Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

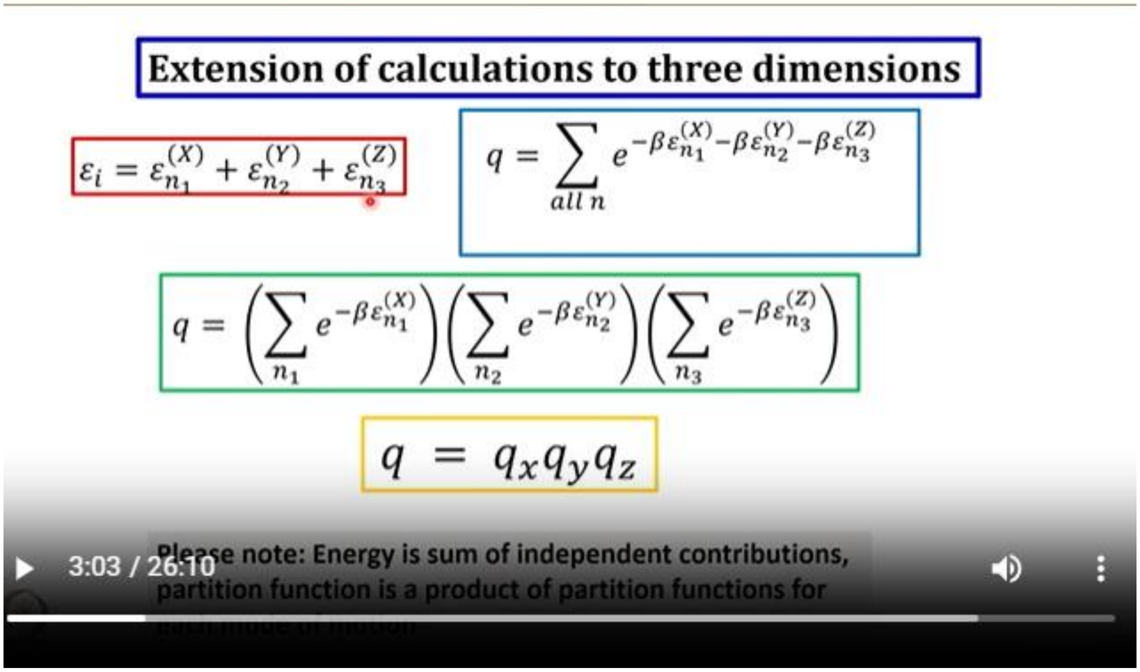
Department of Chemistry

Indian Institute of Technology, Bombay

Lecture - 08

After having discussed partition function for a particle which is free to move only in one dimensional container, now let us start discussing about partition function for a particle which is free to move in two dimension which is free to move in three dimensions. So that means now let us consider a container which has sides x, y, z, three lengths and if we know x, y, z we can then eventually calculate the volume. If you are talking about two dimensions x and y you can calculate the area. So let us discuss now how to derive expression for a particle of mass m which is free to move in three dimensional container and the sides are going to be x, y and z. Before we start doing that let us revisit what we have done in the previous lecture. We derived an expression for the partition function for a particle of mass m which is free to move only in a length x in one dimensional container and we have talked about the meaning of each term in this expression. With this knowledge now let us move forward. Let us consider an i th state. We are talking here about only the translation of a molecule and we are saying that the molecule or particle is free to move in x, y and z dimension. If you want you can stop at x and y derive an expression but the method of deriving the expression is going to be same. Therefore I am directly switching over to a particle which is free to move in three dimensions. The container which has sides x, y, z. Now the expression for the energy of i th state is going to be $E_{n_1}{}^{(x)}$ plus $E_{n_2}{}^{(y)}$ plus $E_{n_3}{}^{(z)}$.

(Refer slide time: 3:03)



Again referring back to your concepts which you learnt in quantum mechanics, quantum chemistry. What are n $_1$, n $_2$ and n $_3$? These are the quantum numbers which are associated with the movement of the particle or movement of the molecule in x direction, y direction or z direction.

Now substitute these energies into partition function expression. We know that the partition function is equal to exponential minus beta E $_{i.}$ So in place of E $_i$ now I am substituting all this summation. So summation all n, all n means we are including n $_1$, n $_2$, n $_3$ and exponential minus beta E $_i$. Instead of E i, I am writing E_{n_1} plus E_{n_2} plus E_{n_3} So therefore I am getting this expression. So what is exponential a into b or a plus b plus c? So this is the expression for the equation. Is exponential a into exponential b into exponential c? Simple mathematics. That is exponential a plus b plus c is equal to exponential a into exponential b into exponential c. I am just going to use this. That is what I am going to do is I am going to now split this and mathematically it is allowed that this can be splitted into individual summation with the corresponding values for the quantum number. For n $_1$, I am summing for all n $_1$ and this is associated with the movement of the particle in x direction or along the side x. The second one is going to be summation from n $_2$ which is basically 1 to infinity exponential minus beta E_{n_2} into y and third one is summation n $_3$ exponential minus beta E_{n_3}into z. Please note this transition from this summation to this. What we are just going to do, what we have done is we have made use of this mathematical transformation and we have now separated each exponential term with the respective summation.

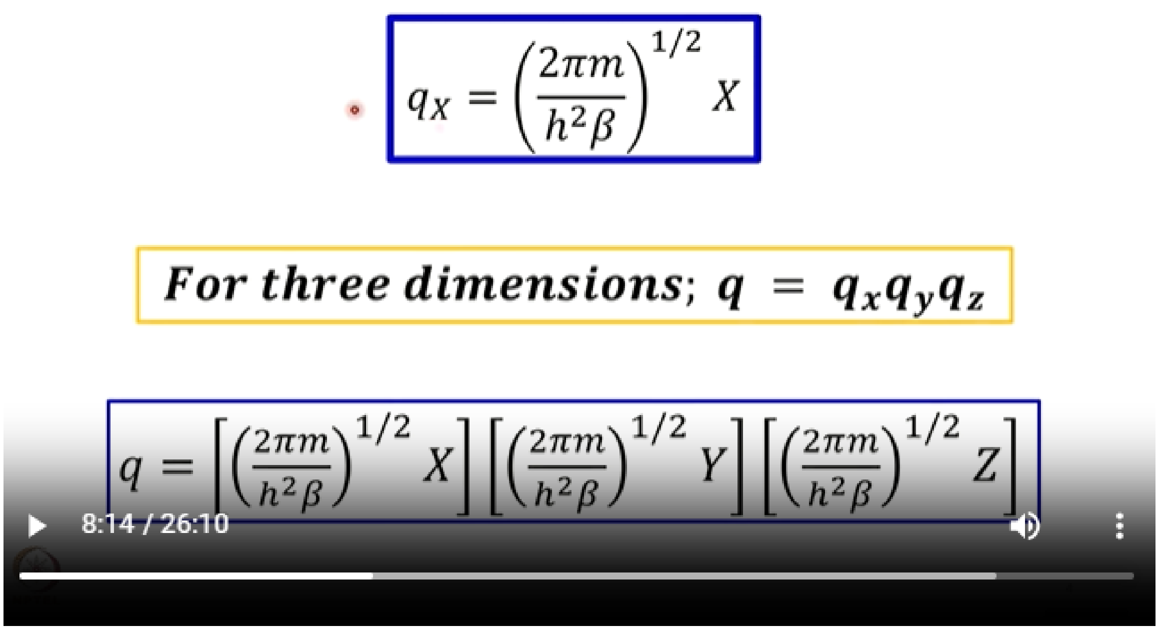
So, the ones which are associated with quantum number n $_1$, n $_2$ and n $_3$ we have separated. Carefully examine this. This first one is q_x, second one is q_y and the third one is q_z. Partition function for the movement of particle in x dimension, this one is partition function for the movement of particle in y dimension and this one is partition function for the movement of particle in z dimension. So therefore, the overall translational partition function for a molecule, for a particle which is free to move in three dimension is q_x into q_y into q_z.

I would like to draw your attention to energy expression and the partition function to energy expression and the partition function expression. The energy we have expressed at summation of energy of the particle in x direction plus y dimension plus z dimension. So if the energy is additive, you see here the partition function is multiplicative. That is one, that is y, that is what is written in the footnote that please note energy is sum of independent contributions that is E_I is equal to this is independent contribution $E_{n_1}{}^{(x)}$, $E_{n_2}{}^{(y)}$, $E_{n_3}{}^{(z)}$. These are independent contribution.

So energy is sum of independent contributions. Partition function is a product of partition functions for each mode of motion. This is an important result that is energy is additive and when you write partition function and there are different modes of motion, then the overall partition function is a product of partition function for individual mode of motion, each mode of motion. Very important result which you will be using in future. We have derived this result

$$q_X = \left(\frac{2\pi m}{h^2\beta}\right)^{1/2} X$$

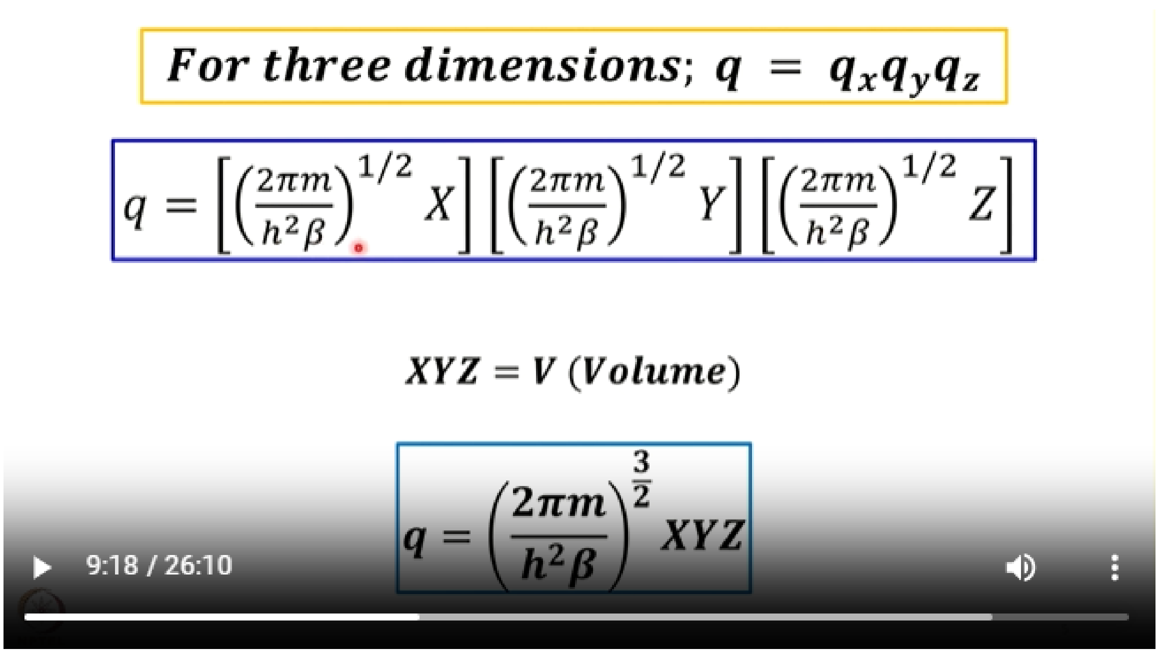
(Refer slide time :8:14)



This was the partition function for a particle which is free to move only in x dimension and for three dimensions we need to multiply q_x, q_y, q_z. So this is q_x first bracket, the second bracketed expression is for q_y only replacement is x with y and the third one is for q_z. So we have used the result here that the partition function is product of partition function for each mode of motion. Combine all these three and let us see what do we get. Once you combine all these three, see x into y into z is volume and 2 pi m over h square beta is appearing three times. So

$$q = \left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} XYZ$$

(Refer slide time: 9:18)



This x y z I can replace by volume, x y z is volume. Therefore the partition function is going to be now instead of in place of x y z let us put volume and this 2 pi m over beta h square raise to the power 3 by 2 I will write as denominator in the form of λ cube. Why we are doing this? What is the significance of λ? Let us discuss that. So if I am writing this 2 pi m over h square beta raise to the power 3 by 2 as λ cube then what will be λ? λ will be simply beta h square over 2 pi m square root, simple mathematics.

You can take h out, you can write λ as h into beta over 2 pi m square root. You can write it as beta is equal to 1 over k T so an alternate form can be h over square root 2 pi m k T.

There are different forms you can use the expression which is more convenient when you are solving, when you are addressing the different type of problems. In this expression once again h is the Planck constant, m is the mass of one particle, k is the Boltzmann constant, T is the temperature in Kelvin. So once you put all the units you will see that the dimensions of λ turn out to be that of the length.

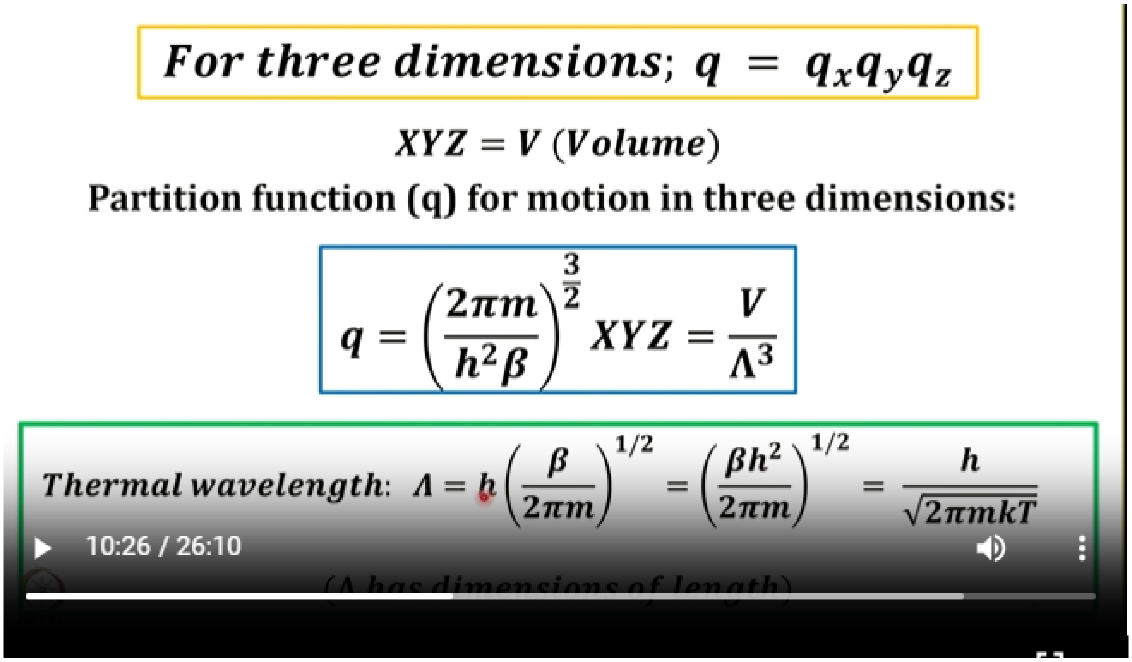
The dimension of λ turns out to be that of the length. Therefore, this λ is given a special name and that is the thermal wavelength. Refer to quantum chemistry. You talked about the wavelength and here partition function since it refers to the relative population of various energy levels, energy states as a function of temperature. Therefore, you put a word before wavelength thermal wavelength. That means this λ is going to decide the value of q. q is equal to V upon λ q. So the smaller is the value of λ, the higher is the value of q. So this is the value. So λ will decide the value of q and q simply refers to how many states are thermally accessible at a given temperature

That is the reason this λ is given this name thermal wavelength. So the point to be noted over here is that q, the partition function is inversely proportional to λ. For one dimension it is inversely proportional to λ. For two dimension it is inversely proportional to λ square and for three dimension it is inversely proportional to λ q So the smaller is the thermal wavelength, the more will be the value of q and the more number of energy levels or energy states will be populated.

So the translational partition function, for a particle, for a molecule which is free to move in three dimensions is given by this expression q is equal to V upon λ q. Once again, again and again I am emphasizing that when you are solving the numerical problems please take care of the dimension, please take care of the units. V is the volume of the container and if we know the thermal wavelength, to know the thermal wavelength we need the temperature and we need the mass, that's it. Other things are constant, h is constant, k is constant, only variables are mass and temperature. Once we have that information we can calculate the value of translational partition function.

Let us now move ahead for further discussion. Let's try to solve a problem. Calculate the translational partition function of a hydrogen molecule confined to 100 centimeter cube vessel at 25 degree centigrade. To solve this problem we need to first of all recognize that what is being asked is translational partition function and we have just derived the expression for qtranslational is V upon λ q where λ was equal to beta h square over 2 pi m square root or you can write this as h over root 2 pi m k T. We are given the volume 100 centimeter cube that can be substituted over here.

(Refer slide time:10:26)

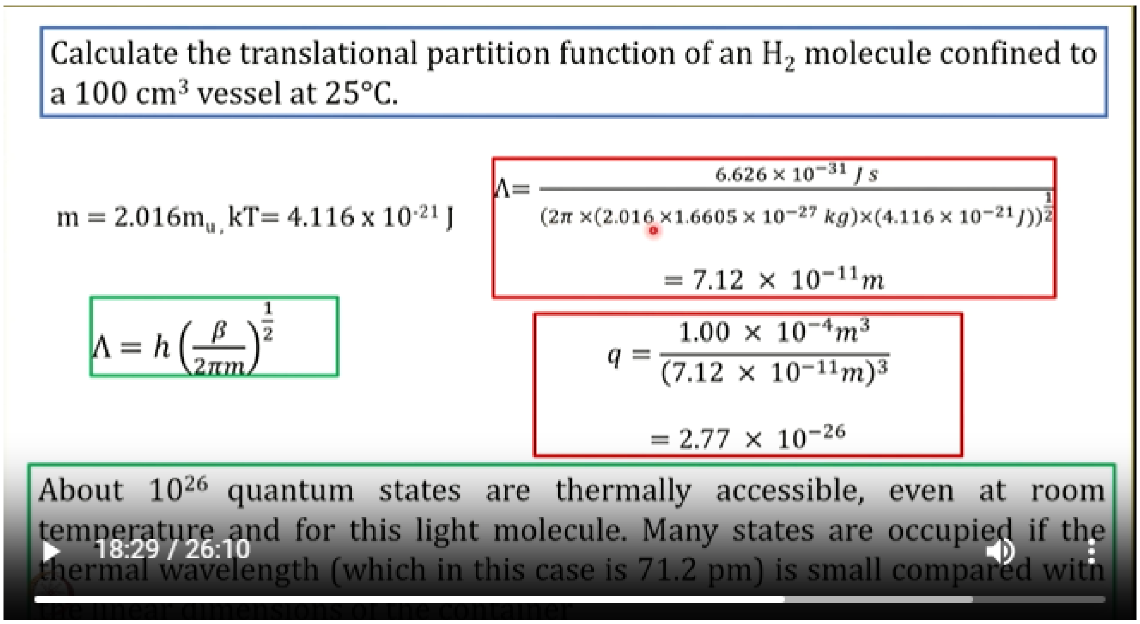


We know the mass, it is hydrogen molecule, but remember what we discussed earlier, since this is the molecular partition function you will need to substitute here mass of 1 hydrogen molecule. So, how will you calculate m is equal to M_r Let's say if I write this m R is the relative molecular weight in gram per mole, I will divide this by Avogadro constant and I will also multiply by 10 to the power minus 3. That is only possible, I mean that can be, factor can be applied if I write M_r in grams per mole. The factor 10 to the power minus 3 is to convert gram into kilogram and factor N_A Avogadro constant is used to convert mass per particle, mass per molecule.

This we need to keep in mind and of course, the given volume is in centimeter cube and since we are using, we have to use the SI units throughout. Therefore, we need to convert this centimeter cube into meter cube once we substitute that value over here. Mass is 2.016 gram per mole, it is hydrogen molecule H_2. kT value at 25 degree centigrade you can individually substitute Planck's constant or Boltzmann constant and temperature and get the expression at 25 degree centigrade K T is 4.116 into 10 to the power minus 21 joule. So, λ just recall λ is H over 2 pi m K T substitute the value h is Planck's constant 6.626 into 10 to the power minus 31 joule second 2 pi m. So, m how you calculate m? You can calculate m by m, m by m is equal to m you see here it is 2.016 which is the relative molar mass to convert this into per molecule or per particle you have to put this factor this conversion factor 1.6605 into 10 to the power minus 27 K g from where this factor comes in this is basically M_R divided by Avogadro constant into 10 to the power minus 3 if the molar mass you use is in gram per mole. So, 1 by N_A into 10 to the power minus 3 is equal to 1.6605 into 10 to the power minus 27 K g and kT is 4.116 into 10 to the power minus 21. Just make sure that all the units are proper in SI units and then calculate the value of thermal wavelength.

Thermal wavelength is 7.12 into 10 to the power minus 11 meter which is equal to 71.2 picometer. Now, qis equal to V upon λ cube the given volume is in centimeter cube. So, you multiply this 100 centimeter cube by 10 to the power minus 6 to convert into meter cube and now you see that meter cube meter cube will cancel you have to take care of the units otherwise there will be an issue. So, the value of q, q comes out to 2.77 into 10 to the power 26 make this correction. So, this is the value of q. q is 10 to the power plus 26. If you look at this value of molecular partition function this value is very high 2.77 into 10 to the power 26.

(Refer slide time: 18:29)



You remember when we talked about interpretation of the molecular partition function the information that you get from the molecular partition function is how many states are thermally accessible. In the derivation of translational partition function we also talked about that the translational energy levels are very close to each other in a laboratory sized vessel. So, if they are very close to each other that means even at room temperature a very large number of energy states energy levels will be accessible and that is what is seen in this number. About 10 raise to the power 26 quantum states are thermally accessible even at room temperature for this light molecule hydrogen in a light molecule. And look at the next comment many states are occupied if thermal wavelength which of course in this case is 71.2 picometer is small compared with the linear dimensions of the container. q is equal to V by λ cube the answer comes from that. Let me just write q is equal to V by λ cube. So, this is the answer V upon λ cube. The smaller the value of λ compared to the linear dimensions of the container the value of Q is going to be very high. So, what is the conclusion from the discussion of this numerical problem? The conclusion is that for gas molecules for example, hydrogen at 25 degree centigrade is in the gaseous form.

Similarly, you can calculate for other gases oxygen nitrogen you can calculate for helium argon etcetera. The value of partition translational partition function is very very high. That means so many quantum states are thermally accessible. That means at room temperature the translational contribution to partition function for the gases is always there. The second conclusion that we draw from this discussion is that if the thermal wavelength is small compared with linear dimensions of the container then many states are occupied. The number for translational partition function turns out to be several orders like you know 2.77 into 10 raise to the power 26. So, what we conclude from today's this part of the lecture is that you can write the expression for the translational motion of a particle of a molecule in one dimensional, two dimension, three dimension. I have done the derivation for one dimension and three dimension, but you can also stop at the derivation for two dimension. A particle which is free to move in along a length, a particle which is free to move on a on an area surface and a particle which is free to move in three dimension in a container with length x y z. All three we have derived we have discussed. Our next goal is not only going to be deriving expression for the partition function for the rotational degree of freedom, vibrational and others, but also start connecting the molecular partition function with different thermodynamic quantities. So, in the next lecture onwards we will start connecting partition function with different thermodynamic quantities and then we will also proceed towards deriving expressions for the partition function for other modes of motion.

Thank you very much.