Ideal Bose-Einstein Gas

Start with the maximum probable distribution $f(\varepsilon_i)$, where:

$$f(\varepsilon_i) = \frac{N_i^*}{g_i} = \frac{1}{e^{-\beta\mu+\beta\,\varepsilon_i} - 1} \tag{1}$$

g_i is the degeneracy of the state and μ is the chemical potential. Define $\alpha = -\mu\beta$, $e^{-\alpha} = e^{\beta\mu} = z$, where z is the fugacity of the gas. With the conservation of energy, it is required that:

$$N = \sum_{\substack{i=0\\(levels)}}^{\infty} N_i^* = \sum_{\substack{i=0\\(levels)}}^{\infty} \langle n_i \rangle = \sum_{\substack{i=0\\(levels)}}^{\infty} \frac{g_i}{z^{-1}e^{\beta\varepsilon_i} - 1} = \frac{g_o}{e^{\beta(\varepsilon_o-\mu)} - 1} + \frac{g_1}{e^{\beta(\varepsilon_1-\mu)} - 1} + \cdots$$
$$= N_o + N_1 + \cdots \tag{2}$$

The summation in Eqn. (2) is sum over (energy) levels. Supposing we do a sum over states, then it is necessary that we give a statistical weight to each state. Since there is no restriction on the number of particles occupying a particular state, each state can be given a statistical weight of **1**.

The condition $e^{-\beta\mu} \geq 1$, or $\mu \leq 0$, is required to have positive numbers of particles. As the total number of particles in the ground state, i.e. $\varepsilon_o = 0$, is $N_o = N$ we have

$$N_o = f(\varepsilon_o = 0) = \frac{1}{e^{\alpha} - 1} = \frac{1}{z^{-1} - 1} = \frac{z}{1-z},$$

then

$$N = \frac{1}{e^{\alpha} - 1} \qquad \Rightarrow \quad \alpha = \ln\left(1 + \frac{1}{N}\right) \approx \frac{1}{N}$$

As $N \to \infty$, we find $\alpha = 0$, or $e^{\alpha} = 1$

Mathematical Description:

$$N_e = N = \sum_{\substack{i=0\\(levels)}}^{\infty} N_i^* = \int_0^{\infty} \frac{g(\varepsilon)d\varepsilon}{e^{\alpha+\beta\,\varepsilon} - 1} \quad . \tag{3}$$

Where $g(\varepsilon) = \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\sqrt{\varepsilon}$ **.** Eqn (3) are often found expressions for a Bose ideal gas in texts.

$$N_e = \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2} \int_0^{\infty} \frac{\sqrt{\varepsilon}\, d\varepsilon}{e^{\alpha+\beta\,\varepsilon} - 1} = \frac{V}{\lambda^3}\frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{\sqrt{x}dx}{z^{-1}e^{x} - 1} \tag{4}$$

Where $x = \beta\varepsilon$, and $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ is the De-Broglie wave function.

By incorporating the density of states, no weight is given to $\varepsilon = 0$ state (zero momentum state) as the kinetic energy of the particles goes to zero in this energy level. In quantum mechanical treatment this is incorrect as the particles essentially occupy the lower energy states in the low temperature and high density limit where quantum effects become dominant. Hence it is necessary that we take this term out of the summation (Eqn. 2) before carrying out the integration.

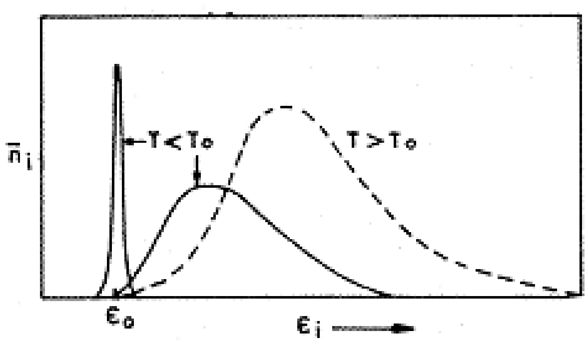
For the density of states we have to revise it in the form:

$$g(\varepsilon) = \delta(\varepsilon) + \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\sqrt{\varepsilon}\,\mathbf{,} \qquad \delta(\varepsilon) = \text{Dirac's delta function}$$

Then we have for the total number of particles:

$$N = \int_0^\infty d\varepsilon \frac{1}{z^{-1}e^{\beta\varepsilon}-1}\left[\delta(\varepsilon)+\left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\varepsilon^{1/2}\right]$$
$$= \underbrace{\left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{z^{-1}e^{\beta\varepsilon}-1}}_{N_e} + \underbrace{\left(\frac{z}{1-z}\right)}_{N_o} \tag{5}$$

where N_e refers to the number of particles in the **excited states** and N_0 is the number of particles in the $\varepsilon = 0$ state.



Schematic diagram of the distribution function for the particles of an ideal BE gas.

When the temperature is very high (classical limit), then z << 1 as $z = e^{\beta\mu}$ and μ is a –ve quantity. Under such conditions, the term $\frac{z}{1-z}$ is well behaved and does not give a significant contribution to *N*. In other words $N_0 << N$ and N_e is large. Hence most particles are in the excited states and not in the $\varepsilon = 0$ state. But as the temperature approaches 0 K, $z \to 1$ and the term $\frac{z}{1-z}$ diverges as $z = 1$ at T = 0 K. The contribution from singularity terms becomes more significant under these conditions. Here N_0 becomes much more significant compared to N_e. Thus the $\varepsilon = 0$ level gets densely populated. This is what is called ***Bose-Einstein condensation***.

Bose-Einstein Integral

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Home work: Prove that (See Pathria Appendix …)

$$g_s(z) = \frac{1}{\Gamma(s)}\int_0^\infty \frac{x^{s-1}dx}{z^{-1}e^x - 1} = \sum_{k=1}^\infty \frac{z^k}{k^s},$$

then plot it for the values $s = \frac{3}{2}, \frac{5}{2}$, $g_\infty(z) = e^{-z}$.

Plot $g_{3/2}(z) = e^{-z}, \quad z = 0 \to 1$

Check $g_{3/2}(1) = \sum_{n=1}^{\infty} \frac{1}{n^{3/2}} = \varsigma(\frac{3}{2}) = 2.612$

where ς is the Riemann zeta function. This is the maximum possible value of $g_{3/2}(z)$.

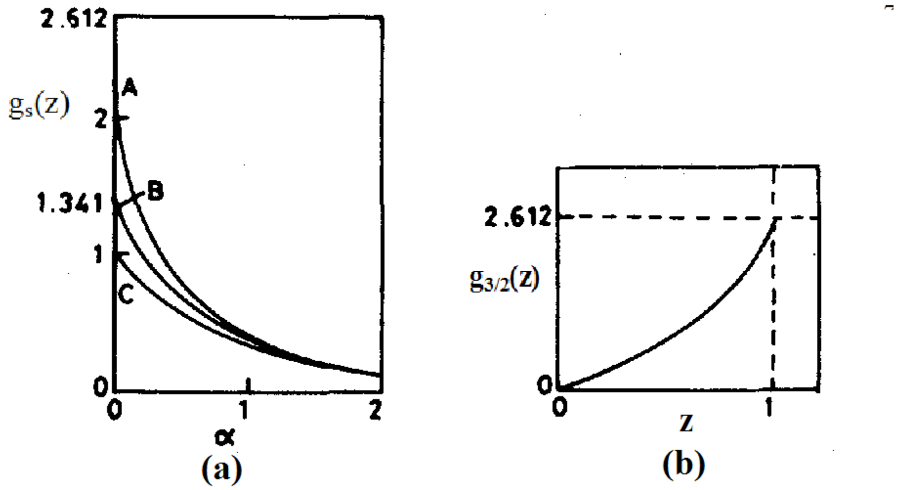

FIg. (a) The functions $g_{3/2}(\alpha)$, curve A; $g_{5/2}(\alpha)$, curve B; and $g_{\infty}(\alpha) = e^{-\alpha}$, curve C.
(b)The function $g_{3/2}(z)$. Note that $z = e^{-\alpha}$

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We can define a (minimum) critical temperature T, at which z has a maximum value 1. Use the value:

$g_{3/2}(1) = \sum_{n=1}^{\infty} \frac{1}{n^{3/2}} = \varsigma(\frac{3}{2}) = 2.612$, we have

$$N_e = 2.612\, V \times \left(\frac{2\pi\, mk_B T}{h^2} \right)^{3/2} \tag{6}$$

As $N = N_e$, and $T = T_c$, we have

$$T_c = \frac{h^2}{2\pi\, mk_B} \left(\frac{N}{2.612\, V} \right)^{2/3} \tag{7}$$

Divider Eq. 6 by Eq. 7 gives the maximum number of particles occupying states above the ground state is

$$N_e = N \left(\frac{T}{T_B} \right)^{3/2} \qquad T < T_c \tag{8}$$

and the rest of the particles

$$N_o = N - N_e = N \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right] \qquad T < T_c \tag{9}$$

must condense into the ground state. This rapid increase in the population of the ground state below T_c is called Bose-Einstein condensation.

HW. For ^4He calculate T_c at 1 atm.

Answer:

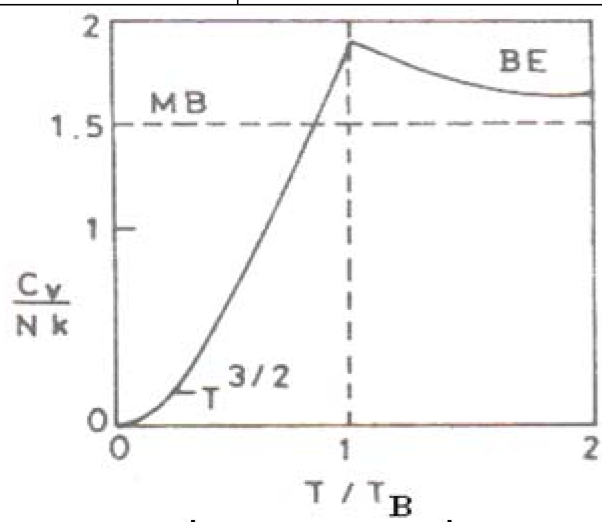
Use $N = N_A = 6.02\times10^{23}$ molecules/mol, $m = 4\times1.66\times10^{-27} = 6.65\times10^{-27}$ kg, and $V = 22.4\times10^{-3}$ m^3/mole, then

$$T_c = \frac{h^2}{2\pi m k_B}\left(\frac{N}{2.612\,V}\right)^{2/3}$$

$$= \frac{(6.63\times10^{-34})^2}{2\pi(6.65\times10^{-27})\times1.38\times10^{-23}}\left(\frac{6.02\times10^{23}}{2.612\times22.4\times10^{-3}}\right)^{2/3} = 0.036\text{ K.}$$

It is small compared to the experimental value 4.21 K.

The Properties of Ideal Bose-Einstein Gas

Physical quantity	$T > T_B$	$T < T_B$
Internal energy (U)	$U_+ \to \frac{3}{2}Nk_BT$	$U_- = 0.77Nk_BT\left(\frac{T}{T_B}\right)^{3/2}$
Specific heat (C_V)	$C_{V+} = \left(\frac{\partial U_+}{\partial T}\right)_V \approx \frac{3}{2}Nk_B$	$C_{V-} = \left(\frac{\partial U_-}{\partial T}\right)_V \approx 1.92\,N\,k_B\left(\frac{T}{T_B}\right)^{3/2}$
		
Entropy (S)		$S_- = \int_0^T \frac{C_{V-}}{T'}dT' = 1.28\,N\,k_B\left(\frac{T}{T_B}\right)^{3/2}$
Helmholtz free energy (F)		$F_- = U_- - TS_- = -1.33\,k_BT\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$

Pressure (P)		$P_{-} = -\left(\frac{\partial F_{-}}{\partial V}\right)_{T,N} = 1.33\ k_B T\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

NOTES:

1. B.E. condensation can occur only when the particle number is conserved. For example, photon do not condense, they have a simpler alternative, namely, to disappear into the vacuum.
2. At $T < T_c$ the system may be looked upon as a mixture of two "phases"
   (a) A gaseous phase [Ne], particles distributed over the excited states ($\varepsilon \neq 0$), and
   (b) A condensed phase, consisting of [N_o] particles accumulated in the ground state ($\varepsilon = 0$).

We can define a (minimum) critical temperature T, at which z has a maximum value 1

$$N = \frac{V}{\lambda_c^3} = V\left(\frac{2\pi m k T_c}{h^2}\right)^{3/2} \times 2.612$$

$$\Longrightarrow T_c = \frac{h^2}{2\pi m k}\left(\frac{\rho}{2.612}\right)^{2/3}, \qquad \rho = \frac{N}{V}$$

If we have one mole of gas, so that N is Avogadro's number,

$$T_c = \frac{115}{M V_M^{2/3}}\mathrm{K}$$

where M is the molecular weight and V_M is the molar volume in cm^3 mol'.
Example: For Helium, M = 4, V_M = 27.6 cm^3 , this implies T = 3.14 K, (exp. = 2.18 K). Bose-Einstein Condensation:-

Bose-Einstein Condensation:-

The expression

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

has no solution for $T < T_c$ because $g_{3/2}(z) < g_{3/2}(1)$. This difficulty does not occur in the original sum. For low temperature, $T < T_c$ this changing from summation to integration cases a serious error. Large contribution from the first few terms are left out because of $g(\varepsilon = 0) = 0$.

For small z (or large $e^{-\mu\beta}$), the terms with the lowest do not contribute much to the sum, and so replacement of the sum with an integral causes little error. However, when z is approaching 1 (or $e^{-\mu\beta}$ is small), the first few terms in the summation become important, and so we can not replace the sum with an integral.

AT low temperature the ground state is important an should be treated separately. So,

$$g(\varepsilon) = \delta(\varepsilon) + \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{\frac{1}{2}}$$

where $\delta(\varepsilon)$ is the Dirac delta function. The total number of particles N could be separated to

Bose_Einstein_condensation

$$N = N_o + N_e = \int_0^\infty \frac{d\varepsilon}{z^{-1}e^{\beta\epsilon} - 1}[\delta(\varepsilon) + \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{\frac{1}{2}}]$$

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

where N0 is the number of particles in the ground state, and Ne is the number of particles in the excited state. Also,

$$N_e = N\left(\frac{T}{T_c}\right)^{3/2} \frac{g_{3/2}(z)}{g_{3/2}(1)}$$

N_e has its maximum value when $\alpha = 0$.

NOTES:

3. B.E. condensation can occur only when the particle number is conserved. For example, photon do not condense, they have a simpler alternative, namely, to disappear into the vacuum.
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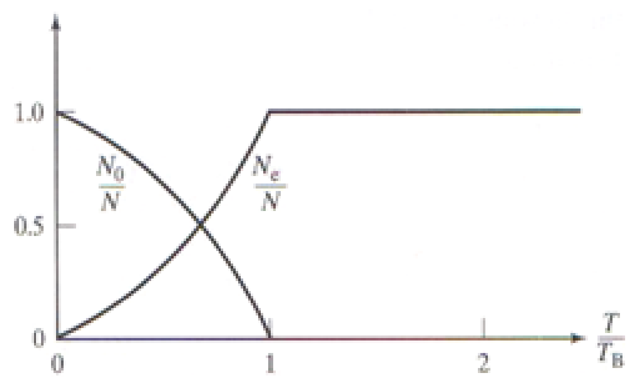

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	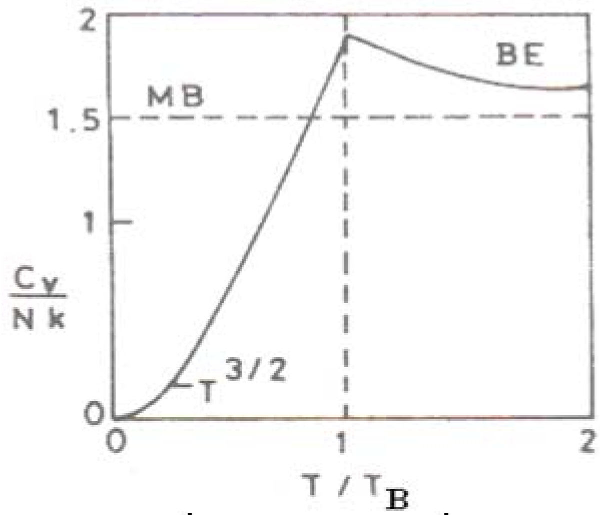	
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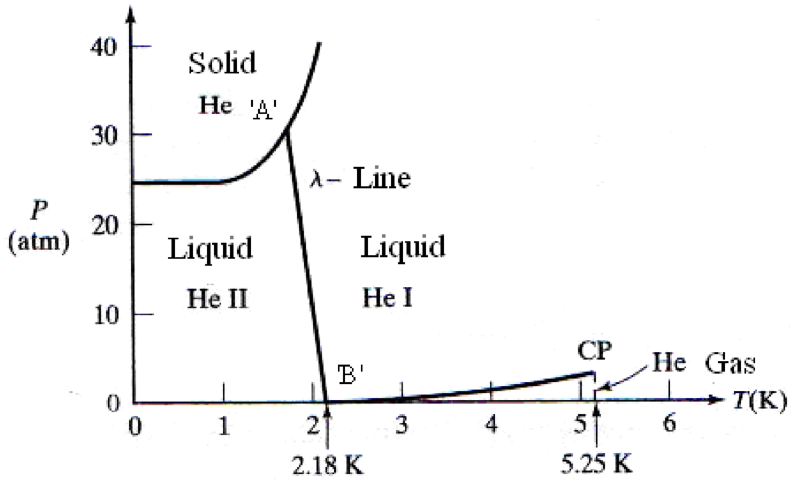
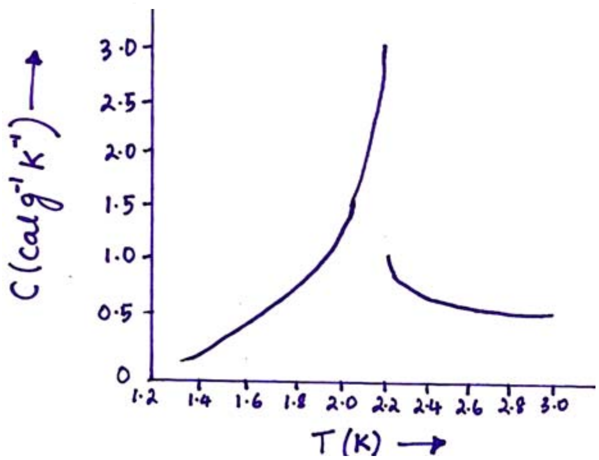
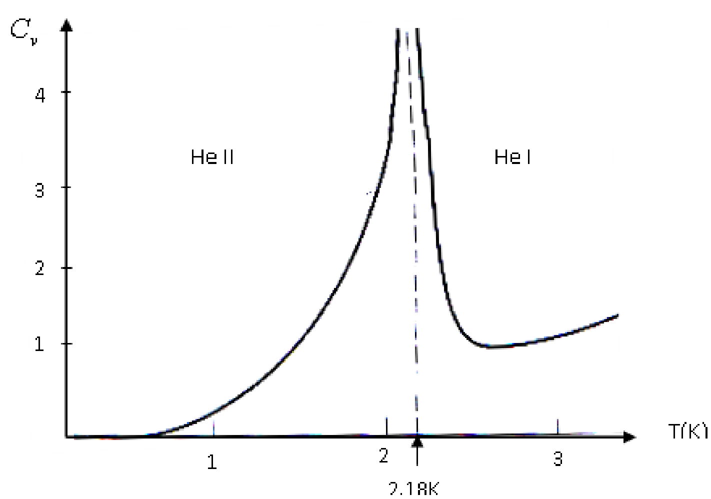
An experimental evidence for Bose–Einstein condensation came from the (C_V, T) relationship of $^4\mathrm{He}$. Phase transition of $^4\mathrm{He}$ was found to occur at 2.19 K. When the mass, $m = 4 \times 1.66 \times 10^{-27} = 6.65 \times 10^{-27}$ kg and volume, $\mathrm{V} = 27.6\ \mathrm{cm}^3/\mathrm{mole}$ cm^3/mole the transition temperature it was found to be 3.13. The two numbers were not drastically different and the similarity between the (C_V vs. T) plot of an ideal Bose gas and that of $^4\mathrm{He}$ was enough evidence to prove that the phase transition in $^4\mathrm{He}$ is actually Bose-Einstein condensation.





Struck by the shape of this graph, the phase transition was given the name $\lambda-$transition by Keesom and the transition point was called $\lambda-$transition point.



H.W. Show that for an ideal boson gas $P = \alpha u$, where P is the pressure, u the energy density and α a constant. What is α?

Answer

Using results in section 7.H.1d., we have

$$U = \langle E \rangle = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle = \sum_{\mathbf{k}} \frac{\varepsilon_{\mathbf{k}}\, z}{\exp(\beta \varepsilon_{\mathbf{k}}) - z}$$

$$= \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty dp\; p^2 \frac{1}{2m} p^2 \frac{z}{\exp\left(\beta \frac{1}{2m} p^2\right) - z}$$

Using $p = \sqrt{2mk_B T}\; x = \frac{2\sqrt{\pi}\,\hbar}{\lambda_T} x$, we have,

$$U = \frac{4\pi V}{(2\pi\hbar)^3} \cdot \frac{1}{2m} \left(\frac{2\sqrt{\pi}\,\hbar}{\lambda_T}\right)^5 \int_0^\infty dx\; x^4 \frac{z}{\exp(x^2) - z}$$

$$= \frac{8V\hbar^2\sqrt{\pi}}{m\lambda_T^5} \int_0^\infty dx\; x^4 \frac{z}{\exp(x^2) - z}$$

$$= \frac{8V\hbar^2\sqrt{\pi}}{m\lambda_T^5} K_4^{(-)}(z) = \frac{8V\hbar^2\sqrt{\pi}}{m\lambda_T^5} \cdot \frac{1}{2} \Gamma\left(\frac{5}{2}\right) g_{5/2}(z)$$

$$= \frac{3V\hbar^2\pi}{m\lambda_T^5} g_{5/2}(z)$$

$$\Rightarrow \qquad u = \frac{U}{V} = \frac{3\hbar^2\pi}{m\lambda_T^5} g_{5/2}$$

Comparing with

$$P = k_B T \frac{1}{\lambda_T^3} g_{5/2}(z) = \frac{2\hbar^2\pi}{m\lambda_T^5} g_{5/2}(z)$$

we have

$$P = \frac{2}{3} u$$