

Maxwell-Boltzmann statistics

Maxwell-Boltzmann distribution

Consider a system of N identical particles in a box of volume V . Each of the above particles is allowed any one of the energy values E_1, E_2, \dots, E_m . These m energy values will be called *single particle energy levels*. Let the number of distinct ways in which a particle can acquire these energy values be g_1, g_2, \dots, g_m respectively. We can call them the degeneracies of the m single particle energy levels. Let n_1, n_2, \dots, n_m be the number of particles in these m energy levels. If the total energy of the system of N molecules is E then they must satisfy

$$N = n_1 + n_2 + \dots + n_m = \sum_{i=1}^m n_i \quad (1)$$

$$E = n_1 E_1 + n_2 E_2 + \dots + n_m E_m = \sum_{i=1}^m n_i E_i \quad (2)$$

We will now derive an expression for the number n_i of particles having energy value E_i , where the index i takes any one the values $i = 1, 2, \dots, m$. This number n_i is the *occupation number* of energy level E_i .

First step to this is to find the number of ways in which N particles can be distributed among m energy levels with n_1 in the first level, n_2 in the second and so on n_m in the m^{th} . The number of ways in which n_1 particles in the first level can be chosen from N particles is

$${}^N C_{n_1} = \frac{N!}{n_1!(N - n_1)!}$$

Now each of these n_1 particles could occupy first level in g_1 ways, implying that the number of ways in which the chosen n_1 particles could occupy energy level E_1 in $g_1^{n_1}$ ways. Thus n_1 particles could be chosen to occupy first energy level in ${}^N C_{n_1} \cdot g_1^{n_1}$ number of ways. Similarly we see that out of the remaining $N - n_1$ particles n_2 particles in the second level can be chosen in ${}^{N-n_1} C_{n_2} \cdot g_2^{n_2}$ ways. Now the number of ways in which the first two levels can be filled in the above manner is clearly

$${}^N C_{n_1} \cdot g_1^{n_1} \cdot {}^{N-n_1} C_{n_2} \cdot g_2^{n_2}$$

as the the second choice is independent of the first. Continuing this we get the number of ways in which N particles can be distributed among m energy levels to be

$$\begin{aligned} & {}^N C_{n_1} g_1^{n_1} \cdot {}^{N-n_1} C_{n_2} g_2^{n_2} \dots {}^{N-n_1-n_2-\dots-n_{m-2}} C_{n_{m-1}} g_{m-1}^{n_{m-1}} \cdot {}^{N-n_1-n_2-\dots-n_{m-1}} C_{n_m} g_m^{n_m} \\ = & {}^N C_{n_1} {}^{N-n_1} C_{n_2} \dots {}^{N-n_1-n_2-\dots-n_{m-2}} C_{n_{m-1}} {}^{N-n_1-n_2-\dots-n_{m-1}} C_{n_m} \cdot g_1^{n_1} g_2^{n_2} \dots g_{m-1}^{n_{m-1}} g_m^{n_m} \\ = & \frac{N!}{n_1! n_2! \dots n_m!} \cdot g_1^{n_1} g_2^{n_2} \dots g_{m-1}^{n_{m-1}} g_m^{n_m} \end{aligned} \quad (3)$$

This quantity in eqn (3) is the thermodynamic probability of the macrostate of the system of N particles with energy E .

$$W(E) = \frac{N!}{n_1! n_2! \dots n_m!} \cdot g_1^{n_1} g_2^{n_2} \dots g_{m-1}^{n_{m-1}} g_m^{n_m} \quad (4)$$

Taking a logarithm of this we get

$$\begin{aligned}
\ln W(E) &= \ln N! - \ln n_1! - \ln n_2! - \dots - \ln n_m! + \ln g_1^{n_1} + \ln g_2^{n_2} + \dots + \ln g_m^{n_m} \\
&= \ln N! + \sum_{i=1}^m (\ln g_i^{n_i} - \ln n_i!) \\
&= \ln N! + \sum_{i=1}^m (n_i \ln g_i - \ln n_i!) \tag{5}
\end{aligned}$$

For $n \gg 1$, we can use the Stirling's approximation to write

$$\ln n! = n \ln n - n \tag{6}$$

Typically, $N \gg 1$ and $n_i \gg 1$ for the system of particles we consider. Thus we can use this approximation in eqn (5) to obtain

$$\ln W(E) = N \ln N - N + \sum_{i=1}^m [n_i \ln g_i - n_i \ln n_i + n_i] \tag{7}$$

Now we put this box in contact with a heat bath and let it reach equilibrium. After it reaches equilibrium if we observe this box for a short enough period of time we see no change in energy, ie. E remains constant¹.

We assume that, at equilibrium the amount of energy supplied or taken by the heat bath is not sufficient to change the single particle energy levels E_i or their degeneracies g_i . Therefore neither the E_i nor g_i varies at equilibrium and all of the change in E is caused by a change in n_i . This requires

$$\Delta E = \sum_{i=1}^m E_i \Delta n_i \tag{8}$$

The heat bath is much bigger compared to the system and thus the change of energy experiences by it is going to be negligible. However at equilibrium, change in energy of the system and of the heat bath will be equal in magnitude but opposite in sign. Thus the change in energy of the system $\Delta E = 0$, implying

$$\Delta E = \sum_{i=1}^m E_i \Delta n_i = 0 \tag{9}$$

Also since particles cannot be added to or removed from the box that we consider, the total number of particles N always remain the same despite the change in the occupation numbers n_i . Thus

$$\Delta N = 0 \Rightarrow \sum_{i=1}^m \Delta n_i = 0 \tag{10}$$

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

$$\Delta \ln W(E) = \frac{\Delta W(E)}{W(E)} = 0 \tag{11}$$

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

Using the form of $\ln W(E)$ obtained in eqn (7), we can write the condition in eqn (11) as

$$\begin{aligned}\Delta \ln W(E) &= \sum_{i=1}^m \left[\Delta n_i \ln g_i - \Delta n_i \ln n_i - n_i \frac{\Delta n_i}{n_i} + \Delta n_i \right] = 0 \\ \Rightarrow \sum_{i=1}^m \ln \frac{g_i}{n_i} \Delta n_i &= 0\end{aligned}\quad (12)$$

We must require the condition in eqn(12) to hold along with the conditions in eqn(8) and eqn(10). But we can require a more general condition.

It is obvious that if we multiply an arbitrary constant γ' (that is independent of n_i) to the left hand side of eqn(12) it must still vanish.

$$\gamma' \sum_{i=1}^m \ln \frac{g_i}{n_i} \Delta n_i = 0 \quad (13)$$

Similarly, multiplying eqn(9) and eqn(10) with arbitrary constants β' and α'

$$\beta' \sum_{i=1}^m E_i \Delta n_i = 0 \quad (14)$$

$$\alpha' \sum_{i=1}^m \Delta n_i = 0 \quad (15)$$

Clearly if we add the left hand sides of eqns(13,14, 15) the sum must vanish too, thus giving a condition

$$\sum_{i=1}^m \left(\gamma' \ln \frac{g_i}{n_i} + \beta' E_i + \alpha' \right) \Delta n_i = 0 \quad (16)$$

Now, the only way eqn(16) can be satisfied for arbitrary variations Δn_i is if its coefficient vanishes for each Δn_i .

$$\gamma' \ln \frac{g_i}{n_i} + \beta' E_i + \alpha' = 0 \quad (17)$$

Dividing through out by γ' and introducing new arbitrary constants $\alpha'' = \frac{\alpha'}{\gamma'}$ and $\beta'' = \frac{\beta'}{\gamma'}$, we can rewrite eqn (17) as

$$\begin{aligned}\ln \frac{g_i}{n_i} + \beta'' E_i + \alpha'' &= 0 \\ \Rightarrow \ln \frac{g_i}{n_i} &= -\beta'' E_i - \alpha''\end{aligned}\quad (18)$$

Exponentiating this eqn(18) and writing n_i in terms of the rest of the quantities

$$n_i = e^{\alpha''} g_i e^{\beta'' E_i} \quad (19)$$

Eqn (19) provides us the promised expression that gives the occupation number n_i of i^{th} level as a function of its energy E_i . But it is still incomplete because we do not know the values of the arbitrary constants α'' and β'' .

First we will evaluate α'' in terms of β'' and other given quantities. This can be done by summing the LHS of eqn (19) over the index i . Doing this we get

$$\begin{aligned} \sum_{i=1}^m n_i &= e^{\alpha''} \sum_{i=1}^m g_i e^{\beta'' E_i} \\ \Rightarrow e^{\alpha''} &= \frac{N}{\left(\sum_{i=1}^m g_i e^{\beta'' E_i}\right)} \end{aligned} \quad (20)$$

Finding α'' from eqn (20) is straightforward, but, for us, it is enough to find $e^{\alpha''}$. Substituting eqn (20) back in eqn (19) we get

$$n_i = \frac{N g_i e^{\beta'' E_i}}{\left(\sum_{i=1}^m g_i e^{\beta'' E_i}\right)} \quad (21)$$

where β'' remains to be evaluated.

In order to evaluate the arbitrary constant β'' we will supply a small amount of energy to this box of particles at fixed volume and find out by how much the entropy of the system 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).

$$\frac{1}{T} = \left. \frac{\Delta S}{\Delta E} \right|_V \quad (22)$$

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 $\Delta E = \sum_{i=1}^m \Delta n_i E_i$. Again the amount of energy supplied is assumed to be insufficient to change the nature of the energy levels E_i of individual fermions or their degeneracies g_i . Nor does the total number of particles change in the process. Thus

$$\Delta E_i = 0; \quad \Delta g_i = 0; \quad \sum_{i=1}^m \Delta n_i = 0; \quad \Delta E = \sum_{i=1}^m \Delta n_i E_i \quad (23)$$

Using eqn(7) we can find the entropy of the system as

$$S = k_B \ln W(E) \simeq k_B (N \ln N - N) + k_B \sum_{i=1}^m [n_i \ln g_i - n_i \ln n_i + n_i] \quad (24)$$

We have used Stirling's approximation to get the final expression in eqn(24).

The change in entropy due to the additional energy ΔE , from eqn(24), is found to be

$$\Delta S = k_B \ln W(E) = \sum_{i=1}^m \ln \frac{g_i}{n_i} \Delta n_i \quad (25)$$

Substituting the expression for n_i from eqn(21) into eqn(25) we get

$$\begin{aligned} \Delta S &= k_B \sum_{i=1}^m \Delta n_i \left(\ln \frac{\sum_{i=1}^m g_i e^{\beta'' E_i}}{N} + \ln e^{-\beta'' E_i} \right) \\ &= k_B \left(\ln \frac{\sum_{i=1}^m g_i e^{\beta'' E_i}}{N} \right) \sum_{i=1}^m \Delta n_i - k_B \beta'' \sum_{i=1}^m \Delta n_i E_i \end{aligned} \quad (26)$$

$$= -\beta'' k_B \Delta E \quad (27)$$

where we have substituted the last two relations in eqn (23) into eqn (26) to obtain eqn (27). Using the result of eqn(27) in eqn(22) we get

$$\begin{aligned}\frac{\Delta S}{\Delta E} &= -\beta'' k_B = \frac{1}{T} \\ \Rightarrow \beta'' &= -\frac{1}{k_B T}\end{aligned}\tag{28}$$

Thus we evaluate the second arbitrary constant β'' . Substituting this into eqn(21) we get the *Maxwell-Boltzmann distribution* or *statistics* for the occupation number

$$n_i = \frac{N g_i e^{-\frac{E_i}{k_B T}}}{\left(\sum_{i=1}^m g_i e^{-\frac{E_i}{k_B T}} \right)}\tag{29}$$

Physical meaning of the above distribution can be understood if we notice that the quantity

$$\frac{n_i}{N} = \frac{g_i e^{-\frac{E_i}{k_B T}}}{\left(\sum_{i=1}^m g_i e^{-\frac{E_i}{k_B T}} \right)}\tag{30}$$

gives us the probability of finding a particle in the i^{th} energy level. Thus MB distribution provides us the estimate for the number of particles in i^{th} energy level in terms of a probability distribution. Important feature of this probability is that the higher a single particle energy level is, **exponentially lesser** is the probability of finding a particle at that level. But one must keep in mind that the probability also depends on the degeneracy g_i of that single particle level.

Maxwell distribution for ideal gas

An immediate use of MB statistics would be to obtain a distribution for ideal gas particles. Ideal gas consists of identical free particles that do not experience any force. Energy of each of the ideal gas is kinetic. Single particle energy levels \mathcal{E} for a free particle take values in the interval $0 \leq \mathcal{E} \leq \infty$. Because it is kinetic energy, in terms of the momentum vector \mathbf{p} of the particle we can express

$$\mathcal{E} = \frac{\mathbf{p} \cdot \mathbf{p}}{2m}\tag{31}$$

We can use MB statistics to find the distribution of the ideal gas molecules at various energies if we generalize the MB statistics to the case where single particle energy is continuous. In addition, we must also know how to find g_i in this case.

MB statistics continuous single particle energy levels will give us number of particles $n(\mathcal{E}) d\mathcal{E}$ that have energy value between \mathcal{E} and $\mathcal{E} + d\mathcal{E}$. First thing to do is to replace E_i in the MB statistics in eqn (29) with \mathcal{E} . We must now find out what takes the place of g_i . For this, we must remember that it basically counts the number of ways in which any particle can achieve energy E_i . Since the single particle energy is now continuous, now we can only say how many ways can a particle have a value of energy between \mathcal{E} and $\mathcal{E} + d\mathcal{E}$. This number

will be proportional on $d\mathcal{E}$ itself, clearly. If $g(\mathcal{E})$ is the number of ways in which the particle could be in a unit energy interval at \mathcal{E} , we see that $g(\mathcal{E})d\mathcal{E}$ gives us the number of ways can a particle have a value of energy between \mathcal{E} and $\mathcal{E} + d\mathcal{E}$. Finally the denominator of eqn (29) contains a summation over energy levels. In this case, it must be replaced with an integral over energy levels.

With all the inputs said above, MB statistics gives for ideal gas,

$$n(\mathcal{E}) d\mathcal{E} = \frac{N g(\mathcal{E}) e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E}}{\int_0^{\infty} g(\mathcal{E}) e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E}} \quad (32)$$

In eqn (32), we still have to say what $g(\mathcal{E})d\mathcal{E}$ the number of ways an ideal gas particle can have energy between \mathcal{E} and $\mathcal{E} + d\mathcal{E}$ is. While studying the phase space of a free particle in a box of volume V we had seen that the number of ways an ideal gas particle can have energy between \mathcal{E} and $\mathcal{E} + d\mathcal{E}$ is

$$\frac{V 4\pi p^2}{h^3} dp = \frac{4\pi m V \sqrt{2m\mathcal{E}}}{h^3} d\mathcal{E} \quad (33)$$

where h^3 was the volume of the smallest volume element in phase space and $p = |\mathbf{p}| = \sqrt{\mathbf{p} \cdot \mathbf{p}}$ is the magnitude of the momentum vector. Thus $g(\mathcal{E})$ is just the density of states for a particle. If ideal gas particle is a free particle $g(\mathcal{E})d\mathcal{E}$ must be given by the RHS of eqn (33). Substituting this into eqn (32) we find

$$n(\mathcal{E}) d\mathcal{E} = \frac{N \frac{4\pi m V \sqrt{2m\mathcal{E}}}{h^3} e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E}}{\int_0^{\infty} \frac{4\pi m V \sqrt{2m\mathcal{E}}}{h^3} e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E}} = \frac{N \sqrt{\mathcal{E}} e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E}}{\int_0^{\infty} \sqrt{\mathcal{E}} e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E}} \quad (34)$$

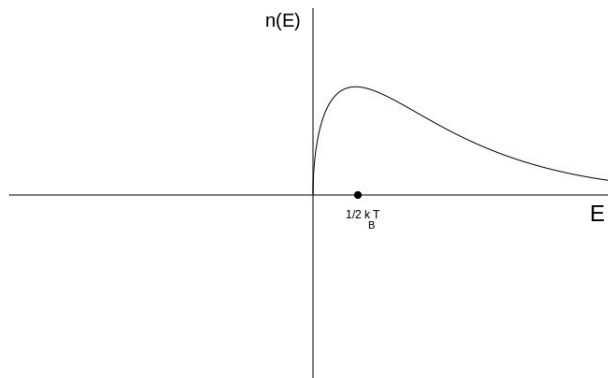
The integral in the denominator of eqn (34) gives

$$\int_0^{\infty} \sqrt{\mathcal{E}} e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E} = \frac{\Gamma\left(\frac{3}{2}\right)}{\beta^{\frac{3}{2}}} = \frac{\sqrt{\pi}}{2\beta^{\frac{3}{2}}} \quad (35)$$

In the above equation we have used $\beta = \frac{1}{k_B T}$. Substituting the above result into eqn (34) we obtain the Maxwell distribution for occupation number as

$$n(\mathcal{E}) d\mathcal{E} = \frac{2N}{\sqrt{\pi}} \left(\frac{1}{k_B T}\right)^{\frac{3}{2}} \sqrt{\mathcal{E}} e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E} \quad (36)$$

Occupation number varies with energy as shown below and has a maximum at $\frac{1}{2}k_B T$.



Notice that energy of the particle specifies a macrostate of the particle. Thus the integral in eqn (33) carries out a sum over the possible macrostates of a particle. We could express the the above also as an integral over the microstates of that particle. What makes up the microstates of the particle? The pair of vectors (\mathbf{r}, \mathbf{p}) specifying position and momentum of the particle, of course. Thus expressing the integral as one over microstates requires us to rewrite the integral over energy as an integral over position coordinates and momentum components. But the energy of an ideal gas particle depends only on the magnitude of the momentum vector as indicated by eqn (31). Thus in the integral over microstates all the three integrals over position coordinates and two of the integrals over momentum components can be carried out. The only integral that remains will be the one over the magnitude of the momentum, resulting in the integral on the left hand side of eqn (33). Substituting equations (31,33) into eqn (36), we get

$$\frac{N \frac{4\pi V p^2}{h^3} e^{-\frac{p^2}{2mk_B T}} dp}{\int_0^\infty \frac{4\pi V p^2}{h^3} e^{-\frac{p^2}{2mk_B T}} dp} = N \frac{4\pi p^2 e^{-\frac{p^2}{2mk_B T}} dp}{(2\pi m k_B T)^{\frac{3}{2}}} = n(p) dp \quad (37)$$

This gives us the number of ideal gas particles having absolute momentum in the range $(p, p + dp)$ namely, Maxwell's momentum distribution for ideal gas particles.

One can easily derive Maxwell's velocity distribution for the ideal gas by putting $p = mv$ in eqn (37) above, where $v = |\mathbf{v}|$ is the magnitude of the velocity \mathbf{v} of an ideal gas particle.

$$N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} 4\pi v^2 e^{-\frac{mv^2}{2mk_B T}} dv = n(v) dv \quad (38)$$

which estimates the number of ideal gas particles with velocity in the range $(v, v + dv)$.

Thermodynamics of ideal gas

From the MB statistics it is easy to calculate the average energy U of the ideal gas in the box, we must multiply the occupation number in eqn (36) with the energy of a particle \mathcal{E} and integrate over all value of energy.

$$\begin{aligned} U &= \int_0^\infty \mathcal{E} n(\mathcal{E}) d\mathcal{E} = \frac{2N}{\sqrt{\pi}} \left(\frac{1}{k_B T} \right)^{\frac{3}{2}} \int_0^\infty \mathcal{E}^{\frac{3}{2}} e^{-\frac{\mathcal{E}}{k_B T}} d\mathcal{E} = \frac{2N}{\sqrt{\pi}} \left(\frac{1}{k_B T} \right)^{\frac{3}{2}} \frac{\Gamma(\frac{5}{2})}{\left(\frac{1}{k_B T} \right)^{\frac{5}{2}}} \\ &= \frac{2N}{\sqrt{\pi}} (k_B T) \frac{3}{4} \Gamma\left(\frac{1}{2}\right) = \frac{2N}{\sqrt{\pi}} (k_B T) \frac{3}{4} \sqrt{\pi} = \frac{3}{2} N k_B T \end{aligned} \quad (39)$$

This is the familiar expression for internal energy of an ideal gas which may be derived also using kinetic theory of gases. It can be seen that each degree of freedom contributes a factor of $\frac{1}{2}k_B T$ to the average energy of a single molecule. As each molecule has 3 degrees of freedom, each molecule contributes a factor of $\frac{3}{2}k_B T$ to the energy of the gas. There being a total of $3N$ degrees of freedom results in the average energy value of $\frac{3}{2}Nk_B T$ of the gas. The fact that the energy is equally partitioned among each degree of freedom is often called *equipartition of energy*.

Specific heat at constant volume C_V is the rate of increase in energy with temperature at constant volume. Using the expression for internal energy above we see

$$C_V = \left. \frac{\partial U}{\partial T} \right|_V = \frac{3}{2} N k_B \quad (40)$$

One often writes this in terms of the gas constant R defined as $N_A k_B$, where $N_A = 6.023 \times 10^{23}$ is the Avogadro's number, to get the familiar expression

$$C_V = \frac{3}{2} n R \quad (41)$$

Here n represents the quantity of gas in moles. One could observe that the specific heat gives a count of the degrees of freedom of the system.

One can proceed further to derive all the known thermodynamics of ideal gas from statistical mechanics and verify the physical description it provides.

Gibb's paradox

Despite the success of MB statistics in describing the thermodynamics of ideal gas it has a severe problem. The problem can be identified by examining the expression for entropy that results from the MB statistics. Let us first calculate the entropy of the gas in the first compartment starting from the expression in eqn (24).

$$\begin{aligned} S_1 &= k_B (N \ln N - N) + k_B \sum_{i=1}^m (n_i \ln n_i - n_i) \\ &= k_B N \ln N + \frac{1}{T} U + k_B N \ln A - k_B N \ln N \end{aligned} \quad (42)$$

In the second step we have denoted

$$\sum_{i=1}^m g_i e^{-\beta E_i} = A \quad (43)$$

after substituting eqn (29) for n_i .

For the ideal gas we have already found U in eqn (39). However to find entropy S from eqn (42) we must calculate A . For ideal gas the single particle energy takes continuous set of values, as discussed in paragraph above eqn (32). Therefore the expression in eqn (43) for A will have to be generalized to

$$A = \int_0^{\infty} d\mathcal{E} g(\mathcal{E}) e^{-\beta \mathcal{E}} \quad (44)$$

For ideal gas, we had seen that number of ways a single particle can have energy between \mathcal{E} and $\mathcal{E} + d\mathcal{E}$ is as obtained in eqn (33)

$$g(\mathcal{E}) d\mathcal{E} = \frac{4\pi m V \sqrt{2m\mathcal{E}}}{h^3} d\mathcal{E}$$

Substituting this into eqn (44) and doing the integral we get

$$A = \frac{4\pi m V \sqrt{2m}}{h^3} \int_0^{\infty} d\mathcal{E} \sqrt{\mathcal{E}} e^{-\beta\mathcal{E}} = V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \quad (45)$$

By substituting eqn (45) into eqn (42), we get the entropy for an ideal gas as

$$S = k_B \left[N \ln N + \frac{3}{2}N + \frac{3}{2}N \ln \left(\frac{V}{N} \frac{2\pi m k_B T}{h^2} \right) \right] \quad (46)$$

Now let us consider same ideal gas in a box with two compartments separated by a wall. Let the volumes of the two compartments be V_1 and V_2 with the number of molecules in them being N_1 and N_2 respectively. The temperature T and densities of the ideal gas in two compartments are taken to be the same.

$$\frac{N_1}{V_1} = \frac{N_2}{V_2}$$

Using eqn (46), the entropies of the gas in the first and second compartments will be, respectively

$$\begin{aligned} S_1 &= k_B \left[N_1 \ln N_1 + \frac{3}{2}N_1 + \frac{3}{2}N_1 \ln \left(\frac{V_1}{N_1} \frac{2\pi m k_B T}{h^2} \right) \right] \\ S_2 &= k_B \left[N_2 \ln N_2 + \frac{3}{2}N_2 + \frac{3}{2}N_2 \ln \left(\frac{V_2}{N_2} \frac{2\pi m k_B T}{h^2} \right) \right] \end{aligned} \quad (47)$$

Now we remove the wall separating the compartments slowly and allow the gas to mix. Easily the density of the gas after mixing will be the same as what it was

$$\frac{N_1 + N_2}{V_1 + V_2} = \frac{N_1}{V_1} = \frac{N_2}{V_2} \quad (48)$$

As the temperature and densities are the same one would expect the entropy S_f after mixing to be the sum of the initial entropies S_1 and S_2 . However if you add the expressions for S_1 and S_2 in eqn (47) one finds

$$S_1 + S_2 = k_B \left[(N_1 \ln N_1 + N_2 \ln N_2) + \frac{3}{2}(N_1 + N_2) + \frac{3}{2}(N_1 + N_2) \ln \left(\frac{V_1 + V_2}{N_1 + N_2} \frac{2\pi m k_B T}{h^2} \right) \right] \quad (49)$$

However using the expression in eqn (46) we get

$$S_f = k_B \left[(N_1 + N_2) \ln(N_1 + N_2) + \frac{3}{2}(N_1 + N_2) + \frac{3}{2}(N_1 + N_2) \ln \left(\frac{V_1 + V_2}{N_1 + N_2} \frac{2\pi m k_B T}{h^2} \right) \right] \quad (50)$$

Clearly the expressions in eqns (49) and (50) have a mismatch, but **only in the first term**. This contradiction is referred to as *Gibb's paradox*. Physically eqn (49) seem to suggest that the entropy of an ideal gas in a box would depend on how we arrived at that configuration. If we obtained that gas starting with many walls and compartments and removing the walls slowly, the gas should have larger entropy than if we have started with fewer walls and compartments. In other words, the gas must have some “memory” of its past, which is physically

just absurd.

The first term in entropy that gives rise to Gibb's paradox would not have been there if the expression for thermodynamic probability $W(E)$ in eqn (4) did not have an $N!$ in the numerator. Thus the factor $N!$ seems to be an overcounting that happened because we treated all the N molecules to be distinguishable. If we divide this factor out and define the entropy as

$$\tilde{S} = \ln \frac{W(E)}{N!} \quad (51)$$

we get an expression for entropy after mixing in the above mentioned case to be

$$\tilde{S}_f = \tilde{S}_1 + \tilde{S}_2$$

Therefore the definition of entropy in eqn (51) does not lead to any paradoxes. We accept this as the entropy for MB statistics.