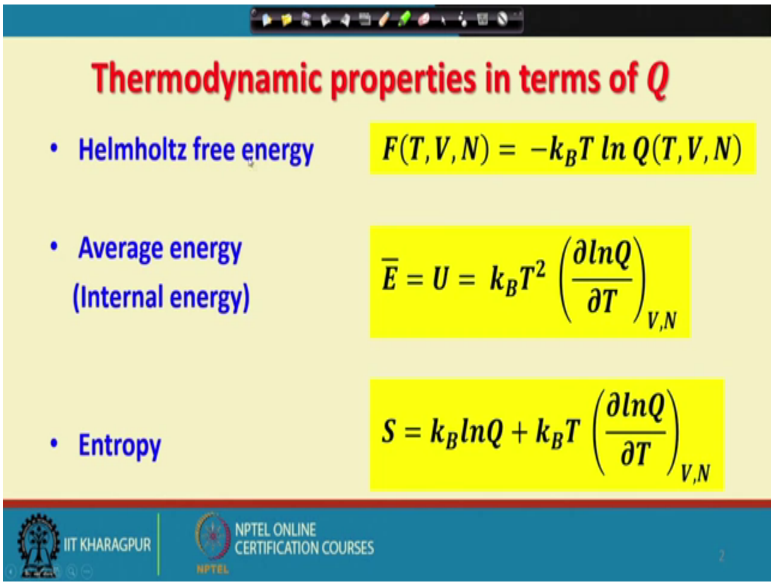
Introduction to Molecular Thermodynamics

Prof. Srabani Taraphder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 20
Canonical Ensemble Part III

Welcome back. So, in this lecture, we are going to discuss the third part of canonical ensembles, where we have already seen that under a given condition of temperature volume and number of particles, if I know the partition function, I can get the thermodynamic properties, where the relationships are given are listed over here.

(Refer Slide Time: 00:42)



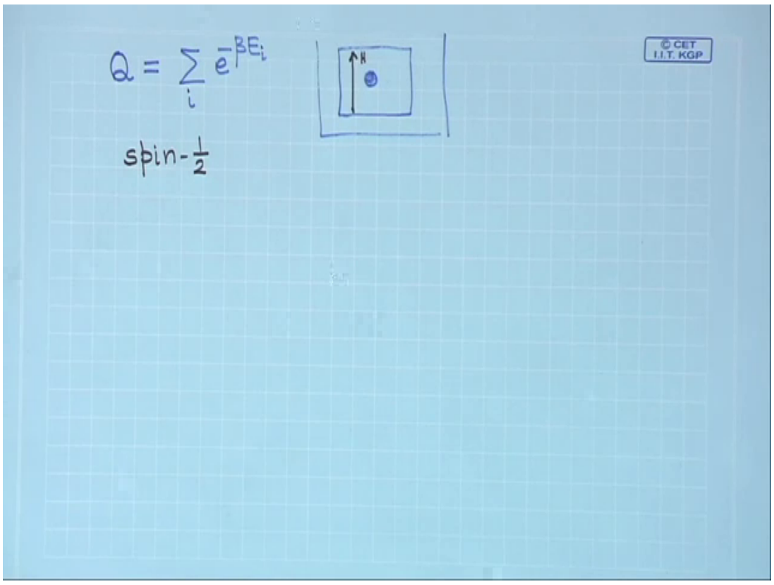
Thermodynamic properties in terms of Q

- Helmholtz free energy $F(T,V,N) = -k_BT \ln Q(T,V,N)$
- Average energy (Internal energy) $\bar{E} = U = k_BT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$
- Entropy $S = k_B \ln Q + k_BT \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

The Helmholtz free energy of average energy, or the internal energy entropy pressure, and even chemical potential. So, all these require the partition function Qas a function of temperature volume and the number of particles and; obviously, you understand that for a given system capital Q that is equal to summation over all possible microscopic states e to the power of minus beta E i, where E i characterizes the i th microscopic state as given by the solution of the Schrodinger equation.

(Refer Slide Time: 01:04)

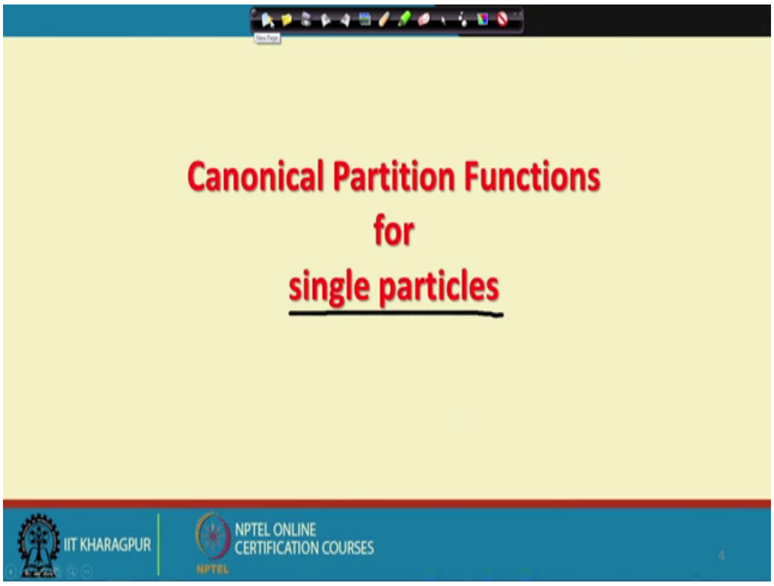


$$Q = \sum_i e^{-\beta E_i}$$

spin-$\frac{1}{2}$

So, therefore, the aim of this particular lecture is to evaluate the canonical partition function of a given system for which the solution of the Schrodinger equation is known.

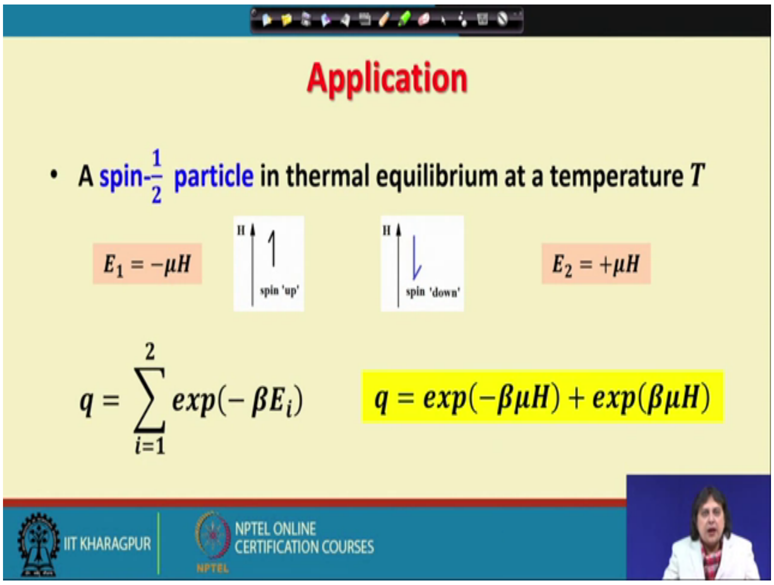
(Refer Slide Time: 01:44)



Canonical Partition Functions
for
single particles

So, we are going to start by calculating the canonical partition function for single particles, we have already seen a lot of single particle systems for which we have discussed in detail the solution of the Schrodinger equation, and how to count them when they are present under the isolated condition, now we are going to use those concepts once again in this particular course.

(Refer Slide Time: 02:09)



Application

- A spin-$\frac{1}{2}$ particle in thermal equilibrium at a temperature T

$E_1 = -\mu H$

$E_2 = +\mu H$

$$q = \sum_{i=1}^{2} exp(-\beta E_i)$$

$$q = exp(-\beta\mu H) + exp(\beta\mu H)$$

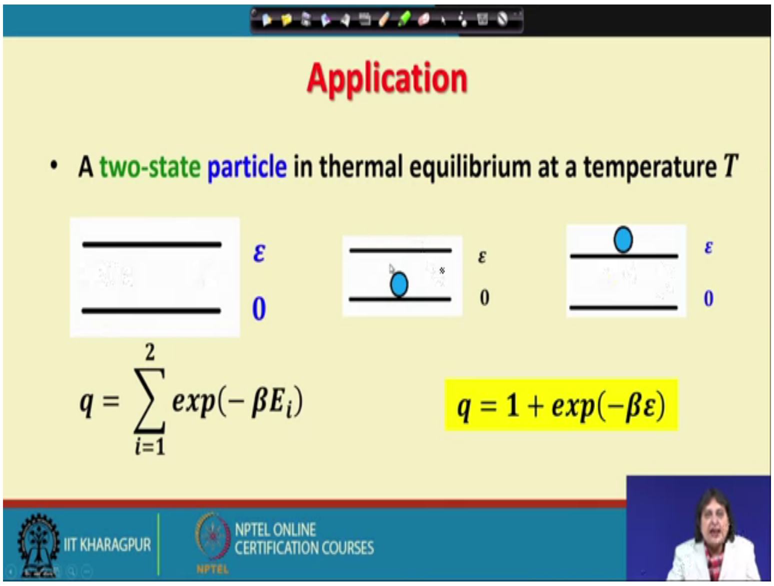
So, the first application that I have in mind is a single spin half particle, and in this case unlike the isolated system, I have the system which is immersed in a thermal reservoir, and here for the sake of simplicity I have a single particle, and this single particle in my first example corresponds to a spin half particle, I assume that that is embedded inside the system some magnetic field H therefore, if the magnetic moment associated with the spin half is mu,, in that case I know that from the solution of Schrodinger equation for the isolated system the allowed energy Eigen states for this spin half particle is going to be the first one the spin up microstate having an energy minus mu H, and the second one which is plus mu H energy having a spin down; that means, the spin is oriented anti parallel to the direction of the applied field.

So, how many microstates are there, under isolated condition there are basically 2 such microscopic states, now when you take any such system and put it in contact with a thermal reservoir, now we are asking the question are they equally probable, because of the presence of a finite temperature you are no longer in the temperature less description of the Schrodinger equation and therefore, the 2 possible microstates are going to be differently populated under the condition of finite temperature, and then correspondingly we will say well, since it is a single particle system I am going to use small q as a representation of the canonical partition function for the single particle, and this is going to be by definition once again summation over I e to the power of minus beta E i now how many microstates are possible for this system 2.

So, I will say this is i equal to 1 to 2, and accordingly I will write in this summation in the expanded form and say that this is equal to e to the power of minus beta e 1 into e to the power of minus beta e 2, I know for this given system what e 1 is this quantity is minus mu H, and this quantity is plus mu H therefore, I can very easily write down that small q is equal to e to the power of minus beta mu H plus e to the power of this one is plus beta mu H, and this is going to be minus beta mu h. As discussed in the last class I am using this particular notation that beta is equal to 1 by the Boltzmann constant multiplied by the temperature in the absolute scale.

Now, once you know this small q, I can very easily answer questions like what is the probability that this single particle in this system has an up spin then; obviously, the answer is e to the power of up spin, which means that is the first energy state that I am talking about. So, that is minus beta of e 1 divided by q, by definition p I is e to the power of minus beta E i by q. So, here my up spin corresponds to the index 1 here, and therefore, I am writing it like this. So, writing it explicitly then I have this is equal to e to the power of beta mu H, divided by e to the power of beta mu H plus e to the power of minus beta mu H clear. So, that is a result that we have put up here. So, this is actually trivial I would say and this can be extended very easily to the general scenario of a 2-state particle.

(Refer Slide Time: 06:35)



Application

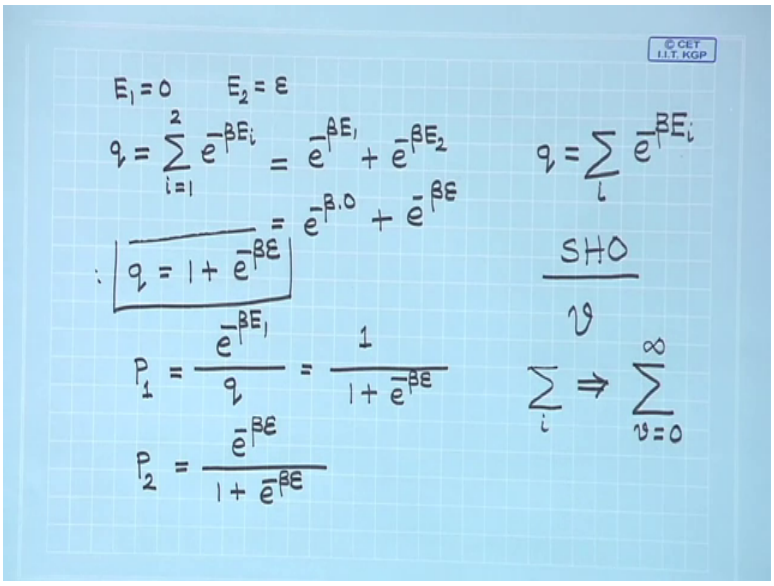
- A two-state particle in thermal equilibrium at a temperature T

$$q = \sum_{i=1}^{2} exp(-\beta E_i)$$

$$q = 1 + exp(-\beta\varepsilon)$$

Where instead of having minus mu H and plus mu H, I would say that my system is comprised of a single particle for which the energy state diagram from the solution of the Schrodinger equation is like this. So, once again how many microscopic states are possible for this system, the Schrodinger equation solution tells you that only 2 microstates are possible, and what are these energy values or energy Eigen values for these 2 states?

(Refer Slide Time: 07:09)



$E_1 = 0 \quad E_2 = \varepsilon$

$$q = \sum_{i=1}^{2} e^{-\beta E_i} = e^{-\beta E_1} + e^{-\beta E_2}$$

$$= e^{-\beta . 0} + e^{-\beta \varepsilon}$$

$$\therefore \boxed{q = 1 + e^{-\beta \varepsilon}}$$

$$P_1 = \frac{e^{-\beta E_1}}{q} = \frac{1}{1 + e^{-\beta \varepsilon}}$$

$$P_2 = \frac{e^{-\beta \varepsilon}}{1 + e^{-\beta \varepsilon}}$$

$$q = \sum_i e^{-\beta E_i}$$

SHO

ϑ

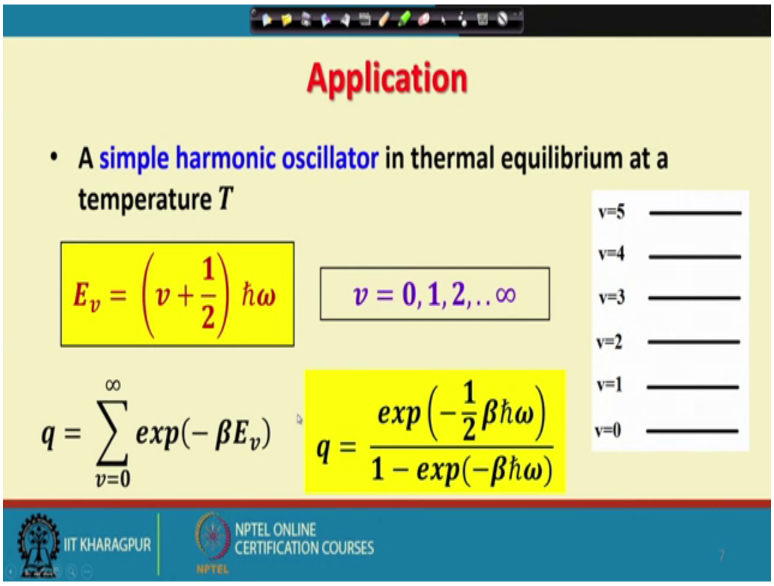
$$\sum_i \Rightarrow \sum_{\vartheta=0}^{\infty}$$

One is e 1 equal to 0 the other one is e 2 is equal to epsilon. So, once again if I write down the single particle partition function for this system I will say that this is equal to I equal to 1 to 2 e to the power of minus beta E I. So, as before I am going to write it as e to the power of minus beta e 1 plus e to the power of minus beta e 2 now I put the values of e 1 and e 2. So, e to the power of minus beta epsilon. So, what is the final form of q the final form of q is 1 plus e to the power of minus beta epsilon. So, this is basically a generalization of what I had from the [vocalize-noise] spin half particle system. So, here as you see that I have 2 distinct microscopic states, and the corresponding partition function for the single particle is this.

So, if I ask you the question what is the probability that this particular microscopic state will be observed, that probability corresponds to my energy e 1 equal to 0 therefore, the probability of observing the system in the lower energy state which has an index 1, that is equal to e to the power of minus beta e 1 by q now what is e 1 that is 0. So, this term becomes 1 and I have 1 plus e to the power of minus beta epsilon, similarly if I want to know what is the probability of observing the system in this particular micro state, that is where the system is present in the upper energy state in that case, I would immediately say that the probability is e to the power of minus beta epsilon divided by 1 plus e to the power of minus beta epsilon.

This is a repetition from the last lecture, but I thought I will highlight it once more before we take up other examples, but there is one more example that we have talked about in the last class.

(Refer Slide Time: 09:26)



Application

- A **simple harmonic oscillator** in thermal equilibrium at a temperature T

$$\boxed{E_v = \left(v + \frac{1}{2}\right)\hbar\omega}$$

$$\boxed{v = 0, 1, 2, .. \infty}$$

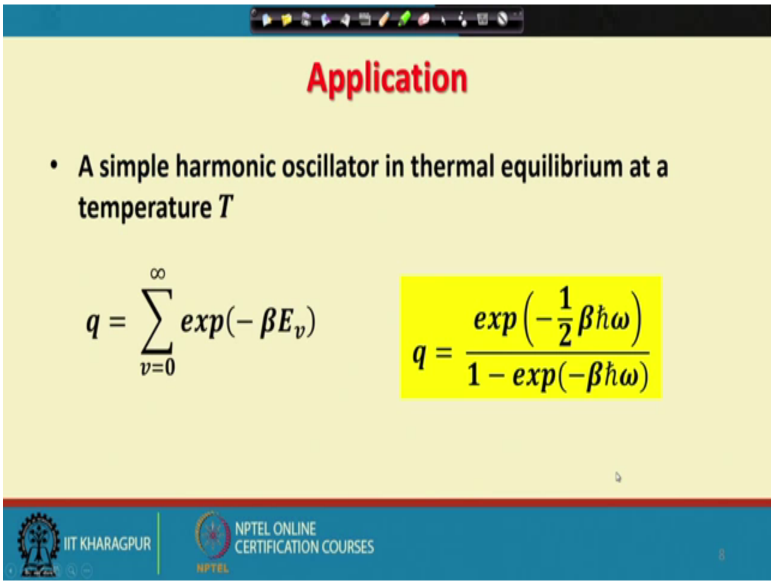
$$q = \sum_{v=0}^{\infty} exp(-\beta E_v)$$

$$q = \frac{exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1 - exp(-\beta\hbar\omega)}$$

And that is the simple harmonic oscillator where unlike the first 2 examples I have an infinite number of solutions of the Schrodinger equation possible, and in the with a given angular frequency of the oscillator. So, in this case when I write down the energy states I write it down in terms of a quantum number that varies from 0 or 1 2 etcetera. So, it can take up integral values and there are infinite number of possibilities, for a given value of this quantum number v, you can find out the associated energy value of this energy state and that is v plus half H cross omega where omega is the angular frequency of the oscillator and therefore, once again since the basic definition of small q is summation over all possible microstates e to the power of minus beta E I.

So, in the case of simple harmonic oscillators, each microstate is characterized by this one quantum number v and therefore, here summation over all microstates as I write as I always right here, is actually a summation over all possible values of the quantum number v. So, following this principle we have shown you how to derive this how to evaluate this infinite summation, and we find that there is a very nice analytical expression as shown over here.

(Refer Slide Time: 11:09)



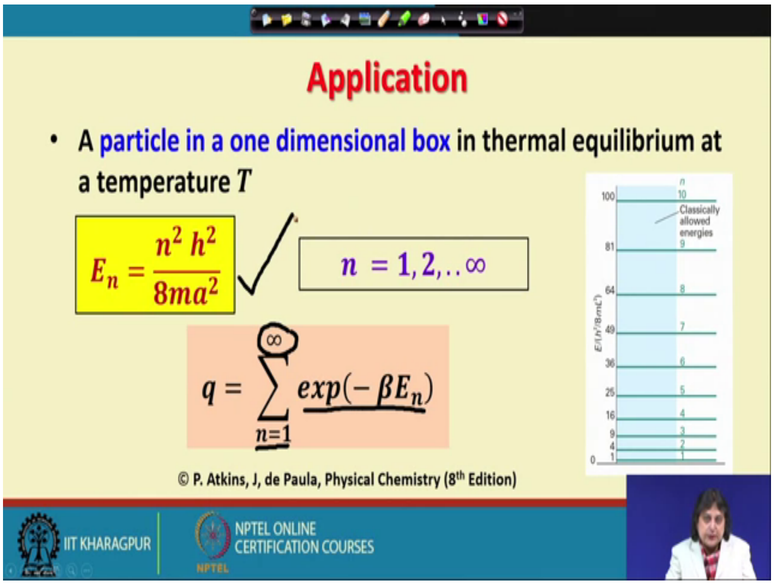
Application

- A simple harmonic oscillator in thermal equilibrium at a temperature T

$$q = \sum_{v=0}^{\infty} exp(-\beta E_v) \qquad q = \frac{exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1 - exp(-\beta\hbar\omega)}$$

Now, in today's class what I am going to do is, I am going to talk about a particle in a 1-dimensional box in thermal equilibrium at a temperature t.

(Refer Slide Time: 11:11)



Application

- A particle in a one dimensional box in thermal equilibrium at a temperature T

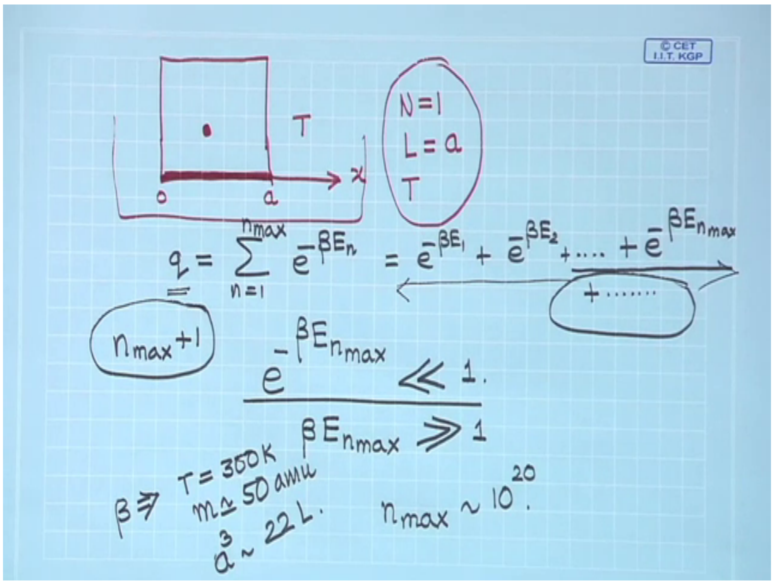
$$E_n = \frac{n^2 h^2}{8ma^2} \checkmark \qquad n = 1, 2, .. \infty$$

$$q = \sum_{\underline{n=1}}^{\infty} \underline{exp(-\beta E_n)}$$

© P. Atkins, J, de Paula, Physical Chemistry (8th Edition)

Now once again this is the picture that I have in mind.

(Refer Slide Time: 11:26)



So, I have a 3-dimensional box. So, I will consider only one direction in it. So, that the particle is moving in this direction which is probably the x direction, and it moves it has to confine itself between 0 and a, there is only one such particle, and this box or whatever this direction is this is in equilibrium with the thermostat maintained at a temperature t. So, I have n equal to 1, instead a volume since I have a single dimension therefore, I have a length that is equal to a within which the particle is confined, and the other thing that I require to define the microstate of the system that is the temperature t.

Now, the question is how shall I obtain the a canonical partition function for a particle like this. So, let us remind ourselves; what is the solution that we know from the solution of Schrodinger equation for any such system we know that once again all the microstates are can be described in terms of a single quantum number which is n. So, what are the possible values of n n must be an integer varying from 1 to infinity, and the corresponding energy values are given by n square multiplied by something which depends on the Planck's constant mass of the particle, and the length a over which it is confined.

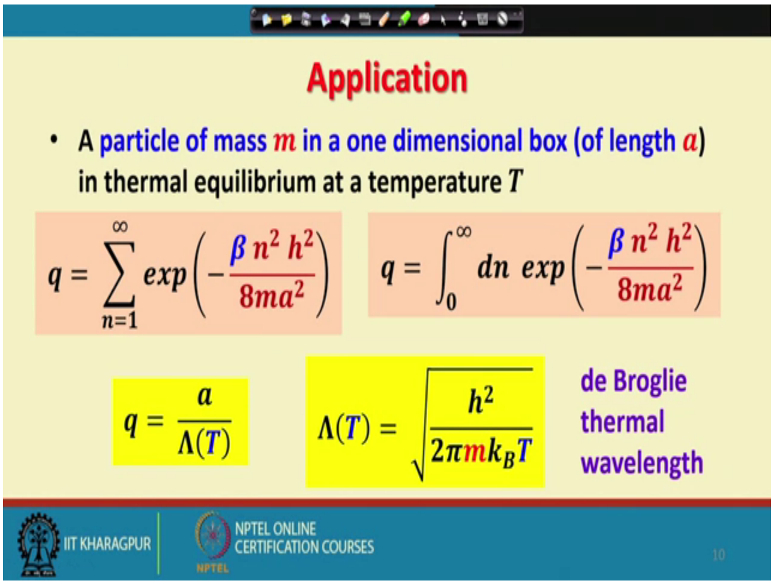
So, it is possible to use this relationship and evaluate the small q for this system. So, small q now just as before would require a summation of this particular term, exponential of minus beta into energy values over all possible microstates, here each and every microstate is characterized by the quantum number n therefore, a summation over all microstates translates to the summation over all possible values of n, now n starts from 1 and goes to infinity right and therefore, I would say that in order to be able to evaluate this q, we need to evaluate this particular expression in keeping with the known solution of Schrodinger equation for a particle confined in a 1 dimensional box.

Now, but it should be easy to do once again we are having this problem of evaluating an infinite series summation, but unlike the previous case of simple harmonic oscillator, what we find is here the summation is not. So, easy and why do I say. So, that is because let us say that I am going to calculate a sum evaluate this sum by hand, can I do it, I mean infinity is a very large number. So, it is not possible to do this summation by hand, you might argue that I can use a computer to do this summation. So, even in that case you will have to specify the maximum value of n up to which you are going to add to this evaluation of q, now my small q is a number like say summation over n going from 1 to some n max say for the purpose of my actual summation of this, e to the power of minus beta E n, now if I do this summation then I will have e to the power minus beta e 1 plus e to the power of minus beta e 2 and so on and so forth.

Let us say that I will go up to e to the power minus beta E n max if that is. So, then there will be other terms as well which will correspond to the value of n greater than n max something like n max plus 1, now if it so, happens that I can truncate it at this position and ignore any of these terms which are present, that will give me a rather accurate evaluation numerical evaluation of this summation, and thereby give me an estimate of accurate estimate of small q. So, the question that I have here is E n max beta E n max when it is exponentiated like this, this number must be much, much less than 1. So, that whatever other terms are there in this particular summation they are going to be very, very insignificant, I mean n max or n max plus 1, this kind of relationship is going to be very, very small or in other words I must be having beta E n max must be much, much greater than 1, actually if you look at what are the possible values for example, say beta corresponding to a temperature of 300 Kelvin, and mass is about 50 a m u, and if your a is roughly a cube is roughly about 22 litres, what you will find that this n max value is going to be roughly of the order of 10 to the power of 20.

So, of course, then there is a very large number of terms that I need to find out I need to add in order to be able to evaluate this infinite series summation, of course, I am not going to do it we the scientists are very smart people. So, they formed out alternative ways of evaluating this sum and that is as follows.

(Refer Slide Time: 17:56)



Application

- A particle of mass m in a one dimensional box (of length a) in thermal equilibrium at a temperature T

$$q=\sum_{n=1}^{\infty} exp\left(-\frac{\beta n^2 h^2}{8ma^2}\right)$$

$$q=\int_0^{\infty} dn\ exp\left(-\frac{\beta n^2 h^2}{8ma^2}\right)$$

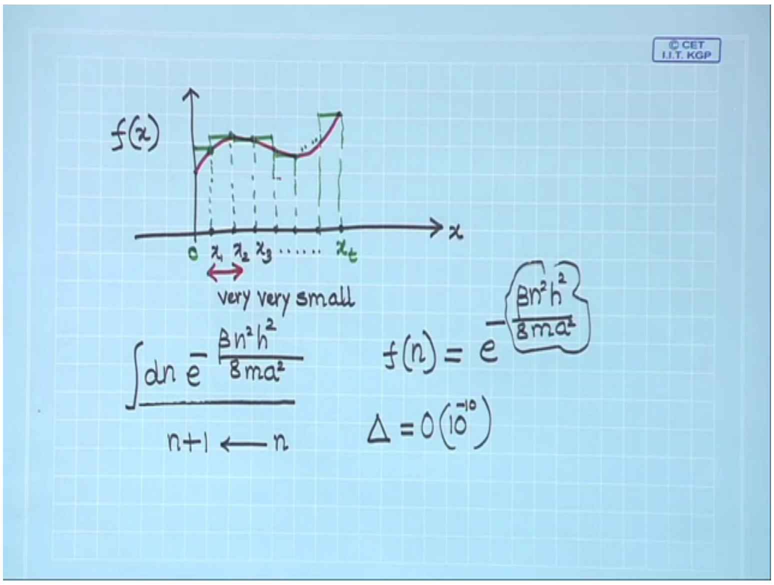
$$q=\frac{a}{\Lambda(T)}$$

$$\Lambda(T)=\sqrt{\frac{h^2}{2\pi m k_B T}}$$

de Broglie thermal wavelength

So, what they did was, they understood that this series summation can be replaced by a by an integral.

(Refer Slide Time: 18:10)



$$\int dn\, e^{-\frac{\beta n^2 h^2}{8ma^2}}$$

$n+1 \longleftarrow n$

$$f(n)=e^{-\frac{\beta n^2 h^2}{8ma^2}}$$

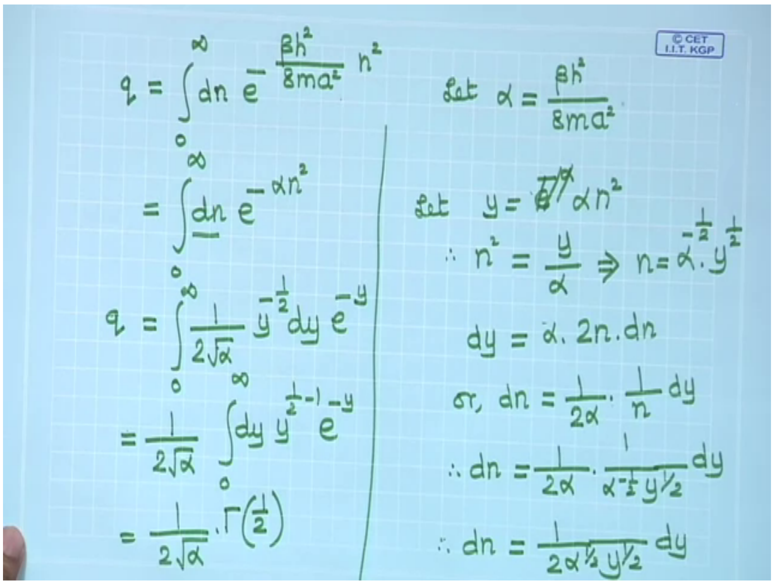
$$\Delta = O(10^{-10})$$

Now when you do this you understand that you are dealing with a situation where you are plotting say x along this direction, and f x along the y direction, and let us say that this is how f x varies as a function of x, now what we are trying to say is x varies from some initial value 0 to some final value here that is say x T right. So, basically what we are looking for here is the we have discretisized the x direction into a few different a values like x 1, x 2, x 3 and so on. And so, forth, and what we can do is we can find out the corresponding values of f x at these points, now why is this discretisization important, this discretisization is important because if you find out the values of these rectangles areas of these rectangles from here in this figure, then that is going to give you a rough approximate value of the area under this curve.

So, and that is exactly what we would look for, but this depends very, very much upon the interval, that you have chosen over here and this interval is something that decides whether the sum of the areas under this rectangle are going to be accurate enough to represent the integral, and we already know that yes this is true if and only if this interval is very, very small, now if you go back and look at like the typical values that we are thinking of here, we are finding that I am going to look for d n e to the power of minus beta n square H square divided by 8 m a square right, I am going to evaluate this. So, which one is my f x or my f n here that is equal to e to the power of minus beta n square H square divided by 8 m a square, now so, in this particular case the n appears with all these numbers and if you go from n to n plus 1, the delta; that means, the change in the values of n the corresponding functional change that is of the order of 10 to the power 10 minus 10.

So, which means that I can indeed replace the summation that I have written here, in terms of this integral, and it is possible to evaluate this integral and, do you know how to do this? I will quickly have a look at how to do this integral and the result is something that I am going to show you first, and the result is something like this. So, what is lambda t? Lambda T is a is a quantity which we will see that it is very important as far as describing the temperature dependent properties are concerned, and this is known as the de Broglie wavelength and it has the dimensions of length.

(Refer Slide Time: 21:59)



$$q = \int_0^\infty dn\, e^{-\frac{\beta h^2}{8ma^2} n^2}$$

$$= \int_0^\infty dn\, e^{-\alpha n^2}$$

$$q = \int_0^\infty \frac{1}{2\sqrt{\alpha}}\, y^{-\frac{1}{2}} dy\, e^{-y}$$

$$= \frac{1}{2\sqrt{\alpha}} \int_0^\infty dy\, y^{\frac{1}{2}-1} e^{-y}$$

$$= \frac{1}{2\sqrt{\alpha}} . \Gamma\left(\frac{1}{2}\right)$$

Let $\alpha = \frac{\beta h^2}{8ma^2}$

Let $y = \alpha n^2$

$\therefore n^2 = \frac{y}{\alpha} \Rightarrow n = \alpha^{-\frac{1}{2}} . y^{\frac{1}{2}}$

$dy = \alpha . 2n . dn$

or, $dn = \frac{1}{2\alpha} . \frac{1}{n} dy$

$\therefore dn = \frac{1}{2\alpha} . \frac{1}{\alpha^{-\frac{1}{2}} y^{1/2}} dy$

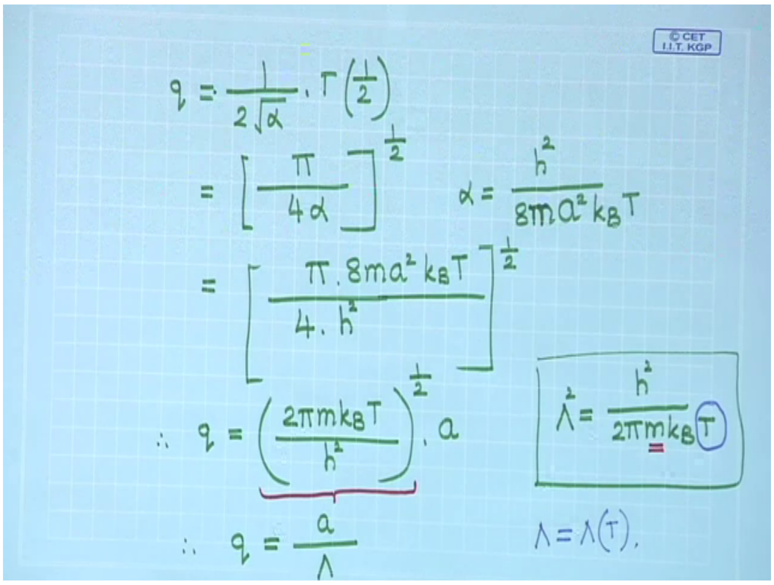
$\therefore dn = \frac{1}{2\alpha^{1/2} y^{1/2}} dy$

© CET I.I.T. KGP

Now, going back let us now try to do this particular integration. So, q is equal to 0 to infinity d d n e to the power of minus beta H square divided by 8 m a square into n square, now what I am going to do is let me use the following notation, let alpha be equal to beta H square divided by 8 m a square, then this integration now looks like 0 to infinity d n e to the power of minus alpha n square, I need to find out the value of this integral in order to do. So, let me do further assumption let me say that y is equal to e to the power of minus, y is equal to alpha n square right. So, what is n square n square is equal to. So, what is n square? N square is equal to y by alpha right, there and now since I know y I can find out what d y is, d y would be alpha into 2 n into d n, now I am going to replace finish doing this change in variable and say that then d n is equal to 1 by 2 alpha into 1 by n into d y, now what is n n square is equal to y by alpha therefore, n is equal to alpha to the power of minus half into, into y to the power of half now I put everything together. So, what I get is d n is equal to 1 by 2 alpha then in place of n I am putting in alpha to the power of minus half, into y to the power of half into d y, a little bit more of algebra and then what I find is that I have here half, alpha to the power of half, y to the power of half into d y, now I am going to use these new variables in order to find what small q is, now when n is equal to 0, what is y? Y is equal to 0.

So, the this is a lower limit replacement, when n is equal to infinity once again alpha is a finite quantity is non0, as a result this stays as infinity instead of d n I am going to write it as 1 by 2 root alpha into y to the power of minus half d y, and I am going to do the replacement here and this is equal to minus y. So, this now turns out to be 1 by 2 into root alpha into integral 0 to infinity d y, y to the power of half minus 1 into e to the power of minus y by now you must have learnt in your maths courses that this is nothing but 1 by 2 root alpha into gamma half right.

(Refer Slide Time: 25:45)



$$q = \frac{1}{2\sqrt{\alpha}} \cdot \Gamma\left(\frac{1}{2}\right)$$

$$= \left[\frac{\pi}{4\alpha}\right]^{\frac{1}{2}} \qquad \alpha = \frac{h^2}{8ma^2 k_B T}$$

$$= \left[\frac{\pi . 8ma^2 k_B T}{4 . h^2}\right]^{\frac{1}{2}}$$

$$\therefore\ q = \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{1}{2}}} . a \qquad \boxed{\Lambda^2 = \frac{h^2}{2\pi \underline{\underline{m}} k_B T}}$$

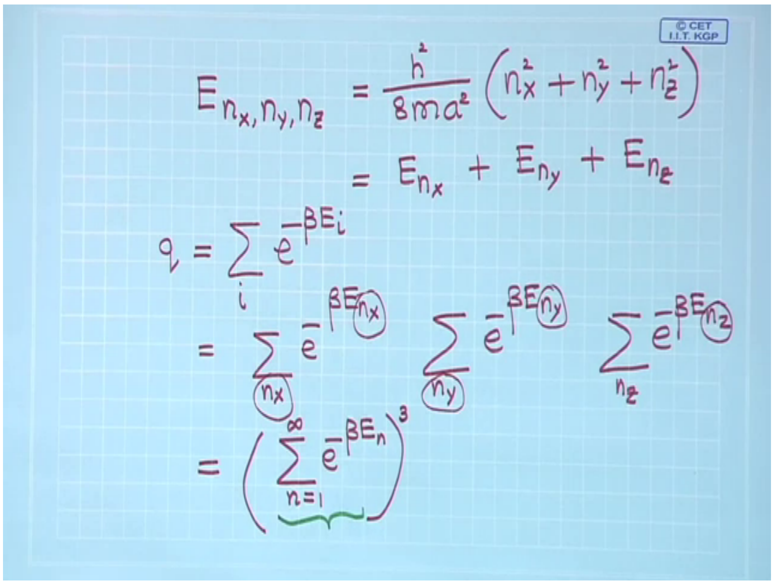
$$\therefore\ q = \frac{a}{\Lambda} \qquad \Lambda = \Lambda(T).$$

So, my small q now turns out to be 1 by 2 into root alpha into gamma half, do you know what the value of gamma half is? Yes, the value of gamma half is root pi. So, what I have here is pi divided by 4 alpha to the power of half, now I do not know the definition of alpha and that is equal to, H square divided by 8 m 8 sorry 8 m a square into k b t, I put it back over here what do I get I get this is pi divided by 4 into H square into 8 m a square k b T to the power of half. So, the final expression that I get is 2 pi m k T by H square to the power of half, and I have taken the a outside, now this is a quantity that I am going to use and you can very easily confirm that it has a dimension of length, and I am going to inverse of length and I am going to define lambda as lambda square as H square divided by 2 pi m k t. So, what is the final expression for q, that is equal to a divided by lambda, now have a look at the definition of lambda.

Lambda is a function of temperature. So, where does the thermodynamic information enter over here, it enters here in terms of the temperature, the and does it depend on the volume no and therefore, I would say that lambda is a function of temperature and temperature only, it does have a dependence on the system property, can you identify which system property, it is depending on yes it depends on the mass of the particle which constitutes the system. So, lambda this is known as the Brawley thermal wavelength, that is giving us the temperature dependence explicitly the temperature dependence of the single particle partition function in this treatment and that is exactly what we have shown here.

Now, what happens if I have this single particle, but it is not present in a 1-dimensional box, but it is present in a 3-dimensional box?

(Refer Slide Time: 28:51)



© CET I.I.T. KGP

$$E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}\left(n_x^2+n_y^2+n_z^2\right)$$

$$= E_{n_x} + E_{n_y} + E_{n_z}$$

$$q = \sum_i e^{-\beta E_i}$$

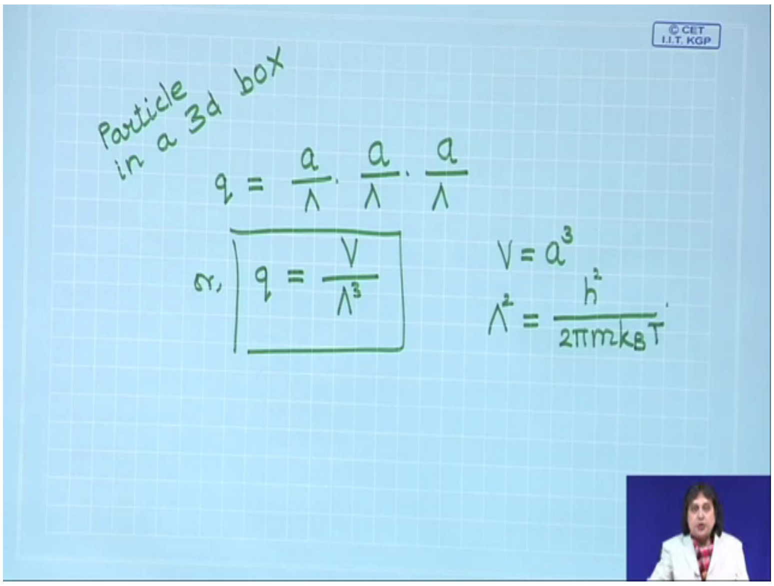
$$= \sum_{n_x} e^{-\beta E_{n_x}} \sum_{n_y} e^{-\beta E_{n_y}} \sum_{n_z} e^{-\beta E_{n_z}}$$

$$= \Bigg(\underbrace{\sum_{n=1}^{\infty} e^{-\beta E_n}}\Bigg)^3$$

So, in that case we would use the same type of argument because I would say that now each energy level is identified in terms of 3 quantum numbers n x, n y, n z, and these values are H square by 8 m a square into n x square plus n y square plus n z, square right and therefore, I would say that this is nothing but E n x plus, E n y plus, E n z, that is because whatever happens in the 3 orthogonal directions, they give you 3 independent degrees of freedom, and therefore, I can write the total energy Eigen state in terms of 3 independent contributions.

So, what is small q now small q is summation over all possible energy Eigen states, into e to the power of minus beta E I, now this can be written very easily as summation over all possible values of n x e to the power of minus beta E n x, similarly this is n y into e to the power of minus beta E n y, and the summation also goes over n z giving you e to the power of minus beta n z, as you see these are dummy indices right all of these 3 summations are the same. So, I can very easily write that essentially what I have is, I need value of this summation e to the power minus beta E n whole cube, the same summation being assumed 3 times in multiplication with each other.

(Refer Slide Time: 30:44)



Particle in a 3d box

$$q = \frac{a}{\Lambda} \cdot \frac{a}{\Lambda} \cdot \frac{a}{\Lambda}$$

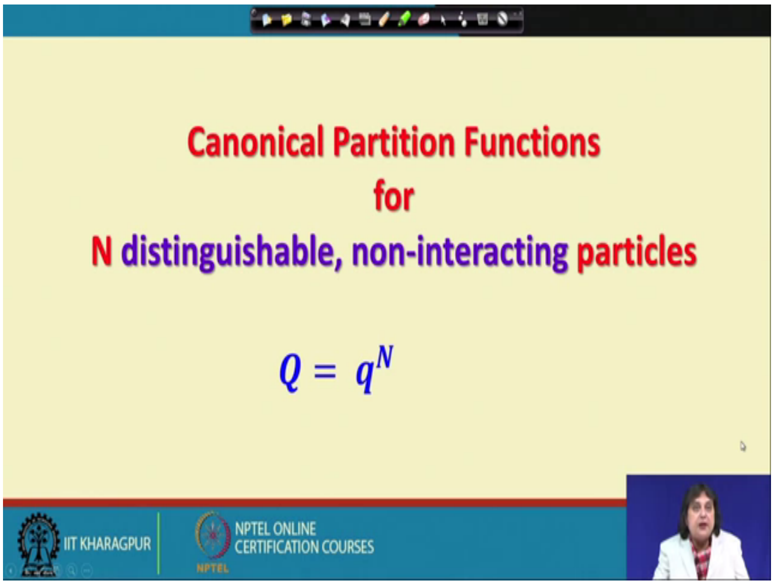
or, $$\boxed{q = \frac{V}{\Lambda^3}}$$

$$V = a^3$$

$$\Lambda^2 = \frac{h^2}{2\pi m k_B T}$$

Now do you know the value of this summation yes we did that for a 1 dimensional box right now and therefore, what I will have for a particle in a 3 dimensional box, is this that small q is going to be equal to a by lambda for the x direction, a by lambda for the y direction, and a by lambda for the z direction, or in other words I can write it as v by lambda cubed where I have assumed that I have a cubic box, such that v is equal to a cube and by definition lambda square is equal to H square divided by 2 pi m k t.

(Refer Slide Time: 31:32)



Canonical Partition Functions

for

N distinguishable, non-interacting particles

$$Q = q^N$$

So, in the last class, I have talked to you about how to write down the canonical partition function for capital, and distinguishable non-interacting particles as capital Q is equal to small q to the power of n. So, there you had n 1 dimensional systems that are independent of each other and today I have shown you 3 independent degrees of freedom associated with 1 particle. So, once again what I found that for every independent degree of freedom you have 1 small q contributing to the overall capital Q now we are going to use this ideas, and look at the application of whatever language that you have developed over here, and start talking about systems that we see every day. So, from the next class onwards we are going to see the, application of the introductory concepts of molecular thermodynamics that we have developed here.

Thank you.