Bose-Einstein statistics

Bose-Einstein distribution

Matter particles that are elementary mostly have a type of angular momentum called *spin*. These particles are known to have a magnetic moment which is attributed to spin. Particles that have integral values of spin $(0, 1, 2, \ldots)$ are called *bosons*. Photon, Weak bosons, Gluons, Gravitons, Higgs particle etc are all bosons. A system with two bosons, labelled A and B, located respectively at $\mathbf{x}_1$ and $\mathbf{x}_2$ have a wavefunction that is symmetric under the exchange of particles.

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \left(\psi^A(\mathbf{x}_1)\psi^B(\mathbf{x}_2) + \psi^B(\mathbf{x}_2)\psi^A(\mathbf{x}_1) \right) = \psi(\mathbf{x}_2, \mathbf{x}_1)$$

It is clear from the above that if we interchange the locations of the two bosons, the wavefunction remains the same. $|\psi(\mathbf{x}_1, \mathbf{x}_2)|^2$ does not change and thus the probability densities do not change under this interchange. The two bosons are said to be *indistinguishable*.
We will consider a box of N bosons. Much like in the case of MB statistics, each boson is allowed to have one of the m different values of energy $E_1, E_2, \ldots, E_m$. Let $g_1, g_2, \ldots, g_m$ be the number of ways of occupying each of these energy levels. If $n_1, n_2, \ldots, n_m$ be the number of particles in each of these energy levels the total energy E, we have

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\begin{align}
N &= n_1 + n_2 + \ldots + n_m = \sum_{i=1}^{m} n_i \tag{1} \\
E &= n_1 E_1 + n_2 E_2 + \ldots + n_m E_m = \sum_{i=1}^{m} n_i E_i \tag{2}
\end{align}
$$

We will now derive a formula for the *occupation number* - the number of particles n_i in the ith energy level as a function of the energy E_i of that level. With this objective we will count the number of ways N bosons can be distributed in the manner described above. Starting with the first energy level E_1, the n_1 particles that occupy this level has g_1 ways to do it. These can be thought of as g_1 cells, all corresponding to energy E_1. Out of the n_1 bosons any number of could go into any one of the g_1 cells as shown in the figure below. Bosons are indicated by dots in the figure.
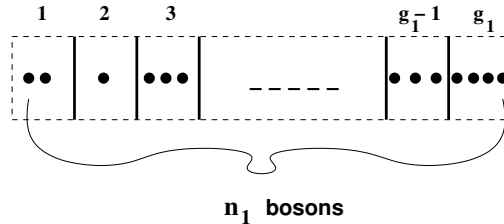
n_1 bosons

We will first find the number of ways n_1 bosons can be distributed into g_1 cells. From the figure above we can see that g_1 cells have been made by inserting $g_1 - 1$ walls (thicker lines in the figure) into a box. All possible distributions of the n_1 bosons into these g_1 cells is

obtained by taking all possible permutations of altogether $n_1 + g_1 - 1$ objects consisting of n_1 dots and $g_1 - 1$ partitions. This can be done in $(n_1 + g_1 - 1)!$ number of ways. Out of this many arrangements of dots and walls, $n_1!$ arrangements must involve just the permutations of the bosons alone. Since the bosons are indistinguishable, these $n_1!$ arrangements should not have been counted as part of the number of ways. To remove this overcounting we divide out a factor of $n_1!$ from the above to get

$$\frac{(n_1 + g_1 - 1)!}{n_1!}$$

Further, the $(n_1 + g_1 - 1)!$ arrangements also include $(g_1 - 1)!$ arrangements of the walls alone which are also indistinguishable as they all lead to the same g_1 cells. We remove this overcounting too by dividing out a factor of $(g_1 - 1)!$

$$\frac{(n_1 + g_1 - 1)!}{n_1! \, (g_1 - 1)!} \tag{3}$$

Eqn (3) provides the number of ways to distribute n_1 bosons into g_1 cells. Needless to say the number of distinct ways to fill n_2 fermions in the g_2 cells corresponding to energy E_2 is

$$\frac{(n_2 + g_2 - 1)!}{n_2! \, (g_2 - 1)!}$$

The number of distinct ways to fill n_1 fermions in g_1 cells, n_2 fermions in g_2 cells, ..., n_m fermions in g_m cells gives us the thermodynamic probability

$$W(E) = \frac{(n_1 + g_1 - 1)!}{n_1! \, (g_1 - 1)!} \, \frac{(n_2 + g_2 - 1)!}{n_2! \, (g_2 - 1)!} \cdots \frac{(n_m + g_m - 1)!}{n_m! \, (g_m - 1)!} \tag{4}$$

Logarithm of this

$$\ln W(E) = \ln \frac{(n_1 + g_1 - 1)!}{n_1! \, (g_1 - 1)!} + \ln \frac{(n_2 + g_2 - 1)!}{n_2! \, (g_2 - 1)!} + \ldots + \ln \frac{(n_m + g_m - 1)!}{n_m! \, (g_m - 1)!} = \sum_{i=1}^{m} \ln \frac{(n_i + g_i - 1)!}{n_i! \, (g_i - 1)!} \tag{5}$$

For $g_i \gg 1$, $n_i \gg 1$, we can use the Stirling's approximation to express eqn(5) as

$$\begin{aligned} \ln W(E) \;=\; & \sum_{i=1}^{m} [(n_i + g_i) \ln(n_i + g_i) - (n_i + g_i) \\ & - n_i \ln n_i + n_i - g_i \ln g_i + g_i] \end{aligned} \tag{6}$$

We put this box in contact with a heat bath and let it reach equilibrium. If we observe this box after it reaches equilibrium, for considerable amount of time we see no change in energy, ie. E remains constant[1]. This requires

$$\Delta E = 0 \implies \sum_{i=1}^{m} E_i \Delta n_i = 0 \tag{7}$$

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[1]Even if we observe for a very long duration, we will see fluctuations of energy ΔE that are too small compared to the energy E. Thus the system can be, practically, considered to be at equilibrium at all times.

At equilibrium, the amount of energy supplied or taken by the heat bath is not sufficient to affect energy values E_i or allowed for the individual particles nor their degeneracies g_i. Therefore neither the E_i nor g_i varies at equilibrium.

Note that the total number of particles N always remain the same despite the variation in the occupation numbers n_i. Thus

$$\Delta N = 0 \implies \sum_{i=1}^{m} \Delta n_i = 0 \tag{8}$$

Further the thermodynamic probability $W(E)$ will be maximum at equilibrium, which requires $\Delta W(E)$ to vanish at the equilibrium value of energy. $\Delta \ln W(E)$ also vanishes at the same values of energy at which $\Delta W(E)$ vanishes.

$$\Delta \ln W(E) = \frac{\Delta W(E)}{W(E)} = 0 \tag{9}$$

Using the form of $W(E)$ obtained in eqn(6), we can write the condition in eqn(8) as

$$\Delta \ln W(E) = \sum_{i=1}^{m} \left[\Delta n_i \ln(n_i + g_i) + (n_i + g_i)\frac{\Delta n_i}{n_i + g_i} - \Delta n_i \ln n_i - n_i \frac{\Delta n_i}{n_i} \right] = 0$$

$$\implies \sum_{i=1}^{m} \left(\ln \frac{n_i + g_i}{n_i} \right) \Delta n_i = 0 \tag{10}$$

We must require the condition in eqn(10) to hold along with the conditions in eqn(7) and eqn(8). It is obvious that if we multiply an arbitrary constant γ' (that is independent of n_i) to the left hand side of eqn(10) it must still vanish.

$$\gamma' \sum_{i=1}^{m} \left(\ln \frac{n_i + g_i}{n_i} \right) \Delta n_i = 0 \tag{11}$$

Similarly, multiplying eqn(7) and eqn(8) with arbitrary constants β' and α'

$$\beta' \sum_{i=1}^{m} E_i \Delta n_i = 0 \tag{12}$$

$$\alpha' \sum_{i=1}^{m} \Delta n_i = 0 \tag{13}$$

Clearly the sum of left hand sides of eqns(11,12, 13) must vanish too.

$$\sum_{i=1}^{m} \left(\gamma' \ln \frac{n_i + g_i}{n_i} + \beta' E_i + \alpha' \right) \Delta n_i = 0 \tag{14}$$

Now, the only way eqn(14) can be satisfied for arbitrary variations Δn_i is if its coefficient vanishes for each Δn_i.

$$\gamma' \ln \frac{n_i + g_i}{n_i} + \beta' E_i + \alpha' = 0 \tag{15}$$

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Dividing through out by γ' and defining new arbitrary constants $\alpha'' = \frac{\alpha'}{\gamma'}$ and $\beta'' = \frac{\beta'}{\gamma'}$, we can rewrite eqn(15) as

$$\ln \frac{n_i + g_i}{n_i} + \beta'' E_i + \alpha'' = 0$$

$$\Rightarrow \ln \frac{n_i + g_i}{n_i} = -\beta'' E_i - \alpha'' \tag{16}$$

Exponentiating this eqn(16) and writing n_i in terms of the rest of the quantities

$$n_i = \frac{g_i}{e^{-\alpha''} e^{-\beta'' E_i} - 1} \tag{17}$$

The quantity $e^{-\alpha''}$ is called *fugacity*[2]. In order to evaluate the arbitrary constant β'' we will supply a small amount of energy to this box of fermions at a fixed volume and find out by how much the entropy changes. The rate of change of entropy with energy at constant volume is the inverse of the temperature of the system in absolute scale (Kelvins).

$$\frac{1}{T} = \frac{\Delta S}{\Delta E}\bigg|_V \tag{18}$$

When a small amount of energy ΔE is supplied it leads to a change in the number of fermions n_i in different energy levels $\Delta E = \sum_{i=1}^{m} \Delta n_i E_i$. The amount of energy supplied will be insufficient to change the nature of the energy levels E_i of individual fermions or their degeneracies g_i and hence these remain constant.

$$\Delta E_i = 0; \qquad \Delta g_i = 0$$

The entropy of the system is found using eqn(6) to be

$$S = k_B \ln W(E) \simeq k_B \sum_{i=1}^{m} \left[(n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i \right] \tag{19}$$

We have used Stirling's approximation to get the final expression in eqn(19).
The change in entropy due to an excess energy ΔE is obtained from eqn(19) as

$$\begin{aligned}
\Delta S &= k_B \, \Delta \ln W(E) \\
&= k_B \sum_{i=1}^{m} \left(\ln \frac{n_i + g_i}{n_i} \right) \Delta n_i
\end{aligned} \tag{20}$$

Substituting the expression for $\frac{g_i}{n_i}$ from eqn(16) into eqn(20)

$$\begin{aligned}
\Delta S &= k_B \sum_{i=1}^{m} (-\alpha'' - \beta'' E_i) \Delta n_i \\
&= -k_B \alpha'' \sum_{i=1}^{m} \Delta n_i - k_B \beta'' \sum_{i=1}^{m} \Delta n_i E_i \\
&= -\beta'' k_B \Delta E
\end{aligned} \tag{21} \tag{22}$$

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[2]The factor α'' is proportional to the amount of work required to insert one more boson into the box, often called the *chemical potential* of the system.

In eqn(21), the first sum is zero as the total number of particle remain unchanged (as in eqn(8) and the second sum gives us the quantity in eqn(22).

Using the result of eqn(22) in eqn(18) we get

$$\frac{\Delta S}{\Delta E} = -\beta'' k_B = \frac{1}{T}$$
$$\beta'' = -\frac{1}{k_B T} \tag{23}$$

This fixes the arbitrary constant β''. Substituting this into eqn(17) we get the *Bose-Einstein statistics* or *distribution* for the occupation number as

$$n_i = \frac{g_i}{e^{-\alpha''} e^{\frac{E_i}{k_B T}} - 1} \tag{24}$$

Blackbody radiation

Photons are bosons. Thus for a gas of photons inside a box of volume V their occupation numbers must be given by BE statistics. This is situation with the radiation inside a cavity held at a fixed temperature T. Let there be a small opening in the cavity through which the radiation can come out of the cavity. If we measure the energy densities of the radiation of different frequencies it has a behaviour as shown in the figure below. This is the famous
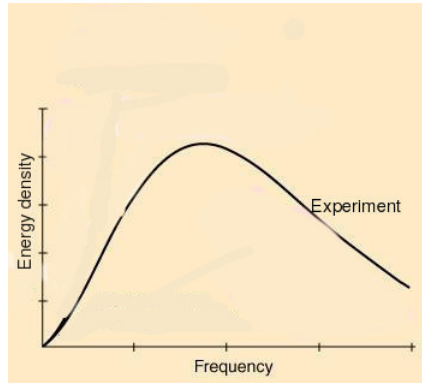
black body radiation distribution. We will now derive an expression for this energy density. We can consider photon approximately as a particle. It is known that photon is massless[3]. The energy $\mathcal{E}$ of a photon with momentum vector $\mathbf{p}$ is

$$\mathcal{E} = pc \tag{25}$$

where $c = 3 \times 10^8 \mathrm{ms}^{-1}$ is the speed of light and $p = \sqrt{\mathbf{p} \cdot \mathbf{p}}$ is the magnitude of the momentum vector.

To apply the BE statistics given in eqn (24) for the case of photons, we first note that allowed value of energy for photons will be in the range $0 \leq \mathcal{E} \leq \infty$. This means, as in the

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[3]This is closely related to the property of electromagnetic fields that they have only transverse polarizations.

case of ideal gas, we must find find how many ways a photon could have an energy in the interval $(\mathcal{E}, \mathcal{E} + d\mathcal{E})$. Clearly this must correspond to a momentum interval $(p, p + dp)$. All the momentum vectors that satisfy this must lie inside a spherical shell of radius p having thickness dp as shown in figure below. The number of such momentum vectors will be
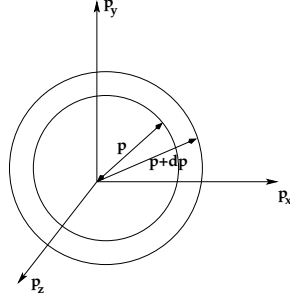
**Volume of the spherical shell gives the number of wavevectors
with magnitude between (p,p+dp)**

proportional to the volume of the shell which is $4\pi p^2 dp$. Multiplying this with the volume V of the box we get the total number of position and momentum vectors corresponding to the energy interval $(\mathcal{E}, \mathcal{E} + d\mathcal{E})$ as

$$4\pi V \ p^2 dp \tag{26}$$

Since we are dealing with particles that can be understood only with laws of quantum mechanics, uncertainty principle holds true for them. According to quantum mechanics, a position coordinate x and the corresponding momentum coordinate p_x of a particle can never be determined more accurately than allowed by the uncertainty relation

$$\Delta x \ \Delta p_x \geq \hbar \tag{27}$$

This implies that in eqn(33) a product of each coordinate, and its corresponding momentum will have a smallest size $\hbar$. The entire phase space can be thought to be filled up by boxes whose edges (or faces) have area $\hbar$. Volume of this smallest box in phase space will be $\hbar^3$. Now we can count the number of states in the phase space - it is the total volume divided by the volume of the smallest box $\hbar^3$. Thus we get

$$\frac{4\pi V \ p^2 dp}{\hbar^3} = \frac{4\pi V \ \mathcal{E}^2 d\mathcal{E}}{\hbar^3 c^3} \tag{28}$$

where RHS above provides the same in terms of energy $\mathcal{E}$ (using of eqn (25)). Photon also has a polarization. There are **two polarizations** possible for each photon. Thus we need to multiply the above number with 2 to get the number of ways $g(\mathcal{E})d\mathcal{E}$ a photon can have an energy in the above range as

$$\frac{8\pi V \ \mathcal{E}^2 d\mathcal{E}}{\hbar^3 c^3} \tag{29}$$

In the BE statistics given in eqn (24), we could replace g_i with $g(\mathcal{E})d\mathcal{E}$ we get the occupation number for the energy range $(\mathcal{E}, \mathcal{E} + d\mathcal{E})$ to be

$$n(\mathcal{E}) \ d\mathcal{E} = \frac{g(\mathcal{E}) \ d\mathcal{E}}{e^{-\alpha''} e^{\frac{\mathcal{E}}{k_B T}} - 1} = \frac{8\pi V}{\hbar^3 c^3} \frac{\mathcal{E}^2 d\mathcal{E}}{e^{-\alpha''} e^{\frac{\mathcal{E}}{k_B T}} - 1} \tag{30}$$

Photons inside a box get absorbed by the wall and get re-emitted continuously. Thus the number of photons is never conserved. Therefore we set $\alpha'' = 0$ for the case of photon gas[4]. The blackbody radiation has an occupation number given by the distribution

$$n(\mathcal{E}) \; d\mathcal{E} \; = \; \frac{8\pi V}{\hbar^3 c^3} \; \frac{\mathcal{E}^2 d\mathcal{E}}{e^{\frac{\mathcal{E}}{k_B T}} - 1} \tag{31}$$

Energy density of the photons in this range of energy is obtained by multiplying the occupation number by energy $\mathcal{E}$ and dividing the result with volume V.

$$\frac{\mathcal{E} \; n(\mathcal{E})}{V} \; d\mathcal{E} \; = \; \frac{8\pi}{\hbar^3 c^3} \; \frac{\mathcal{E}^3 d\mathcal{E}}{e^{\frac{\mathcal{E}}{k_B T}} - 1} \tag{32}$$

Quantum mechanically, energy of a photon is proportional to its (angular) frequency, $\mathcal{E} = \hbar\omega$, where h is the Planck's constant. Using this in the distribution in eqn (32) we get

$$\frac{\mathcal{E} \; n(\mathcal{E})}{V} \; d\mathcal{E} \; = \; \frac{8\pi\hbar}{c^3} \; \frac{\omega^3 d\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \tag{33}$$

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[4]In other words, it takes no extra work to insert one more photon into the box and the chemical potential is zero.