

Advanced Thermodynamics and Molecular Simulations
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Lecture - 02
Molecular Basis of Energy and Entropy

Hello, all of you. So welcome to this course on Advanced Thermodynamics and Molecular Simulation the second lecture of the course. So in the last lecture, I introduced you to this course, and I gave you some motivation to study thermodynamics, and we already briefly recapped the laws of thermodynamics.

In this lecture, we will talk about the idea of energy and entropy and how do they come from the molecular level principles.

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Energy and Entropy

Energy is the **ability** to do work

Energy = Potential Energy + Kinetic Energy

Then what is Internal Energy (U), Enthalpy (H), Helmholtz Free Energy (F), and Gibbs Free Energy?

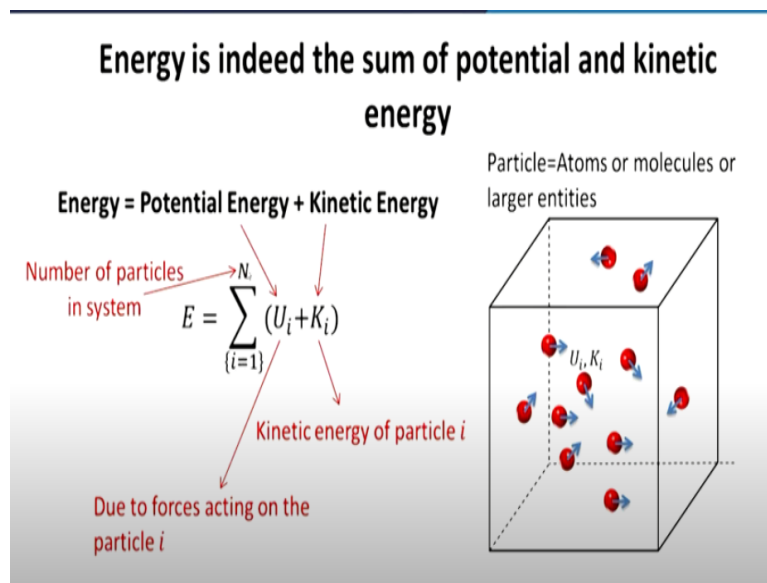
Entropy is the measure of **disorder** or **randomness** → why it is so important?

So if you remember the first definition of energy you may have read in school, energy is the ability to do work, and the way we define energy in high school, is energy is a sum of potential energy and kinetic energy. Potential energy comes in the classical example of a ball as from the height of the ball from the ground, and kinetic energy comes from the velocity of the ball as it moves and ultimately, energy happens to be an interplay between the potential and kinetic energy. However, if you recall in thermodynamics, you should have used energy quite differently. We did not talk about potential energy and kinetic energy, instead we talk about internal energy, enthalpy, Helmholtz free energy and Gibbs free energy.

So the first thing I will try to address is what exactly the energy mean in thermodynamics, and I want to argue that it is no different from what it meant in high school energy is still potential plus kinetic energy if I look at the molecular level system.

The second idea I will introduce and we have already discussed that is the idea of entropy but again, we will try to argue from the molecular level how the idea of entropy comes into existence and why is that important?

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So this is the picture that is there, right so energy is the sum of potential and kinetic energy if we indeed look at the system at the molecular level. So if I look at any particular molecule in the system, the molecules is under influence of forces that can be external to the system or that can be coming from other molecules in the system that give rise to what we know as potential energy just the same way as we had for a ball sitting at a height because there was a gravity force, it was giving rise to a potential energy. So in similar manner, when we have molecules, molecules experience a force and therefore, they have a potential energy. Similarly, molecules move, say they do have the kinetic energy. So at a molecular level, energy is still a sum of potential and kinetic energy.

Now the question is then, why we do not define it in this particular way in thermodynamics and the reason was, we were not looking at one particular molecule or few molecules, we were looking at a large system composed of many molecules. So ultimately, these potential and kinetic energy should somehow lead to the idea of energy of a thermodynamic system, which

it indeed does, right. So what I am showing here, for example, is a box containing many molecules by the way, I want to make a point clear here that I will use the term atoms and molecules interchangeably. Sometimes I will call that particles when we discuss that when it is important in the course I will tell you specifically whether it corresponds to atoms or molecules. But in general, whenever I talk about a particle, the particle can be atoms or molecules and as you will see later, it can also be somewhat larger entities than molecules, may be a combination of molecules or a collection of molecules.

So let us say you have a box containing molecules, that pretty much would be like any small part of any system, let us say a drop of water contains plenty of molecules. Now those molecules all of them has a potential energy and a kinetic energy. Let us say if I look at a particle i , the particle i may have a potential energy U_i by virtue of the forces acting on the particle i and it can have a kinetic energy K_i by virtue of the motion of that particular particle. So the energy of the system would then be the sum of the potential and kinetic energy for all the particles in the system. So in this case, I am summing from i equal to 1 to N , where N is the number of particles in the system and I am summing over all the potential and kinetic energies of the molecules or particles.

$$\text{Energy} = \text{Potential Energy} + \text{Kinetic Energy}$$

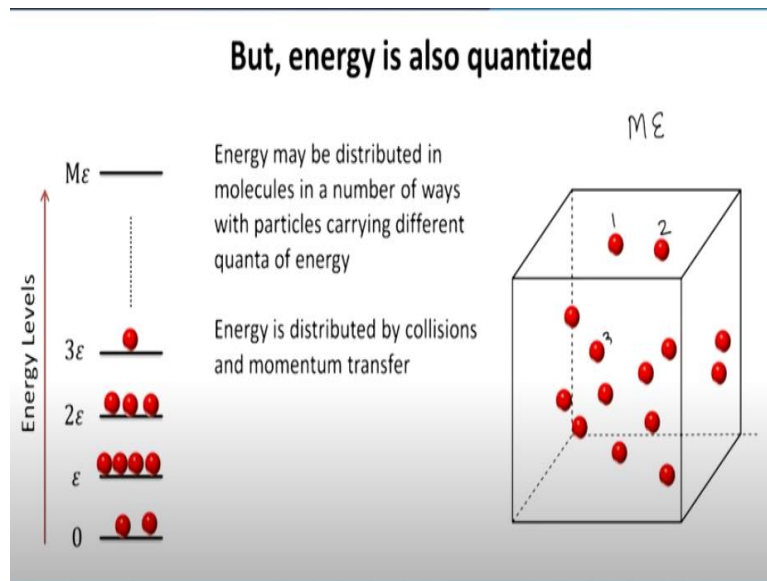
$$E = \sum_{\{i=1\}}^N (U_i + K_i)$$

So this is the thermodynamic energy, energy is not any different from that. Now the reason why we have defined three or four different energies in thermodynamics is more subtle and we will come to that in this course. Before we get there, the other point here is that, if I when I said that the molecules or particles have a potential and kinetic energy, what we are talking about is a classical mechanics description that's where we start to believe in Newton's laws of motion. If I really go to a molecular system or if I particularly go in a subatomic level, we actually have a regime of quantum mechanics and that works quite differently from classical mechanics. Classical mechanics applies to large systems and quantum mechanics applies to small systems, particularly atomic and molecular system.

In this particular course, we are at the interface of quantum and classical mechanics because we are talking of molecular entities, but we want to represent the behavior of large systems as thermodynamics does, right. So if I talk in a quantum mechanical terms, energy of any system

is actually it cannot take any value it has to be discrete packets of energy coming together to give the energy of a system. That means the energy is quantized.

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So let us say if I again look at the same system I was looking at, in the quantum mechanical picture, they do not have a potential and kinetic energy as in what we discussed. Of course, the electrons in the atoms have a kinetic energy. But when we talk about the energy of a molecule that actually is composed of in parts, the kinetic energy of electrons, but also in parts by the nuclear energies and all those things, right. So and that energy happens to be quantized, it can only take certain discrete values.

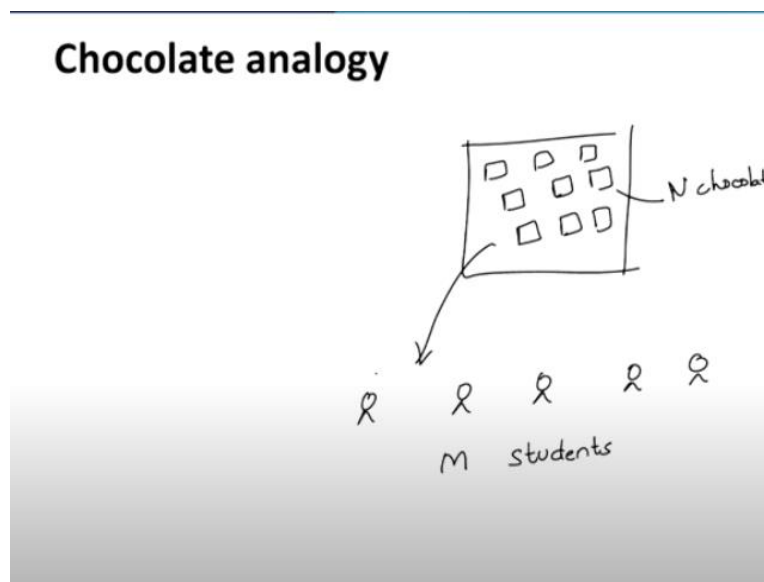
So let us say for example, that discrete I would say unit of energy is ϵ , then a particle can take an energy 0, it can take an energy ϵ , 2ϵ , 3ϵ , 4ϵ and so on. It cannot take any value between 0 and ϵ the energy it can take is only discrete in packets of energy. Of course, it need not be like a uniform packet. There can be for example, a non-uniform energy spacing, but nonetheless, the key point here is that the energy has to take discrete values we are assuming the spacing is uniform it is in multiples of ϵ . It need not be, the key point is it has to be discrete.

So then, if I look at this particular system of molecules, now as you may imagine, different molecules have different kinetic energy in classical mechanics. In quantum mechanics, it corresponds to different energies or different number of quanta of energy.

Let us say for example, two of these particles may have energy of zero, they may be in the ground state four of them may be having an energy of ϵ , they may be in the first excited state, three of them may have energy of 2ϵ , they may be in the second excited state. When we talk about say for example, hydrogen atom this corresponds to 1s, 2s, 3s orbitals and so on. Similarly, 3ϵ we have like one particle, so it has three packets of energy, right. And whenever the molecules collide, they exchange these quanta of energy and essentially the exchange must be again following the law of quantum mechanics, must again be in the same discrete units. So for example, all ϵ can be exchanged, but half ϵ cannot be exchanged, right. So energy exchange must also happen in units of ϵ .

So an easy way to start thinking about this is to make an analogy of like, let us say some chocolates.

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Let us say for example, I have a box of chocolates. And I want to distribute it to the class. So let us say for example, I have some N chocolates in a box and let us say if I want to distribute to some M students in the class. Now the question is, in how many ways we can do that, right and as you may imagine, the possibilities are endless. I can give all the N chocolates to one particular student, I can distribute them equally, I can give the first person 1 chocolate, the second person 2 chocolates, the third person 3 chocolates, the fourth person 4 chocolates. I can give the first person 5 chocolates, second person 3 chocolates, right. So there are a wide range of distribution of chocolates within every student that I am distributing into.

In a similar manner, once the system has certain energy, let us say the energy of system is $M \epsilon$ that means we have M units of or M packets of energy available those are in some sense M chocolates we have that I am distributing to the molecules which are like students in the analogy, right. So this M , I can give all the M to one person, I can distribute them equally, I can distribute it like 1 to this molecule, 2 this molecule, 3 to this molecule, 1 again to this molecule and so on and I can have many-many possible distributions and it is this way of distribution that is what gets into the idea of entropy. Entropy refers to these ways of distribution and that's how it comes in thermodynamics. Of course, energy is a very important concept. Energy is ultimately dictates how much energy a system has and how much capability it has therefore to do some work but at the same time, how the energy is being distributed is also extremely important. The behavior of a system depends on how much energy do the molecules have and how it is being distributed among the molecules.

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Number of ways characterize entropy

entropy = $f(\underbrace{\# \text{ ways of distribution}}_W)$

S

$S = k \log W$

$\log W_1 + \log W_2$

$\underbrace{\log W_1}_{S_1} \quad \underbrace{\log W_2}_{S_2}$

$= \log (W_1 W_2)$

$W = W_1 \times W_2$

So if this is clear, then we can characterize the entropy as sum function of the number of ways of distribution. So although I said that entropy refers to the number of ways of distribution, I have not said that the entropy is the number of ways of distribution. There is some relation, but we do not know what the relation is, right. So typically we call the entropy by S and this number, let us say I call W .

$$\text{entropy}(S) = f(\# \text{ number of ways of distribution})(W)$$

So in order to define entropy, what I will do is try to do a thought experiment. Let us say for example, I divide the box into two halves then the one half of the box, there may be some W_1 ways of distributing the energy in those molecules and second half, there may be some W_2 ways of distributing energy in the second half. So now if you think of it the total number of ways must be the number of ways in the first half multiplied by number of ways in the second half, right.

$$W = w_1 \times w_2$$

However, if you recall, entropy happens to be additive in nature. If I double the system, entropy actually doubles. If I make the system four times entropy becomes four times and so on, okay. So with this kind of a argument, then we will justify this why entropy is additive later but with this kind of an argument, I may argue that entropy could be defined as something like this, S equal to \log of W .

$$S = \log W$$

Because if I do that, then in this particular case, I will add the entropy of the first half and second half. Let me call that S_1 for the first half and S_2 for the second half. And entropy of the total system will be $S_1 + S_2$. It will not be S_1 multiplied by S_2 . However, the number of ways by the property of \log will get multiplied, okay. So now there is something here, so \log of W , W is a number. So by doing this, entropy becomes a unit less quantity, but we know that entropy is not unit less there has to be some constant, let me call it k for the time being and that already gives me a measure of entropy. It simply refers to the number of ways of distribution but if we assume a logarithmic dependence, then only the entropy can be an additive property.

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Definition of entropy

$$S = k \log W$$

\downarrow
 Boltzmann
 \downarrow
 Boltzmann constant
 k_B



So with this we have got the basic idea of entropy and the equation that I basically derived

$$S = k \log W$$

is the equation that was given by the scientist named Boltzmann. And it is a very unfortunate story that when Boltzmann discovered this particular equation or derived this particular equation, no one believed in that back then, and he pretty much was so sad because of that, he committed suicide and much much later after his death, this equation found so much value that he is very popular now and this particular constant is given the name of Boltzmann constant, although he did not define it that way. And we will use the word k_B for that where B stands for Boltzmann and such is the importance of this particular equation to his life and to thermodynamics in general, that this equation is actually engraved on his grave.

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Ideal Gas Example

Kinetic theory $\langle v^2 \rangle \propto \frac{1}{m}$

$\langle v^2 \rangle \propto T$

$E = N \frac{1}{2} m T$

$E \propto NT$

$E \sim Nk_B T$

$E = \sum \frac{1}{2} m v_i^2$

$E = N \frac{1}{2} m \langle v^2 \rangle$

$\langle v^2 \rangle = \frac{1}{N} \sum v_i^2$

$U_i \equiv 0$ $\chi_i \neq 0$

$m = \text{mass}$

point like \equiv occupy no volume
non-interacting

$PV = nRT$

Pressure Volume

number of moles

temperature

$R = k_B N_A$

Avagadro number

$N = \# \text{molecules}$

So with this definition of entropy, let us first start with the simplest example that we discussed in thermodynamics of an equation of state that is the ideal gas law and you may recall the ideal gas law essentially says

$$PV = nRT$$

Where P stands for pressure, V stands for volume, n stands for the number of moles and T stands for temperature and this R happens to be essentially the Boltzmann constant multiplied by the Avogadro number. And I will argue and we will show later in the course that this actually comes from we can actually derive this equation using the idea of statistical mechanics, okay.

So how do we define an ideal gas? So an ideal gas what we do say is that, the picture is that we have molecules present in any substance again we can think of a box containing molecules and each of these molecules are assumed to be point like that means they occupy no volume, right which pretty much means that there cannot be any ideal gas because how do we find something which has no volume. It should have mass, but it cannot have volume. But nonetheless, it is an approximation we can we make it will hold true when the volume is very small in comparison to the box.

And the second assumption we make is that the molecules are non-interacting. Non-interacting meaning that if the molecule is there and another molecule is there, these two molecules do not have any attraction or repulsion whatsoever between them. They can of course collide and they can transfer momentum that is of course possible, it will be an elastic collision but if they are far apart, not colliding, they do not have any attraction or repulsion between them that is the ideal gas law.

So as you may imagine, in ideal gas entropy is the only driving force that dictates how the energy is being distributed and energy in this case is simply the kinetic energy of the molecules. The potential energies have to be equal to 0, because there is no interaction between the molecules. But the K_i is not equal to 0, the kinetic energies are there. And of course, as the molecules collide, they transfer momentum. So kinetic energy of every molecule can be different. And there can still be a distribution of velocity in the system but there is no potential energy so as to speak, okay.

So for this ideal gas, the energy would then

$$E = \sum \frac{1}{2} m v_i^2$$

I am assuming that all the molecules have the same mass, that is for a pure component system and it has some velocity. The velocity can be different in the molecules, right.

So this I can also write as the

$$E = N \frac{1}{2} \langle v^2 \rangle$$

Where v^2 is defined as the average of the squares of the velocity of the molecule and therefore, we can actually get the energy of a system, right.

Now when we talk about a thermodynamic system, as you may had in your undergrad, we do not talk about velocities what we talk about is temperatures, right. So it turns out that the collision of the molecules, the fact that they have velocity and they can collide is what is giving rise to the notion of temperature. In fact, what the kinetic theory of gases tells you is that the squared of the velocity, the mean squared of the velocity should be proportional to the temperature. So therefore, our energy should be something like,

$$E = N \frac{1}{2} m T$$

However, one other thing also comes from this basic notion. Let us say for example if mass of the particles become larger and larger. Let us say for example, I am not talking about molecules, I am talking about human beings who have larger mass. So of course, we are not going undergoing motions because of temperature. So naturally, the velocities because of temperature must apply to very small mass particles larger particles should not be undergoing that velocity or the effect must be smaller. So what this means is that my v^2 must also be something like inversely proportional to the mass, right.

$$v^2 \propto \frac{1}{m}$$

So we should have something like that here,

$$E = N \frac{1}{2} m \frac{T}{m}$$

and that pretty much gives you E being proportional to N multiplied by T.

$$E \propto NT$$

and again the constant happens to be the Boltzmann constant.

$$E \sim Nk_B T$$

If you do it formally, there are some pre factors here and the pre factors can change whether the molecule is mono atomic or polyatomic, or whatever but the key idea remains the same the energy is proportional to the number of molecules multiplied by temperature and the Boltzmann constant. The Boltzmann constant anyway is a constant.

$$E = (Wk_B T)$$

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The image shows a handwritten derivation in red ink on a white background. It starts with the equation $E = (Nk_B T)$. Below this, it shows $\left(\frac{E}{V}\right) = \frac{N}{V} k_B T$. A bracket is drawn under $\left(\frac{E}{V}\right)$ with the text $\sim P$ written below it. This leads to $P \sim \frac{N}{V} k_B T$. Then, it shows $P \sim \frac{n(N_{A0} k_B) T}{V}$. Finally, it shows $P \sim \frac{nRT}{V} \Rightarrow PV \sim nRT$.

So now if you trust me on that I am just putting a equality here, but there can be some pre factor appearing here, some geometric pre factor.

$$\left(\frac{E}{V}\right) = \frac{N}{V} k_B T$$

So then I can define an energy by volume and that will be N by V $k_B T$ and if you think of the energy by volume, this will have the unit same as pressure because energy is force multiplied by length. So energy by volume will be something like force by area and force by area is equal to pressure. So this I can say should be something like pressure. So this I can say should be something like pressure that means pressure should be something like this.

$$P \sim \frac{N}{V} k_B T$$

Now N is the number of molecules. So if I want to write in terms of the number of moles, this will be small n that is the number of moles multiplied by the Avogadro number multiplied by k_B by V into and we essentially have got the ideal gas equation.

$$P \sim \frac{n(N_{AV}k_B)}{V}T$$

$$P \sim \frac{nRT}{V}$$

$$PV \sim nRT$$

That is not a very rigorous derivation, we will derive that more formally later in the course but you can see how the pressure is also coming from the same kind of principle. So the system has energy because of the potential and kinetic energy in the ideal gas case, it is simply the kinetic energy. And those energies also corresponds to the idea of pressure.

So now I have tried to convince you that both pressure and temperature are essentially related to the motion of molecules at the molecular level and in the ideal gas case, the motion is pretty random and temperature happens to be a consequence of the collisions and pressure happens to be a consequence of the energy stored in the system we can say as a result of molecules having certain velocity, right. This is example of an equation of state.

If for example, if I go from an ideal gas model to a Van der Waals model, the only change that we do is that we say that the particles are not of zero volume, they are having some finite size and with that small change, I can actually derive a new equation of state again from the same molecular level principles. So by this we can see how this idea starting from molecular level can be used to actually derive the equation of states than just taking them from granted, right. So that is the whole idea behind the statistical mechanics being used in thermodynamics, and the whole idea about the molecular simulations that we will do for more complicated systems and the key idea is that the systems in the universe are not like ideal gas. Ideal gas is only an approximation that holds true for very few of the gases and even that it does not hold true for all the conditions.

If I look at more complicated molecular systems, the relation between the pressure, volume and temperature that is what is given by the equation of state is going to be different and that is the purpose of statistical mechanics that is the purpose of this particular course on advanced thermodynamics and the molecular simulations that we perform on these systems.

So with this, I stop here. Thank you so much.

