XII. Ideal Bose Gas

[Focus on 3D (Non-relativistic) Ideal Bose Gas]

g_s = spin degeneracy

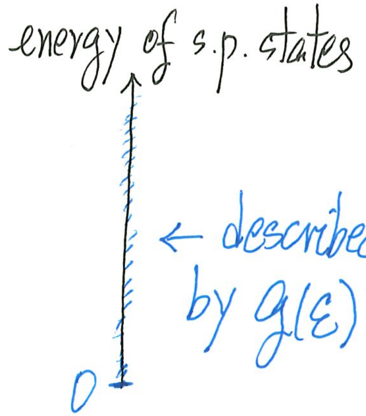
<u>Note</u>: We will use $g_{3D}(\varepsilon) = \frac{V}{4\pi^2} g_s \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}$ for "particle-in-a-big-box".

Experiments in Bose-Einstein Condensation, however, typically use "particle-in-a-harmonic trap"

∴ Pay attention to the concepts and skills, so that you can generalize the treatment to other situations.

We use $g_s = 1$ (spin-zero bosons).

The T=0 K Physics is Simple but illustrative



System: N non-interacting Bosons

$T=0 \Rightarrow$ What is the lowest-energy N-boson state?

Easy! $\boxed{\text{All N Bosons go into the } \underbrace{\text{lowest s.p. state}}_{\varepsilon=0 \text{ state}^{+}}}$

$\boxed{\text{Key Concept: The "N-equation" should carry this case!}}$ (Does it?)

$E(T=0) = 0$ (all bosons in $\varepsilon = 0$ s.p. state)

Does the "E-equation" carry this case? (It does!)

[+] The box is big, so the lowest s.p. state has energy approaches zero. Or you may call it ε_{GS}.

Inspect "N-equation"

$$N \overset{?}{=} \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\mu)/kT}-1}\,d\varepsilon$$

$g(\varepsilon) \sim \varepsilon^{1/2} \Rightarrow g(0) = 0$

$\Rightarrow$ $\int_{\boxed{0}}^{\infty} g(\varepsilon) f_{BE}(\varepsilon)\,d\varepsilon$ does NOT carry the bosons in the s.p. ground state at $\varepsilon = 0$

But Many Bosons can be in the $\varepsilon=0$ state at low temperatures

$\Rightarrow$ Should pay special attention to number of bosons in $\varepsilon=0$ state

There is N, there is $\int_0^\infty g(\varepsilon) f_{BE}(\varepsilon)\,d\varepsilon$, difference should be those in $\varepsilon=0$ state.

N-equation should be modified to

$$N = N_0 + \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\mu)/kT}-1}\, d\varepsilon$$

bosons in lowest s.p. state

But the "E-equation" works [∵ $\underbrace{\text{contribute energy } (\varepsilon = 0) \text{ to total energy}}_{\text{captured in } \int_0^\infty g(\varepsilon)\cdot\varepsilon\cdot f_{BE}(\varepsilon)\,d\varepsilon}$]

Since $pV = \frac{2}{3}E$, we also don't need to modify the "pV" (3^{rd}) equation.

Remark: Why don't we need to worry about the Fermions in the $\varepsilon=0$ s.p. state in Ideal Fermi Gas?

- Only 2 fermions (↑ and ↓) in $\varepsilon=0$ s.p. state out of N fermions (low and zero temp.)
- Also only 2 fermions in $\varepsilon=0$ s.p. state out of a scaled-up system of $2N$ fermions.
  i.e. Occupation of $\varepsilon=0$ s.p. state does NOT scale with N

A. The Governing Equation

$$N = N_0 + \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\mu)/kT}-1}\,d\varepsilon \qquad (1)$$

[The interesting question is: When is the 2nd term insufficient to account for N, so that N_0 (# bosons in lowest s.p. state) must be included as N_0 will scale with N? When this happens, it is called Bose-Einstein Condensation.]

$$E = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{(\varepsilon-\mu)/kT}-1}\,d\varepsilon \qquad (2)$$

$$pV = -kT\,\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \varepsilon^{1/2}\ln\left[1-e^{-(\varepsilon-\mu)/kT}\right]d\varepsilon \qquad (3)^+$$

integration by parts

$$pV = \frac{2}{3}E \qquad (4)$$

$^+$ Eq. (3) can be derived in a way analogous to Ch. X, Sec. H (Eq. (38)) for ideal Fermi gas.

B. $n_i/g_i = f_{BE}(\varepsilon_i)$ cannot be negative and μ is bounded

Recall: $$f_{BE}(\varepsilon_i) = \underbrace{\frac{n_i}{g_i}}_{\underbrace{\text{\# bosons}}_{\boxed{\text{number of particles} \geq 0}} \text{ per s.p. state at energy } \varepsilon_i} = \frac{1}{e^{(\varepsilon_i-\mu)/kT}-1}$$

number of particles ≥ 0 by physical meaning!

$\therefore$ $e^{(\varepsilon_i-\mu)/kT} > 1$ for all s.p. states (ε_i is energy of s.p. states)

$(\varepsilon_i-\mu)/kT > 0 \Rightarrow \varepsilon_i > \mu$ all s.p. states

This sets a condition on μ (recall $\mu(T)$ is determined by N-equation)

$\mu < \varepsilon_i$ (μ must be lower than any s.p. states' energy)

$\therefore$ $\boxed{\mu < \varepsilon_{GS} \quad \text{OR} \quad \mu < 0}$ (5) Bosons (free, non-interacting)

Key Concept $\boxed{\mu \text{ (for Bosons) is bounded from above due to physical meaning of } f_{BE}(\varepsilon)}$

C. Something Unusual should happen at Low Temperature: Bose-Einstein Condensation

Indications

(a) Bosonic nature of particles matters when classical ideal gas fails

$$\left(\frac{V}{N}\right)^{1/3} \approx \lambda_{th}(T_0) = \frac{h}{(2\pi m k T_0)^{1/2}} \quad \text{at some } T_0{}^{+}$$

m: mass of (bosonic) particles

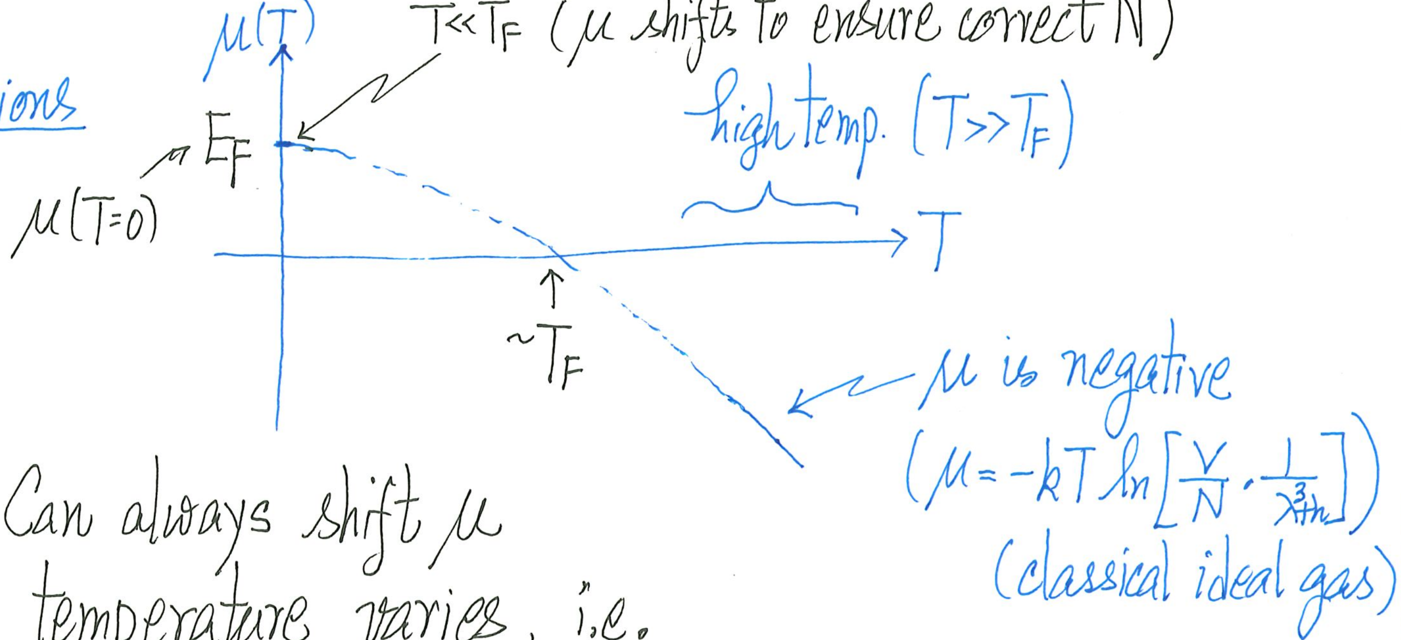
$$\Rightarrow T_0 \sim \frac{h^2}{2\pi m k}\left(\frac{N}{V}\right)^{2/3}$$

When $T < T_0$, something related to the $\underbrace{\text{bosonic nature}}_{\text{many going into s.p. ground state } (\varepsilon = 0 \text{ state})}$ of particles occurs!

+ To be called T_c

(b) $\mu < 0$ ($\mu <$ lowest s.p. state energy) for Bosons

Recall: Fermions



Key Point is: Can always shift μ as temperature varies, i.e.

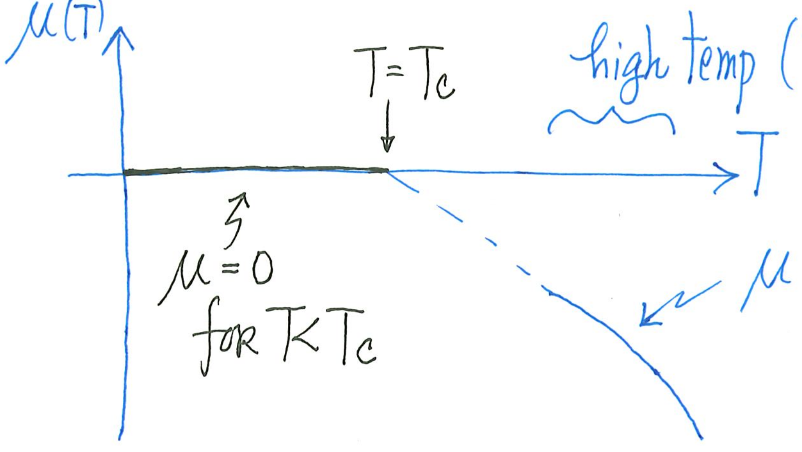
Can always find $\mu(T)$ such that

$$\frac{V}{4\pi^2} g_s \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\mu(T))/kT}+1}\, d\varepsilon = N \quad \text{(fermions)}$$

and the fermions (at most 2 of them⁺) in the $\varepsilon = 0$ won't matter

⁺ The point here is that the "2" doesn't scale with N.

But for <u>Bosons</u>: $\mu < 0$ (can't shift above 0)



μ is negative (expected to behave like classical gas)

$T < T_c$ ($\mu = 0$)

$$\underbrace{\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{\varepsilon/kT}-1}\,d\varepsilon < N}_{\text{can't account for } N}$$

So <u>N_0</u> grows and <u>N_0 scales with N</u>

<u>$T > T_c$</u>, <u>can</u> shift μ as temperature varies so that

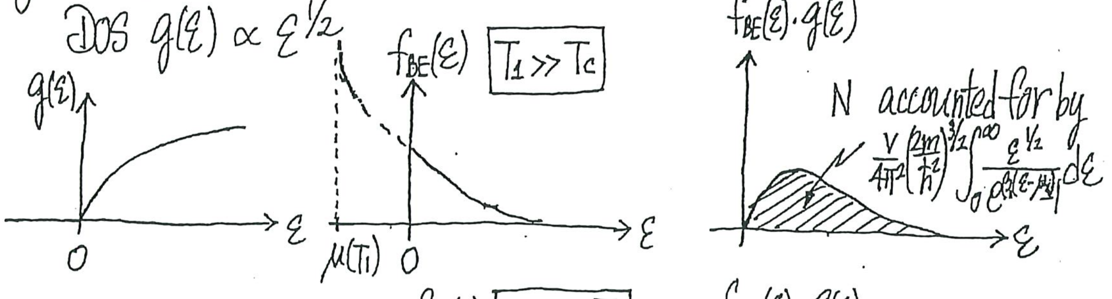
$$\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\mu(T))/kT}-1}\,d\varepsilon \underbrace{= N}_{\text{can account for } N}$$

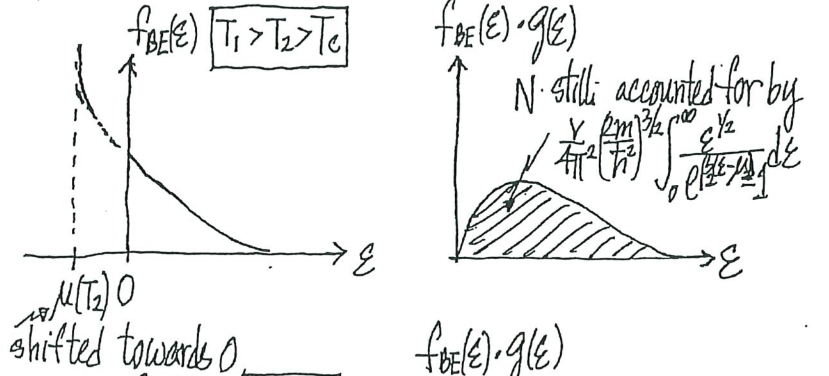
and # bosons in $\varepsilon = 0$ state won't matter

(Bosons "Condense" into s.p. $\varepsilon = 0$ state $\Rightarrow$ Bose-Einstein Condensation (BEC))

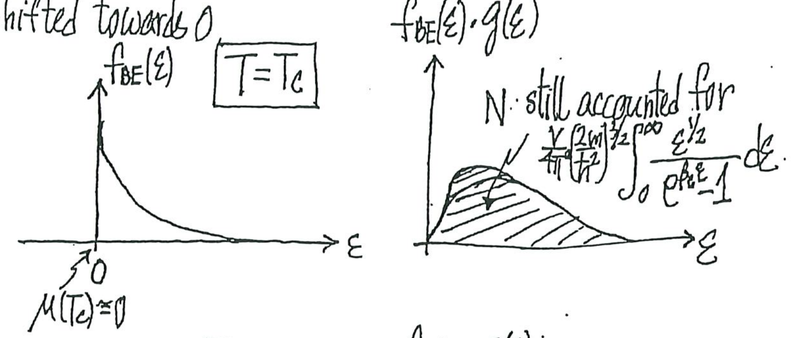
Pictures of Physics of Ideal Bose Gas

DOS $g(\varepsilon) \propto \varepsilon^{1/2}$

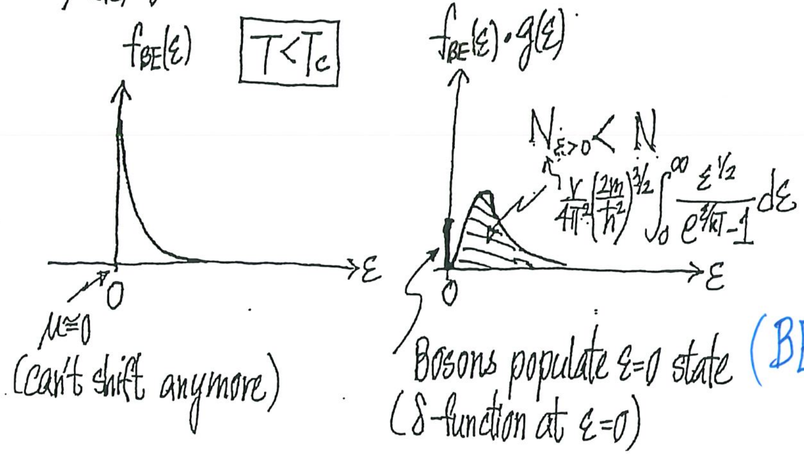




$\left(\beta_c = \frac{1}{kT_c}\right)$



$\mu \to 0$ (first touches 0) at $T = T_c$



Bosons populate $\varepsilon=0$ state (BEC)
(δ-function at $\varepsilon=0$)

Macroscopic Occupation of $\varepsilon=0$ s.p. state

Summary

- μ can't shift anymore when it hits its ceiling at $T=T_c$
- $T<T_c$, $\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{\varepsilon/kT}-1}\,d\varepsilon$ can't account for N
- N_0 grows $T<T_c$
- $\underbrace{\text{Macroscopic}}$ occupation of s.p. ground $(\varepsilon=0)$ state

  $\frac{N_0}{N}$ is a percentage OR N_0 scales with N
- This is Bose-Einstein Condensation (BEC)
  - Bosons "condense" into $\varepsilon=0$ (OR k.e. $=0$) state

    [not condense in real space]

D. The Condensation Temperature T_c and $N_0(T)$ for $T < T_c$

$T > T_c$, can shift μ (from negative to less negative (towards zero)) to account for N

$\boxed{\text{At } T = T_c,\ \mu \text{ first hits } \mu = 0 \text{ AND } \mu = 0 \text{ can still account for } N}$

T_c is the last temperature the integral gives N

$\therefore$

$$\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon - 0)/kT_c} - 1}\, d\varepsilon = \boxed{\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{\varepsilon/kT_c} - 1}\, d\varepsilon = N} \quad (6)$$

Equation for T_c

Key physics idea!

Evaluating T_c : $x \equiv \varepsilon / kT_c$, $\varepsilon^{1/2} = (kT_c)^{1/2} x^{1/2}$, $d\varepsilon = (kT_c)\, dx$ (change variable)

$$\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} (kT_c)^{3/2} \underbrace{\int_0^\infty \frac{x^{1/2}}{e^x - 1}\, dx}_{\text{just a number (if integral is finite)}} = N$$

this step is important!

check behavior near upper and lower limits

it is $\frac{\sqrt{\pi}}{2} \cdot (2.612) \approx \underbrace{2.315}_{\text{a number of order 1}}$

$$(kT_c)^{3/2} = \left(\frac{\hbar^2}{2m}\right)^{3/2} 4\pi^2 \frac{2}{\sqrt{\pi}} \frac{1}{2.612} \frac{N}{V}$$

$$\Rightarrow \boxed{kT_c = \frac{\hbar^2}{2m}\left[\frac{8\pi^{3/2}}{2.612} \frac{N}{V}\right]^{2/3} \quad \text{OR} \quad T_c = \frac{2\pi\hbar^2}{km}\left[\frac{1}{2.612} \frac{N}{V}\right]^{2/3}} \quad (7)$$

Bosons

(c.f. $kT_F = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3}$ for Fermions)

BEC Condensation Temperature (3D Ideal Bose Gas)

$$T_c = \frac{2\pi\hbar^2}{km}\left[\frac{1}{2.612}\frac{N}{V}\right]^{2/3} = \frac{h^2}{2\pi km}\left[\frac{1}{2.612}\frac{N}{V}\right]^{2/3}$$

$\sim \frac{1}{m}$ (mass of bosons)

$\sim \left(\frac{N}{V}\right)^{2/3}$

$\boxed{\text{c.f. } \left(\frac{V}{N}\right)^{1/3} \approx \lambda_{th}(T_c) \text{ gives } T_c = \frac{h^2}{2\pi km}\left(\frac{N}{V}\right)^{2/3}, \text{ consistent!}}$

Why BEC had to take 70 years† to be observed experimentally?

- $\frac{1}{m}$ for atoms (bosons) makes T_c very low
- Can't make $\frac{N}{V}$ higher (denser) to increase T_c, because denser Bose gas will turn into liquid as temperature decreases (before reaching T_c)

† From 1925 to 1995.

At $T = T_c$,
[μ first hits 0]

$$\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{\varepsilon/kT_c}-1}\,d\varepsilon = N$$

↑ just made it to N

For $T < T_c$,
[$\mu = 0$]

$$\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{\varepsilon/kT}-1}\,d\varepsilon = \underbrace{N_{\varepsilon>0}} < N$$

↑ account only for bosons in s.p. states with $\varepsilon > 0$

bosons in $\varepsilon = 0$ s.p. state at T ($< T_c$)

$$N_0(T) = N - N_{\varepsilon>0}$$

$$= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\underline{(kT_c)}^{3/2}\int_0^\infty \frac{x^{1/2}}{e^x-1}\,dx - \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\underline{(kT)}^{3/2}\int_0^\infty \frac{x^{1/2}}{e^x-1}\,dx$$

$$= N - \left(\frac{kT}{kT_c}\right)^{3/2}\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(kT_c)^{3/2}\int_0^\infty \frac{x^{1/2}}{e^x-1}\,dx$$

$$= N - \left(\frac{T}{T_c}\right)^{3/2}N = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]$$

$$\boxed{\begin{aligned} N_0(T) &= N\left[1-\left(\frac{T}{T_c}\right)^{3/2}\right] \quad \text{of bosons in } \varepsilon=0 \text{ s.p. state} \\ N_{\varepsilon>0}(T) &= \underbrace{N\left(\frac{T}{T_c}\right)^{3/2}}_{\text{keep dropping as } T \text{ drops from } T_c} \quad \text{of bosons in } \varepsilon>0 \text{ s.p. states} \end{aligned}} \qquad (8)$$

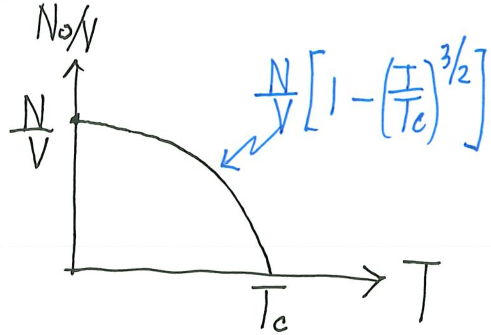
<u>Concept</u>: $N_0(T) \propto N$ for $T < T_c$ $\underbrace{\text{(scales with } N\text{)}}$

this is what <u>macroscopic occupation</u> <u>of</u> <u>$\varepsilon=0$</u> <u>s.p.</u> <u>state</u> means!

OR

$$\frac{N_0(T)}{V} = \underbrace{\frac{N}{V}}_{\text{number density of bosons in system}}\left[1-\left(\frac{T}{T_c}\right)^{3/2}\right]$$

density in s.p. $\varepsilon=0$ state.



Aside (Optional): What is that "$\frac{\sqrt{\pi}}{2}\cdot(2.612)$" for $\int_0^\infty \frac{x^{1/2}}{e^x-1}\,dx$?

$$\int_0^\infty \frac{x^{1/2}}{e^x-1}\,dx = \int_0^\infty \frac{x^{1/2}e^{-x}}{1-e^{-x}}\,dx = \int_0^\infty x^{1/2}e^{-x}\left(\sum_{j=0}^\infty e^{-jx}\right)dx$$

$$= \sum_{j=0}^\infty \int_0^\infty x^{1/2}e^{-(j+1)x}\,dx \qquad \left[y=(j+1)x,\ x^{1/2}=\frac{y^{1/2}}{(j+1)^{1/2}},\ dx=\frac{dy}{(j+1)}\right]$$

$$= \sum_{j=0}^\infty \int_0^\infty \frac{y^{1/2}}{(j+1)^{1/2}}\,e^{-y}\,\frac{dy}{(j+1)}$$

$$= \left(\int_0^\infty y^{1/2}e^{-y}\,dy\right)\cdot\left(\sum_{j=0}^\infty \frac{1}{(j+1)^{3/2}}\right) = \Gamma(3/2)\cdot\underbrace{\left(\sum_{j=1}^\infty \frac{1}{j^{3/2}}\right)}_{\text{this is called } \zeta\left(\frac{3}{2}\right)}$$

(Riemann Zeta function†)

$$= \Gamma\left(\frac{3}{2}\right)\cdot\zeta\left(\frac{3}{2}\right) \qquad (9)$$

$$= \frac{\sqrt{\pi}}{2}\cdot(2.612)$$

† $\zeta(n) = \sum_{j=1}^\infty \frac{1}{j^n}$, $\zeta\left(\frac{3}{2}\right) = \sum_{j=1}^\infty 1/j^{3/2} = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \frac{1}{4^{3/2}} + \cdots$

E. More $T<T_c$ Properties

$T<T_c$, particles in $\varepsilon>0$ s.p. states contribute to $E(T)$

$$\underset{(T<T_c)}{E(T)} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{\varepsilon/kT}-1}\,d\varepsilon \qquad (\mu=0,\ T<T_c)$$

$$= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(kT)^{5/2}\underbrace{\int_0^\infty \frac{x^{3/2}}{e^{x}-1}\,dx}_{\text{just a number}} \propto T^{5/2}$$

$$N_{\varepsilon>0} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(kT)^{3/2}\underbrace{\int_0^\infty \frac{x^{1/2}}{e^{x}-1}\,dx}_{\text{just another number}}$$

$$\therefore\ E(T) \sim N_{\varepsilon>0}\cdot(kT) = \underbrace{(0.770)}_{\text{after working out the numbers}}\cdot N_{\varepsilon>0}\cdot kT \qquad (10)$$

$$\frac{E(T)}{N_{\varepsilon>0}(T)} = 0.770\ kT \qquad (11)$$

Heat Capacity $C_V = \frac{\partial E}{\partial T}$; $E(T) \sim T^{5/2} \Rightarrow C_V \sim T^{3/2}$

$$E(T) = 0.770 \cdot N_{\varepsilon>0}(T) \cdot kT = 0.770 \cdot N\left(\frac{T}{T_c}\right)^{3/2} \cdot kT$$

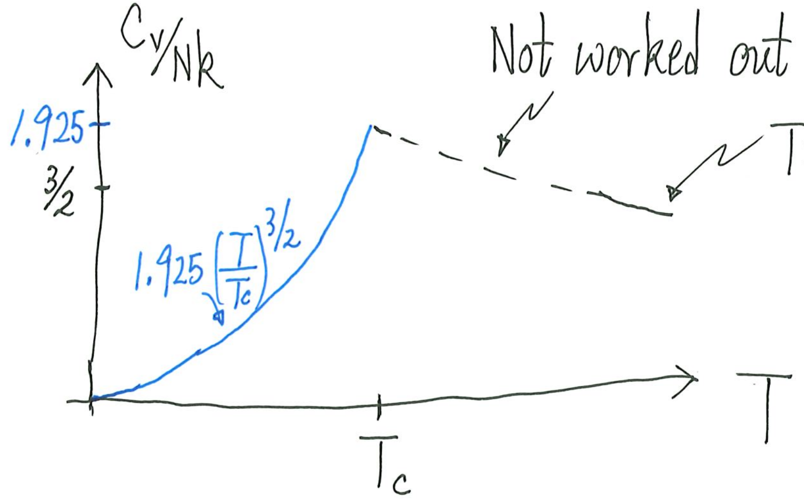
$$C_V(T) = \frac{\partial E}{\partial T} = 0.770 \times \frac{5}{2} \cdot \underbrace{N\left(\frac{T}{T_c}\right)^{3/2}}_{N_{\varepsilon>0}(T)} \cdot \underbrace{k}_{\text{correct unit}} \qquad (12)$$

$$= 1.925 \cdot N_{\varepsilon>0}(T) \cdot k \qquad (13)$$

(i) $T \to 0$, $C_V \to 0$ (OK with thermodynamics 3rd law)

(ii) $T = T_c$, $C_V = 1.920\, Nk$ ($> \frac{3}{2} Nk$ of classical ideal gas, which is $T \gg T_c$ limit)

(iii) $T < T_c$, $C_V = 1.925 \frac{N_{\varepsilon>0}(T)}{N} \cdot Nk = 1.925 \cdot Nk \cdot \left(\frac{T}{T_c}\right)^{3/2} \sim T^{3/2}$



Not worked out here (but we have the equations)

$T \gg T_c$, $C_V = \frac{3}{2} Nk$ (classical gas behavior)

Ideal Bose Gas (3D)

- $C_V(T)$ is continuous across T_c, but it has a <u>cusp</u>

$$pV = \frac{2}{3} E = \frac{2}{3} \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (kT)^{5/2} \cdot [\text{some number}]$$

(compressibility) $\frac{\partial V}{\partial p} \to \infty$

$$\Rightarrow p = \frac{2}{3} \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (kT)^{5/2} \sim T^{5/2} \text{ and does } \underline{\text{not}} \text{ depend on } V \qquad (14)$$

drops as T decreases to zero

(bosons going into $\varepsilon = 0$ s.p. state don't contribute to p)

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

$$(T<T_c,\ \mu=0) \Rightarrow TS = E + pV = E + \frac{2}{3}E = \frac{5}{3}E$$

$$\Rightarrow S = \frac{5}{3}\frac{E}{T} = \frac{5}{3}\cdot(0.770)\cdot Nk\cdot\left(\frac{T}{T_c}\right)^{3/2} \quad (15)\ (T<T_c)$$

One can get all the thermodynamics for $T<T_c$

We also have the equations for all T.

How does the $T<T_c$ physics play out in 2D, 1D Ideal Bose Gas?