The Bose-Einstein distribution, the Fermi-Dirac distribution and the Maxwell-Boltzmann distribution

This article closely follows the famous textbook *Introduction to Quantum Mechanics* by David J. Griffiths. Suppose there are states $S_1, S_2, S_3, \cdots$ with one-particle energies $E_1, E_2, E_3, \cdots$ and with degeneracies $d_1, d_2, d_3, \cdots$. It means that there are d_1 number of S_1 states, d_2 number of S_2 states and so on, and it costs E_1 of energy for a single particle to occupy state S_1, and so on. It implies the following. If $N_1, N_2, N_3, \cdots$ particles occupy states $S_1, S_2, S_3, \cdots$ respectively, the total number of particles N and the total energy E are given as follows[1]:

$$N = \sum_{n=1}^{\infty} N_n, \qquad E = \sum_{n=1}^{\infty} N_n E_n \tag{1}$$

Given this, Griffiths asks the following question. How many distinct ways are there to achieve this, given $(N_1, N_2, N_3, \cdots)$? The answer $Q(N_1, N_2, N_3, \cdots)$ depends on whether the particle concerned are distinguishable, identical bosons, or identical fermions.

At this point, I would like to remind you that we have considered this problem in two simple cases in our earlier article "Bosons, Fermions and the statistical properties of identical particles." The example given in the main text had

$$d_1 = 2, \quad d_2 = d_3 = \cdots = 0, \qquad N_1 = 2, \quad N_2 = N_3 = \cdots = 0 \tag{2}$$

And, for the problem 1 in that article, we had $d_1 = 2$, $N_1 = 3$, and all the other ds and Ns being zero, and the case being identical bosons.

Now, all we need to do is finding a general expression. First, let $q_n(N_n, d_n)$ be the number of ways N_n particles can be distributed over state S_n with d_n degeneracy. In other words, it is the number of ways distributing N_n particles in d_n slots. Then, it is easy to see the following:

$$Q(N_1, N_2, N_3, \cdots) = \prod_{n=1}^{\infty} q_n(N_n, d_n) \tag{3}$$

where $\prod$ means multiplying every element similar in a way $\sum$ means adding every element.

What is $q_n(N_n, d_n)$ for identical bosons? You can line up the d_n slots. Then, we need $d_n - 1$ screens to distribute N_n particles into the d_n slots. Let's visualize this. For example, let $d_n = 5$, $N_n = 7$, and we have the following figure, in which $\bullet$ represents particles and $|$ represents screens:

$$\bullet\bullet \,||\, \bullet\bullet\bullet \,|\, \bullet \,|\, \bullet \tag{4}$$

[1] $N_1, N_2, N_3, \cdots$ are called "occupation numbers."

You see that there are two particles in the first slot, zero particle in the second slot, three particles in the third slot, one particle in the fourth slot, one particle in the fifth slot. So, the number of $q_n(N_n, d_n)$ for identical bosons can be obtained by counting how many possible ways the $d_n - 1$ screens can be placed. There are total $N_n + d_n - 1$ number of screens and particles, which means that there are total $N_n + d_n - 1$ number of places the screens can be placed. Therefore, we conclude:

$$q_n(N_n, d_n) = \binom{N_n + d_n - 1}{d_n - 1} = \frac{(N_n + d_n - 1)!}{(d_n - 1)!N_n!} \tag{5}$$

What is $q_n(N_n, d_n)$ for identical fermions? At most one particle can occupy each slot. In other words, if a slot is occupied, it is occupied with one particle. Therefore, among d_n slots, N_n slots are occupied. Of course, it is not important which particles occupy certain slots, as particles are not distinguishable. Therefore we conclude:

$$q_n(N_n, d_n) = \binom{d_n}{N_n} = \frac{d_n!}{N_n!(d_n - N_n)!} \tag{6}$$

In case of distinguishable particles, it is more convenient to dispense with (3) and obtain Q more directly. As a first step, let's ignore degeneracies. What is the number of possible ways to divide N particles to S_1, S_2, S_3 and so on? From the section 2 of our earlier article "Combination" we know that they are given by

$$\frac{N!}{N_1!N_2!N_3!\cdots} = N!\prod_{n=1}^{\infty}\frac{1}{N_n!} \tag{7}$$

Let's now consider the degeneracies. In the state S_1, there are N_1 particles and each such particle can be labeled by any number from 1 to d_1. Then, the possible way of labeling these N_1 particles is $d_1^{N_1}$. And, similarly for S_2, S_3 and so on. Therefore, multiplying (7) by $d_1^{N_1}d_2^{N_2}d_3^{N_3}\cdots$, we get

$$Q(N_1, N_2, N_3, \cdots) = N!\prod_{n=1}^{\infty}\frac{d_n^{N_n}}{N_n!} \tag{8}$$

Now, we will find the most probable N_n given $Q(N_1, N_2, N_3, \cdots)$ for each case and (1). This is when $Q(N_1, N_2, N_3, \cdots)$ is maximum. This is also the case in which things actually happen. Remember our discussion in our earlier article "What is entropy? From a microscopic view" Entropy doesn't decrease because such a probability is extremely small, especially when the system concerned is composed of very large numbers of particles. As a similar example, let's say you throw a coin 100000 times and count how many heads we will have. Then, you divide this number by 100000 times. Then, it is very very likely that you will get a number close to 0.5 as this is most probable; the probability that you will get 0.4 or 0.6 is very small. Cases that are most probable are cases that happen when the number of particles or the number of experiments is large.

As the maximum of Q occurs when the maximum of $\ln Q$ occurs, we can find the latter instead. However, we have two constraints as in (1). Therefore, we can use the method of

Lagrange multipliers; we can find the maximum of G which is given by

$$G \equiv \ln Q + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right] \tag{9}$$

What we need to do is solving the following equation:

$$0 = \frac{\partial G}{\partial N_n} \tag{10}$$

To solve this equation, we assume $N_n, d_n \gg 1$ and use Sterling's approximation. In case of identical bosons, we have:

$$G = \sum_{n=1}^{\infty} \ln[(N_n+d_n-1)!] - \ln(N_n!) - \ln[(d_n-1)!] + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right] \tag{11}$$

which means, upon using Sterling's approximation,

$$\begin{aligned} G \quad \approx \quad & \sum_{n=1}^{\infty} \{ (N_n + d_n - 1) \ln(N_n + d_n - 1) - (N_n + d_n - 1) - N_n \ln(N_n) + N_n - \ln[(d_n - 1)!] \\ & -\alpha N_n - \beta E_n N_n \} + \alpha N + \beta E \end{aligned} \tag{12}$$

which implies,

$$0 = \frac{\partial G}{\partial N_n} = \ln(N_n + d_n - 1) - \ln N_n - \alpha - \beta E_n \tag{13}$$

which, in turn, implies:

$$N_n = \frac{d_n - 1}{e^{\alpha + \beta E_n} - 1} \tag{14}$$

However, as $d_n \gg 1$, we can ignore -1 in the numerator. Moreover, in Stirling's formula, we used $\ln n! \approx \int_0^n \ln n$. If we used $\ln n! \approx \int_1^{n+1} \ln n$, -1 in the numerator would be also absent. In any case, we can write:

$$N_n = \frac{d_n}{e^{\alpha + \beta E_n} - 1} \tag{15}$$

For identical fermions (**Problem 1.**), we have:

$$N_n = \frac{d_n}{e^{\alpha + \beta E_n} + 1} \tag{16}$$

Notice that N_n is always less than d_n in this case, since at most one particle can occupy the same state. For distinguishable particles (**Problem 2.**), we have:

$$N_n = \frac{d_n}{e^{\alpha + \beta E_n}} \tag{17}$$

Now, remember in our earlier article "Planck's law of blackbody radiation," we had:

$$\langle s \rangle = \frac{1}{e^{hf/(kT)} - 1} \tag{18}$$

Notice that in the notation of this article we have $\langle s \rangle = N/d$. So, this is exactly (15), provided $\alpha = 0$ and $\beta = 1/(kT)$. In other words, in this article we have derived (18), which is an intermediary step to derive Planck's law of blackbody radiation, in another way using

Lagrange multipliers method. Also, that $\alpha = 0$ must hold can be seen in the following way. As the number of photons is not conserved, the first condition of (1) is absent. Therefore, the second term in (9) must be absent. This can be conveniently done by setting $\alpha = 0$.

Also, it is customary to write $\alpha = -\mu/(kT)$. μ is called "chemical potential" and can depend on the temperature. Using this notation (15), (16) and (17) implies that $n(\epsilon)$ the average number of particles in a particular state (i.e. average "occupation number") with energy ϵ is given as follows (this we can obtain by dividing N_n by number of states d_n):

$$n(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/kT} - 1} \tag{19}$$

for bosons,

$$n(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/kT} + 1} \tag{20}$$

for fermions,

$$n(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/kT}} = e^{-(\epsilon-\mu)/kT} \tag{21}$$

for distinguishable particles. (19) is called "Bose-Einstein distribution," (20) is called "Fermi-Dirac distribution," (21) is called "Maxwell-Boltzmann distribution." All these expressions can be derived by using methods other than Lagrange multipliers. These methods are similar to the method which we used in deriving (18) in our earlier article "Planck's blackbody radiation."

Notice also that the Bose-Einstein distribution (19) and the Fermi-Dirac distribution (20) become approximately equal to (21) in the limit $e^{(\epsilon-\mu)/kT}$ is much larger than 1 (i.e. in the limit $n(\epsilon)$ is small). In other words, in such a limit there is no big difference among the Bose-Einstein distribution, the Fermi-Dirac distribution and the Maxwell-Boltzmann distribution.

Actually, the concept of identical particles along with the one of bosons and fermions is quantum mechanical in nature, and not of classical mechanics origin. Before the advent of quantum mechanics, most physicists, if not all, thought that particles were distinguishable. Therefore, it is not surprising that Bose, Einstein, Fermi, Dirac were physicists who all contributed to quantum mechanics in the early 20th century, while Maxwell and Boltzmann were physicists who contributed to statistical mechanics in the late 19th century, before the advent of quantum mechanics.

In our earlier article "Kinetic theory of gases" we have calculated the average kinetic energy of monatomic molecules in terms of the temperature. Now, having learned Maxwell-Boltzmann distribution, we can do more; we can obtain the speed distribution of monatomic molecules given temperature. This was first derived by Maxwell in 1860. Let's derive it. From our earlier article "Density of states" we know that number of states between the speed between v and $v + dv$ is given by

$$\frac{d^3p\, d^3q}{h^3} = \frac{4\pi p^2 dp\, V}{h^3} = \frac{4\pi m^3 v^2 dv\, V}{h^3} \tag{22}$$

To get the actual number of states occupying the speed between v and $v + dv$, we have to multiply this expression by (21). Thus, we get

$$\left(\frac{4\pi m^3 V}{h^3} e^{\mu/kT}\right) dv\, v^2 e^{-mv^2/2kT} \tag{23}$$

Now, let's calculate the probability distribution $P(v)dv$ for a molecule to have the speed between v and $v + dv$ if the gaseous molecules have temperature T. Notice that the term in the parenthesis in the above expression doesn't depend on the speed of individual molecule v. In other words, the probability distribution is proportional to $dv\, v^2 e^{-mv^2/2kT}$. This implies,

$$P(v)dv = Cv^2 e^{-mv^2/2kT} dv \tag{24}$$

for some C. As the total probabilities must add up to 1, we have

$$1 = \int_0^\infty P(v)dv = C \int_0^\infty v^2 e^{-mv^2/2kT} dv \tag{25}$$

Problem 1. Find C. Hint: Use

$$\int x^2 e^{-Ax^2} dx = -\frac{\partial}{\partial A} \int e^{-Ax^2} dx$$

Problem 2. From the explicit form of speed distribution, check that the average kinetic energy is indeed given by

$$\frac{1}{2} mv^2 = \frac{3}{2} kT \tag{26}$$

Finally, let me mention that the derivation of the Planck's law of blackbody radiation (i.e. the Bose-Einstein distribution with $\mu = 0$) presented in this article was crucial to my research on Hawking radiation spectrum. We will review it in our later article "Quantum corrections to Hawking radiation spectrum." If you have already read "Discrete area spectrum and the Hawking radiation spectrum II" you will be able to understand it as long as you take granted some formulas that relate black hole size, mass and temperature.

Summary

- The Bose-Einstein distribution, the Fermi-Dirac distribution, and the Maxwell-Boltzmann distribution can be derived by finding the most probable occupation numbers.

- $n(\epsilon)$ the average number of particles in a particular state with energy ϵ is given by

  $$n(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/kT} \pm 1} \tag{27}$$

  The plus sign is for bosons and the minus sign is for fermions. For the Maxwell-Boltzmann distribution, there is no ± 1 part.

- When $n(\epsilon)$ is much smaller than 1, there are not much differences between the BE distribution, the FD distribution and the MB distribution; the MB distribution can be used for the BE and FD distribution.