Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Science – Roorkee

Lecture 06
First and Second Law of Thermodynamics

Hello all of you. So in the last lecture I have been discussing how the energies are distributed in molecular systems and we have been discussing about the number of ways of distribution and the idea of entropy and all that. So in today's lecture, we will take the argument further and also include the discussion on the energy itself. So as we have discussed earlier on the course and you must have read in thermodynamics that there are two essential things in thermodynamics that is energy and entropy.

So let’s first discuss the idea of energy and will introduce the first law of Thermodynamics and then in future classes will introduce the other law of thermodynamics that includes both the energy and entropy in discussion.

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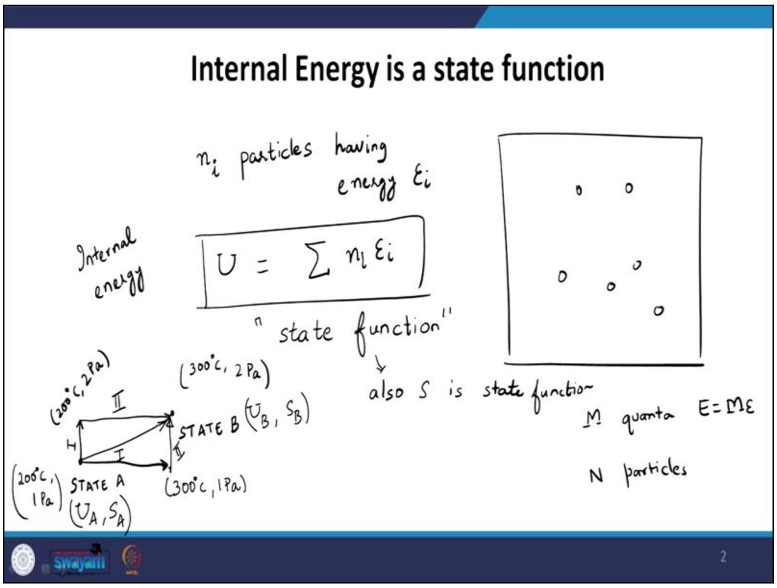

Internal Energy is a state function

So what is internal energy? In some ways, we already have discussed that in the class. So when we said, that we will distribute. M quanta of energy in my N particles then the energy that we had from the M quanta assuming a uniform distribution Mϵ that is my internal energy, actually there is some totalities here but will come to that but this is the energy of the system.

So in general we can say that if you have for example n_i particles having energy ϵ_i and as we have been discussing there is a distribution in reality you can have n_0 having ϵ_0, n_1 having ϵ_1 and so on and I am writing in a manner now it does not matter whether the energy levels are uniformly spaced or not by talking about energy of those energy levels. So in that case the internal energy is given by-

$$U = \sum n_i \epsilon_i$$

that is simply summing over energy of all the molecules in the system because you have n_i molecules having energy ϵ_0 say for example you have n_0 having ϵ_1, n_1 having ϵ_2 and so on you simply add the number multiplied with energy levels and that will give you the internal energy.

So what is a very important thing about the internal energy is it is a state function, in fact although we have not specifically mentioned that earlier entropy is also a state function. What a state function means is that it only depends on the state of a particular system it does not depend on how it got here, so just to give you an example. Let us say for example, I have run stair to come to the second floor building. So now finally I am at second floor of the building so I could have come running fast but I could have come running slow how I came here it does not change the Energy in this particular state even when I am talking about myself it is the potential energy that corresponds to MGH so always I am coming to the second floor. So ultimately what matters is the height from the ground from coming to the same height, every time that means the energy that I am in only depends on my final state that is, not how I came here.

On the other hand if for example look at how much work I have to spend for coming here then of course coming slowly or coming fast may correspond to different amounts of work, how much sweat comes out when I am coming here it corresponds to different values depending on how I got here. So when I say something as state function there is no dependence on the path or the previous history how we got to this particular state this is what we refer to as a state function and ‘U’ is a state function and I will come to path functions in a minute.

Similarly ‘S’ is also a state function and we kind of already had that because what S depends on, S depends on number of ways of distribution. We did not say anything about what was the past of the system and how it got here and things of that sort out there was no discussion on how we got to a particular point only a discussion of like, what is the final state.

However, the system may go from a state A to state B and this can be done in multiple possible ways. So let's say for example just to make our discussion easier for those coming from the thermodynamics background. Let's say for example, I want to go from 200 degree Celsius and 1Pascal to say 300 degree Celsius and 2pascal. So there are many ways of doing it.

In one way what I do is first, I change the pressure to 2 Pascal. I go from 1 Pascal to 2 Pascal keeping the temperature fixed at 200 degree Celsius. So I go from here to state where you have 200 degree Celsius and 2 Pascal. Now since I was the final pressure what I now do is I keep the pressure constant and I simply increase the temperature. In the first part of it, what I was essentially doing was a constant temperature process that is an isothermal process. In the second part what I am doing is a constant pressure process that is isobaric process.

The other possibility of doing that is that I could have changed the temperature first keeping the pressure constant and from there I could have kept the temperature constant and increase the pressure so in that case I am starting from an isobaric process that is a constant pressure process followed by an isothermal process constant temperature process. Now both of this is going to the same final state. So what I am saying from here is that whatever the energy U in the state A or the entropy in the state A and what about the value of U in the state B and the entropy in state B, these values are completely independent of like how exactly the process have been conducted.

You could have also done in a linear manner. So I changed both the temperature and pressure together and probably the same proportion so that I linearly go from 200 to 300 and linearly go from 1 Pascal to 2 Pascal in by changing both of these together whatever the process is called. So the point being is that of course, these processes are different the way we are conducting a different and they may have something else that is dependent on that will come to that in a minute, but the key point is that the energy and entropy does not regard how we have got to a particular state or where do I go from there?

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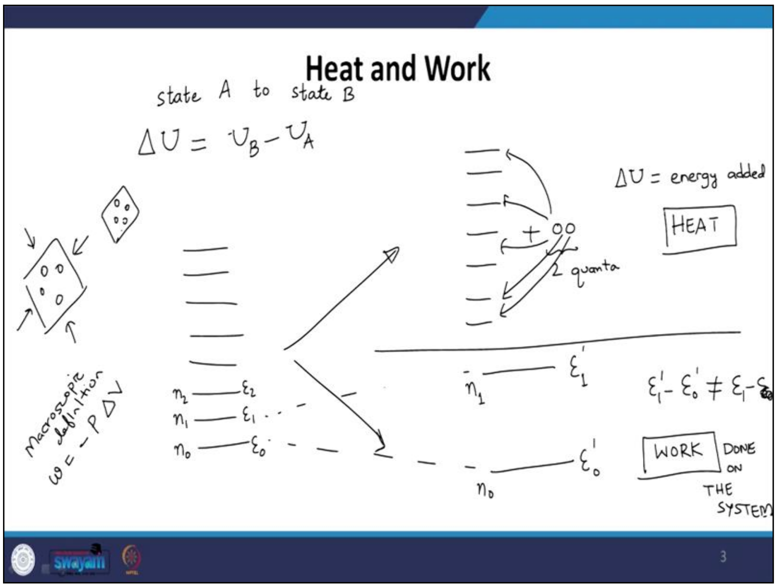

Heat and Work

So now if I look at the previous example we went from state A to state B and these of course have given me some change in the internal energy that is-

$$\Delta U = U_B - U_A$$

Now go back to the molecular level and think of how the energy can come into the system. So we have said that the energy is the number of quanta of energy available in the system. So the only way possibly for energy to come when we have somehow a way to increase the quanta of energy, some probable input to the quanta of energy so energy go from $M\epsilon$ or M quanta to say M +1 or M + 2 or whatever this is the only way the energy can be increased. For a particular energy the distributions may change but the energy can only increase when we are adding the extra energy in the system.

I am going back to our picture of molecules present in different energy levels we can think of two possibilities where this can happen. So let us say we have n_0 molecules having energy ϵ_0, n_1 having energy $\epsilon 1$.

So the notation now we are using it does not quite matter whether the energy levels are uniformly spaced or not because we are not resuming that in the notation now. So in this particular case, there are two possibilities, in one of the way what may happen is that we can add some additional quanta of energy in the system and that will happen, so let’s say for example we had this system and I add some additional let us say 2 quanta of energy, now as the entropy suggest this 2 quanta of additional energy, the system has got it may go to any of the energy levels entropy again comes in but the number of ways of distribution has now increased simply because we have more point of energy and the system has now got two additional quanta of energy. So ΔU will correspond to the energy that we have added and this energy is referred as the heat.

One thing to keep in mind that should be made clear from the definition itself is that when we say heat, it does not always mean although that may be the intuitive way of thinking about it that once we add heat the temperature does not need to increase. Let us say for example, you add heat and water boils, so in that case temperature increases at the same time you can have a case where you have an ice at zero degree Celsius is heated, you can have water at 0 degree Celsius. So in that case we have added heat but it did not go into changing the temperature of the system, it went into changing the phase.

So, all though we have we call it as heat it does not mean that the system gets heated necessarily. It may happen that the system temperature may increase but it may also not happen, although we referred it as heat keep in mind that system need not get heated by adding it. It simply refers to the energy added in the system and that energy may go towards increasing temperature or it may go towards changing phase or something else so it is not always going in the in the heating of the system.

The other possibility is that maybe the system gets energy somehow but instead of like this having these extra quanta of energy that gets like distributed and therefore we should have more number of ways, what may also happen, at least it is easier to imagine is that whatever the energy spacing that you have between the levels they increase. For example by some means we still have the same number of molecules in the 0 level and 1 level. So, n_0 and n_1 remains the same but the energy gap between the two states has changed that means-

$$\epsilon_1' - \epsilon_0' \neq \epsilon_1 - \epsilon_0$$

And you see what will this correspond to because if that is happening then the number of ways of distribution has not been quite altered really because the number of molecules can still be there in 0 state 1 state what has changed is energy spacing between the labels, of course when you discuss about the Boltzmann distribution then this will become important because number of molecules depend on the energy of the state but that is indirect consequence not like the case that we had when we are adding heat and this particular thing is called as work on the system.

So work you may imagine the work as the energy levels in the molecular system are becoming broader in sense and this is the work done on the system. Since this may be slightly confusing for those of you who are coming from like thermodynamics background in undergrad. Let us look at how we define work earlier. So we defined work as typically a pressure volume work.

$$W = P\Delta V$$

So there is a pressure the system possess and that pressure gives rise to some volume change. Now pressure is property of the system so when we talk about the pressure volume work that is the work done by the system. If I want to look at the work done on the system, it is going to be minus of that that is the macroscopic definition of work.

However when this work is added what really happens is that let say for example, if I do work on a system then the system gets compressed. So the number of molecules may remain the same but now they may become closer to each other when they get closer to each other, now the collisions will start to become more frequent in some in some sense they can easily exchange energy. So once they can exchange energy easily, where is that effect being accounted for? This may be accounted for in some changes happening at the level of energy levels because now more exchanges are possible that was probably not possible earlier because the molecules were farther apart. So what we say in the language of energy levels is that the energy levels may become farther from each other or in the in the other case, it may get compressed with some change in energy level as we add work on the on the system. So this basically gives me the definition of the first law of thermodynamics.

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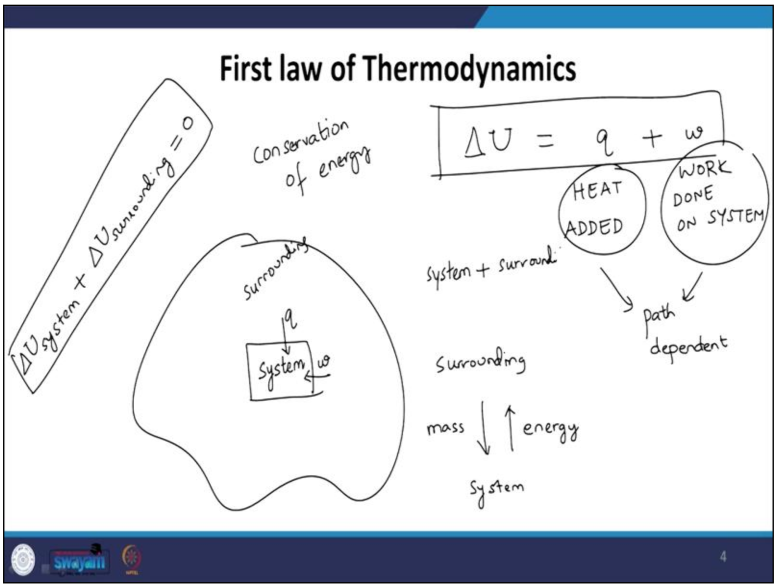
First law of Thermodynamics

So now we have said that there are two ways we can change internal energy. One of them is what I refer as heat added to the system and one of them is the work done on system.

$$\Delta U = q + w$$

The first one and the second one on the right hand side q and w both of them are path dependent. So although the initial and final states do not care when we look at the internal energy or entropy the heat that is needed or the work that is needed for this to be made possible that is going to change when I change the path. If I first do isothermal and then do isobaric or if I first do isobaric and then do isothermal they may corresponding to different levels of heat and work. But the key point is that the sum of that remains a state functions, so whatever path dependence we have there that path dependence must in some way cancel each other or counteract each other so that in the end the net result is a state function.

So this one can also think of the law of conservation of energy because there are only two possible way the energy of a system can change either heat or work and both of them again forms of energy so therefore basically, it is just telling that if I add energy to the system by means of a heat or by work the energy of system will increase by the same amount so it is pretty much a restatement of the law of conservation of energy.

There is something interesting now, let’s say for example, we will look at any particular system containing molecules in thermodynamics we always consider a system along with its surrounding because the surrounding may exchange energy and may exchange mass with the system. So surrounding and system we already discussed the cases. Let us say when the system is isolated then there is no mass and energy exchange. When the system is closed there is no mass exchange, but energy exchange when the system is open, you can have mass and energy exchange. All these exchanges may be there may not be there but the basic notion of system and surrounding is always used.

So what do we mean when I say that I do some work done w on the system or I add some heat on the system, where is that heat and work coming from? That heat and work must be coming from the surrounding. Let's say, for example, if I increase the energy of the system by means of heat and work from the surrounding that must be giving rise to a decrease in the surrounding energy because energy has to be conserved that means that if I add the energy change of the system with the energy change of the surrounding this must be equal to 0.

$$\Delta U_{system} + \Delta U_{surrounding} = 0$$

Now here is a very interesting point now. So this has to be satisfied other ways to say that is that the energy of universe is constant because system + surrounding basically constitute the universe. So what I mean say that energy of the universe is constant so yes you can have a local increase in the energy of a system or any part of the universe, but that local increase must be accompanied by a local decrease in some other part of the universe or surrounding of the system.

So then the bigger question is that then what is the motivation for the system to do any particular thing, because if energy has to be constant then what is the reason that a certain process is being followed and a certain process is not being followed because all the processes will correspond to the same energy for the universe so there is no change in the energy, energy is not if you think about it is not the driving force for processes happening in nature because energy is constant.

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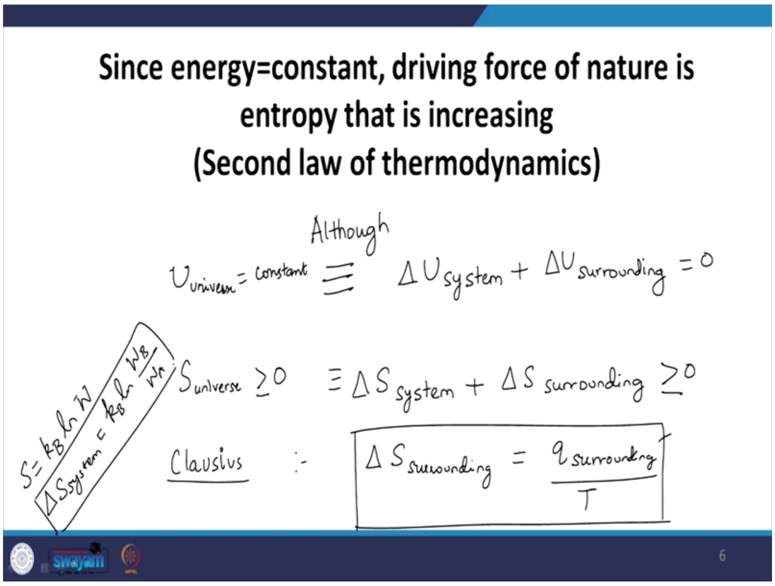

Since energy=constant, driving force of nature is entropy that is increasing (Second law of thermodynamics)

Although

$U_{univer} = constant \equiv \Delta U_{system} + \Delta U_{surrounding} = 0$

$S_{universe} \geq 0 \equiv \Delta S_{system} + \Delta S_{surrounding} \geq 0$

Clausius :- $\boxed{\Delta S_{surrounding} = \frac{q_{surrounding}}{T}}$

$S = k_B \ln W$

$\boxed{\Delta S_{system} = k_B \ln \frac{W_B}{W_A}}$

So here comes the second law of thermodynamics to our help and what it tells me is that although I am copying the statement of the first law although the ΔU of the system plus ΔU of the surround is equal to 0, the same is not true for the entropy.

$$U_{universe} = constant \equiv \Delta U_{system} + \Delta U_{surrouding} = 0$$

If I add the ΔS of the system with the ΔS of surrounding this must be higher than 0. So what this tells me, is that the U of the universe is equal to constant what this tells me and we have already discussed this point that S of the universe must increase in fact that actuality you should have something like-

$$S_{universe} \geq 0 \equiv \Delta S_{system} + \Delta S_{surrounding} \geq 0$$

So what this tells me, is that the U of the universe is equal to constant what this tells me and we have already discussed this point that S of the universe must increase in fact that actuality you should have something like greater than equal to sign and when it is equal we call the process as reversible and will come to the discussion in the next lecture.

So now we have the driving force clearly identified that is my entropy, energy is of course important. If I want to look at the energy of a system I need to look at what is the heat being added work being done and those pretty much because energy is the ability of doing work that is extremely important but nonetheless, it is not the driving force in real sense because energy of the entire universe has to be constant. It is the entropy at the driving force and this particular finding is because of the scientist name Clausius thought of the same question as a just post that energy cannot be the driving force if energy remains constant there has to be something else. So although he did not know how the entropy has to be that defined he had this argument that there must be something called entropy, and then he also claimed and it came out to be correct that ΔS for the surrounding should be defined as-

$$\Delta S_{surrounding} = \frac{q_{surrounding}}{T}$$

In fact this also becomes a definition of temperature if I go back to Clausius argument.

So heat added to the surrounding is actually negative of the heat added to the system because if I had heat to the system the heat comes from the surrounding. So when q surrounding is positive it means the system is giving off heat to the surrounding and when q surrounding is negative it means that the surrounding is giving of heat to the system nevertheless ΔS surrounding is always given by this-

$$\Delta S_{surrounding} = \frac{q_{surrounding}}{T}$$

So ΔS of system we can find using the arguments we just made in the previous lectures that is I know that entropy is given by-

$$S = k_B \ln W$$

$$\Delta S_{system} = k_B \ln \frac{W_B}{W_A}$$

If I am going from state A to state B.

Now why would not be used the same formula for the surrounding simply because surrounding is much, much larger than compared to the system so therefore a description of the surrounding entropy in terms of the number of ways is going to be pretty much impossible. But for the system we can manage to do that, even though formula should be applicable for surrounding as well we will go with the Clausius formula because of the practical difficulties in counting the number of ways for the surrounding part of system.

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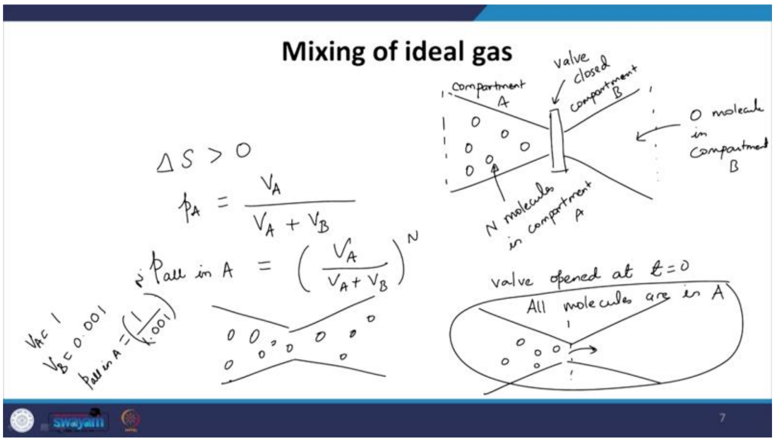

Mixing of ideal gas

$$\Delta S > 0$$

$$p_A = \frac{V_A}{V_A + V_B}$$

$$p_{\text{all in A}} = \left(\frac{V_A}{V_A + V_B}\right)^N$$

$V_A = 1$

$V_B = 0.001$

$p_{\text{all in A}} = \left(\frac{1}{1.001}\right)$

Let’s take an example of why this entropy of the driving force and we take a simple example again of the ideal gas that we had taken earlier. So let us say for example, you have two compartments where gas can be present and the compartments are connected using a valve and this valve is closed to begin with it that means there cannot be any flow of energy or mass between the compartments A and compartment B.

Now the question I am posing let us say for example in the beginning of experiment we have some N molecules in compartment A and 0 in compartment B. Let’s say at time T = 0 whatever reference time what time we want to define we open this particular valve that means now molecules can go from compartment A to compartment B, it was earlier not possible.

Now let us say how the laws of thermodynamics will approach this problem, even though we have assumed that it is an ideal gas and there is no interactions the molecule may have some kinetic energy or whatever but energy of the entire system is going to be constant. If you think about it energy cannot really drive the motion from compartment A to Compartment because by doing that energy remains the same so why going towards compartment B should be a favourite things be a favoured process, so energy cannot explain that,what can explain is the fact that the entropy of this particular arrangement must increase in this case there is no surrounding, in this case the system is composed of compartment A and compartment B. At time T = 0 anyway the molecules cannot move from A to B compartment but as soon as the valve is opened now the molecules can go and they will go if ΔS for this is higher than 0 because the entropy must increase, it is true for the universe but in this case the surrounding has no effect. So the ΔS of this compartment A and B system must increase for this particular motion and let us see if it is indeed true. Let us for doing that. Let us compare two different states in one state the valve is open but all the molecules are in compartment A and the second state the molecules can just be anywhere it can be in compartment A or compartment B. Now let us find the probability for this to happen.

What is the probability that all the molecules are in A and the way to answer that is that let us find what is the probability for one molecule to be in A? So if I ask this question that molecule a is as happy being in compartment A and as so being in compartment B, all that matters is that what is the volume of these compartment from the probabilistic argument. So ultimately for the molecule to be in A the probability is-

$$p_A = \frac{V_A}{V_A + V_B}$$

because there is no difference it makes for the molecule to be in compartment A or compartment B it will pretty much want to be just anywhere only depending on volume. Of course if the volume is small the probability there is also a small.

However if I look at all the molecules in A then I am looking at basically power of these probability. Let's say a first molecule in A and second molecule is also in compartment A the probability is going to p_A^2. If first, second and third are all in A the probability is going to p_A^3. So the probability for all being in A is going to be-

$$p_{all\ in\ A} = \left(\frac{V_A}{V_A + V_B}\right)^N$$

Now let us say its molecular system and N is very large, but you can see from there is the probability of this to happen becomes extremely small as N is large even if V_B is like a very small number compared to V_A. Let us say, for example, if V_A is 1 and V_B is 0.001 so even then what it tells me is the probability of all in A is like-

$$p_{all\ in\ A} = \left(\frac{1}{.001}\right)^N$$

and N is like 10^{23} or higher and you can imagine this number is pretty much going to be zero.

So what is establishes again is that entropy indeed is a driving force for a process to happen. Energy is extremely important than ideal gas case we did not consider that the interactions were not present. It may be important but none the less energy itself cannot be the driving force for a particular process.

So with this particular argument I will close the discussion today and we will see in the next classes. How do we define the third law of Thermodynamics and how can then we go towards description of other energies that we may have heard of like enthalpy and free energy and so on.

So with this is stop here, thank you.