Quantum Statistics and Bose-Einstein Condensation

Let us consider a system consisting of non-interacting molecules, denoted by *a*, *b*, *c* …., whose energy levels are given by E_a, E_b, E_c, …In the classical statistical mechanical treatment of ideal gases, the particles/molecules/atoms are assumed to be ==distinguishable==. Therefore, every possible occupation of energy levels by particles is admissible. Hence the following decomposition of the Hamiltonian, total energy and the partition function holds good.

$$H = H_a + H_b + H_c + ...$$

$$E = E_a + E_b + E_c + ...$$

$$q_a = \sum_a e^{-\beta E_a} \quad , \qquad q_b = \sum_b e^{-\beta E_b}$$

$$Q = q_a q_b q_c ..... \qquad \text{where a, b, c etc are the particle indices.}$$
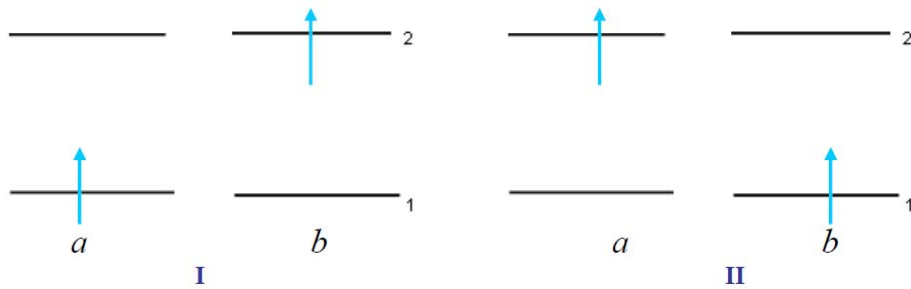
Owing to the distinguishability of the particles '*a*' and '*b*', arrangements I and II are different and each should be counted separately.

　　　However, when particles are ==indistinguishable==, the arrangements I and II are one and the same and hence should be counted only as one arrangement. Evaluating the total partition function as

$$Q = q_a q_b q_c .....$$

is incorrect as it has those extra terms.

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Justification:

I. Take five balls that are distinguishable.

The total number of ways in which the balls can be arranged in <u>three</u> levels such that

　　　　　　　　　2 balls in level 1
　　　　　　　　　2 balls in level 2
　　　　　　　　　1 ball in level 3

are 　$\dfrac{5!}{2!2!1!} = 30$

Generically, $\dfrac{N!}{n_1! n_2! n_3! ..}$ where $n_1, n_2, n_3...$ are the numbers of balls occupying levels 1, 2, 3.. etc respectively.

II. Supposing the balls were indistinguishable,

*Then the number of ways is which the above arrangement can be done is just **1** !*

Supposing an arrangement with only one ball occupying each level is desired, then again there only one possible way to obtain it in the indistinguishable balls case. Whereas with distinguishable balls there are *N*! possible ways of obtaining this arrangement.

Therefore, classical statistics vastly over-estimates the number of configurations. In classical statistical mechanics, this is of course taken into account by the 1/N! terms (Boltzmann factor) in front of the partition function. This method does not work at low temperature where quantum nature of the particles become important that impose further restrictions on the occupancy of the energy levels of the system. In a system of Bose particles, any number of particles can occupy any given energy level. On the other hand, particles obeying Fermi-Dirac statistics, maxium of one particle can occupy a given energy level. That is, the occupation number of a given energy level can be 1 or 0.

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High Temperature Limit

When the temperature is high, a system has a large number of accessible energy states such as translational, rotational, electronic…. The number of states is much more than the number of atoms/molecules. At high temperatures, a large number of states become accessible, especially the translational states. In such a case, the possibility of multiple occupancy of a state will be greatly reduced. *Thus the occupied energy levels are mostly non-degenerate*. Thus, the occupation due to quantum statistics is not important and classical Boltzmann statistics works well. This is exactly like case **II** in justification. So the surplus contributions that will feature for the indistinguishable particles in the expression

$$Q = q_a q_b q_c \ldots..$$

N! compared to distinguishable particles.

For an ideal gas the atoms/molecules are independent (negligible intermolecular forces) and indistinguishable. In the expression

$$Q = q^N$$

there are *N*! surplus contributions in the thermodynamic limit for an ideal gas. Thus the exact partition function for an ideal gas in this limit is

$$Q = \frac{q^N}{N!} \rightarrow (1)$$

In the thermodynamic limit, $n\lambda^3 \ll 1$ (where *n* is the number density, λ is the de-Broglie wavelength,

$\lambda = \left(\dfrac{h^2}{2\pi n k_{\mathbf{B}} T} \right)^{\frac{1}{2}}$ and $n\lambda^3$ is a dimensionless quantity) because *m* >> 1, *T* >> 1 and *n* << 1. This is the classical

regime where Maxwell-Boltzmann statistics holds good and indistinguishability can be exactly accounted for. But as we go on to *low temperatures and high densities* multiple occupancy of states increases. $n\lambda^3 \approx 1$ is in this limit. Under such conditions, the indistinguishability of particles becomes much more significant. This is where the quantum effects creep in and there is need for a revised statistics.

Quantum Statistics

All known indistinguishable particles, fall in to the class of either *Fermions* or *Bosons*. These two statistics or distributions lay different constraints on the occupancy of a particular state but under the conservation of two quantities, the total number of particles and the total energy.

$$\sum_i n_i = N$$

$$\sum_i n_i \varepsilon_i = E$$

These constraints become very significant when there is degenerate/multiple occupancy of energy levels.

To understand the effects of these statistics on the distribution of energy levels, we first group the energy levels with energy within a small interval together and assign a degeneracy factor to each group according to the number of energy levels in each group. Let us denote the energy and degeneracy of i-th group by ε_i and g_i, respectively. The picture below illustrates the grouping.
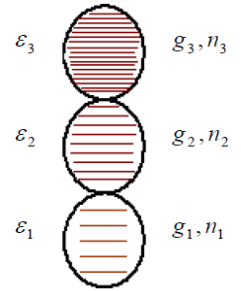
Fermions obey the condition on the occupation of a state is that: a state can have 1 particle or 0 particle in it, but never two or more. So, n_i is always less than or equal to g_i. This is because they obey the Pauli exclusion principle.

$$n_i = 0,1$$
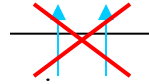
Let n_i be the number of particles occupying an energy level ε_i in a particular configuration. If g_i is the degeneracy of ε_i, (such that the degeneracy of that energy is $\geq$ the number of particles occupying that energy level), then the number of possible arrangements amongst the degenerate levels of ε_i is

$$w_{FD}^{(i)} = \frac{g_i!}{n_i!(g_i - n_i)!} \rightarrow (2)$$

(This is exactly like picking '*n*' white balls out of '*g*' white balls.)

Bose-Einstein Statistics

Bosons obey this statistics. There is no constraint on the occupation of a particular state in an energy level as these particles do not obey the Pauli principle. Any number of particles can occupy a state in an energy level.

$$n_i = 0, 1, 2, 3, \ldots\ldots$$

$$n_i^{max} = \infty$$

Let n_i be the number of particles occupying an energy level ε_i in a particular configuration. If g_i is the degeneracy of ε_i, then the number of possible arrangements amongst the degenerate levels of ε_i are

$$w_{BE}^{(i)} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \rightarrow (3)$$

Justification:

Suppose we take five indistinguishable balls (bosons, n_i) and arrange them into three distinct boxes (degenerate levels, $g_i = 3$) with no restriction on the occupation numbers in each box.

Box 1   Box 2   Box 3
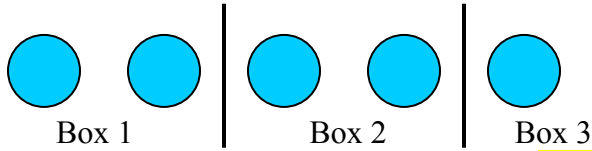
Here there are five balls and two sticks (the <mark>number of sticks will always be one lesser than the number of degenerate levels</mark>). The total number of possible arrangements for the balls in the boxes is

$$\frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} = \frac{(5 + 3 - 1)!}{5!2!} = \frac{7!}{5!2!} = 21$$

We are justified in doing $(g_i - 1)!$ because only the boxes are distinct, the sticks are not. The sticks are indistinguishable.

Example 1: Compare the Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics when four particles are arranged in two energy levels. Three particles are at energy level ε_1 having a degeneracy $g_1 = 4$ and one particle at energy level ε_2 having a degeneracy $g_2 = 2$.

Solution:
Note that: n1 = 3, g1 = 4 , n2 = 1, g2 = 2

$$w_{MB} = N! \prod_{i=1}^{n} \frac{g_i^{N_i}}{N_i} = 4! \frac{4^3 \times 2^1}{3!1!} = 512$$

$$w_{BE} = \prod_{i=1}^{n} \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} = \frac{(3+4-1)!}{3!3!} \frac{(1+2-1)!}{1!1!} = 40$$

$$w_{FD} = \prod_{i=1}^{n} \frac{g_i!}{N_i!(g_i - N_i)!} = \frac{4!}{3!1!} \frac{2!}{1!1!} = 4$$

Example 2: Consider a system of *two* particles in a volume V, each of which can be in any one of three quantum states of respective energy $\varepsilon_1 = 0$, $\varepsilon_2 = 1\varepsilon$, and $\varepsilon_3 = 3\varepsilon$. The system is in contact with a heat reservoir at temperature $T = (k\beta)^{-1}$. Write an expression for the **partition function** if the particles obey:

1- the classical Maxwell-Boltzmann statistics and are consider *distinguishable*.
2- the classical Maxwell-Boltzmann statistics and are consider *undistinguishable*.
3- the particles obey Fermi-Dirac statistics.
4- the particles obey Bose-Einstein statistics.

Solution:

Configuration				Number of states		
0	1ε	3ε		MB	BE	FD
xx				1	1	--
	xx			1	1	--
		xx		1	1	--
x	x			2	1	1
x		x		2	1	1
	x	x		2	1	1

$$Z_{MB} = \sum_{\{n_i\}} e^{-\beta \sum_s n_s \varepsilon_s} = \sum_{i(energy\ levels)} g_i e^{-\beta \varepsilon_i}$$

$$= 1 + e^{-2\beta\varepsilon} + e^{-6\beta\varepsilon} + 2e^{-\beta\varepsilon} + 2e^{-3\beta\varepsilon} + 2e^{-4\beta\varepsilon}$$

$$Z_{BE} = \sum_i g_i e^{-\beta\varepsilon_i} = 1 + e^{-2\beta\varepsilon} + e^{-6\beta\varepsilon} + e^{-\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}$$

$$Z_{FD} = \sum_i g_i e^{-\beta\varepsilon_i} = e^{-\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}$$

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  The total number of arrangements possible for a particular configuration for both F-D as well as B-E are (this is over all the energy levels of a particular configuration)

$$W\{n_i\} = \prod_i w^{(i)}(n_i) \rightarrow \qquad (4)$$

The total number of arrangements possible over all configurations is

$$\Omega(N,V,E) = \sum_{\{n_i\}} W(\{n_i\}) \rightarrow \qquad (5)$$

where $\Omega(N,V,E)$ is the partition function in microcanonical ensemble.

Thus the entropy is

$$S = k_B \ln \Omega \cong k_B \ln W\left(\{n_i^*\}\right)$$

Maximizing the entropy and **finding out the maximum term by Lagrange's method of undetermined multipliers.**

$$\delta \ln W\left(\{n_i\}\right) - \left[\alpha \sum_i \delta n_i - \beta \sum_i \varepsilon_i \delta n_i\right] = 0 \rightarrow \qquad (7)$$

$$W\{n_i\} = \prod_i w^{(i)}(n_i)$$

$$\ln\left[W\{n_i\}\right] = \ln\left[\prod_i w^{(i)}(n_i)\right] = \sum_i \ln w^{(i)}(n_i)$$

$$\delta \ln W\left(\{n_i\}\right) = \sum_i \delta \ln w^{(i)}(n_i) \rightarrow \qquad (8)$$

  For F-D statistics,

$$w^{(i)} = \frac{g_i!}{n_i!(g_i - n_i)!}$$

$$\ln w^{(i)} = \ln g_i! - \ln n_i! - \ln(g_i - n_i)!$$

$$= g_i \ln g_i - \cancel{g_i} - n_i \ln n_i + \cancel{n_i} - (g_i - n_i)\ln(g_i - n_i) + \cancel{g_i} - \cancel{n_i}$$

$$= g_i \ln g_i - n_i \ln n_i - (g_i - n_i)\ln(g_i - n_i)$$

$$= g_i \ln\left(\frac{g_i}{g_i - n_i}\right) + n_i\left(\frac{g_i - n_i}{n_i}\right) = -g_i \ln\left(1 - \frac{n_i}{g_i}\right) + n_i \ln\left(\frac{g_i}{n_i} - 1\right) \rightarrow (9)$$

For B-E statistics,

$$w^{(i)} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

$$
\begin{aligned}
\ln w^{(i)} &= \ln(n_i + g_i - 1)! - \ln n_i! - \ln(g_i - 1)! \\
&= (n_i + g_i - 1)\ln(n_i + g_i - 1) - \cancel{n_i} - \cancel{g_i} + \cancel{1} - n_i \ln n_i + \cancel{n_i} - \cancel{(g_i - 1)}\ln(g_i - 1) + \cancel{g_i} - \cancel{1} \\
&= (n_i + g_i - 1)\ln(n_i + g_i - 1) - n_i \ln n_i - (g_i - 1)\ln(g_i - 1) \\
&= n_i \ln\frac{(n_i + g_i - 1)}{n_i} + (g_i - 1)\ln\frac{(n_i + g_i - 1)}{(g_i - 1)} \cong n_i \ln\left(1 + \frac{g_i}{n_i}\right) + g_i \ln\left(1 + \frac{n_i}{g_i}\right) \rightarrow
\end{aligned}
$$
(10)

General form of $\ln w^{(i)}$ **for F-D and B-E statistics is**

$$\ln w^{(i)} = n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a}\ln\left(1 - a\frac{n_i}{g_i}\right) \rightarrow$$
(11)

where $\quad a = -1 \quad$ for BE
$\qquad\qquad a = 1 \quad$ for FD
$\qquad\qquad a = 0 \quad$ for MB

$$
\delta \ln w^{(i)} = \left[\ln\left(\frac{g_i}{n_i} - a\right) + n_i \frac{\left(-g_i/n_i^2\right)}{\left(\frac{g_i}{n_i} - a\right)} - \frac{g_i}{a}\left(\frac{-a/g_i}{1 - a\frac{n_i}{g_i}}\right) \right]\delta n_i = \left[\ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{n_i}\left(\frac{1}{\frac{g_i}{n_i} - a}\right) + \left(\frac{1}{1 - a\frac{n_i}{g_i}}\right) \right]\delta n_i
$$

$$
= \left[\ln\left(\frac{g_i}{n_i} - a\right) - \left(\frac{\cancel{1}}{\cancel{1 - a\frac{n_i}{g_i}}}\right) + \left(\frac{\cancel{1}}{\cancel{1 - a\frac{n_i}{g_i}}}\right) \right]\delta n_i = \left[\ln\left(\frac{g_i}{n_i} - a\right) \right]\delta n_i \rightarrow \qquad (13)
$$

From eqns (7) and (8),

$$\delta \ln W(\{n_i\}) - \left[\alpha \sum_i \delta n_i - \beta \sum_i \varepsilon_i \delta n_i\right] = 0 \qquad \Rightarrow \quad \delta \ln W(\{n_i\}) = \sum_i \delta \ln w^{(i)}(n_i)$$

Thus,

$$\sum_i \left[\ln\left(\frac{g_i}{n_i} - a\right) - \alpha - \beta\varepsilon_i\right]\delta n_i = 0 \qquad \Rightarrow \qquad \ln\left(\frac{g_i}{n_i^*} - a\right) - \alpha - \beta\varepsilon_i = 0$$

$$n_i^* = \frac{g_i}{e^{\alpha + \beta\varepsilon_i} + a} \rightarrow (14)$$

n_i^* *is the distribution that maximizes the entropy.* Hence

$$\frac{S}{k_B} \cong \ln W\left(\{n_i^*\}\right) = \sum_i \ln w^{(i)}(n_i^*)$$

From eqn (11)

$$\frac{S}{k_B} = \sum_i \left[n_i^* \ln\left(\frac{g_i}{n_i^*} - a\right) - \frac{g_i}{a} \ln\left(1 - a\frac{n_i^*}{g_i}\right)\right] = \sum_i \left[n_i^* \ln\left(\frac{g_i}{g_i/e^{\alpha+\beta\varepsilon_i}}\right) - \frac{g_i}{a} \ln\left(1 - a\frac{g_i/e^{\alpha+\beta\varepsilon_i}}{g_i}\right)\right]$$

$$\frac{S}{k_B} = \sum_i \left[n_i^*(\alpha + \beta\varepsilon_i) + \frac{g_i}{a} \ln(1 + ae^{-\alpha-\beta\varepsilon_i})\right] \rightarrow (15)$$

$$\sum_i n_i^* = N \quad ; \quad \sum_i n_i^* \varepsilon_i = E$$

$$\frac{S}{k_B} - \alpha N - \beta E = \frac{1}{a}\sum_i g_i \ln(1 + ae^{-\alpha-\beta\varepsilon_i})$$

$$\alpha = -\frac{\mu}{k_B T} \quad ; \quad \beta = \frac{1}{k_B T}$$

Thus,

$$\frac{S}{k_B} + \frac{\mu N}{k_B T} - \frac{E}{k_B T} = \frac{1}{a}\sum_i g_i \ln(1 + ae^{-\alpha-\beta\varepsilon_i})$$

From thermodynamics,

$$\frac{S}{k_B} + \frac{\mu N}{k_B T} - \frac{E}{k_B T} = \frac{G - (E - TS)}{k_B T} = \frac{PV}{k_B T} \rightarrow (16)$$

Equation of state for a quantum ideal gas is

$$PV = \frac{k_B T}{a}\sum_i g_i \ln(1 + ae^{-\alpha-\beta\varepsilon_i}) \rightarrow \qquad\qquad (17)$$

In the high temperature limit,

$$\alpha, \beta \approx 0$$

Hence Taylor expansion can be done, $\ln(1 + x) \approx x$

$$\frac{PV}{k_B T} = \frac{1}{a}\sum_i g_i ae^{-\alpha-\beta\varepsilon_i} = \sum_i g_i e^{-\alpha-\beta\varepsilon_i} \rightarrow (18)$$

For an ideal gas with Maxwell-Boltzmann distribution, the equation of state is

$$\frac{PV}{k_B T} = \sum_i n_i^* = N \qquad \text{(Ideal gas law)}$$

But from eqn (14)

$$n_i^* = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}}$$

Thus,

$$\frac{PV}{k_B T} = \sum_i g_i e^{-\alpha-\beta\varepsilon_i} \rightarrow (19)$$

(Compare eqn (18) and (19)). Irrespective of whether it is a Bose gas or a Fermi gas, in the thermodynamic limit it goes over to Maxwell-Boltzmann distribution.

Ideal Bose gas

From eqn (17), the equation of state of a Bose gas is

$$\frac{PV}{k_BT} = -\sum_i g_i \ln(1 - e^{-\alpha - \beta\varepsilon_i})$$

$e^{-\alpha} = e^{\frac{\mu}{k_BT}} = z$, where z is the fugacity of the gas.

The equation of state can be rewritten as

$$\frac{PV}{k_BT} = -\sum_i g_i \ln(1 - ze^{-\beta\varepsilon_i}) \rightarrow (20)$$

$$N = \sum_i \langle n_i \rangle = \sum_i \frac{g_i}{e^{\alpha + \beta\varepsilon_i} - 1} = \sum_i \frac{g_i}{z^{-1}e^{\beta\varepsilon_i} - 1} \rightarrow (21)$$

The summations in eqn (20) and (21) are 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 equation of state of the Bose gas as a sum over all states is

$$\frac{PV}{k_BT} = -\sum_k \ln(1 - ze^{-\beta\varepsilon_k}) \rightarrow (22)$$

The total number of particles is

$$N = \sum_k \frac{1}{z^{-1}e^{\beta\varepsilon_k} - 1} \rightarrow (23) \text{ , where the index k is for the states.}$$

Eqns (22) and (23) are oft found expressions for a Bose ideal gas in texts.

The summation can be replaced by an integral if the density of states in the neighbourhood of each energy level is included.

$$\frac{PV}{k_BT} = -\int d\varepsilon G(\varepsilon) \ln(1 - ze^{-\beta\varepsilon})$$

$$N = \int d\varepsilon G(\varepsilon) \frac{1}{z^{-1}e^{\beta\varepsilon} - 1}$$

Density of states around each energy level is

$$G(\varepsilon)d\varepsilon = \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2} \varepsilon^{1/2} d\varepsilon$$

The equation of state thus becomes

$$\frac{PV}{k_BT} = -\left(\frac{2\pi V}{h^3}\right)(2m)^{3/2} \int_0^\infty d\varepsilon \left\{\ln(1 - ze^{-\beta\varepsilon})\right\} \varepsilon^{1/2}$$

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 (20)) before carrying out the integration. Now,

$$\frac{PV}{k_BT} = -\left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\left[\left\{\int_0^\infty d\varepsilon \left\{\ln(1 - ze^{-\beta\varepsilon})\right\} \varepsilon^{1/2}\right\} + \ln(1 - z)\right]$$

$$\frac{P}{k_B T} = -\left(\frac{2\pi}{h^3}\right)(2m)^{3/2}\left[\left\{\int_0^\infty d\varepsilon \left\{\ln(1 - ze^{-\beta\varepsilon})\right\}\varepsilon^{1/2}\right\} + \frac{1}{V}\ln(1 - z)\right]$$

Similarly for the total number of particles

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

The total number of particles present in the system can be classified into

$$N = N_e + N_0$$

$$N = \underbrace{\left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{z^{-1}e^{\beta\varepsilon} - 1}}_{N_e} + \underbrace{\left(\frac{2\pi}{h^3}\right)(2m)^{3/2}\left(\frac{z}{1 - z}\right)}_{N_0} \rightarrow (24)$$

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.

When the temperature is very high (classical limit), then z << 1 as $z = e^{\beta\mu}$ and μ (chemical potential) 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, $z \rightarrow 1$ 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**.

B-E Integral
In the following expressions,

$$\frac{P}{k_B T} = -\left(\frac{2\pi}{h^3}\right)(2m)^{3/2}\left[\left\{\int_0^\infty d\varepsilon \left\{\ln(1 - ze^{-\beta\varepsilon})\right\}\varepsilon^{1/2}\right\} + \frac{1}{V}\ln(1 - z)\right] \rightarrow (25)$$

$$\frac{N}{V} = \left(\frac{2\pi}{h^3}\right)(2m)^{3/2}\left[\int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{z^{-1}e^{\beta\varepsilon} - 1} + \frac{1}{V}\frac{z}{1 - z}\right] \rightarrow (26)$$

$\frac{z}{1 - z} = N_0$ (from eqn (24)) and thus, $z = \frac{N_0}{N_0 + 1}$.

The last terms in eqn (24) and (25) are significant only at low temperatures. The last terms in eqn (24) is

$$-\frac{1}{V}\ln(1 - z) = \frac{1}{V}\ln(N_0 + 1) \rightarrow (27) \qquad\qquad \text{Volume } V,$$

generally scales as *N*. At low temperature most particles are in the $\varepsilon = 0$ state. Hence $N_0 \approx N$. The upper bound on eqn (27) is $N^{-1}\ln N$ which is negligible for all z and hence the last term can be dropped. The eqns (25) and (26) can now be rewritten as

$$\frac{P}{k_B T} = -\left(\frac{2\pi}{h^3}\right)(2m)^{3/2} \int_0^\infty d\varepsilon \left\{\ln(1 - z e^{-\beta\varepsilon})\right\} \varepsilon^{1/2} \rightarrow (28)$$

$$\frac{N - N_0}{V} = \left(\frac{2\pi}{h^3}\right)(2m)^{3/2} \int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{z^{-1} e^{\beta\varepsilon} - 1} \rightarrow (29)$$

Substituting $\beta\varepsilon = x$

$$\frac{P}{k_B T} = -\left(\frac{2\pi}{h^3}\right)(2mk_B T)^{3/2} \int_0^\infty dx \left\{\ln(1 - z e^{x})\right\} \varepsilon^{1/2} \rightarrow (30)$$

$$\frac{N - N_0}{V} = \left(\frac{2\pi}{h^3}\right)(2mk_B T)^{3/2} \int_0^\infty dx \frac{x^{1/2}}{z^{-1} e^{x} - 1} \rightarrow (31)$$

Integrals like those in eqns (30) and (31) are very common in Bose-Einstein systems.

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 Aside
They essentially of the form

$$G_\nu(z) = \int_0^\infty \frac{x^{\nu-1} dx}{z^{-1} e^{x} - 1} \rightarrow (32) \qquad 0 \le z < 1, \; \nu > 0 \; ; \; z = 1, \nu > 1$$

$$\underset{z \to 0}{Lim} G_\nu(z) = \int_0^\infty z e^{-x} x^{\nu-1} dx = z \Gamma(\nu)$$

It is useful to introduce another function $g_\nu(z)$ such that

$$g_\nu(z) \equiv \frac{1}{\Gamma(\nu)} G_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1} dx}{z^{-1} e^{x} - 1} \rightarrow (31)$$

For small vales of z, the integrand in eqn (33) can be in powers of z as

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty x^{\nu-1} \sum_{l=1}^\infty (z e^{-x})^l dx$$

$$= \sum_{l=1}^\infty \frac{z^l}{l^\nu} = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \dots.$$

For $z \ll 1$, the function $g_\nu(z)$, for all ν, behaves like z itself. For $z = 1, \nu > 1$ $g_\nu(z)$ approaches the Riemann *zeta function* $\varsigma(\nu)$

$$g_\nu(1) = \sum_{l=1}^\infty \frac{1}{l^\nu} = 1 + \frac{1}{2^\nu} + \frac{1}{3^\nu} + \dots = \varsigma(\nu) \rightarrow (34)$$

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Rewriting eqns (30) and (31) in terms of $g_\nu(z)$,

$$\frac{P}{k_B T} = -\left(\frac{2\pi}{h^3}\right)(2mk_B T)^{3/2} \int_0^\infty dx \left\{\ln(1 - z e^{x})\right\} \varepsilon^{1/2} = \frac{1}{\lambda^3} g_{5/2}(z) \rightarrow (32)$$

(Integration of eqn (30) by parts will give eqn (32))

$$\frac{N - N_0}{V} = \left(\frac{2\pi}{h^3}\right)(2mk_BT)^{3/2}\int_0^\infty dx \frac{x^{1/2}}{z^{-1}e^x - 1} = \frac{1}{\lambda^3}g_{3/2}(z) \to (33)$$

$$\text{where } \lambda = \left(\frac{h^2}{2\pi mk_BT}\right)^{\frac{1}{2}}$$

Eqn (32) gives

$$\frac{PV}{k_BT} = -\left(\frac{2\pi V}{h^3}\right)(2mk_BT)^{3/2}\int_0^\infty dx\{\ln(1 - ze^x)\}\varepsilon^{1/2} = \frac{V}{\lambda^3}g_{5/2}(z) \to (34)$$

What are the conditions necessary for Bose-Einstein condensation?
Eqns (33) and (24) give us that

$$N_e = \frac{1}{\lambda^3}g_{3/2}(z) = V\frac{(2\pi mk_BT)^{3/2}}{h^3}g_{3/2}(z) \to (35)$$

At high temperatures, $z \ll 1$ and $N_e \approx N$ i.e. most particles reside in the excited energy levels. $g_{3/2}(z)$ can be written as a summation in terms of z

$$g_{3/2}(z) = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + ...$$

The upper bound on the value of $g_{3/2}(z)$ is when $z = 1$

$$g_{3/2}(1) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + ... = \varsigma(\upsilon) \cong 2.612$$

The upper bound on the value on N_e is

$$N_e = V\frac{(2\pi mk_BT)^{3/2}}{h^3}\varsigma\left(\frac{3}{2}\right) \to (36)$$

Thus at high temperatures with z of interest,

$$g_{3/2}(z) \le \varsigma(z) \to (37)$$

From eqns (35) and (36)

$$N_e \le V\frac{(2\pi mk_BT)^{3/2}}{h^3}\varsigma\left(\frac{3}{2}\right) \to (37)$$

So long as the total number of particles is lesser that the limiting value of N_e, almost all particles occupy the excited states, $N_e \approx N$. But if the total number of particles exceeds the upper bound of this upper bound of N_e, then the excited states receive only as much as it can hold (as dictated by the upper bound on N_e). The rest of the particles will be pushed to $\varepsilon = 0$ ground state. $\varepsilon = 0$ energy level has no limitations on the number of particles that it can hold under all conditions. Number of particles occupying the ground state now becomes

$$N_0 = N - \left\{V\frac{(2\pi mk_BT)^{3/2}}{h^3}\varsigma\left(\frac{3}{2}\right)\right\} \to (38)$$

The condition necessary for the onset of Bose-Einstein condensation can hence be summarized as
I   Number of particles in the system should be greater than the limiting value on N_e

$$N > VT^{3/2} \frac{(2\pi m k_B)^{3/2}}{h^3} \varsigma\left(\frac{3}{2}\right) \rightarrow (39)$$

II If we hold N and V constant and vary only T, we find that T has to be lesser than a particular value T_c such that N is greater than the limiting value of N_e.

$$T < T_c = \frac{h^2}{2\pi m k_B} \left\{ \frac{N}{V\varsigma\left(\frac{3}{2}\right)} \right\}^{2/3} \rightarrow (40)$$

The following plot shows how the complementary fractions $\dfrac{N_e}{N}$ and $\dfrac{N_0}{N}$ vary with temperature. For $T > T_c$, the particles are essentially in the excited states and negligible in the ground state. Below T_c, there is significant population $\varepsilon = 0$ energy level which drops with increase in temperature. The drop in N_0 when approached from $T = 0$ follows the equation

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2} \approx \frac{3}{2}\frac{T_c - T}{T_c} \rightarrow (41)$$

This eqn (41) is obtained from eqns (38) and (40).
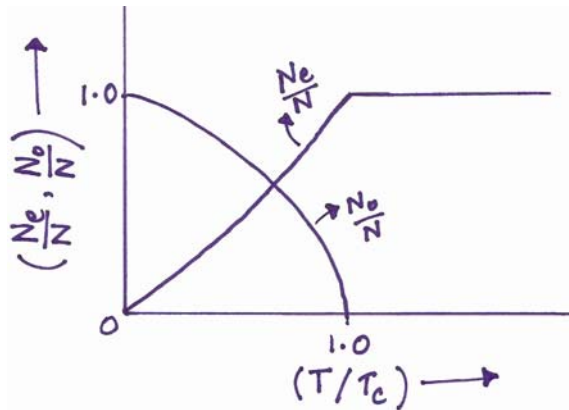
Thermodynamic properties of an ideal Bose gas

Pressure dependence on temperature

From eqn (34), it can be seen that,

$$P(T) = \frac{k_B T}{\lambda^3} g_{5/2}(z) \rightarrow (42)$$

For unit fugacity,

$$P(T) = \frac{k_B T}{\lambda^3} \varsigma\left(\frac{5}{2}\right)$$

λ^3 has a $T^{3/2}$ dependence. Thus $P(T)$, in all has $T^{5/2}$ dependence.

At the critical temperature the value of pressure is,

$$P(T_c) = \left(\frac{2\pi mn}{h^2}\right)^{3/2} (kT_c)^{5/2} \varsigma\left(\frac{5}{2}\right) \rightarrow (43)$$

From eqn (40), eqn (43) can be rewritten as

$$P(T_c) = \frac{\varsigma\left(\frac{5}{2}\right)}{\varsigma\left(\frac{3}{2}\right)} \left(\frac{N}{V} k_B T_c\right) \cong 0.5134\left(\frac{N}{V} k_B T_c\right) \rightarrow (44)$$

According to the ideal gas law,

$$P = \frac{N}{V} k_B T$$

Hence the pressure exerted by an ideal Bose gas is almost half of that applied by an equivalent Boltzmannian (classical ideal gas) at the critical temperature.

The pressure exerted by the ideal Bose gas above the critical temperature, $T > T_c$ is

$$P(T_c) = \frac{g_{5/2}(z)}{g_{3/2}(z)} \left(\frac{N}{V} k_B T\right)$$

Internal energy of an ideal Bose gas

Statistical thermodynamics gives us

$$\frac{PV}{k_B T} = \ln \Xi$$

where Ξ is the grand canonical partition function.

The internal energy of a system can be evaluated using the grand canonical partition function (using eqn (34)).

$$U \equiv -\left(\frac{\partial}{\partial \beta} \ln \Xi\right)_{z,V} = k_B T^2 \left\{\frac{\partial}{\partial T}\left(\frac{PV}{k_B T}\right)\right\}_{z,V} = k_B T^2 V g_{5/2}(z)\left\{\frac{d}{dT}\left(\frac{1}{\lambda^3}\right)\right\}$$

$$U = \frac{3}{2} k_B T \frac{V}{\lambda^3} g_{5/2}(z) \rightarrow (35)$$

For an ideal gas

$$P = \frac{2}{3}\left(\frac{U}{V}\right)$$

Specific heat of a Bose ideal

Specific heat is given by

$$C_v = \frac{\partial U}{\partial T} = \frac{3}{2} k_B V g_{5/2}(z) \frac{d}{dT}\left(\frac{T}{\lambda^3}\right) \rightarrow (36)$$

An implicit assumption is that

$$g_{3/2}(z) = \frac{N}{V} \frac{h^3}{(2\pi mn k_B T)^{3/2}} \rightarrow (37)$$
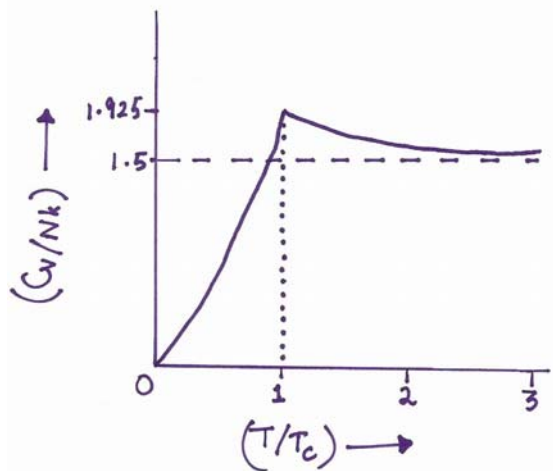
For unit fugacity,

$$\frac{C_v}{Nk_B} = \frac{3V}{2N} \varsigma\left(\frac{5}{2}\right) \frac{d}{dT}\left(\frac{T}{\lambda^3}\right) = \frac{15}{4} \frac{(2\pi nk_B T)^{\frac{3}{2}} V}{Nh^3} \varsigma\left(\frac{5}{2}\right) \rightarrow (38)$$

It has a $T^{\frac{3}{2}}$ dependence on temperature. This is how the specific heat behaves in the low temperature limit.
At the critical temperature $T = T_c$ (from (37) and (38)),

$$\frac{C_v(T_c)}{Nk_B} = \frac{15}{4} \frac{\varsigma\left(\frac{5}{2}\right)}{\varsigma\left(\frac{3}{2}\right)} \cong 1.925$$

For $T > T_c$ ($z \rightarrow 0$), it is the classical limit of an ideal gas. Assuming the gas to be monoatomic, the specific heat is

$$C_V = \frac{3}{2}$$

A cusp can be seen in the plot. This is a consequence of a phase transition that occurs at $T = T_c$ which gives rise to a sudden change in the density.

An experimental evidence for Bose –Einstein condensation came from the (C_V, T) relationship of He^4. Phase transition of He^4 was found to occur at 2.19 K. When the mass, $m = 6.65 * 10^{-24}$ and volume, $V = 27.6$ cm^3/mole were substituted in eqn (40) to find theoretically find out 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 He^4 was enough evidence to prove that the phase transition in He^4 is actually Bose-Einstein condensation.
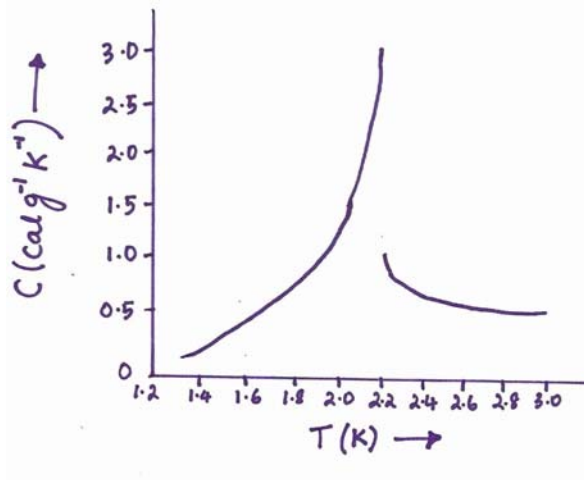
Struck by the shape of this graph, the phase transition was given the name $\lambda-$transition by Keesom and the transition point was called $\lambda-$transition point.