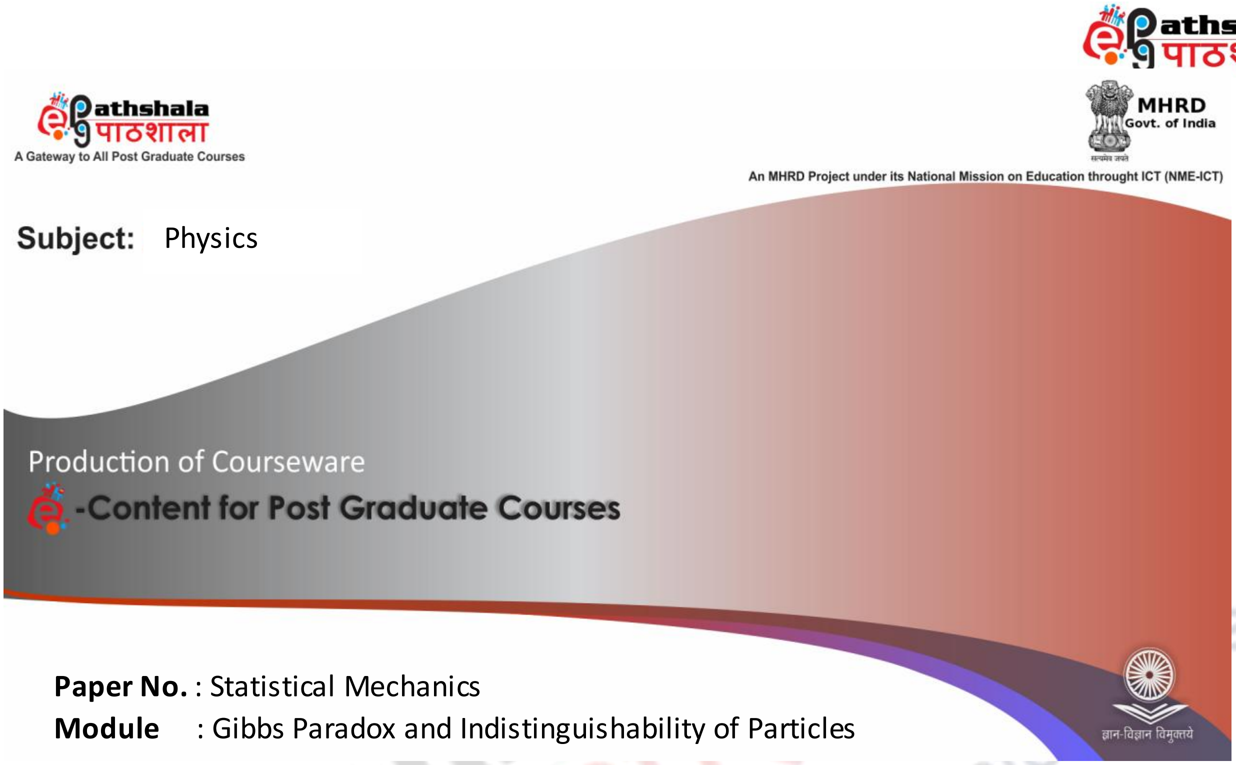

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Paper No. : Statistical Mechanics

Module : Gibbs Paradox and Indistinguishability of Particles

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Description of Module	
Subject Name	Physics
Paper Name	Statistical Mechanics
Module Name/Title	Equilibrium, Thermodynamic Parameters and Response Functions
Module Id	M9

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1. Learning Outcomes

After studying this module, you shall be able to

- Comprehend the logical consequences of violation of extensiveness of a thermodynamic physical quantity while applying statistical methods
- Appreciate paradoxical situation which arises on mixing of same type of ideal gases together, namely Gibbs Paradox.
- Infer the importance of indistinguishability of particles even in a classical system
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- Learn that quantum statistical mechanics reduces to classical statistical mechanics results only when correct enumeration rules are applied in the classical limit..

2. Introduction

In this module we pay attention to the expression obtained for entropy of a monoatomic ideal gas derived in module 8 as given below

$$S = Nk_B \ \ln\left[\left(\frac{V}{h^3}\right)\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}Nk_B \tag{1}$$

Where $E = \frac{3}{2}N\, k_B T$. One of the interesting observations is that entropy as given in equation (1), led to correct equation of state for an ideal gas and other thermodynamic properties. Despite these successes this expression lacks one of the most important properties of entropy called extensiveness which implies that entropy scales if we scale the extensive parameters involved in the expression. This implies $S(\alpha N, \alpha V, \alpha E) = \alpha\, S(N, E, V)$. In this module we seek to look for the implications of the lack of extensiveness of entropy S leading to Gibbs Paradox, and how this paradox can be resolved, bringing into focus the issue indistinguishability of particles involved.

3. Violation of extensiveness of Entropy (S)

To check the extensiveness of entropy $S(NE,V)$ given in equation (1), let us change $N \to \alpha N$, $V \to \alpha V$ and $E \to \alpha E$ keeping the intensive variables unchanged then equation (1) becomes

$$S(\alpha N, \alpha V, \alpha E) = \alpha N k_B \ \ln\left[\left(\frac{\alpha V}{h^3}\right)\left(\frac{4\pi m\alpha E}{3\alpha N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}N\alpha k_B \ \neq \alpha S(N,E,V) \tag{2}$$

Obviously, α sitting with V inside the argument of ln fails to make entropy extensive. This means that if system is made up of α parts each having entropy S then sum of the entropies of each part is $\neq \alpha \textit{ times } S$. This is physically unacceptable situation.

4. Entropy of Mixing of Two Ideal Gases

To fully see the implication of the violation of extensiveness of entropy, Gibbs went for a thought experiment of mixing of two samples of different ideal gases at the same temperature T, followed by mixing of two samples of same ideal gas at the same temperature. It is worth noting that first experiment involving mixing of different ideal gases is an irreversible process for which $\Delta S > 0$, where as second experiment mixing of two samples of same gas is a reversible process i.e. $\Delta S = 0$.

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Case 1: Mixing of two samples of two different ideal gases at same temperature having same number density

Figure 1 below shows the two different ideal gases 1 and 2 at the same temperature and having same number density i.e. $\left(\frac{N_1}{V_1} = \frac{N_2}{V_2}\right)$.**6. Entropy of N Three Dimensional Classical Harmonic Oscillators**

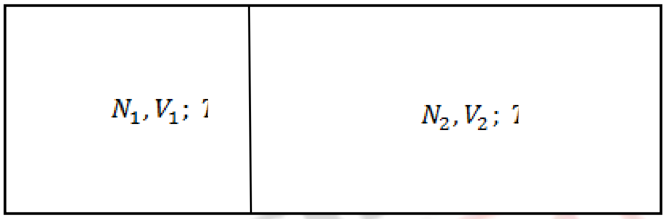

Figure 1 Mixing of two ideal gases

Before mixing the ent

$$S_i = N_i k_B \ln\left[\left(\frac{V_i}{h^3}\right)(2\pi m_i k_B T)^{\frac{3}{2}}\right] + \frac{3}{2} N k_B \quad \text{where } i=1,2 \tag{3}$$

Or

$$S_i = N_i k_B \ln v_i + \frac{3}{2} N_i k_B \left[\ln\left(\frac{2\pi m_i k_B T}{h^2}\right) + 1\right] \quad \text{where } i=1,2 \tag{4}$$

After the mixing has taken place, the total entropy can be written easily keeping in mind that now the partition of figure 1 has been removed and each particle of the gas can roam in total volume $V = V_1 + V_2$, so that total entropy can be written as

$$S_{Total} = \sum_{1=1}^{2}\left[N_i k_B \ln V + \frac{3}{2} N_i k_B \left[\ln\left(\frac{2\pi m_i k_B T}{h^2}\right) + 1\right]\right] \tag{5}$$

Now we can define entropy of mixing as

$$\Delta S = S_{total} - \sum_{i=1}^{2} S_i \tag{6}$$

Using (4) and (5), this leads to

$$\Delta S = k_B \left[N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2}\right] \text{, where } V = V_1 + V_2 \qquad (7)$$

Since $V > V_1$and $V > V_2$, $\Delta S > 0$. Hence process is irreversible, expected for mixing. Furthermore, since we assumed that number density is same, equation (7) can be written as

$$\Delta S = k_B \left[N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{V_2}\right] \qquad (8)$$

Once again $\Delta S > 0$.

Case 2: Mixing of two samples of same ideal gases at same temperature having same number density

Now let us look at the same mixing process by taking in the two compartments same gas and remove the partition allowing for mixing the gases of the two compartments. Only difference now is that $m_1 = m_2 = m$.

So that S_{total} becomes

$$S_{Total} = Nk_B \ln V + \frac{3}{2} Nk_B \left[\ln\left(\frac{2\pi m k_B T}{h^2}\right) + 1\right] \text{ where } N = N_1 + N_2 \qquad (9)$$

Using this expression, and the expression the entropy of mixing again remains the same as given in equation (8) with $\Delta S > 0$. This is where the paradox arises, mixing of two samples of the same gas again when temperature T and Number density are same can be undone merely by inserting the partition, making the whole process reversible and the entropy of mixing ΔS should be equal to zero, which is not the case. In literature this is known as Gibbs Paradox.

4. **Adhoc Resolution of Gibbs Paradox**

As discussed in Case 2, there is a need to give a careful look to equation (1)so that entropy does not remain non-extensive and paradox of entropy of mixing ΔS of two samples of same gas does not become greater than zero for a reversible process. Gibbs proposed an adhoc way of overcoming this paradox by suggesting that from equation (1) if we subtract $\ln N!$. the entropy of mixing for case 2 becomes zero and restores extensive ness of the entropy of a nonoatomic ideal gas. This is equivalent to diminishing S_1 by $\ln N_1!$, S_2 by $\ln N_2!$ And S by $\ln N!$

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$$S = Nk_B \ln\left[\left(\frac{V}{h^3}\right)\left(\frac{4\pi m E}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2} Nk_B - k_B \ln N! \qquad (10)$$

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$$S = Nk_B \ln\left[\left(\frac{V}{h^3}\right)\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}Nk_B - k_B(N\ln N - N) \tag{11}$$

Or

$$S = Nk_B \ln\left[\left(\frac{V}{N}\right)\left(\frac{4\pi mE}{3Nh^3}\right)^{\frac{3}{2}}\right] + \frac{5}{2}Nk_B \tag{12}$$

And hence energy E, after simplification , can be written as

$$E = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}} exp\left(\frac{2S}{3Nk} - \frac{5}{3}\right) \tag{13}$$

A mere glance tells us that entropy has become extensive with a factor of N dividing V inside the logarithmic term.

Let us see introducing this adhoc term physically amounts to doing what. This amounts to diminishing the number of microstates of the monoatomic ideal gas by a factor of $N!$ involving new counting procedure called correct Boltzmann Counting Process. If we recall problems which we have done in permutations and combinations which allow us to count without counting, the number of permutations of N different things taken N at a time is given by N!, but if all the N things are identical it should lead to 1 possibility only this requires us to divide N! by N!.

So while checking the extensiveness of the equation (1), therefore, need is to revisit the process of counting of microstates of a monoatomic ideal gas and division by N! an adhoc solution to Gibbs paradox amounts to saying that though we are dealing with the classical particles constituting the ideal gas still these should be treated as identical to get physically correct entropy. This expression for entropy of an ideal gas was first calculated by O. Sackur and H. Tetrode in a series of papers separately during 1911-12 using for the first time quantization of phase space in classical statistical mechanics.

Now in the following we derive three very important properties which we left out in module 8, since without correct for S and hence E these physical quantities would not have come correct.

Chemical Potential

Chemical potential is defined as $\mu = \left(\frac{\partial E}{\partial N}\right)_{V,S}$, therefore

$$\mu = \frac{3h^2 N^{\frac{5}{3}}}{4\pi\, mV^{2/3}}\left[\frac{5}{3N} - \frac{2S}{3N^2 k_B}\right] exp\left(\frac{2S}{3Nk_B} - \frac{5}{3}\right) \tag{14}$$

Or

$$\mu = \left[\frac{5}{3N} - \frac{2S}{3N^2 k_B}\right] E \tag{15}$$

In terms of N, V, T, (15) can be written as

$$\mu = k_B T \ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}\right] \tag{16}$$

It is interesting to note that in classical limit, when particle density is low and temperature very high i.e. $\frac{N}{V} \ll \left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}$. This implies that the argument of logarithmic term is always less than 1 and hence chemical potential is always negative. The quantity $\frac{(2\pi m k_B T)^{\frac{1}{2}}}{h}$ is called thermal de Broglie wavelength.

Gibbs Free Energy

Gibbs free energy is defined as $G = \mu N$

$$G = Nk_B T \ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}\right] \tag{17}$$

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Helmholtz free energy has been defined as $F = E - TS = G - PV = \mu N - Nk_B T$,

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9. Indistinguishability and Enumeration of Microstates

Indistinguishability of particles in a classical ideal gas means that by no means you can tag these particles as particle A, particle B, particle C, and so on. At the most we can talk about is the distribution of these indistinguishable particles over different states, say n_i particles over the state ϵ_i, giving a set of number of particles $\{n_i\}$ distributed over a set of states $\{\epsilon_i\}$ such that $\sum_i n_i = N$ and $\sum_i n_i\epsilon_i = E$.

We shall carefully look at the emerging situation, the total number of permutations of N particles distributed according to the set $\{n_i\}$ is like distributing N particles such that n_1 particles are of the kind sitting in state ϵ_1, n_2 particles are of the kind sitting in state ϵ_2 and so on. Thus the total number of permutations turn out to be

$$\frac{N!}{n_1!\,n_2!\,\dots\dots\dots\dots\dots.} \quad (19)$$

Where the set $\{n_i\}$ satisfies the two constraints corresponding to total number of particles and total energy stated above. If all the particles had been distinguishable this would have given us the correct number of microstates of a given macrostate (N, V, E). But because particles are indistinguishable, each of these microstates gives one and only one microstate. So Gibbs remedy dividing by $N!$ still leaves us with a spurious weight factor

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The only way to make it 1 is probability of each of n_i greater than 1 becomes smaller and smaller and most of the time it takes values either 0 or 1and rarely greater than 1. This will bring the expectation value of $n_i \ll 1$, which defines the classical limit. This leads to correct enumeration of microstates of a given macrostate, which, however, can be understood only by quantum statistics and not other wise.

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In this module we have learnt

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- That to resolve Gibbs paradox, number of microstates need to be reduced implying treating gas as made up indistinguishable particles.
- That corrected form of entropy allows calculation of thermodunamic properties such as chemical potential (μ), Gibbs free energy G and Helmholtz free energy F, which would have otherwise been wrong
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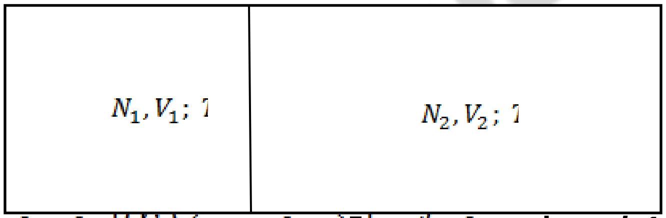

Figure 2 Mixing of two ideal gases

Before mixing the

$$S_i = N_i k_B \ln\left[\left(\frac{V_i}{h^3}\right)(2\pi m_i k_B T)^{\frac{3}{2}}\right] + \frac{3}{2} N k_B \quad \text{where } i=1,2 \tag{23}$$

Or

$$S_i = N_i k_B \ln v_i + \frac{3}{2} N_i k_B \left[\ln\left(\frac{2\pi m_i k_B T}{h^2}\right) + 1\right] \quad \text{where } i=1,2 \tag{24}$$

After the mixing has taken place, the total entropy can be written easily keeping in mind that now the partition of figure 1 has been removed and each particle of the gas can roam in total volume $V = V_1 + V_2$, so that total entropy can be written as

$$S_{Total} = \sum_{1=1}^{2} \left[N_i k_B \ln V + \frac{3}{2} N_i k_B \left[\ln\left(\frac{2\pi m_i k_B T}{h^2}\right) + 1\right]\right] \tag{25}$$

Now we can define entropy of mixing as

$$\Delta S = S_{total} - \sum_{i=1}^{2} S_i \tag{26}$$

Using (4) and (5), this leads to

$$\Delta S = k_B \left[N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2}\right], \text{ where } V = V_1 + V_2 \tag{27}$$

Since $V > V_1$and $V > V_2$, $\Delta S > 0$. Hence process is irreversible, expected for mixing. Furthermore, since we assumed that number density is same, equation (7) can be written as

$$\Delta S = k_B \left[N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{V_2}\right] \tag{28}$$

Once again $\Delta S > 0$.

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Using this expression, and the expression the entropy of mixing again remains the same as given in equation (8) with $\Delta S > 0$. This is where the paradox arises, mixing of two samples of the same gas again when temperature T and Number density are same can be undone merely by inserting the partition, making the whole process reversible and the entropy of mixing ΔS should be equal to zero, which is not the case. In literature this is known as Gibbs Paradox.

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Or

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And hence energy E, after simplification , can be written as

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In terms of N, V, T, (15) can be written as

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It is interesting to note that in classical limit, when particle density is low and temperature very high i.e. $\frac{N}{V} \ll \left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}$. This implies that the argument of logarithmic term is always less than 1 and hence chemical potential is always negative. The quantity $\frac{(2\pi m k_B T)^{\frac{1}{2}}}{h}$ is called thermal de Broglie wavelength.

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- That enumeration of correct microstates is basically a quantum phenomenon and in the context of a classical ideal gas requires classical limit to be satisfied i.e. expectation value of occupation number must be $\ll$ one.

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After studying this module, you shall be able to

- **Comprehend the logical consequences of violation of extensiveness of a thermodynamic physical quantity while applying statistical methods**
- **Appreciate paradoxical situation which arises on mixing of same type of ideal gases together, namely Gibbs Paradox.**
- **Infer the importance of indistinguishability of particles even in a classical system**
- **Correct the expression of entropy of an ideal gas by applying so called correct Boltzmann counting rule.**
- **Learn that quantum statistical mechanics reduces to classical statistical mechanics results only when correct enumeration rules are applied in the classical limit..**

2. Introduction

In this module we pay attention to the expression obtained for entropy of a monoatomic ideal gas derived in module 8 as given below

$$S = Nk_B \ \ln\left[\left(\frac{V}{h^3}\right)\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}Nk_B \qquad \textbf{(41)}$$

Where $E = \frac{3}{2}N\,k_BT$. One of the interesting observations is that entropy as given in equation (1), led to correct equation of state for an ideal gas and other thermodynamic properties. Despite these successes this expression lacks one of the most important properties of entropy called extensiveness which implies that entropy scales if we scale the extensive parameters involved in the expression. This implies $S(\alpha N, \alpha V, \alpha E) = \alpha\, S(N, E, V)$. In this module we seek to look for the implications of the lack of extensiveness of entropy S leading to Gibbs Paradox, and how this paradox can be resolved, bringing into focus the issue indistinguishability of particles involved.

3. Violation of extensiveness of Entropy (S)

To check the extensiveness of entropy $S(NE, V)$ given in equation (1), let us change $N \to \alpha N$, $V \to \alpha V$ and $E \to \alpha E$ keeping the intensive variables unchanged then equation (1) becomes

$$S(\alpha N, \alpha V, \alpha E) = \alpha N k_B \ \ln\left[\left(\frac{\alpha V}{h^3}\right)\left(\frac{4\pi m\alpha E}{3\alpha N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}N\alpha k_B \ \neq \alpha S(N, E, V) \qquad \textbf{(42)}$$

Obviously, α sitting with V inside the argument of ln fails to make entropy extensive. This means that if system is made up of α parts each having entropy S then sum of the entropies of each part is $\neq$ $\alpha\ times\ S$. This is physically unacceptable situation.

4. Entropy of Mixing of Two Ideal Gases

To fully see the implication of the violation of extensiveness of entropy, Gibbs went for a thought experiment of mixing of two samples of different ideal gases at the same temperature T, followed by mixing of two samples of same ideal gas at the same temperature. It is worth noting that first experiment involving mixing of different ideal gases is an irreversible process for which $\Delta S > 0$, where as second experiment mixing of two samples of same gas is a reversible process i.e. $\Delta S = 0$.

Let us see these two case separately, and calculate explicitly using equation (1)

Case 1: Mixing of two samples of two different ideal gases at same temperature having same number density

Figure 1 below shows the two different ideal gases 1 and 2 at the same temperature and having same number density i.e. $\left(\frac{N_1}{V_1} = \frac{N_2}{V_2}\right)$.

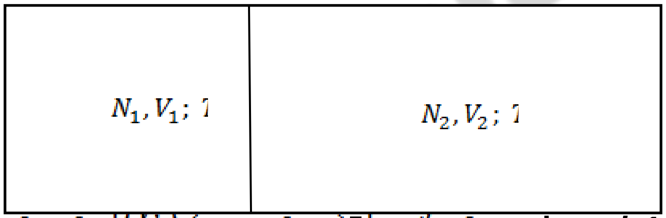

Figure 3 Mixing of two ideal gases

Before mixing the

$$S_i = N_i k_B \ln\left[\left(\frac{V_i}{h^3}\right)(2\pi m_i k_B T)^{\frac{3}{2}}\right] + \frac{3}{2} N k_B \quad \text{where } i=1,2 \qquad (43)$$

Or

$$S_i = N_i k_B \ln v_i + \frac{3}{2} N_i k_B \left[\ln\left(\frac{2\pi m_i k_B T}{h^2}\right) + 1\right] \quad \text{where } i=1,2 \qquad (44)$$

After the mixing has taken place, the total entropy can be written easily keeping in mind that now the partition of figure 1 has been removed and each particle of the gas can roam in total volume $V = V_1 + V_2$, so that total entropy can be written as

$$S_{Total} = \sum_{1=1}^{2}\left[N_i k_B \ln V + \frac{3}{2} N_i k_B \left[\ln\left(\frac{2\pi m_i k_B T}{h^2}\right) + 1\right]\right] \qquad (45)$$

Now we can define entropy of mixing as

$$\Delta S = S_{total} - \sum_{i=1}^{2} S_i \qquad (46)$$

Using (4) and (5), this leads to

$$\Delta S = k_B\left[N_1 \ln\frac{V}{V_1} + N_2 \ln\frac{V}{V_2}\right], \text{ where } V = V_1 + V_2 \qquad (47)$$

Since $V > V_1$and $V > V_2$, $\Delta S > 0$. Hence process is irreversible, expected for mixing. Furthermore, since we assumed that number density is same, equation (7) can be written as

$$\Delta S = k_B\left[N_1 \ln\frac{N_1 + N_2}{N_1} + N_2 \ln\frac{N_1 + N_2}{V_2}\right] \qquad (48)$$

Once again $\Delta S > 0$.

Case 2: Mixing of two samples of same ideal gases at same temperature having same number density

Now let us look at the same mixing process by taking in the two compartments same gas and remove the partition allowing for mixing the gases of the two compartments. Only difference now is that $m_1 = m_2 = m$.

So that S_{total} becomes

$$S_{Total} = Nk_B \ln V + \frac{3}{2}Nk_B\left[\ln\left(\frac{2\pi m k_B T}{h^2}\right) + 1\right] \text{ where } N = N_1 + N_2 \qquad (49)$$

Using this expression, and the expression the entropy of mixing again remains the same as given in equation (8) with $\Delta S > 0$. This is where the paradox arises, mixing of two samples of the same gas again when temperature T and Number density are same can be undone merely by inserting the partition, making the whole process reversible and the entropy of mixing ΔS should be equal to zero, which is not the case. In literature this is known as Gibbs Paradox.

4. Adhoc Resolution of Gibbs Paradox

As discussed in Case 2, there is a need to give a careful look to equation (1)so that entropy does not remain non-extensive and paradox of entropy of mixing ΔS of two samples of same gas does not become greater than zero for a reversible process. Gibbs proposed an adhoc way of overcoming this paradox by suggesting that from equation (1) if we subtract $\ln N!$. the entropy of mixing for case 2 becomes zero and restores extensive ness of the entropy of a nonoatomic ideal gas. This is equivalent to diminishing S_1 by $\ln N_1!$, S_2 by $\ln N_2!$ And S by $\ln N!$

If we do this equation (1) becomes

$$S = Nk_B \ln\left[\left(\frac{V}{h^3}\right)\left(\frac{4\pi m E}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}Nk_B - k_B \ln N! \qquad (50)$$

Or

$$S = Nk_B \ln\left[\left(\frac{V}{h^3}\right)\left(\frac{4\pi m E}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}Nk_B - k_B(N\ln N - N) \qquad (51)$$

Or

$$S = Nk_B \ln\left[\left(\frac{V}{N}\right)\left(\frac{4\pi m E}{3Nh^3}\right)^{\frac{3}{2}}\right] + \frac{5}{2}Nk_B \qquad (52)$$

And hence energy E, after simplification , can be written as

$$E = \frac{3h^2 N^{\frac{5}{3}}}{4\pi m V^{\frac{2}{3}}}\, exp\left(\frac{2S}{3Nk} - \frac{5}{3}\right) \tag{53}$$

A mere glance tells us that entropy has become extensive with a factor of N dividing V inside the logarithmic term.

Let us see introducing this adhoc term physically amounts to doing what. This amounts to diminishing the number of microstates of the monoatomic ideal gas by a factor of $N!$ involving new counting procedure called correct Boltzmann Counting Process. If we recall problems which we have done in permutations and combinations which allow us to count without counting, the number of permutations of N different things taken N at a time is given by N!, but if all the N things are identical it should lead to 1 possibility only this requires us to divide N! by N!.

So while checking the extensiveness of the equation (1), therefore, need is to revisit the process of counting of microstates of a monoatomic ideal gas and division by N! an adhoc solution to Gibbs paradox amounts to saying that though we are dealing with the classical particles constituting the ideal gas still these should be treated as identical to get physically correct entropy. This expression for entropy of an ideal gas was first calculated by O. Sackur and H. Tetrode in a series of papers separately during 1911-12 using for the first time quantization of phase space in classical statistical mechanics.

Now in the following we derive three very important properties which we left out in module 8, since without correct for S and hence E these physical quantities would not have come correct.

Chemical Potential

Chemical potential is defined as $\mu = \left(\frac{\partial E}{\partial N}\right)_{V,S}$, therefore

$$\mu = \frac{3h^2 N^{\frac{5}{3}}}{4\pi\, m V^{2/3}}\left[\frac{5}{3N} - \frac{2S}{3N^2 k_B}\right] exp\left(\frac{2S}{3Nk_B} - \frac{5}{3}\right) \tag{54}$$

Or

$$\mu = \left[\frac{5}{3N} - \frac{2S}{3N^2 k_B}\right] E \tag{55}$$

In terms of N, V, T, (15) can be written as

$$\mu = k_B T \ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}\right] \tag{56}$$

It is interesting to note that in classical limit, when particle density is low and temperature very high i.e. $\frac{N}{V} \ll \left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}$. This implies that the argument of logarithmic term is always less than 1 and hence chemical potential is always negative. The quantity $\frac{(2\pi m k_B T)^{\frac{1}{2}}}{h}$ is called thermal de Broglie wavelength.

Gibbs Free Energy

Gibbs free energy is defined as $G = \mu N$

$$G = Nk_BT \ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}\right] \qquad (57)$$

Helmholtz Free Energy

Helmholtz free energy has been defined as $F = E - TS = G - PV = \mu N - Nk_BT$,

$$F = \; Nk_BT\left[\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}\right] - 1\right] \qquad (58)$$

9. Indistinguishability and Enumeration of Microstates

Indistinguishability of particles in a classical ideal gas means that by no means you can tag these particles as particle A, particle B, particle C, and so on. At the most we can talk about is the distribution of these indistinguishable particles over different states, say n_i particles over the state ϵ_i, giving a set of number of particles $\{n_i\}$ distributed over a set of states $\{\epsilon_i\}$ such that $\sum_i n_i = N$ and $\sum_i n_i \epsilon_i = E$.

We shall carefully look at the emerging situation, the total number of permutations of N particles distributed according to the set $\{n_i\}$ is like distributing N particles such that n_1 particles are of the kind sitting in state ϵ_1, n_2 particles are of the kind sitting in state ϵ_2 and so on. Thus the total number of permutations turn out to be

$$\frac{N!}{n_1!\, n_2! \ldots \ldots \ldots \ldots \ldots} \qquad (59)$$

Where the set $\{n_i\}$ satisfies the two constraints corresponding to total number of particles and total energy stated above. If all the particles had been distinguishable this would have given us the correct number of microstates of a given macrostate (N, V, E). But because particles are indistinguishable, each of these microstates gives one and only one microstate. So Gibbs remedy dividing by $N!$ still leaves us with a spurious weight factor

$$\frac{1}{n_1!\,n_2!\,\dots\dots\dots\dots\dots} \qquad (60)$$

The only way to make it 1 is probability of each of n_i greater than 1 becomes smaller and smaller and most of the time it takes values either 0 or 1and rarely greater than 1. This will bring the expectation value of $n_i \ll 1$, which defines the classical limit. This leads to correct enumeration of microstates of a given macrostate, which, however, can be understood only by quantum statistics and not other wise.

9. Summary

In this module we have learnt

- That treating monoatomic ideal gas as made up of distinguishable particles leads to physically incorrect expression for entropy violating its extensiveness.
- That mixing two samples of same ideal gas wrongly leads to this process to be irreversible, once again unacceptable physically called Gibbs paradox.
- That to resolve Gibbs paradox, number of microstates need to be reduced implying treating gas as made up indistinguishable particles.
- That corrected form of entropy allows calculation of thermodunamic properties such as chemical potential (μ), Gibbs free energy G and Helmholtz free energy F, which would have otherwise been wrong
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- That enumeration of correct microstates is basically a quantum phenomenon and in the context of a classical ideal gas requires classical limit to be satisfied i.e. expectation value of occupation number must be $\ll$ one.

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