Advanced Chemical Thermodynamics and Kinetics
Prof. Arijit kumar De
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 23
Introduction to statistical thermodynamics 02

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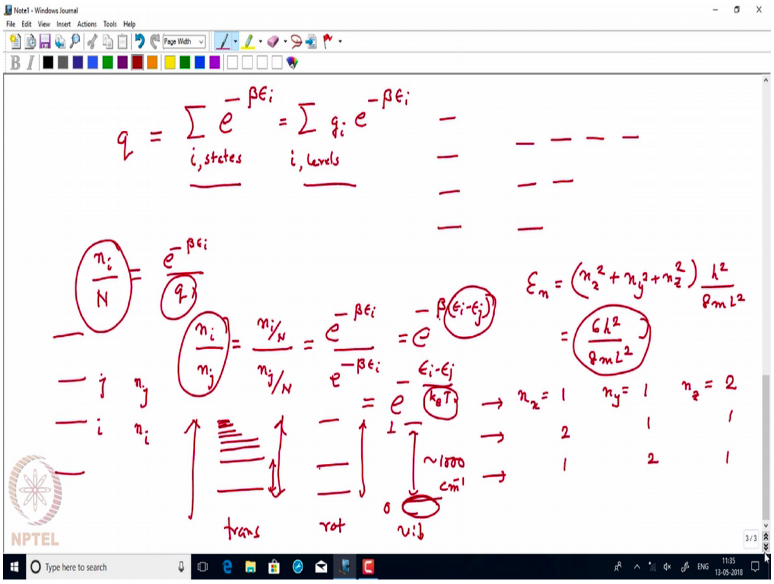

So, the partition function was defined as in the previous section as the molecular partition function, as the sum of over energy levels, and we wrote it at e to the power minus beta epsilon i. Now, this i remember we said that we have some let say energy levels. And each energy level in this case has one particular state, meaning this sum is actually over the energy states.

However, you may encounter a situation where suppose you have some degeneracy for the states. And then we have to be very careful. So, then what I do is that, we take simply this number e to the power minus beta epsilon i the Boltzmann factor. And then you multiply it by the degeneracy of that state. And then take the sum over all the energy levels.

So, in this case actually it is the sum over levels. So, each level i has g i g i fold degenerate. In the earlier case actually we are taking some over states. So, we have to be very careful when whether this i corresponds to levels or i corresponds to states. Let me give you an example. So, for practical in 1D box, we know that the 3D box, and it suppose a think about there is this is an cubic box. So, what we have the total energy, there I am using epsilon notation. Let me just use the epsilon notation here. So, that is given by n square h square by 8 m L square. But in this case actually it is it have 3 quantum numbers; n x square plus n y square plus n z square h square by 8 m L square, where L is the length of the box and n is the mass of the particle.

Now, the interesting thing is that suppose we say that we just take an energy levels, let us say 6 h square by 8 m L square. Now this energy level is how many states are there at this energy level? We can see that there are 3 states. Why? Because, I can choose n x to be equal to 1 and y to be equal to 1 and n z to be equal to 2, that will satisfy this energy level. Because, 1 square plus 1 square plus 2 square is 6, I could have chosen n x to be 2 n y to be 1 and n z to be 1 or n x to be 1 and y to be 2 and z to be 1. So, I see that there are basically 3 steps 1 1 2, 2 1 1 and 1 2 1, but all these 3 states corresponds to the same energy.

So, each energy level at this particular energy level is 3-fold degenerate. So, in order to calculate that the g i will be 3; so, that way you have to be very careful that whether we are taking it the sum over states or sum over the levels. Also one important thing for the Boltzmann factor is that, if you remember the way we wrote it the probability; like, we wrote it as n i by N, and that is basically equal to the e to the power minus beta epsilon i divided by that q, where q is the molecular partition function.

So, we wrote it as n i divided by capital N, or the probability is nothing but e to the power of minus beta epsilon i by q. That is another way of writing in. Now, suppose I have 2 energy levels, I have many energy levels and I am just talking about the 2 particular energy levels. And if there are number of particles in these energy levels are n i and n j, then we can also predict their ratios n i by n j will be nothing but you can see here, that I can actually directly use this formula for the probability.

And the, I can easily see that this q actually gets cancelled out. So, I will have e to the power minus beta epsilon i divided by e to the power minus beta epsilon j, which together we could write it as e to the power minus beta epsilon i minus epsilon j. I will see that the relative population which is the ratio of the population is dependent on the difference in the energy levels and that is a very interesting thing. Because, you can actually now think in terms of the real energies. For example, if I have translational energy levels. And we know that the translational energy levels will, according to the particle in a box model will go like this. So, it goes as 1 by n square; so, the as we increase in energy the gap between the energies decrease.

Now, what we say is that at room temperature considered these things. You will find that these the beta is nothing but, 1 over k B T. So, I could write it as e to the power minus epsilon i minus epsilon j divided by k B T. Now let us at 300 Kelvin temperature. You can actually calculate for particle in a box model that: what is this energy gap, with respect to the thermal energy which is k B T. And you will find as it is energy gap is extremely small.

So, you will see that the difference in the population would be much in a sense all our in other words, there will be many many energy levels which will be populated the many many translational energy levels which will be populated. Similar thing will also happen for the rotational energy levels. And where we have some energy levels like this, and then the energy levels are also degenerate. So, and we will also see that for rotation also many many energy levels will be populated at room temperature.

But for vibrational energy levels, the energy gap is pretty big. And you will see that you can actually calculate this particular ratio. If I have the total number of molecules like say, or you do not need to know the total number of molecules, you can just calculate the fraction. And you will figure out that for vibrational any amplitude of course, depends on which vibration you are talking out what is the exact energy that will get difference between them whether it is a low frequency vibration, or high frequency vibration for what for any general calculation.

Let us say if you take thousand wave number vibration land frequency, you can actually convert it into energy scale, in terms of joule or something like that. And then you can actually calculate you can take the temperature to be 300 Kelvin. And you can calculate that if I have let us say this is the 0-point energy of vibration, and this is the first vibrational energy level v equal to 0 and v equal to 1.

So, how many molecules are there in or related to the total number of molecules what is the fraction? That you can easily calculate, and then you figure out you can also I mean by fraction, I mean, this number also you can calculate for individual energy levels, you can also calculate the ratios. But if you calculate that then you will see that more than 99.99 percent molecules are reciting only the 0 energy level.

So, vibrational energy level at room temperature is very much beards like a discrete. So, you see a quantum mechanical effect from that. But usually for translational and rotational partition function. We will treat them as if they are continuous. So, that is the meaning of this continuous distribution in the Boltzmann sense, that if you talk about a translational or rotational you do not really see the quantum mechanical effect at room temperature.

Because many energy levels are populated and because cavity is much higher compared to the energy levels; however, for vibrational or electronic electronic energy levels will be much far more separated. You see only the ground vibrational state is predominantly forming I mean populated for electronic. It is you will see exclusively the electronic ground state is a populated, because it is they are very difficult to thermally activate the second electronic states. Although, I mean, there are there are examples of thermally activity the energy levels electronic energy levels, but let us not go into those details.

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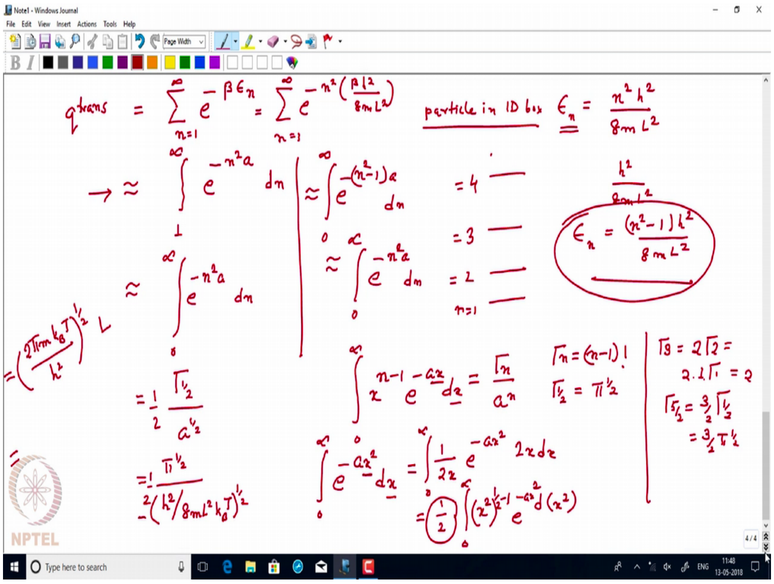

$$q^{trans} = \sum_{n=1}^{\infty} e^{-\beta\epsilon_n} = \sum_{n=1}^{\infty} e^{-n^2\left(\frac{\beta h^2}{8mL^2}\right)}$$

particle in 1D box $\underline{\underline{\epsilon_n}} = \frac{n^2h^2}{8mL^2}$

$$\rightarrow \approx \int_1^{\infty} e^{-n^2a}\,dn \approx \int_0^{\infty} e^{-n^2a}\,dn = \frac{1}{2}\frac{\Gamma_{1/2}}{a^{1/2}} = \frac{1}{2}\frac{\pi^{1/2}}{\left(h^2/8mL^2k_BT\right)^{1/2}} = \left(\frac{2\pi m k_BT}{h^2}\right)^{1/2} L$$

$$\approx \int_0^{\infty} e^{-(n^2-1)a}\,dn \approx \int_0^{\infty} e^{-n^2a}\,dn$$

$=4$

$=3$

$=2$

$n=1$

$\frac{h^2}{8mL^2}$

$$\epsilon_n = \frac{(n^2-1)h^2}{8mL^2}$$

$$\int_0^{\infty} x^{n-1}e^{-ax}\,dx = \frac{\Gamma_n}{a^n}$$

$\Gamma_n = (n-1)!$

$\Gamma_{1/2} = \pi^{1/2}$

$\Gamma_3 = 2\Gamma_2 = 2.1\Gamma_1 = 2$

$\Gamma_{5/2} = \frac{3}{2}\Gamma_{1/2} = \frac{3}{2}\pi^{1/2}$

$$\int_0^{\infty} e^{-ax^2}\,dx = \int_0^{\infty}\frac{1}{2x}e^{-ax^2}\,2x\,dx = \boxed{\frac{1}{2}}\int_0^{\infty}(x^2)^{\frac{1}{2}-1}e^{-ax^2}\,d(x^2)$$

Now, let us try to calculate this partition function. First thing first we are going to calculate: what is the translational partition function. Now, what is the translational energy level? If I take let us say, the energy level particle in a box energy level for a 1D box, let us say particle in 1D box. So, for that the energy level is given by, I have only one quantum number n square h square h is the Planck constant divided by it is not h square, but it is n square h squared. We could write it in terms of h square also by 8 m L square. And then I am denoting the energy level with an suffix n.

And for so, then I can just use the sum over state formulation because, in this case actually there is no degeneracy. So, I am taking sum over n, the index I is arbitrary because usually the, I am denoting it in terms of the quantum number. And it is nothing but e to the power minus beta epsilon n. And which is nothing but if I take the sum, it is nothing but e to the power minus. So, it will be n square h square by 8 m L square. So, it will be n square times the constant which is nothing but beta h square by 8 m L square, something like that.

Now, since as I said that compared to the beta or 1 over k B T; so, the at room temperature, the energy levels are far more closed or closely packed. So, then I can think that instead of the sum I can actually integrate this quantity. And then I will have e to the power of minus n square into some constant like which is write this constant as a. And then integrating it, and the variable is now n and where actually the energy levels are going from 0 to infinity.

So, although it is a true this begins a discrete energy level I need to take the values of 0 1 2 3. But since at room temperature the many many translational states are (Refer Time: 11:37) and the space between the levels are much less. So, you can think that it is as if it is a continuous distribution. Now, there is one interesting thing here, that if you if you remember that for particle in a box, I will have the energy levels like this which is ever increasing n equal to 1 2 3 4 something like that. Now the question is whether this partition function we are measuring with respect to the ground state or not. So, if we do with respect to the ground state so, the for the ground state the energy level is n is equal to 1.

So, the energy level would be the energy would be the 8 m L a per by 8 m L square. So, all the energies with respect to the ground state, that if I if I had written it then I should write it as n square minus 1 into h square by 8 m L squared. And then we basically write in this thing as remember that n actually goes from 1 to infinity, you know in our case, but it is a discrete sum again. So, but then we are writing n equal to 0 and the denominator. But if we do this transformation that we are measuring everything with respect to n equal to 1.

Then actually I could write the lower limit as n minus 1 and the lower limit will be 1 minus 1 which is 0. And then this thing instead of the integration writing as this I should have written it as e to the power minus n square minus 1 into a into d n where n is going from 0 to infinity. After this level actually I have n equal to actually one to infinity. But then for the, if you write it in this way, then the next stage we say that find e to the power of minus n since n is very large. So, I can actually approximate it as n squared and there is a here something like this. But we are not actually following that notation; rather we are saying that fine the n is going from one to infinity.

But I can actually add in from 0 to infinity to because it is adding nothing if I just add n equal to 0 in the in the sum it will of course, add some number to the partition function. But if I start from 0, the energy level is not changing I mean there is no energy yet correspond to 0. So, you could use either way. So, remember that we used one of this notation that approximation notation for going from summation to integration. And the second one I am writing here, that changing the limit from one to 0, on the other convention I think at kins has used this convention that he was measuring energies with respect to the ground state. So, in that case I write it as n square minus 1. And automatically the limit is from 0 to infinity. And, but then you would approximate it as n square minus 1 as n square.

Now, how do you calculate how to evaluate this integral? So, this is a very straightforward integral, but we can actually use the gamma function integral for this. What is a gamma function? The gamma function is defined as so, you can use standard integrals for this. And the gamma function is defined as like this. So, if I have an integral like this e to the x to the power n minus 1 e to the power of minus a x d x. That is equivalent to gamma n by a to the power n; where gamma n is nothing but n minus 1 factorial. And if I have something like gamma half it will be root pi.

So, for example, if I have say gamma 3, it will be 2 into so, n minus 1 factorial is 2 factorial. We can actually write it as a 2 gamma 2, it will do basically 2 times 1 and gamma 1 and gamma 1 is nothing but 1. Because gamma 1 is 0 factorial so, that will be 2. So, this is how we will evaluate it. If I have something like say gamma 5 by 2 so, it will be 3 by 2 gamma half, and gamma half is root pi. So, it will be 3 by 2 root 5. So, in that way we just evaluate the gamma function.

Now, let us see the mathematical form here. It is e to the power minus x square a into d x. So, I have to write it in terms of the gamma function. It is something like e to the power a x square d x. I have just written write I am just writing x in place of n, but this is exactly the same. Now how to write it in terms of gamma function? Let us see, that here I have actually x square. So, I am here like if I have d x, then I have e to the power minus a x; x is the variable, but now can I have to change it to x square variable; so, that I can easily do. So, I will just write it as d of x square now maybe I can actually use one more step. So, that you understand more clearly. So, my final goal is that I will just write it as d of x square. Now d of x square is what? It is 2 x d x.

Now, so if I write it like this 2 x d x in the next line I will write it as d of x square, but this is an extra 2 x d x. So, I have to write it like 1 over 2 x also I have to introduce 1 over 2 x, e to the power minus a x square, that is the integral. So, I just introduced divided and I mean multiply the entire thing by (Refer Time: 18:06). Now, now let us see how I can actually write this 2 x. So, it is nothing but half half I can take out of the integration it is just a constant. Now it is x to the power minus 1. X to the power minus 1 is x square to the power minus half. And minus half I can write it as 1 minus half. So, you see 1 minus half is minus half, and x squared to the power minus half is x to x to the power minus 1 which is 1 over x. And then I have e to the power of minus a x square.

Now, you see it the beauty, now it actually matches with the gamma function. I can actually switch now the variable right x square as y. So, it will be y e to the power n minus 1 e to the power minus a y d y that is a gamma function. So, instead of the variable x, it is now x squared. And what is n here? N is basically 1, sorry I made a mistake here so, it is a minus 1. So, it will be half minus 1 that way I have to write it here.

So, since I had minus half I have to write it as half minus 1. So, this integral is nothing but gamma n by a to the power n. And which is nothing but gamma half by a to the power half. Now gamma half is root pi. And what is a? A is we approximated a to be this entire thing, beta h square by 8 m L square. So, beta is 1 over k bit you can just write it h square divided by 8 m L square into k B T raise to the power half.

So, and then remember that there was a half here. So, I have to also use this half here, there is a half here. So, this is the translational partition function. Let me actually write it in a more compact form. So, this 8 square root of 8 it will be in the numerator, a square root of 8 that we could write it as 4 into 2. So, that 2 4 comes out so, that cancels with the 2 in the numerator the denominator. So, these 2 gets cancelled with that square root of 4.

So, I would left with 2 and I have a pi, and then all these things m k B T divided by h square entire thing to the power half and into l. So, this l square I am taking out. So, this is the formula for translational partition function. 2 pi m cavity in 2 to the power half into l divided by h bar squared.

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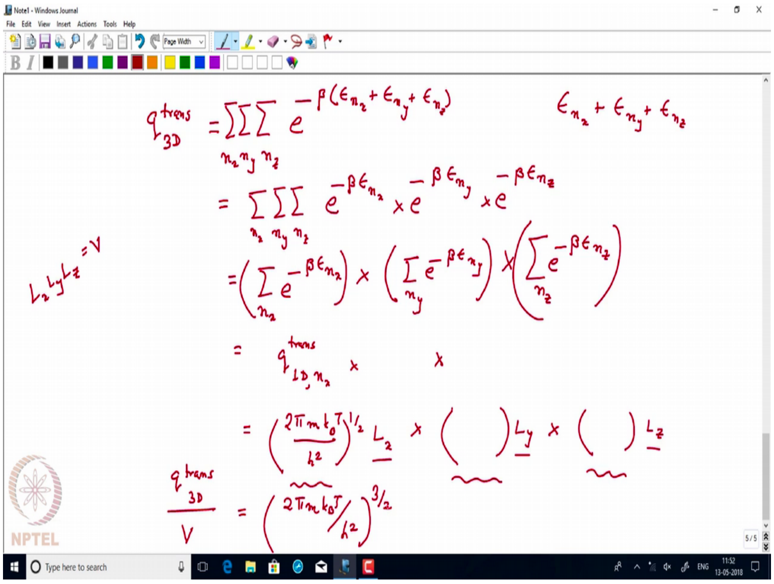

$$q^{trans}_{3D} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta(\epsilon_{n_x}+\epsilon_{n_y}+\epsilon_{n_z})} \qquad \epsilon_{n_x}+\epsilon_{n_y}+\epsilon_{n_z}$$

$$= \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta\epsilon_{n_x}} \times e^{-\beta\epsilon_{n_y}} \times e^{-\beta\epsilon_{n_z}}$$

$$L_x L_y L_z = V$$

$$= \left(\sum_{n_x} e^{-\beta\epsilon_{n_x}}\right) \times \left(\sum_{n_y} e^{-\beta\epsilon_{n_y}}\right) \times \left(\sum_{n_z} e^{-\beta\epsilon_{n_z}}\right)$$

$$= q^{trans}_{1D,n_x} \times \qquad \times$$

$$= \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{1/2}}\underline{L_x} \times \underbrace{\left(\qquad\right)}\underline{L_y} \times \underbrace{\left(\qquad\right)}\underline{L_z}$$

$$\frac{q^{trans}_{3D}}{V} = \left(2\pi m k_B T/h^2\right)^{3/2}$$

Now if you have h the practical in a free box, let me just write it. So, q translational for 1D we got it as like this. But remember that if I have particle near 30 box the energy levels are basically additive, because the total energy level instead of writing it as e n the summation will be now I will have 3 energy levels I will have E n X plus E n y plus E n z. And how the partition function will go for this?

So, then you can easily think that the partition function will be like summation over n x n y and n z. Now it is a basically e to the power minus beta into energy, now energy is additive. So, it is basically n x plus n y plus n z. And then actually this is a triple sum over n x n y and n z. I will say that, I can actually since it is a exponential to the power something which is a addition of 3 terms. I could actually write it as the multiplication of the exponentials.

So, and then I will have the triple sum e to the power minus beta epsilon n x times e to the power minus beta epsilon n y, times e to the power of minus beta epsilon n z. And there is a triple sum so; I can actually evaluate them separately. So, e to the power e to the power minus beta epsilon n x, times the second term n y e to the power minus beta epsilon n y. And similarly I will also have n z e to the power minus beta epsilon n z. So, now you see that these are basically translational partition function for 1D, but for n x for n y and for n z.

So, we see that since the energies are additive. So, the partition functions, since it goes as exponential to the power n achieve at the energies are relative we will get all this a multiplication of the partition function. So, this is the 3D partition function, and each of them will give you the same value 2 pi m k B T divided by h squared raised to the power of half into l. And then what we will have here is something like 2 pi m k B T raise 2 divided by h square to the power 3 by 2 into L x where L x is the length along x

Similarly, the so, this will be half this factor will be 1 over 2. And similarly the same factor into L y into the same factor into L z. So, together what we see here. So, this L x into L y into L z is if it is a rectangular box. So, that is nothing but the volume of the system. So, what we usually do? You usually calculate the cross sectional partition function per unit volume.

And then you said that this things basically gets multiplied. So, you get transition and partition function per unit volume as 2 pi m k B T divided by h square raised to the power 3 by 2. So, this is the total part translational partition function for a molecule. Now, we will see: what are basically the rotational partition functions. And eventually we will see: what are the vibrational partition functions.