Advanced Thermodynamics and Molecular Simulations
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Lecture - 05
Energy Distribution in Molecular Systems

Hello, all of you. So in the previous lectures, I was basically giving you a motivation to study thermodynamics. We discussed the molecular origin of entropy and things of that sort and then finally, we have been discussing that how the idea of chemical equilibrium is also driven by this idea of entropy and so on.

So in today's lecture, I will take the argument a bit further and go back to the example of a molecular system, where we talked about that, the molecules exchanged quanta of energy with each other and then using that, I will build the idea of a most probable distribution that is called the Boltzmann distribution.

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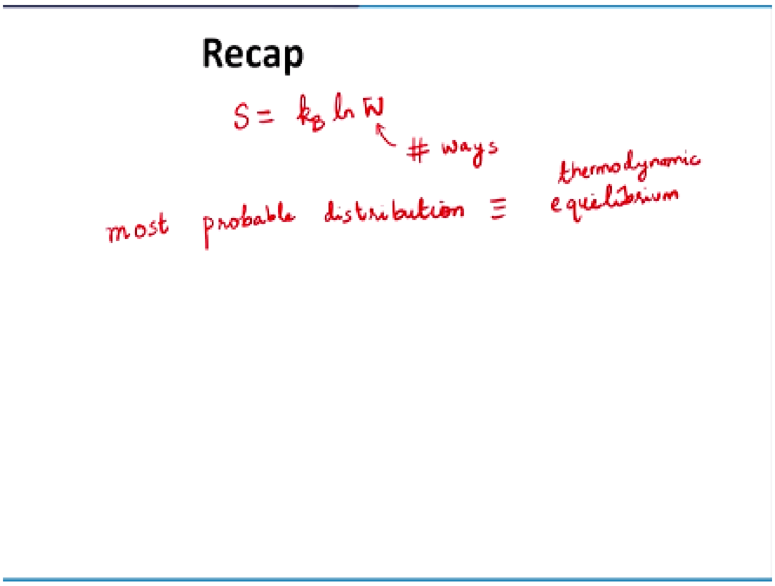

Until so far I have discussed that there is something called entropy that is a measure of disorder and entropy is related to the number of ways of distribution is-

$$S = k_B \ln W$$

where W is the number of ways and this idea is because of Boltzmann and then we discussed examples as I said, in various context starting from a coin toss example and the second thing I have said is that there is something called a most probable distribution, which actually refers to what I know in thermodynamics as a condition of equilibrium we showed this also in the context of a chemical equilibrium so idea is more general although we talk in this course, particularly about thermodynamic equilibrium.

So before we discuss the molecular system, let us step back a bit and look at a simpler example I have been discussing so for example, you may imagine that you have a box of chocolates.

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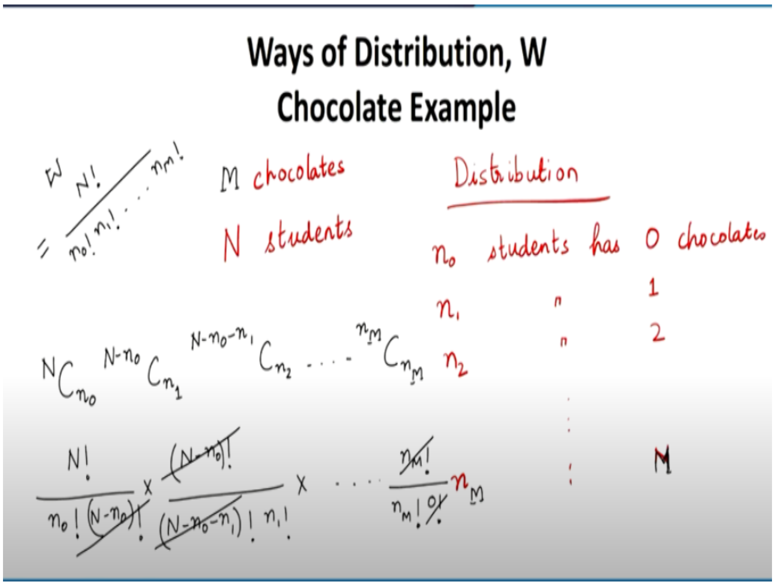

So let us say for example, you have N chocolates that you want to distribute to some N students and the question is in how many ways can we do it, and what is the most probable distribution for that so now as I have been telling you that there are too many possibilities here either one student runs away with all the chocolates, or all the students get some same number of chocolates, because the number of chocolate is same as the number of students or you can have one student having one other student having two other having three other having four so you can have a variety of distributions. So I can characterize one particular distribution as the following.

So I can say that n_0 students has no chocolates, n_1 has 1, n_2 has 2 and so on until, n_N students have N chocolates, right. So one thing to keep in mind that although in the example we have taken the number of chocolates to be same as the number of students, it need not always be the case. Let us say for example, instead of N you have M chocolates distributed among N students. So in this case, all that will change is that now you have more possibility starting from n_0 to n_1 to n_2 and ultimately you can have n_M students having M chocolates.

So the idea of like the number of chocolates being same as the number of students are only a simplicity, it can be even more general and we will see how it comes in next example as well. So now how many ways we can do that, right and one of the way to think about it is that first out of this N students I will pick n_0 students who will get zero chocolates and how many ways we can do that? We can do that in ${}^{N}C_{n0}$ way.

Now once we have done that, then we have N - n_0 students remaining and I can again pick n_1 students from the remaining one in ${}^{N - n0}C_{n1}$ ways and after that we will have N - n_0 – n_1 students remaining and we can pick n_2 students from there and I can keep on doing it until I have only n_M students remaining and they get n M chocolates, right. So this is where we use the idea of and probability. So first we pick n_0 students and then we pick n_1 students from remaining and so on. So we have to multiply the combinations to find the number of ways. So if I do that, you know the formula of combination is the following-

$$\frac{N!}{n_0!\,(N-n_0)!}\ x\ \frac{(N-n_0)!}{(N-n_0-n_1)!\,n_1!}\ x\ \dots\dots\dots..\frac{n_M!}{n_M!\,0!}n_M$$

So what you will notice here is there will be certain cancellations for example, this cancels with this. Similarly, this will cancel and we can keep on going and even the last one, these will also cancel 0 factorial anyway is equal to 1. So the answer then is the number of ways is given by-

$$W = \frac{N!}{n_0!\,n_1!\dots\dots..n_M!}$$

So we can take simpler examples to carry home this particular point.

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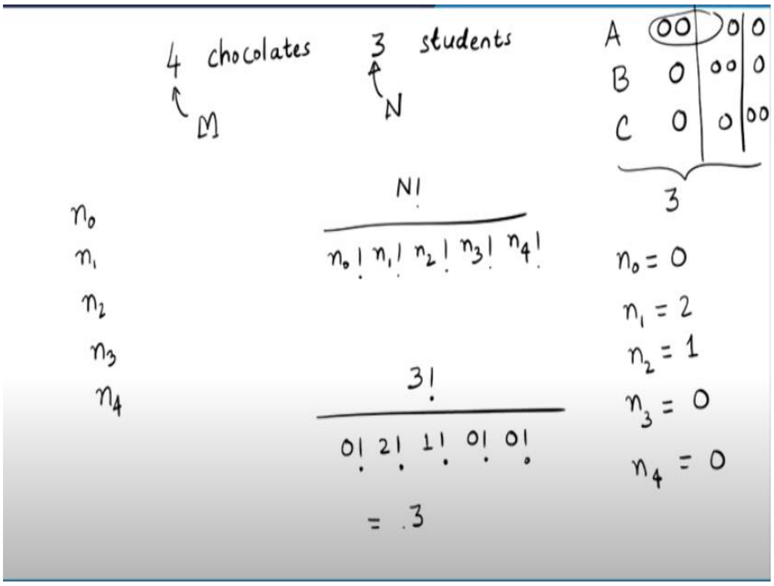

Let us say for example, you have 4 chocolates and you want to distribute in 3 students. So in how many ways we can do that, so we can see what is the N and M here. So N is this, that is the number of students, M is this and the possibilities in here are either you can have 0 chocolates, or you can have 1, or you can have 2, or you can have 3, or you can have 4 and the number of ways to do that is given by-

$$\frac{N!}{n_0!\,n_1!\,n_2!\,n_3!\,n_4!}$$

So let us say for example, if I look at one particular distribution, where let us say there are three students A, B and C. Then one of them gets 2, the other one gets 1 and the last one also gets 1, right. So in this case, I have labeled the students as A, B and C that means that the students are different. In molecular systems, that distinction is not really important, the distribution is more important. So if you do not have the distinction, in that case we can say, we can pick the student containing two chocolates in three possible ways because whether A has two or B has two or C has two, all of them basically give you the same distribution that one student gets two chocolates, right.

So it can be done in this particular way. It can be done in this way, or it can be done in this way. So the number of ways to do that is equal to three that we can also get from this formula, because in this case, $n_0 = 0$, there are no students having 0 chocolates; $n_1 = 2$, two students have one chocolate each; $n_2 = 1$, that is one student; $n_3 = 0$ and n_4 is again equal to 0 so we can do the math here. So we have-

$$\frac{3!}{0!\,2!\,1!\,0!\,0!} = 3$$

that is the same as the number of ways we have seen in the example.

So one very important point to mention here is that even though intuitively we will think that the number of ways in which the distribution is even is more favored that is not always true.

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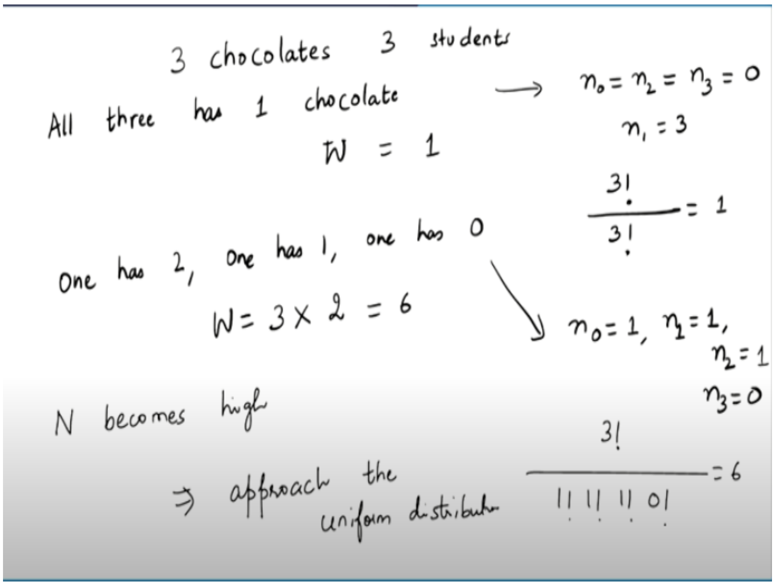

Let us say for example, we have 3 chocolates and 3 students. Now your intuition may say that, if all three has 1chocolate, that should be like most favored, but let us count how many ways that corresponds to and you see that the number of ways of doing that is equal actually simply 1, because in that case, you will have $n_0 = n_2 = n_3 = 0$ and $n_1 = 3$. So W will be equal to-

$$W = \frac{3!}{3!} = 1$$

On the other hand, if in the same example, we consider that one has 2, and one has 1, and one has 0, what you will find is that in three ways, I can find the person having 2 chocolates and now I have 2 students remaining so out of this in two ways, I can pick the one containing 1 chocolate. So the number of ways in this case is going to be 6. We can also see it using the same formula in that case, you will have $n_0 = 1$, $n_1 = 1$, and $n_2 = 1$ and $n_3 = 0$. And the answer will be-

$$W = \frac{3!}{1!\,1!\,1!\,0!} = 6$$

So even though our intuition suggest that all should have even distribution, it need not be the case for fewer number of chocolate what will however be true is that as the number of students increases, you will have a near even distribution that is what the point I was trying to make also in the coin toss example. Let us say for example, if N becomes high, we are going to approach the uniform distribution and you can see why it has to be true because let us say for example, if you have 100 students, and you have 100 chocolates. Now you may imagine that yes, it is very unlikely that all of them gets one chocolate but it is also extremely unlikely and it is more unlikely in the case of 100 students than compared to 3 students, that one student runs away with all the 100 chocolates. The distribution also becomes narrower as the number of students increases. So let us say for example, one gets 50, then others cannot get like a large number of chocolates then others will have the number of chocolates close to 1 or 2 or 3 so the point is although the possibility of all the students getting the same number of chocolate is very small, the probability of all the student getting close to one chocolate is actually increasing as the number of students increases.

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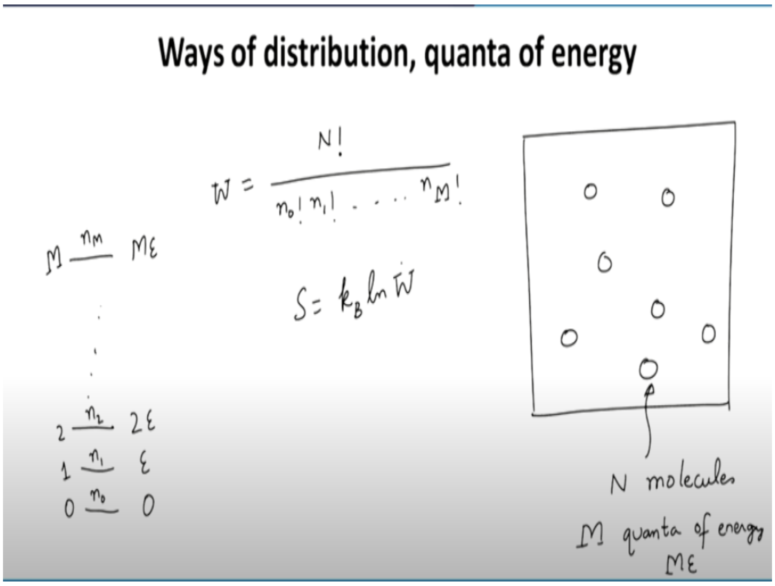

Now let us see how this idea also is useful when we look at the distribution of energy in molecular system. So I was telling you that in general you can have N molecules in a system and then you may have some M quanta of energy and for the sake of argument, let us assume that the energy levels are equally spaced that means total energy is equal to M multiplied by ϵ although you can extend to a non-uniform distribution, but that does not really change the main findings.

So now what is possible, right? So now just like chocolates, every molecule can have 0quanta, 1quanta, 2quanta, 3quanta and maximum number of quanta it can have is M, right. So now I can talk about number of molecules having 0, 1, 2 and M quanta of energy or in the units of energy it can have Mϵ, 2ϵ, ϵ and 0 and the number of molecules which have these labels are again maybe n_0 having this, n_1 having 1, n_2 having 2 and n_M having M and the number of ways is again going to be same as the case of chocolates. It is-

$$W = \frac{N!}{n_0!\,n_1!\,n_2!\ldots\ldots\ldots.n_M!}$$

And as I said, the entropy can now be defined once we know the number of ways and we will see how to deal with factorials later in the course but the key idea is that the number of ways of distributing energy in terms of quanta is pretty much following the probability arguments that we have discussed earlier.

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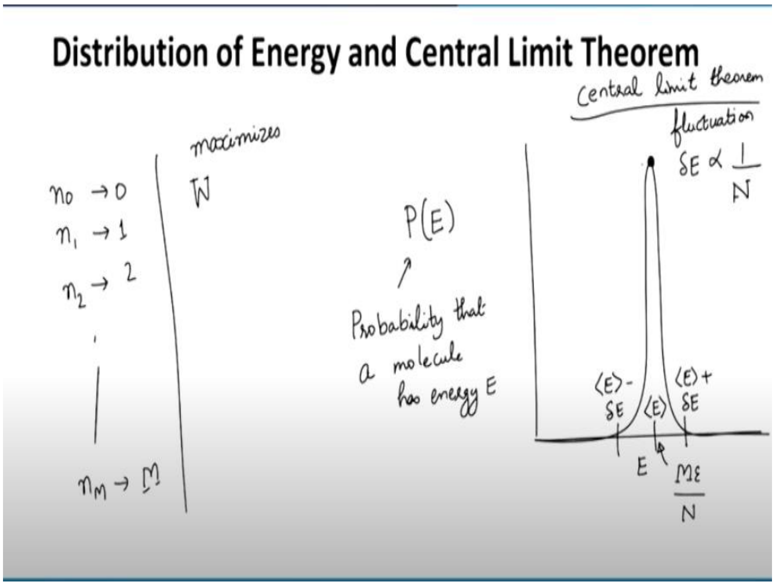
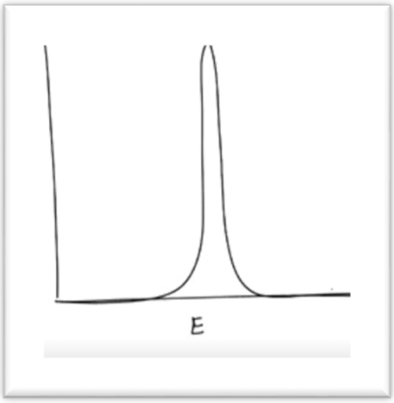


So now going back to the argument I was making regarding the uniform distribution, if for example, I look at the probability that a molecule has energy E versus the energy E, although, all the molecules having the same energy is highly unlikely, but the energy having near that value is going to increase or the distribution will get narrow as n increases the number of molecules increases and in molecular system, we have like n of the order of 10^{23} or higher so clearly, in that case, the distribution is going to be extremely narrow. So let us say for example, the distribution looks like this-



So clearly, as you increase n further it will be more and narrower and approach towards a δ function close to δ function as n becomes close to ∞. So the average value of the energy we can easily find will correspond to the case when you have a uniform distribution, and that will correspond to the total energy available divided by the number of quanta number of students or a number of molecules that you have in this particular case. So this is my average energy, let me call it something like this-

$$< E > = \frac{M\epsilon}{N}$$

However, we are not talking about that particular value really we are talking about a value near about that, right. So what you will start to see, as the number of molecule increases is the fluctuation let me call it something like a δ E in the distribution will start to decrease as N increases and fluctuation you can define in many ways. One way to think of them is like a standard deviation, or some multiple of a standard deviation if the probability of having an outcome is less than 0.01 we discard that so at that particular point where the probability is 0.01 maybe the average plus fluctuation or minus fluctuations, we can put a cutoff like that or we can have other ways.

The key point is that the width of the distribution starts to decrease as I increase the number of molecules, so the width δE that is a measure of fluctuation is going to be decreasing as N starts to increase and this is a statement of the central limit theorem. There is a very interesting fact about the central limit theorem that it does not really matter even what is the distribution like so it may look like a Gaussian distribution a normal distribution or some other type of distribution all of them actually approaches a narrower distribution as N increases and the fluctuation always is inversely proportional to the number of molecules in this particular case actually, it goes like 1 over square root of N. We will show that later and that is the beauty of the central limit theorem, although we will not be deriving for a general case. But I will show you how it works out for simple distributions.

So we haven't yet answered the question of like, what is going to be the most probable distribution we have said that we can have n_0 molecules having 0 quanta, n_1 having 1 quanta, n_2 having 2 and n_M having M quanta but then there can be many possible ways where we can pick n_0, n_1, n_2 and so on. So the question is how do we know which of these values will be true, which distribution will be picked, and the answer to the question is that we should be looking at something that maximizes my number of ways, so even though for the case of like three students and three chocolates, that gave rise to an uneven distribution, what you will find for large number of molecules is that when you maximize it, you will be close to this peak value that you see here. So as you increase the number of molecules, you will be approaching towards a uniform distribution is the point where the W is maximized. However, keep in mind that, that is still a distribution that means, that you still have particles containing 0, 1, 2, 3 and M quanta of energy we are not saying that all of them will have only one quanta of energy. There is still a distribution, but the distribution is narrowed as in as N increases, and it has a peak at the point when we have the uniform distribution.

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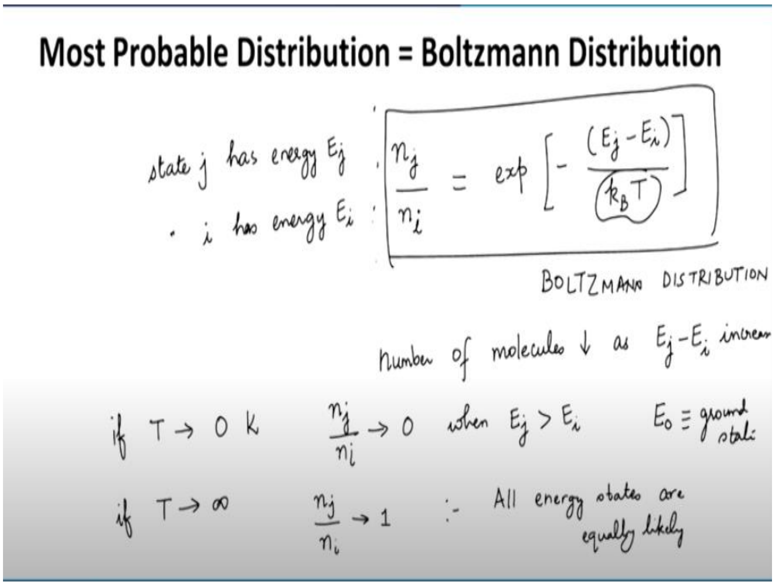

So what Boltzmann also found is that or what is attributed to him actually is that, we can find the number of molecules in a state j where I define a state j has an energy E_j in our notation that we just followed it can be j quanta of energy like j ϵ or if it is non-uniform distribution, it might be something else but the key point is that you can define states having some energy E_j

right. So if I find the number of molecules in a state j and divide by the number of molecules in a state i, where state i has an energy E_i, then this number is given by-

$$\frac{n_j}{n_i} = \exp[-\frac{E_j - E_i}{k_B T}]$$

And this is what is known as the Boltzmann distribution.

Now we will derive this equation particularly and we will talk about when there can be small violations from this particular formula I have written but you can see the key points from this equation already what it tells you is that as E_j is higher than E_i, as soon as that happens when E_j is higher than E_i, then you get a negative number inside the exponential. So that means that the higher energy states are going to have lower probability than compared to the lower energy states that means, the number of molecules decreases as E_j - E_i increases, right so the higher energy levels are going to be less occupied than compared to lower energy levels.

What it also tells you is that, if I increase the temperature, if I increase the temperature, what is going to happen is that this denominator becomes large. So the net magnitude of the term inside the exponential will decrease and therefore, the difference between the higher and lower energy states will decrease that means, if I increase the temperature, then we will have lesser difference between the particles at higher energy level and particles at lower energy level.

On the other hand, if I for example go to lower temperatures, the reverse happens. Then for example, if I go to very small value of T, the denominator decreases. So any small energy change E_j - E_i is magnified more and therefore, higher energy states become lesser and lesser probable and you can already find the limiting behavior in here that is, if T goes to 0 Kelvin, what you will have is n_j by n_i practically goes to 0 when E_j is higher than E_i and what it tells you is that the lowest possible energy state let me call that E_0 or the ground state will be the one where all the molecules are going to be, that means as soon as the molecules want to go to a higher energy state, you have very less likelihood of that to happen because the temperature is very small and this is what we call a condition for zero entropy that is how we define the third law of thermodynamics that at zero Kelvin, we should have zero entropy, and that basically correspond to the condition that all the molecules are in a ground state.

On the other hand, if I go to a very large T, just for the arguments sake let us say if T goes to ∞, what you will see is that n_j by n_i will now go towards 1 because the term inside exponential goes towards 0 and in that case, what you will have is all energy states are going to be equally likely. Of course, we will never have ∞ temperature, but you already know the asymptotic behavior so at 0Kelvin, you only have molecules in the ground state as the temperature increases, the other energy levels, the higher energy levels start getting populated and at infinitely high temperature or very high temperature, you can have molecules present in all the possible energy level.

So it is this particular argument that pretty much drives the energy exchange in the molecular system. The energy exchange is going to be larger when the temperatures are larger and this is pretty much gives you a definition of temperature and how it gives you the energy distribution inside the molecular system.

So with this particular argument, I am going to stop the discussion here. In the next class, we will talk about the other aspect of thermodynamics that is the energy. So far we have focused on the entropy part and we have discussed entropies and function of number of ways and so on. And now we go towards including the discussion of energy as well. So with that I stop here.

Thank you so much.