Chemical Principles 2
Professor Dr. Arnab Mukherjee
Department of Chemistry
Indian Institute of Science Education and Research, Pune
Microscopic Definition of Heat and Work

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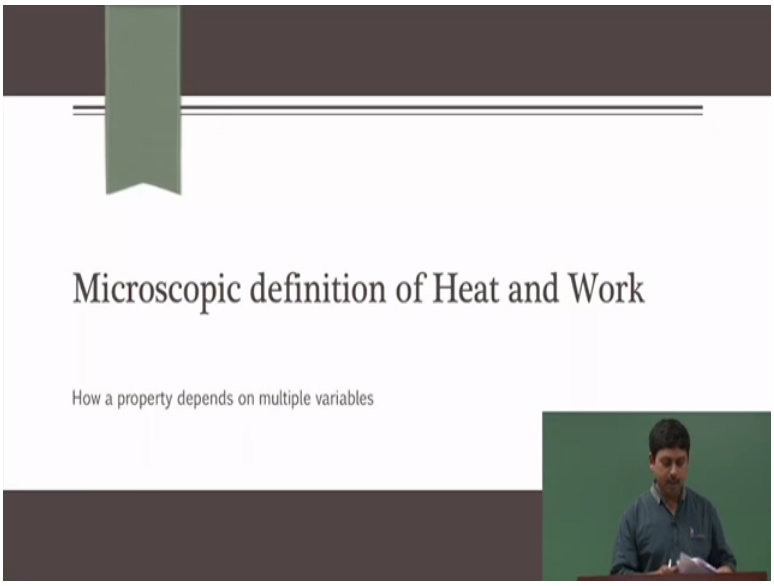

So now let us understand, let us review little bit about the microscopic definition of heat and work. So how do we understand you know heat and work in terms of atoms and molecules?

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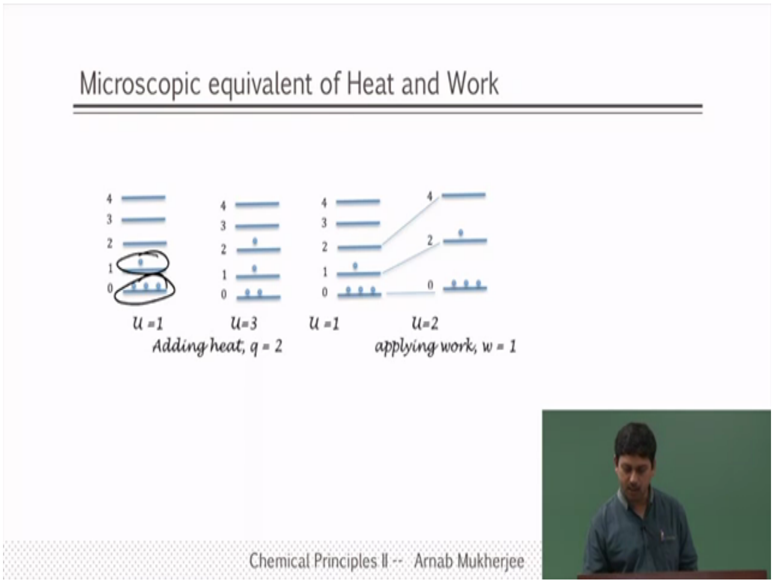

So let us say I have the system, so you know that every atom or every molecule is arranged you know according to you know different different energy labels according to quantum mechanics, right. Even though classically the labels are very very close together but the energies are discrete or quantized. So let us say I think about I design a system very restrictive system where there are four particles, three particles are on the ground state and one particle is in the excited state.

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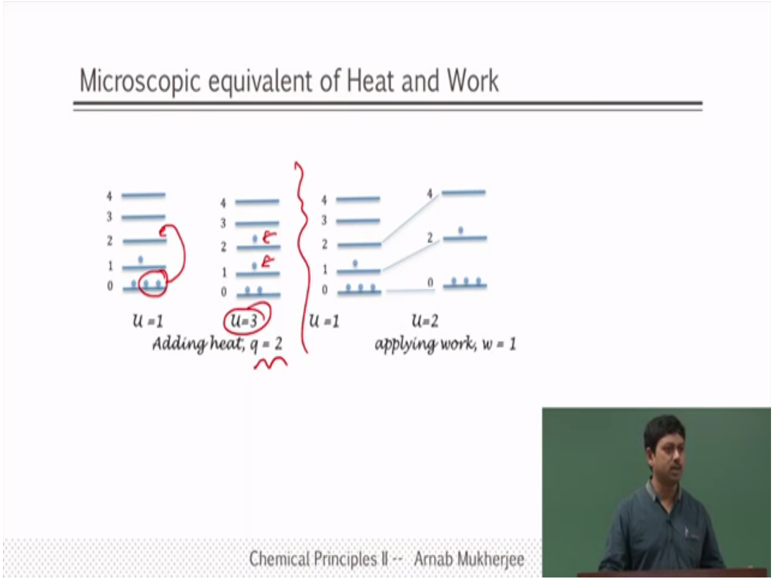

Now total energy of the particular system is how much? 1, right total energy of the system is 1 because 3 particles are in 0 and I add heat to the system, so what is going to happen? So whenever I put heat to the system the energy of the system is going to increase and since we know that internal energy and heat they are of all the same thing, so I put q equal to 2 means my total energy is going to be 3, now. Now how it site going to 3? It is going to be 3 by sending some particles to higher energy level.

So here I am showing that these two particles, one of them actually goes to label 2, so now the total energy of the system becomes 2 plus 1, 3. So when I add heat to the system, what happens is that there is a redistributions of particles in different energy label that take place, okay you will understand later that it is because of the Boltzmann distribution. So you will see that the particles are distributed depending on the temperature and the energy labels in such a way that it satisfies the Boltzmann distribution.

However, the adding work on the system is little bit more complicated, okay. So what happens when you do work on the system? Actually I should write it here, so let us say do you remember the particle in a box formula? Particle in the box you remember, right.

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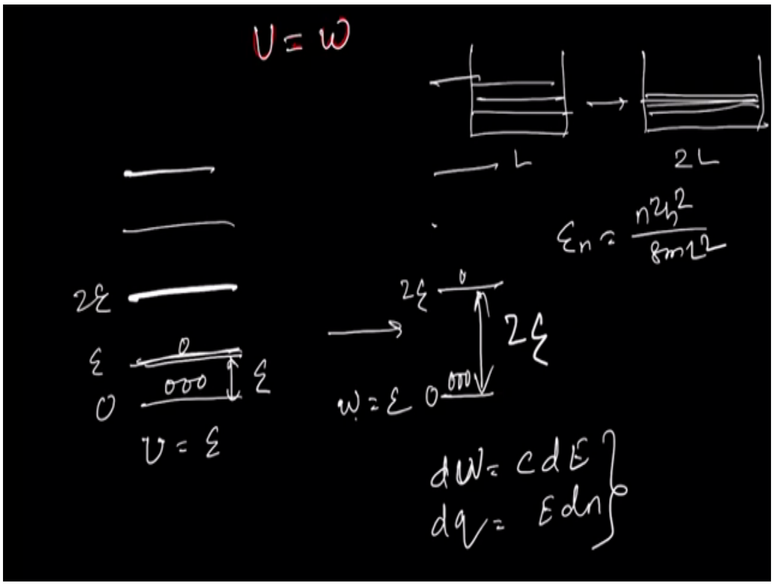

So using particle in a box can you tell me that when you do work on the system, so we know that from the first law of thermodynamics U equal to w when there is no heat supplied, right (I should change the colour) So U equal to w when there is no heat supplied to the system that we know. Now I am asking you that given a distribution of particles where let us say some particles are there in this label the total energy of the system is now epsilon or 1 whatever you can say.

If I do work on this particular system what is going to happen will the particle go to the higher label? Let us say I do you know 1 unit of work w equal to epsilon let us say, what do you expect that is going to happen? Do you have any idea? What is work? What happens in work? When you do work, then the volume changes, right volume of the system changes. Now imagine particle in a 3D box, so particle in a 3D box has 3 different lengths, lengths, widths and heights, right.

So there okay from 3D box let us come to 1D box, so let us say for a 1D box if the box length changes let us say it goes from L to 2L, what happens to the energy label? The gap between the energy labels decreases, right they become more closer. So similarly when you do a particle in a 3D box when you are let us say isotropically your volume changes such that all from all different size the length changes, what is going to happen? Your energy labels now going to be more closer and opposite will happen when you compress the system when you compress the system then what is going to happen is your energy labels are going to be now separated from each other more separated and you know the formula, right.

So En atleast for particle in a box is n square h square by 8m L square. Now if L becomes smaller the difference is going to be larger, right. So a compression work I told you is the work in which the internal energy of the system increases because that is the positive work. So therefore we are going to look at compression work, we are going to look at when volume decreases or L decreases what happens in that case then? Energy separation increases.

So now when that happens this E is going to become 2E, so the gap separation so it is just an example that in this particular case when you do work upto you know the amount of epsilon then instead of the difference epsilon now the difference becomes 2 epsilon. However, the distribution of particles need not change here, without distribution of particles being changed the energy can change when the labels itself changes.

So this is this way you can understand that when we heat the system, how the energy you know going to be distributed in the system by distributing the particles, or when you do work on the system work meaning a compressing or expanding the box size there the energy labels of the particle itself is changing. For example we talked about gas particles, so this is like a 1 dimensional system, we are taking the example of a 3 dimensional ideal system and you will see that using this information that in case of work done dW it is a constant multiplied by dE the label itself the energy label itself changes, whereas for q it is your E dn that is going to change from a microscopic point of view.

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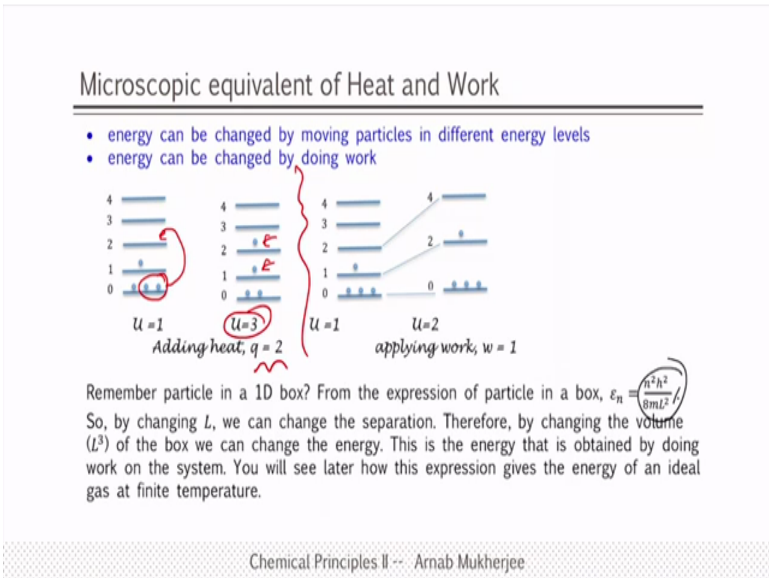

So energy can be changed by moving the particles in different energy labels or it can be changed by doing the work we have shown that and from the particle in a box we can understand that how changing the box length or rather box volume is going to affect the different energy labels, okay.

Here I am going to show you so all of you remember the particle in a box system, right and imagine that you know particle in a box system of course there is only one particle kept you know typically we discussed about one particle which can be at any different labels.

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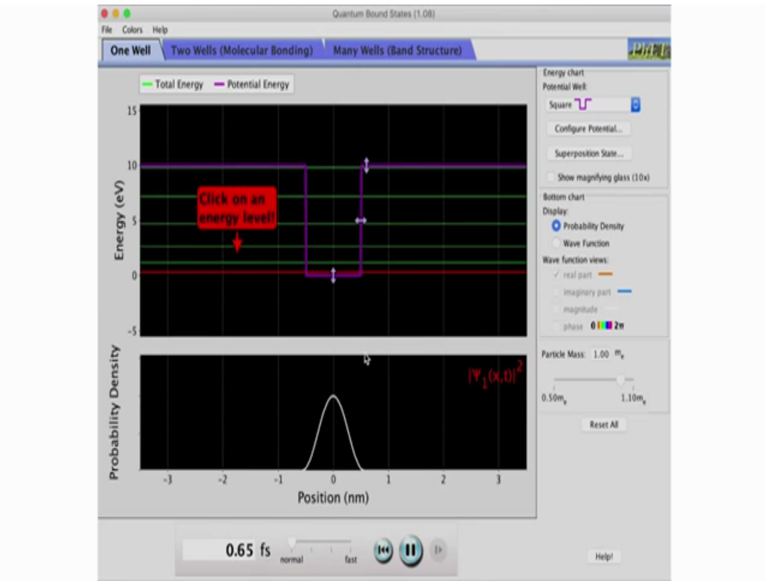

However, imagine that there are many many different particles are there at different different energy labels, so when we heat the particles they will get redistributed in the same energy label because we are heating the system and assuming that there is no work done which means that as long as the box length remains fixed as you can see the box length remains fixed, then the energy labels itself do not change, right.

So if you heat the system, total energy of the system is going to change. However, energy labels do not change because the box length is fixed in case of 3 dimensional box it will be box volume that will remain fixed. So therefore when you heat the system the way in order to change the internal energy the particle distribution in the different labels will need to be changed, right that is how we can think about a microscopic description of heat in which distribution of the particles change.

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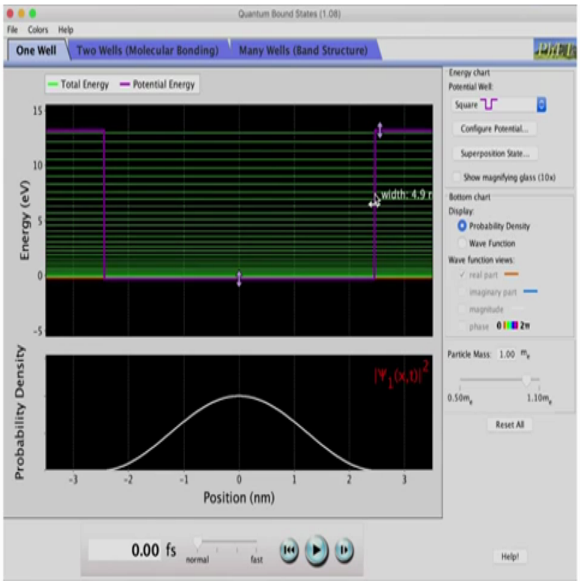

However, when you do the work remember what we do is that we change the volume of the box, now here we are showing the one dimensional box which is the length, but if it is an isotropic box of all equal sides which means that length is changing as V to the power 1 by 3, so by changing the length we can understand how the energy labels change and when you let us say compress the system that means you make the L smaller and smaller you see now the difference between energy labels become larger, now you see the difference between two energy labels is let us say 0.97 and 3.78, now if I make it bigger the difference is much smaller, right.

So by just doing the work what we are doing is that assuming there is no heat given to the system that means the particles are in the same label where they were. However, now they are of different energy, is it clear? Yes, so that is how we can understand microscopic descriptions of heat and work from you know particle in a box or very simplistic system itself, you know one can show later on that the energy that we get for a particle in a box let us say 3 by 2 k B T or 3 by 2 n k B T that can be also obtained from particle in a box systems as well, both from quantum mechanics and classical.

So classically it is half mv square equal to k B T half k B T is the energy that is there, assuming there is no interaction among the particles in ideal gas systems there is no potential energy so all the energy that is there is the kinetic energy and we already discussed that kinetic energy is half mv square or V square average which is half a k B T, right. So now that is only the velocity in one direction, now if you now take all the three different directions it will be half k B T plus half k B T plus half k B T which is 3 by 2 k B T, so 3 by 2 k B T is the total energy that is available for one particle in an ideal gas situation, 3 by 2 n k B T is the total energy that is there for n particles of an ideal gas, okay.

So and the same thing you can get and we also discussed that you know quantum mechanics we only get the kinetic energy because there is no potential energy, remember the potential energy operator was 0, so what was all there is the kinetic energy operator and one can show that using this particle in a box systems your average energy you can get as 3 by 2 k B T as well, okay we are not doing that right now but it can be shown later on.