

Statistical Mechanics
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Lecture – 14
Entropy of Mixing

Good afternoon students. So, we will basically start of from where we left.

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$$\Omega(N, V, E) = \frac{V^N}{n!} \cdot \frac{(2\pi)^{3N/2}}{(3N-1)!} \cdot (2mE)^{(3N-1)/2} \cdot \left(\frac{2m}{E}\right)^{1/2} \Delta E$$

$$S = k_B \ln \Omega = N k_B \ln \left[\frac{eV}{N} \cdot \left(\frac{4\pi m e E}{3N h^2}\right)^{3/2} \right]$$

... assuming $(3N-1) \approx \frac{3N}{2}$

In the last class, where we showed that the entropy of an ideal gas can be written as well we derive an expression for the number of assessable microstates for an ideal gas at N, V, E conditions as this expression. And we remarked that the n factorial here purely stands for the fact that the particles of a gas or indistinguishable. And hence for each microstate, there was a serious over counting by a factor of n factorial that is the number of permutations you can do with n objects. So, purely respecting the fact that we want to only take the microstates, where duplication is not permitted; we have to divide the entire number of microstates with the n factorial.

And this division by n factorial actually makes the entropy purely extensive; as we shall see we did derive the expression for entropy. And I am going to write down the expression for the entropy by taking a logarithm. So, you can compute the entropy, which is K B ln omega. And this can be seen very easily if you take logarithms assuming

n is very large, then you can write it as $N k_B \ln \left(\frac{e V}{N} \right)^{3/2}$.

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$S = k_B \ln \Omega$
 $\Omega \propto \frac{N!}{\left(\frac{3N}{2}\right)! \left(\frac{3N}{2}\right)!}$
 .. assuming $\left(\frac{3N}{2}-1\right)! \approx \left(\frac{3N}{2}\right)!$
 $\ln \left(\frac{3N}{2}-1\right)! \approx \ln \left(\frac{3N}{2}\right)! \approx \frac{3N}{2} \ln \left(\frac{3N}{2}\right) - \frac{3N}{2}$
 dropped terms $\ln N$, $\ln E$, etc in comparison to $N \ln N$, $N \ln E$

Now, this derivation of S from omega you know we have assumed that N is very large, which means I have taken $3N/2 - 1$ as just $3N/2$. And hence I have taken factorial $3N/2$ as just $3N/2$. And logarithm of $3N/2$ factorial minus 1 is hence just a logarithm of $3N/2$ factorial, and this has been taken to be from Stirling's approximation just $3N/2 \ln 3N/2 - 3N/2$ ok.

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$\ln \left(\frac{3N}{2}-1\right)! \approx \ln \left(\frac{3N}{2}\right)! \approx \frac{3N}{2} \ln \left(\frac{3N}{2}\right) - \frac{3N}{2}$
 dropped terms $\ln N$, $\ln E$, etc in comparison to $N \ln N$, $N \ln E$
 $N \sim 10^4$
 $\ln N \sim 4$ $N \ln N \sim 4 \cdot 10^4$

We have also dropped terms like you know $\ln N$, $\ln E$, etcetera. In comparison to $N \ln N$ or $N \ln E$, so these terms are much larger compared to these terms, which we have taken to be as almost negligible ok. Because, you can simply see that if I take N as a large number let us say, then $\ln N$ approximately goes as 4. If I take a $\ln 10$ to the base E as 1, it is close to 1. But, $N \ln N$ is approximately 4 into 10 to the power 4. So, I am definitely going to drop $\ln N$ in comparison to $N \ln N$ ok, so that is the reason why I have dropped several terms in taking logarithm fine.

So, let us go back to expression for an entropy which is a nice beautiful expression sitting here. So, I am going just copy this expression ok. So, let us so I am going to copy this expression to a new page where I am going to do something with it, all right. But, I said in the last lecture that I want to do some thermodynamics in this system.

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Macro observations

Microscopic information

Recalling: $T ds = dE + PdV - \mu dN$

$$T \left. \frac{\partial S}{\partial E} \right|_{V,N} = 1$$

$$\Rightarrow T N k_B \frac{3}{2} \frac{1}{E} = 1$$

$$\Rightarrow E = \frac{3}{2} N k_B T$$

So, the route to thermodynamics is often laid by this bridge between microstates this beautiful expression given by Boltzmann, and that this is the microscopic world or microscopic information. And Boltzmann's bridge connects this with the thermodynamic or macroscopic observations. So, this is a beautiful bridge that connects the microscopic world to macroscopic world.

So, let us take advantage of this bridge, and construct quantities that we require. So, if you recall the first law of thermodynamics, you can write down ok. So, I am going to write down the first law of thermodynamics as $T ds$ the heat given to a system equals to

the change in internal energy plus work done by the system may expand, and let us also include the chemical work or minus μdN ok.

Now, μ here is the chemical potential. So, if I want to compute the energy of the ideal gas. So I can use this expression and write down get an expression for energy by simply saying that $T ds$ over dE at constant value of V and N should be 1 ok. Just take the differentiation with respect to E keeping volume and number of particles constant. So, you will see that this will go to 0, and this will go to 0, because N and V are taken to be as constants. And what you get on the right hand side is just one, because you have taken derivative with respect to E .

So, this will give us T times if you look at your entropy impression, taking derivative with respect to E will give us nothing but $N K_B$ over E equals to 1. And there will be a factor of $3/2$, which is precisely this factor ok. So, if I take a logarithm of E raise to $3/2$, it is just $3/2$ logarithm of E ok.

So, what I will get here is basically $3/2$ into $1/E$ ok, because logarithm of E is derivative is $1/E$. This will give me the internal energy of a gas as $3/2 N K_B T$ that is the expression for the internal energy of a gas perhaps, we knew it already from kinetic theory, but here you derive it using statistical mechanics. So, another result you can obtain is the relationship between pressure and temperature. Now, here in this case you take from the first law at and you take the derivative at constant E and constant N ok.

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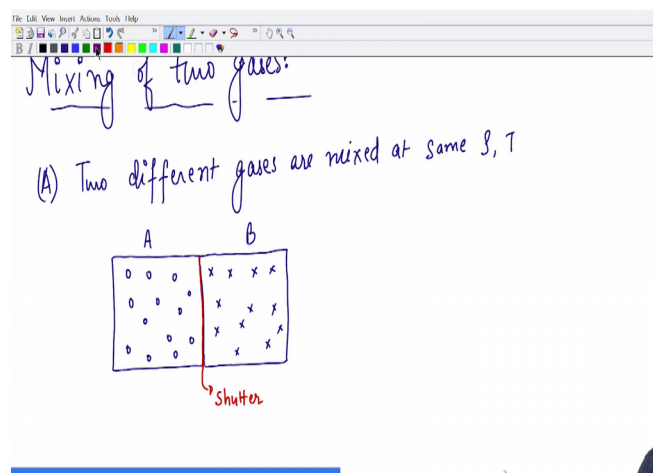
The image shows a handwritten derivation on a whiteboard. At the top, there is a box containing the number '2'. Below this, the first law of thermodynamics is written as $T \frac{\partial S}{\partial V} \Big|_{E,N} = T \cdot \frac{N K_B}{V} = P \dots 1^{st} \text{ law}$. Below this equation, the ideal gas law is boxed: $PV = N K_B T$.



So, when you do that you basically you are doing, you are taking the derivative of S with respect to volume at constant energy N number of particles ok. And that will simply give you T times, if you look at the expression of an entropy taking derivative with respect to volume is simply giving you $N K B$ over V ; because everything else is a constant, and does not depend on the volume. So, it just gives you T times $N K B$ over V , but this is equal to if you look at the first law, this is equal to pressure from the first law.

So, you get the ideal gas law as $P V$ equals to $N K B T$ ok. So, this is the equation of state for an ideal gas derived from statistical mechanics. And we are now in a position to generalize our argument of the entropy of an ideal gas to mixing of a two gases. So, this is an important subject. So, I am going to simply take this expression here ok.

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So, I am going to talk about a new subject, which is mixing of two gases right. So, I am going to basically construct an experiment, I experiment quite similar to the Gedanken experiments done by Gibbs, when he was puzzled by the entropy increase that a company is mixing of two gases. He did two types of experiments thought experiments one was mixing gases, which were of the same type, and he did experiment on mixing gases of different types.

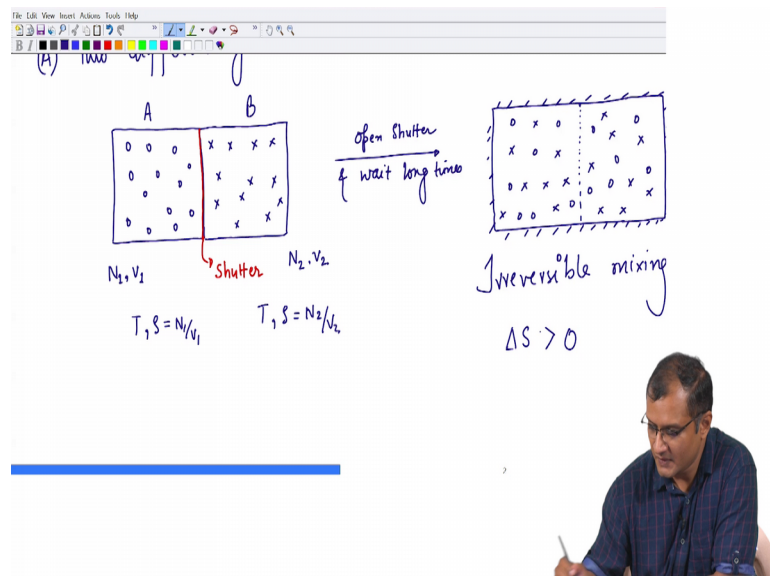
So, in a quite surprisingly he found that when you mix gases at of the same type, at same temperature, and densities if you do not properly account for a indistinguishability, this mixing apparently leads to rise in entropy of the universe, which is wrong. Because,

when you are mixing two gases at same temperature and density, and the gases of the same type ok, suppose you mix oxygen with oxygen at same temperature and same density, then this mixing leads to no rise in overall entropy of the universe. Because, if you look at the system after a long time as a (Refer Time: 13:48), you cannot distinguish the macro state; after you have mixed with the macro state that you had in the beginning of the experiment ok. So, we will discuss these two different cases.

And I am going to talk about the first case, when two different gases are mixed ok. And let us for the simple simplicity, you take the density and temperature to be same at same rho and T just to keep things simple. So, I am going to draw the schematic, you take one gas in a container call it gas of type A. And you indicate A type particles with or I think it is even better if I take let us take circles, and you take in another chamber gases is of type B ok.

Now, if you see that these particles are of different types. So, let us say there is a shut shutter here in between which can be opened and closed ok. So, I am going to basically indicate the shutter by a by a red line let us say ok. So, this is a shutter that can be open or closed.

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And I have started for the case of for the case of simplicity; you know N_1 particles on this side, N_2 particles. And I have taken volume V_1 and have taken volume V_2 . I have taken the temperature to be same, and have taken the density to be same. So, the rho here

is N_1 by V_1 , and the density here is also the same, number densities are taken to be the same.

So, if you open the shutter and wait for long times, so what do you see? What will you see after you come back; let us say go for a cup of coffee, and you come back after long time, what will you see? There are two different gases at identical temperature and density. So, the shutter has been opened, so I am going just to indicate that there was a shutter here, I will draw a virtual line.

And what you will see after a very long time is that these two part systems have mixed ok. And I am going to ask you one question is this mixing reversible or irreversible. When in can I recover my old system A and B, two gases have mixed, I cannot put the shutter back and recover my whole system ok. So, what you have seen is basically a mixing that is purely irreversible, so I am going to conclude that this is an irreversible mixing.

And we know that the entire system A plus B is mechanical and thermally isolated ok. So, the entire system is isolated from surrounding completely isolated, which means no amount of heat is exchange, no amount of work is exchange, and particles also cannot escape. So, no heat can come in or leave the system no work can be done on the system, and certainly particle cannot escape, so the complete isolation.

And, what you have seen is that in this isolated system something irreversible has happened. So, it is well known from the second law of thermodynamics that I must see the total entropy of the universe to increase ok, it is in fact greater than 0, the equality should not be there. And I will call this as the entropy of mixing.

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The image shows a handwritten slide with the following content:

$$S = Nk_B \ln \left[\frac{eV}{N} \left(\frac{4\pi m e E}{3N h^2} \right) \right] \quad \left| \quad S_f - S_i = \text{Entropy of mixing} \right.$$

$$S_i = \underbrace{k_B N_1 \ln \left[\frac{e}{\Omega} \left(\frac{4\pi m_1 e E_1}{3h^2 N_1} \right)^{3/2} \right]}_A + \underbrace{k_B N_2 \ln \left[\frac{e}{\Omega} \left(\frac{4\pi m_2 e E_2}{3h^2 N_2} \right)^{3/2} \right]}_B$$



Now, what is delta is here is basically the entropy of mixing or the total entropy difference initially and finally ok. So, this delta s is nothing but the entropy of the final configuration minus the entropy of the initial configuration, and this is a positive number, we can calculate this. And this delta is precisely called entropy of mixing ok.

Now, if we recall this expression for entropy, so I can use this expression here ok. So, I can use this expression to compute the entropy of mixing. So, you write down the initial entropy first, now initially what you have is basically these two gases A and B. So, you write down the entropy of these two gases and add them up.

So, initially the entropy using this expression for the A type particles is simply N_1 , because you had N_1 particles into $k_B \ln$, I am going to write down e by ρ_1 , because N_1 by V_1 is ρ_1 into $4\pi m_1 e E_1$ by $3h^2 N_1$ to the power $3/2$. This is just a entropy of first gas ok. I can in fact take k_B constant outside.

Student: (Refer Time: 23:36).

No this is just S_i initial entropy. So, initial entropy I am taking the sum of A and B plus I am going to write down the entropy of 2nd which is $N_2 \ln e$ by, and since the densities are the same. I am going to write down just ρ ok, because ρ_1 and ρ_2 are just ρ .

So, I think for the presentation it is better to write down k_B multiplied to each one of them just improves the presentation. So I am going to write down shift this entire object

towards slightly on the ok. And I am going to write down. So, this is basically the entropy of the A plus I am going to write down the entropy of the system B, and this is initial entropy ok. This would be k_B in two particles $\ln e$ by rho into $4 \pi m^2 e E^2$ by $3 h^2$ N 2 to the power 3 half that is it fine, this is for B, so right.

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$$S_f = k_B N_1 \ln \left[\frac{eV}{N_1} \left(\frac{4\pi m_1 e E_1}{3h^2 N_1} \right)^{3/2} \right] + k_B N_2 \ln \left[\frac{eV}{N_2} \left(\frac{4\pi m_2 e E_2}{3h^2 N_2} \right)^{3/2} \right]$$

$$\Delta S_{\max} = S_f - S_i = k_B N_1 \ln \left[\frac{V}{N_1} \right] + k_B N_2 \ln \left[\frac{V}{N_2} \right]$$

$$= k_B \left[N_1 \ln \left(\frac{V}{V_1} \right) + N_2 \ln \left(\frac{V}{V_2} \right) \right]$$



So, now what we can do here, we can write down the final entropy also. Finally, if you look at the system here on the right hand side, N_1 particles of A now have access to the entire volume. So, if I call that the final volume is the sum of the initial volumes which is V , V being the joint volume of the two boxes. So, I can see that my zeros and the crosses have both occupying volume B .

So, if I want to write down the final entropy, the same expression gives me the expression that I have written here for entropy gives me $N_1 \ln e$ by I am going to write it as e by N_1 into totally V into $4 \pi m_1 e E_1$ upon $3 N_1 h^2$ or I am going to write it as a h^2 into N_1 to the power 3 half plus for the 2nd system B system k_B into \ln , but now it has access to the full volume divide by N_2 into $4 \pi m_2 e E_2$ over $3 h^2 N_2$ whole raise to 3 by 2 fine.

So, this is now the entropy of A and B ok. So, to compute the difference entropy of mixing, I have to subtract the final entropy minus the initial entropy fine. So, you can clearly see that there a couple of term that I can straight away cancel. So, the term that I can straight way cancel from the from these two expressions is the; well, I can straight

away cancel the log e and log e raised to 3 by 2 terms, because both of the pre factor K B and 1 ok.

So, if you if you look at the expression, I can from the A types I can simply write down K B N 1 into ln into rho, because it is minus of S i and it is only lon 1 by rho. And from the 2nd term everything else cancels, in the second term I can write down K B N 2 ln V by N 2 into rho, because S i component is minus of lon 1 by rho, which is already lon rho and that is it. Everything else cancels, because if you look at here for example the m 2 to the power 3 half will it simply become 3 by 2 lon m 2, and the pre factor is K B N 2 numerator upstairs if you see there is one more K B N 2, and that is also multiply to 3 by 2 lon m 2.

So, all these terms will cancel, what you will have in the end is just this expression, where an I can simply write down one more step. If I take K B outside, this simply gives me N 1 ln see rho is already N 1 by V 1, so this becomes V by V 1 plus N 2 ln V by V 2 ok.

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The image shows a handwritten derivation of the entropy change of mixing for two gases, A and B. The derivation is written on a whiteboard and includes the following steps:

$$\Delta S_{mix} = S_f - S_i = k_B N_1 \ln \left[\frac{V}{N_1} \right] + k_B N_2 \ln \left[\frac{V}{N_2} \right]$$

$$= k_B \left[N_1 \ln \left(\frac{V}{V_1} \right) + N_2 \ln \left(\frac{V}{V_2} \right) \right]$$

A boxed equation states: $\Delta S_{mix} > 0$

Additional notes include: $V > V_1, V_2$ and $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surround} > 0$.

The image also shows a man in a blue shirt sitting at a desk, looking at the whiteboard.

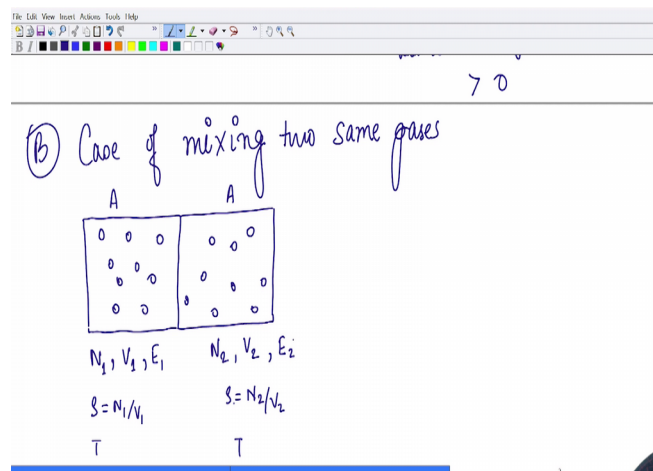
And as you can tell that V is greater than V 1 and V 2; V over V 1 is a number greater than 1, which means logarithm of V over V 1 and V over V 2 is greater than 0. So, S f minus S i is a positive quantity. So, what we ended up showing the delta S mixing is a positive quantity, and it should be, because my final configuration is a state of irreversible mixing look at the crosses and the circles. There is no way I can recover

initial system, where crosses are sitting in one compartment and circles are sitting in the other compartment.

So, by the pure nature of the mixing, there will be a positive entropy of mixing. So, basically I would I will say that my entropy of the universe has increased ok. So, the total entropy of the universe is precisely increasing by a factor ΔS_{mix} ok. So, if you want to understand, what is meant by this argument it is like I can say that the entropy of the change in entropy of the universe is nothing but the change in entropy of the systems plus change in entropy of the surrounding; now nothing happened to the surrounding.

The surrounding is basically shielded say I have shielded A plus B this means that I have seen that the surrounding. Now nothing that happens inside my A plus B influences the surroundings, surroundings entropy is not changed ok. In fact, if I come back after my cup of coffee the surrounding looks the same nothing has happened there. But, my system inside which is enclosed inside isolated boundary or boundary, which isolates my system, then I see the ΔS of the system has become positive. And so this is in fact greater than 0, what we have observed fine.

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So, now you will take different case, the case of mixing two same gases ok. And as usual I am going to take the case of ideal these is the case of mixing, when the temperature on both the sides is same, and the density in both the sides are same.

So, now I am going to do this experiment. So, as usual you take two compartments, and you take particles of the same type on both sides, because I am mixing two gases of the same type. And I have taken N_1 particles, N_2 particles, the volume of the container here is a V_1 , and volume the container is V_2 , and I am taking the density to be the same. So, both sides I am taking density ρ , and I am taking the temperature to be the same ok.

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wait for long time

N_1, V_1, E_1 N_2, V_2, E_2

shutter

$\rho = N_1/V_1$ $\rho = N_2/V_2$

$T = \frac{2}{3} \frac{E_1}{N_1 K_B}$ $T = \frac{2}{3} \frac{E_2}{N_2 K_B}$

$V_1 + V_2 = V$

ρ, T

$\rho = \frac{N_1 + N_2}{V_1 + V_2} = \frac{V_1 \left(\frac{N_1}{V_1}\right) + V_2 \left(\frac{N_2}{V_2}\right)}{(V_1 + V_2)}$

$T = \frac{2}{3} \frac{(E_1 + E_2)}{(N_1 + N_2)} \frac{1}{K_B}$

So, if you taking the energy as E_1 and energy here as E_2 ; well, then this is nothing but 2 by $3 N_1$ ok, and the temperature here is 2 by $3 E_2$ over $N_2 K_B$ ok. So, in some sense times keeping same temperature in both side means energy density same even by N_1 is the same as E_2 by N_2 on the other side.

Now, again as usual we have the shutter here that we can open and close as per our wish, so I have my shutter here. So, I am going to open the shutter and allow the gases to make. So, basically I will wait for long time allow them to mix. So, when I come back after sometime, so what do I get, you can you might have already guessed it. So, if I come back after long time, let me draw virtual vertical line just to remind us that there was a shutter here before we went for a coffee, and what you see is basically A type particles uniformly spread across the two compartments.

Now, I am going to ask you a simple question. The final volume is V_1 plus V_2 , which is V , the final density remains the same, and the final temperature is also the same, because you did nothing to the temperature and densities the temperature density on both sides

whether it is same. So, they remain the same, after you have mixed it well if you want to see, why they remain the same is simple.

The final density is nothing but they with final number of particles divide by the final volume right. So, you just take a numerator multiply by 1 upon V to both the terms. So, you take V 1 into N 1 by V 1 plus V 2 into N 2 by V 2 divide by V 1 plus V 2 this is just this is just N 1 by V 1. If I take it as rho, it can be written just as a it remains the same, so it is either a N 1 by V 1 or it is N 2 by V 2, which is nothing but your rho ok. So, N 1 by V 1 is rho, and N 2 by V 2 is also rho like I have taken here. So, I can substitute rho from both sides what I get is rho plus rho divided by 2, so it is just rho itself, fine.

So, you can see the right hand side. **So, you can take** V 1 into rho plus V 2 into rho divided by V 1 plus V 2, which is just rho ok. So, the final density does not change remains the same and the final temperature also does not change. Because, you can write down the final temperature by the same logic that it is 2 by 3 into total energy, which is now sum of the two energies divided by the total number of particles, which is the sum of two particles divided by K B. Hence, E 1 plus E 2 the same logic like N 1 plus N 2 divide by V 1 plus V 2 did not change, it remained N by V 1. Similarly, E 1 plus E 2 divide by N 1 plus N 2 remains as E by N.

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The image shows handwritten notes on a whiteboard. At the top, there are two boxes representing initial states of two gases. The left box contains N_1, V_1, E_1 and the right box contains N_2, V_2, E_2 . A vertical line between them is labeled "Shutter". Below these, the initial density $S = N_1/V_1$ and temperature $T = \frac{2}{3} \frac{E_1}{N_1 k_B}$ are written for the first gas, and $S = N_2/V_2$ and $T = \frac{2}{3} \frac{E_2}{N_2 k_B}$ for the second. To the right, under "Reversible mixing", it says $V_1 + V_2 = V$ and S, T . The final density is derived as $S = \frac{N_1 + N_2}{V_1 + V_2} = \frac{V_1 \frac{N_1}{V_1} + V_2 \frac{N_2}{V_2}}{V_1 + V_2}$. The final temperature is derived as $T = \frac{2}{3} \frac{(E_1 + E_2)}{(N_1 + N_2)} \frac{1}{k_B}$, which is then shown to be equal to $\frac{2}{3} \frac{E_1}{N_1} \frac{1}{k_B} = \frac{2}{3} \frac{E_2}{N_2} \frac{1}{k_B}$. At the bottom right, there is a small inset image of a man in a blue shirt, looking thoughtful with his hand to his chin.

So, this remains as E by N 1 or it remains as so the final temperature also is the same ok, you can do the same trick. You can multiply the first term by 1 by N 1, and 2nd term by 1 by N 2 and just the same trick.

So, now when you look at the final configuration, when A plus A has been mixed, you see that this is reversible scenario. In the sense that the final I am going to write down here, this is a state of it is completely reversible mixing. Because, I cannot distinguish between the final macro state and the initial macro state, no distinction can be made here. The system is this in the same macro state ok. So, when that has happened, you cannot tell that this is systems entropy has changed ok. So, this configuration after we have waited for a long time is in the same state. And you cannot distinguish that an experiment has happened by any a test of any investigation.

So, clearly the final system is in a completely reversible you know in this entire change is completely reversible, and we do not expect any entropy difference to have you know arisen. So, so clearly when you are macro state has not has not change, you do not expect any you remain in equilibrium, you are in equilibrium to begin with you are in equilibrium now, so you are not going away from the equilibrium, which means entropy has not changed the system is isolated, and the configurations are indistinguishable.

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Recalling ...

$$S = Nk_B \ln \left[\frac{eV}{N} \cdot \left(\frac{4\pi m e E}{3N h^2} \right)^{3/2} \right]$$

$$T = \frac{2}{3} \frac{(E_1 + E_2)}{(N_1 + N_2)} \frac{1}{k_B}$$

$$= \frac{2}{3} \frac{E_1}{N_1} \frac{1}{k_B} = \frac{2}{3} \frac{E_2}{N_2} \frac{1}{k_B}$$

So, you can check it from your expression. So, if you write down your entropy here, so I am going to write down let us take this; so I am going to I just want to copy this

expression, I guess we just recalling that this is expression for entropy. You can compute the total change in the entropy.

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The slide contains the following mathematical derivations:

$$S_i = N_1 k_B \ln \left[\frac{e}{8} \left(\frac{4\pi m_1 e E_1}{3h^2 N_1} \right)^{3/2} \right] + N_2 k_B \ln \left[\frac{e}{8} \left(\frac{4\pi m_1 e E_2}{3h^2 N_2} \right)^{3/2} \right]$$

Each term in the above equation is underlined and labeled 'A'.

$$S_f = (N_1 + N_2) k_B \ln \left[\frac{e}{8} \left(\frac{4\pi m_1 e [E_1 + E_2]}{3h^2 [N_1 + N_2]} \right)^{3/2} \right]$$

The above equation is underlined and labeled 'A+A'.

$$\Delta S_{mix} = S_f - S_i = 0 \quad \because \frac{E_1 + E_2}{N_1 + N_2} = \frac{E_1}{N_1} = \frac{E_2}{N_2}$$

So, as usual you write down the initial entropy, which is the sum of two entropies of A and B. So, our particles of were now distributed A type wherein compartment A with volume V 1 and B type wherein compartment B. So, we can write down as N 1 K B ln e V 1 by we can write down V 1 by N 1 as simply e by rho into 4 pi m m 1.

Student: (Refer Time: 46:16).

I am going to take m 1 for both of them. E 1 by 3 h square N 1 fine, this is for just A type for just one compartment plus N 2, because the compartment volumes could be different, they we have taking a type in both the compartments. The compartment volumes could be different, which means the number particles in the two compartments may be different, because we are keeping density the same.

So, we are going to write down as K B ln e by rho 4 pi m 1 e and 2, because the masses are same upon 3 h square N 2 to the power 3 half fine, this is for the B type ok, before we open the shutter. After we open the shutter, and waited for a very long time.

So, the final entropy becomes, now you have N 1 plus N 2 sitting in volume V 1 plus V 2 ok. So, here it is going to be just N 1 plus N 2 that is going to be a total number of particles. So, they are of the same type multiplied by K B e v by n is simply rho, because

that has not change the density into $4 \pi m^{-1} e$ upon $3 h$ square. Now, you can write E_1 by N_1 or you can write E_2 by N_2 , it is the same thing ok.

So, I am going to write down as E_1 plus E_2 divide by N_1 plus N_2 with the realization that they two are the same is the same as individual density. Now, this is the final entropy for the A plus A . In fact, there is no B here,, we will be going to write it as it is A only in the two compartments.

Now if you take the difference what you think should happen, I am going to I have actually missed an lon here. So, I am just going to write it again, because I have missed a lon here I we will have to rewrite it again, I missed a lon just there is a lon here that was missing e by ρ into $4 \pi m^{-1} e$ into E_1 plus E_2 divided by N_1 plus N_2 all raised to $3/2$ divided by $3 h$ square here. Now, you can see E_1 plus E_2 divide by N_1 plus N_2 is the same as E_1 by N_1 or E_2 by N_2 .

So, the entire (Refer Time: 50:39) logarithm argument is the common argument in all the three terms. And if you look at S_i , there is $N_1 K_B$ plus $N_2 K_B$, whereas in the denominator is the same $N_1 K_B$ and $N_2 K_B$. Say if you take the difference of S_i minus S_f , you are going to get nothing but 0. Because, of the fact that your energy density is the same as initial energy density, we have already shown this, we are mixing them with constant temperature, and so the logarithm of argument is the same in all three terms, and when you take the difference what you get is essentially 0.

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$$\Delta S_{mix} = S_f - S_i = 0$$

There is no change in entropy for this mixing

H.W. "Gibbs Paradox"

$$\Omega(N, V, E) = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{(3N-1)!} (2mE)^{(3N-1)/2} \left(\frac{2m}{E}\right)^{N/2} \Delta \epsilon$$

So, there is absolutely they take a messages that there is no change in entropy for this mixing. And the entropy did not change simply, because the macro state remain in equilibrium, and did not change. So, you had the same macro state to begin with and you go the same macro state when you end it, there is absolutely no way you can tell that an experiment was actually was performed ok, when you come back, you can put the shutter back and recover the old system with the same density on either sides, and the same temperature either sides.

So, clearly the change that happen happened in this isolated system was reversible, and for such systems for such changes you do not incur in incur a change in a positive change in entropy. So, hence the entropy of mixing turns out to be purely 0. So, if you had taken in your expression for number of microstates, so I am going talk about this expression now. Remember this N factorial, which is highlighted in red colour. This stands only to safeguard your computation, and to make entropy purely extensible extent extensive. So, if you see your entropy expression, if I scale E by λ , N by λ , and E by λ the entire entropy expression is killed by λ , which is known as pure extensive scaling of entropy with respect to its arguments.

So, if I had not taken this care and not divided by N factorial, it would have given me an entropy which was not purely extensively. And as consequence of that the case of mixing of two same gases would have given me an entropy change that was that that would be positive. So, you can do this calculation mix two gases of the same type, at same temperature, and same density using an expression for S that does not have this, S correction factor, and you will see an entropy change that is positive.

I will leave that exercise as homework. And this is precisely the problem that puzzled Gibbs for a long while, and this problem is called the Gibbs paradox. Today, we resolve that paradox. We stated that there is absolutely no change in the entropy. If you correctly can count, you know a numerate the number of microstates by taking into account indistinguishability of the particles. So, the Gibbs paradox stands resolved, we did not encounter it, because we computed the states correctly.

And, we shall give you one problem as homework that will so write down the homework problem, so I am just going to state here. So, we will give you the solutions, but you should do this problem yourself. Say, if you take the let me copy this expression, so the

problem is in Gibbs paradox, it is very simple thing to understand. We did not encounter it, because we did the calculation correctly.

But, suppose you were to do this calculation incorrectly, and this is where Gibbs paradox comes. So, suppose you so suppose you took the wrong expression for you know the number of microstates, you did not take the N factorial ok.

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The whiteboard contains the following handwritten text:

Suppose you missed it.

$$S^* = N k_B \ln \left[v \left(\frac{4\pi m e E}{3 h^2 N} \right)^{3/2} \right]$$

↑
over computation

$$N \rightarrow \lambda N, \quad v \rightarrow \lambda v, \quad E \rightarrow \lambda E$$

$$S^* \rightarrow \lambda S + \lambda N k_B \ln \lambda$$

The man in the bottom right corner is looking thoughtful, with his hand on his chin.

Suppose you missed it. Then without this N factorial the expression for entropy, and I am going to write down the super script to just tell you the fact that this is over computation, this would be just N K B. You can do the calculation without the N factor just a take logarithm on both sides. You would get V into 4 pi m e E over 3 h square N to the power 3 half. Now, you can see that your entropy is not extensive. In the sense that if I scale N by lambda N, and volume by lambda V, and E by lambda E, my overall entropy S star is killed by you know S original plus; so this would become my this would become my lambda S plus N K B ln lambda ok, because E by N does not matter.

So, E by N remains E E by N, because they both killed by lambda. And V scaled by lambda V, so I can take N K B lambda N K B lambda ok, and 1 lambda N K B into V into this thing is just lambda into S ok. So, this extra factor that I get should have been 0, if entropy was you know this not 0, so that is how I say that my entropy is not extensive I get I got an extra contribution. And you can see this is positive in nature, because I have over counted omega.

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over count

$$N \rightarrow \lambda N, \quad V \rightarrow \lambda V, \quad E \rightarrow \lambda E$$
$$S^* \rightarrow \lambda S + \lambda N k_B \ln \lambda$$

Mix two ^{same} gases at same S, T .

You should get $\Delta S_{\text{mix}} > 0$ "Gibbs paradox"

So, now if you mix to you know, you redo this mixing of gases take the case of two gases at two same gases, at same temperature, and density you will get, you should get the entropy of mixing as non-zero. In fact, there should be you will get it as a quantity which is positive. So, this is basically Gibbs paradox.

A little while ago when we did this calculation, we saw that the entropy change is 0. But, if you do this calculation at home at you know you know at temperature and density which are same on both sides, and you mix two same gases, when you do the calculation the same spirit like we did just a few minutes ago, you will find that entropy of mixing comes out to be positive. And that is completely wrong, because it should not be positive, it should be 0.

So, the heart of the Gibbs paradox lies the incorrect enumeration of microstates, precisely because you did not take into account that there are N factorial microstates that are indistinguishable, when you over counted them. And thereby made the entropy non-extensive and hence you ran into this issue.

So, we will close this lecture here. And the next class when we meet, we will talk about canonical ensemble. And this is an ensemble where you allow for the energies to exchange in order to maintain constant temperature. So, we will start the next lecture from canonical ensemble and taken from there.

Thank you.