Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

Lecture - 07

Welcome back to the next lecture on Statistical Thermodynamics. In the previous lectures, we have derived expression for molecular partition function and we have tried to understand what is the meaning of partition function, what is the interpretation of partition function. Then we tried to understand further the meaning of partition function by considering a two level system and then we derived an expression for partition function for a uniform ladder of energy levels. We also derived expressions for the fractional population and from the discussion on temperature dependence of fractional population, we arrived at a very important conclusion that as the temperature approaches infinity, all the states are going to be equally likely populated. With that background, now let us proceed further. Today we are going to discuss the partition function for a particle or a molecule which is free to move in one dimension, two dimension, three dimensions. That means today we will derive expressions for the translational partition function. How we will develop is that first we will consider a particle or a molecule which is free to move only in one dimension, x dimension let us say. And once we have derived some expressions, then we will extend this to a particle or a molecule which is free to move in two dimensions or three dimensions. So today in the discussion, I will refer back to particle in one dimensional box.

You remember when you studied quantum chemistry, particle in 1D box, 2D box, 3D box, there you derived expressions for the energy levels for a particle in 1D box, 2D box, 3D box. We are going to use that result over here also. Let us begin our discussion. So, let us consider the energy levels of a molecule of mass m in a container of length x. That means you are allowing the molecule or the particle to move only in one dimension. You are not allowing it to move in y direction or z dimension, only one dimension length x. And as I said, we are going to use the expression for energy levels which you derived for particle in one dimensional in a box which essentially was a length. And this is the expression you got, E_n is equal to n square h square over 8 m x square. x is the length of that box. n is the quantum number.

The energy levels of a molecule of mass m in a c... length X are given by

$$E_n = \frac{n^2 h^2}{8mX^2} \qquad n = 1, 2, 3, \ldots\ldots$$

For $n=1$ (Lowest level); $E_1 = \frac{h^2}{8mX^2} = \varepsilon$

4:26 / 27:18

Remember that the values, permitted values of n were 1, 2, 3 onwards. Remember n is equal to 0 was not permitted.

$$E_n = \frac{n^2 h^2}{8mX^2} \qquad n = 1, 2, 3, \ldots\ldots$$

For $n=1$ (Lowest level); $E_1 = \frac{h^2}{8mX^2} = \varepsilon$

$$\varepsilon_n = (n^2 - 1)\varepsilon$$

So, once again n is the quantum number, h is plant constant, m is mass of the molecule or particle and x is the length. Now, I refer back to our original discussion where we talked about the ground state. We set the value of energy of ground state equal to 0. So, how do we bring that modification over here? Here the lowest state is corresponding to n equal to 1. So, what is n equal to 1? n equal to 1, the lowest level E 1, you substitute here n equal to 1. So, you have h square over 8 m x square. And let me write this equal to E.
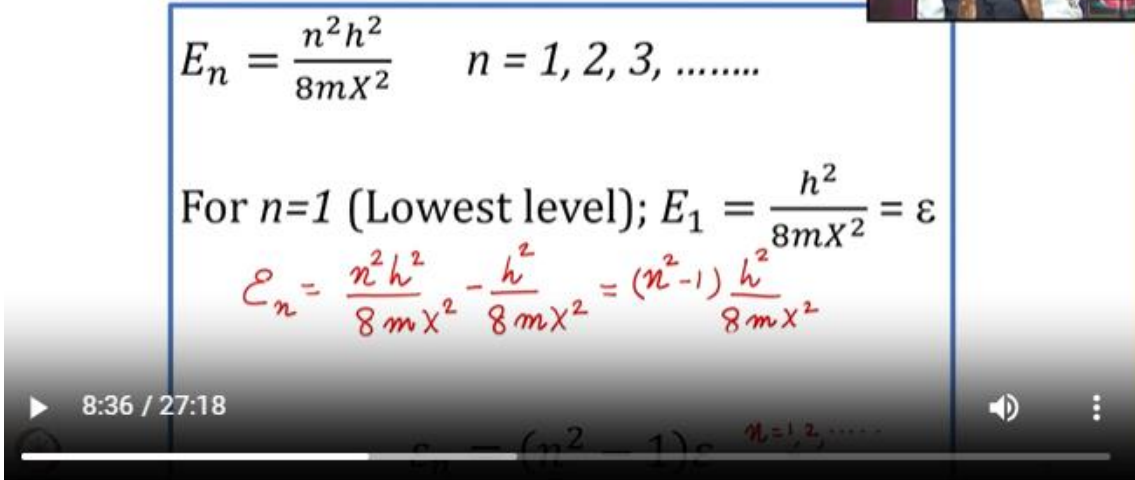
The energy levels of a molecule of mass m in a c... length X are given by

$$E_n = \frac{n^2 h^2}{8mX^2} \qquad n = 1, 2, 3, \ldots\ldots$$

For $n=1$ (Lowest level); $E_1 = \frac{h^2}{8mX^2} = \varepsilon$

$$\mathcal{E}_n = \frac{n^2 h^2}{8mX^2} - \frac{h^2}{8mX^2} = (n^2-1)\frac{h^2}{8mX^2}$$

$$\mathcal{E}_n = (n^2 - 1)\varepsilon \qquad n = 1, 2, \ldots\ldots$$

This is the energy of the lowest level. So, therefore, in order to set the value of energy corresponding to n equal to 1 to 0, what I will do? I will write E n is equal to n square h square over 8 m x square minus I will subtract this value, the lowest value which is h square over 8 m x square. What I have done? Pay attention that we took the expression n square h square over 8 m x square and from this we subtracted an expression which is the energy level for n equal to 1. So, this way we are setting the lowest level energy equal to 0. So, what we have now here is equal to n square minus 1 into h square over 8 m x square. And this h square over 8 m x square we have set equal to E. That means now I can write E n is equal to n square minus 1 into E. And now let's say if I set n equal to 1, 2, etcetera, etcetera, etcetera, for n equal to 1, if you substitute n equal to 1, then the lowest energy is going to be equal to 0. So, note this step that how we have set the ground level, the lowest level energy equal to 0. We have just subtracted a constant and we will account for this subtraction, we will account for this constant later on. So, what we have done?

$$\varepsilon_n = (n^2 - 1)\varepsilon$$

$$q_X = \sum_{n=1}^{n=\infty} e^{-(n^2-1)\beta\varepsilon}$$

This expression is exact. However, the sum cannot be evaluated explicitly (other than numerically for specific value of βε

The translational energy levels are very close together in a container of the size of a typical laboratory vessel. Therefore, the sum can be approximated by an integral

9:11 / 27:18

$$q_X = \int^{\infty} e^{-(n^2-1)\beta\varepsilon} dn \simeq \int_0^{\infty} e^{-n^2\beta\varepsilon} dn$$

We have set the energy level E_n is equal to n square minus 1 into E. And now we need to write the expression for partition function. And what is the expression for partition function? You remember is equal to summation j exponential minus beta E_j and wherever degeneracy needs to be accounted, we need to account for. So q_x, the subscript x identifies the movement only in one dimension in a length x equal to x. n value we will now write summation, summation n value can assume from 1 to infinity exponential minus beta E, beta is there and instead of E, I am writing n square minus 1 into E.

This step should be noted carefully. We have basically used this formula and we have substituted for n, n can vary from 1 to infinity and exponential minus beta E, Ej or E_n here instead of j I am writing E_n. So, therefore, you have writing n square minus 1 into E. This expression is exact. In order to evaluate this expression, you have to keep on adding, adding, adding for different values of n.

 Even though this expression is exact, the sum cannot be evaluated explicitly other than numerically for specific value of beta E. See n can vary from 1 to infinity. So therefore, when you expand this summation, you will have to keep on changing n equal to 1, n equal to 2, n equal to 3, etcetera, etcetera, etcetera, go up to infinity. So there should be an easier way of evaluating this expression. So what approximation we are going to use now? Translational energy levels are very close together in a container of the size of a typical laboratory vessel.

The energy spacing between translational energy levels is very small. You have studied this in quantum chemistry. So when the spacing is very small, when they are very, very close to each other, therefore, you can then approximate this summation by integration whenever there is a very, very small increment or very, very small spacing. So we are

going to use this approximation, that is, instead of summation, let us write integration. n equal to 1 to n equal to infinity exponential minus n square minus 1 beta E d_n

$$\varepsilon_n = (n^2 - 1)\varepsilon$$

$$q = \sum_j \bar{e}^{-\beta\varepsilon_j}$$

$$q_X = \sum_{n=1}^{n=\infty} e^{-(n^2-1)\beta\varepsilon}$$

This expression is exact. However, the sum cannot be evaluated explicitly (other than numerically for specific value of βε

The translational energy levels are very close together in a container of the size of a typical laboratory vessel. Therefore, the sum can be approximated by an integral

▶ 13:05 / 27:18 $q_X = \int_1^\infty e^{-(n^2-1)\beta\varepsilon} dn \simeq \int_0^\infty e^{-n^2\beta\varepsilon} dn$ ◀) ⋮

I am just from here I am switching over to here. .

$$q_X = \int_1^\infty e^{-(n^2-1)\beta\varepsilon} dn \simeq \int_0^\infty e^{-n^2\beta\varepsilon} dn$$

But now if you look at this expression, this integration is not that easy to solve. So we are going to do minor modification over here, that is, instead of starting from 1, you start integration from 0 and ignore 1 over here. Okay, note the step. You start integration from 0 and ignore 1 over here, then you have 0 to infinity exponential minus n square beta E dn.

I am not saying that you randomly do that, but if you do this kind of modification, the error introduced is negligible. So this form, perhaps you can recognize that you can easily evaluate this integral. Let us work on that. We need to evaluate this integral. How do we evaluate? Very easy.

Let us substitute x square is equal to n square beta E. So what we have? 2x dx is equal to 2n dn and of course you have that beta E over here. So what is dn? dn here is equal to x upon n into 1 over beta E. What is x upon n? x upon n can be found out from this. Let us use that. x upon n is equal to root beta E into 1 over beta E and you have dx. So what do we have? Here is 1 over root beta E dx. Now let us act upon this. So q_x is equal to, I have to write for dn. So I have integration 0 to infinity exponential minus x square and instead of dn, I am going to write 1 upon beta E dx.

Let me write just appropriately 1 upon beta E integration 0 to infinity exponential minus x square dx. Now I am sure that you remember the value of this standard integral. 0 to infinity exponential minus x square dx.

$$q_X = \int_1^{\infty} e^{-(n^2-1)\beta\varepsilon}\,dn \simeq \int_0^{\infty} e^{-n^2\beta\varepsilon}\,dn$$

$$x^2 = n^2\beta\varepsilon$$

$$2x\,dx = 2n\,dn\,\beta\varepsilon$$

$$dn = \left(\frac{x}{n}\right)\frac{1}{\beta\varepsilon}\,dx = \sqrt{\beta\varepsilon}\cdot\frac{1}{\beta\varepsilon}\cdot dx = \frac{1}{\sqrt{\beta\varepsilon}}\,dx$$

$$q_X = \frac{1}{\sqrt{\beta\varepsilon}}\int_0^{\infty} e^{-x^2}\,dx = \frac{1}{\sqrt{\beta\varepsilon}}\int_0^{\infty} e^{-x^2}\,dx$$

$$\frac{1}{\sqrt{\beta\varepsilon}}\cdot\frac{\sqrt{\pi}}{2} = \sqrt{\frac{\pi}{4\beta\varepsilon}} = \sqrt{\frac{\pi\,8mx^2}{4\beta\,h^2}} = \left(\frac{2\pi m}{\beta h}\right)^{1/2} x$$

19:20 / 27:18

This standard integral, the value is root pi by 2. Let us use that. So what we have now? qx is equal to 1 over beta E into root pi by 2. Can I write this as? Let me bring everything under root. Here is pi by 4 beta E. Now what is this equal to? root pi by 4 beta and E was h square over 8 m x square. This was E. What we have here is 2 pi m over beta h square raised to the power half and let me take out x. It is a very simple derivation. What we did was that we converted this form of integration which was relatively more difficult to evaluate into a simple one by ignoring 1 over here, setting 1 equal to 0 over here and then substituting this equal to x square then working out what we have here is qx is equal to 2 pi m square root beta h square. So what we have is qx is equal to 2 pi m over beta h square into x. What is this? x over here is the length of the container.

Beta is equal to 1 upon kT. m is mass of the particle, mass of the molecule, h is Planck's constant. So this I will write as partition function for a particle or for a molecule free to move in let's say x dimension, x direction, x dimension whatever you want to say. And what is this? x is the length of the container. Let me compare or give some comments about partition function and wave function. You see here we used some result from quantum chemistry, quantum mechanics.

There you talked about wave function. Wave function had all the information about the particle about the molecule whereas, here the partition function we will interpret as partition function has all the thermodynamic information of the molecule. This is how

you can complement each other. Let's move ahead. So what we have done is we have derived an expression for the translational partition function of a particle that is free to move in one dimensional container of length x and that we are referring to as qx. This is the expression qx is equal to 2 pi m over h square beta or beta h square the way you want to read it square root into x. Before you start applying this result, this derivation, it is very important to understand in what units you need to substitute the value. We are talking about partition function of a molecule. We are talking about partition function of a particle. When we say molar mass, what do we understand when we say molar mass? The units of molar mass is gram per mole.

The translational partition function Of a particle that is free to move in one-dimensional container of length X is q_X

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

- m is mass of one particle
- h is Planck constant
- $\beta = \frac{1}{kT}$; k is Boltzmann constant

22:13 / 27:18

For example, if we say oxygen, we say 16 grams per mole. How many molecules per mole? How many molecules or let's say oxygen atom if I say 1 mole of oxygen atom, how many atoms are there? Avogadro constant. And since here we are talking about per molecule per particle, so therefore, when you use a number for m, this is going to be mass of one molecule atom particle whatever you are applying to. Remember this, it is the mass of one particle. Do not substitute it equal to the molecular weight.

You need to convert the mass of one particle. h is Planck constant and beta is 1 over kT where k is Boltzmann constant. So once again when you apply these results to solve numerical problems, you need to be very very careful about the units. If you are using SI units, stick to SI units and remember that one common mistake many times the students do is put m equal to molecular weight, but if you put m equal to molecular weight, you need to account for the Avogadro constant somewhere because m is mass of one particle. Similarly, the length, if it is one dimensional, you are talking about a length.

The units have to be appropriate. Let's say if you are sticking to SI units, stick to SI units. When we switch over from one-dimensional container to two-dimensional container, that is x, one length is x, other length is y, it can be even a square and then if it is a square, then we can allow the particle to move on the surface of a square. We can evaluate an expression or we can derive an expression for the partition function for a particle or a molecule which is free to move on the surface of a square. So what we have done in this lecture is that we have moved towards deriving expression for translational partition function. We are only allowing the molecule or particle to move in different dimensions.

To begin with, we stuck to one dimensional container which has a length x. We used the results of quantum chemistry for energy levels of particle or molecule which is free to move in one dimensional and then we expressed it in the form of partition function and then we solved it to get a result which is listed over here that Qx is equal to 2 pi m over h square beta square root into the length. We will switch over from one dimensional container to two and three dimensional container in the next lecture.

Thank you very much.