\]

\( n_x, n_y, n_z \) integer

Ground state condensate wavefunction

\[ \Psi_0(r) \sim e^{-r^2/2a^2} \text{ with } a = \left( \frac{\hbar}{m \omega_0} \right)^{1/2} \]

\( a \approx 1 \mu \text{m} \) for current traps
\[ \Rightarrow \text{Condensate has spatial extent } \sim a \]

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

\[ m\omega_0^2 \langle r^2 \rangle \sim E(n) \approx n \hbar \omega_0 \]

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

For \( k_B T \gg \hbar \omega_0 \), the atoms are excited up to level \( n \sim \frac{k_B T}{\hbar \omega_0} \)

\[ \Rightarrow \text{spatial extent of the normal component of the gas is} \]

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

\[ R \sim a \left( \frac{k_B T}{\hbar \omega_0} \right)^{1/2} \Rightarrow a \]

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 \( R \sim a \left( \frac{k_B T}{\hbar \omega_0} \right)^{1/2} \Rightarrow a \), 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 the center of cloud—this peak has a radius \( a \ll R \)
To find $T_c$, 

\[
m = m_0 + \int_0^\infty \int_0^\infty \int_0^\infty \frac{1}{e^{(n_x+n_y+n_z)+\hbar\omega_0/k_B T}-1} x^2 y^2 z^2 \, dx \, dy \, dz
\]

\[
= m_0 + \left(\frac{k_B T}{\hbar\omega_0}\right)^3 \int_0^\infty \int_0^\infty \int_0^\infty e^{-(x+y+z)} - 1 \, dx \, dy \, dz
\]

\[
= m_0 + \left(\frac{k_B T}{\hbar\omega_0}\right)^3 \mathcal{S}(3)
\]

At $T_c$, $m_0 = 0 \Rightarrow k_B T_c = \hbar \omega_0 \left(\frac{m}{\mathcal{S}(3)}\right)^{\frac{1}{3}}$

Condensate density

\[
m_0(T) = m \left(1 - \left(\frac{T}{T_c}\right)^3\right)
\]

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

\[
\mathcal{S}(3) = 1 + \frac{1}{2^3} + \frac{1}{3^3} + \frac{1}{4^3} + \cdots
\]