Basic Statistical Mechanics
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Lecture – 25
Ideals Gas of Diatomic Molecules: Microscopic Expression for Rotational and Vibrational Entropy and Specific Heat (Part 4)

Welcome back to the course continued course on statistical mechanics. I hope you are having fun. Good morning or good afternoon wherever you are. So, we continuing with the basics and we did the monatomic gas in a very detailed form the reason of that wanted to you to go through the working of monatomic gas. It is not just monatomic gas is the simplest system. But it also you get the beautiful wonderful stuff that is used repeatedly which is kind of unbelievable.

There are giving that it is such a simple thing. But then I always draw the analogy to quantum mechanics. In quantum mechanics you have simple systems like particle in box, harmonic oscillator, rigid rotators. But those three models play enormous role in condensed matter science and physical chemistry. The particle in a box you know goes over to be used in explaining spectra of conjugated polymers like butadiene and dependence that a 8 ml square term.

Then it goes on to use as I showed in the last class the density of states and that is the model of free electron gas a very well-known model and with its root over energy dependence of density of states. That plays very important role. So, there is amazing that how so if you read the book that is given, I was done by Feynman statistical mechanics. You will find that and also Landau lifshitz the statistical mechanics these two are the best books in the field.

Earlier things who dealt with foundations and earlier parts so then you will find that are amazing that how much importance this very simple results find in those master books of those masters. So, now I want to spend some more time with that because we have again done it little but we did little in bit of hurry. Now, I want to review and now again it is kind of you can say that we did fast in as I analyzed your painting, painting of a wall we do it in not in one shot.

You paint it once and then you paint it again any wait for his time let it dry then you paint it in the final coat. Usually the third coat that comes and we through that you know the way our mind also works it very much like that we get to do. So, now we will do term that is ideal you know ideal and that it is diatomic. So, now we have not monatomic spheres but we have molecules like nitrogen. We have more of oxygen you know this kind of molecules.

Then we will do polyatomic also which will particularly we talk of water and we will talk of ammonia and some other molecules. So, first we will do diatomic then we will do polyatomic and the equations you might have seen before but it will be done more rigorously now and need more connection to the real world. Okay, so let us start then.

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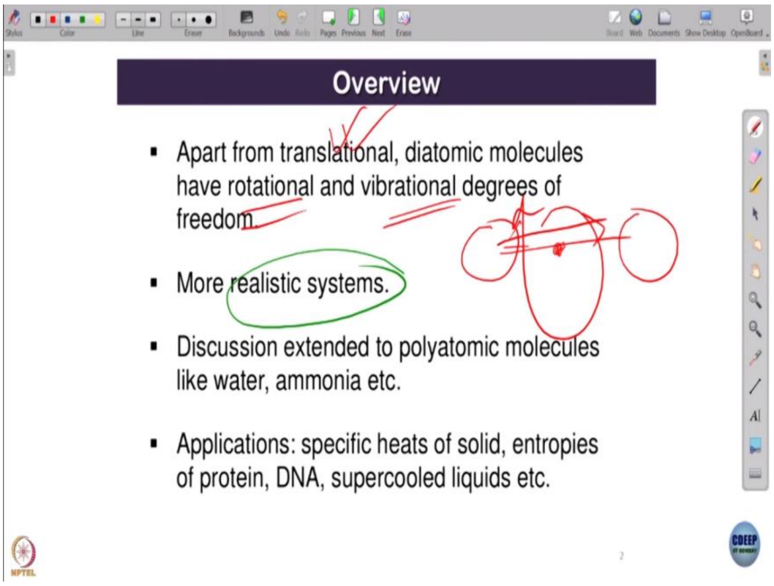

Overview

- Apart from translational, diatomic molecules have rotational and vibrational degrees of freedom.
- More realistic systems.
- Discussion extended to polyatomic molecules like water, ammonia etc.
- Applications: specific heats of solid, entropies of protein, DNA, supercooled liquids etc.

So we now have in case of molecules that these molecules are more realistic systems and that they continue to have the (if this is the diatomic molecule) they continue to have translational motion of the centre of mass but they also vibration their vibration and they have rotation. Now, we have to know translational part we have done and we can now you have done a law.

Probably a lot of these things that you go to a reduced mass description where I can consider translation is that of the centre of mass with m1 m2 by m1 by m2 the reduced mass of that and if they are the same then it becomes half. But we do we have to take care of now rotation and we do have to take up vibration and as I repeatedly say will again go back to quantum mechanics and find the energy levels from the vibrational rotation and use them.

We can also do it classically we can also find out the rotational kinetic energy and vibrational kinetic energy and if you can integrate them the same way we did in the translation. However, in translation we did both classical and quantum. See we basically did classical when you evaluate the partition function but when you went to density of states we did quantum.

And quantum show if I evaluate the partition function from the quantum particle in a box energy levels then I temperature limit I will go over to quantum mechanics. That you can work it out yourself or we will does somewhere down the line. However, in the rotational vibration things a little bit dicey particularly in case of vibration. In vibration vibrational frequencies many times in thousands of centimetre it was like OH is stretching 3600 centimetre inverse.

And you know one $k_B T$ at 300 K is 206 cm^{-1}. So now thermal energy these so the energy of these molecules are 15 times more than thermal energy. So that means gap between two vibration energy levels is 15 times $k_B T$ and that you cannot treat by classical mechanics in work. So energy levels are discrete and you have to do it quantum mechanical not and the situational rotation is not that add adverts to classical mechanics.

But it has also need to be treated quantum mechanically particularly in low temperature. We will see high temperature we can still get away by doing classical mechanics but not at low temperature so. Then also as we said that many we need the talk of vibrations in many things and again what do we learn from the class is simple non ideal diatomic and polyatomic gas. We will go over to very complex systems.

That is my reason to do these systems repeatedly because in this in chemistry in physical chemist we need this much more than physicist do not need them that much. Physicist very easily go to interacting systems and they do up general phenomena like phase transition but we in physical chemist we think of the molecules they are flowing from one part to the other they are undergoing a chemical reaction.

And when they undergo a chemical reaction then entropy changes the amount of entropy changes in a chemical reaction or the vibrational degrees of freedom that play a role in chemical reaction or spectrum vibrational spectroscopy rotational spectroscopy. So we are more in the microscopic world and we explaining our mandate are to explain these properties and that require a much more detail understanding of the spectrum. So let us continue then with this after this motivation.

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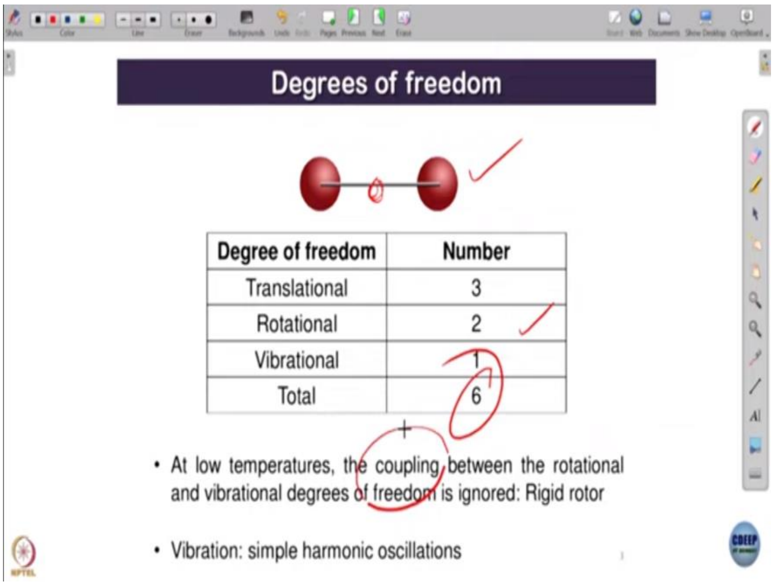

Degrees of freedom

Degree of freedom	Number
Translational	3
Rotational	2
Vibrational	1
Total	6

- At low temperatures, the coupling between the rotational and vibrational degrees of freedom is ignored: Rigid rotor
- Vibration: simple harmonic oscillations

So the data so consider just as diatomic you can consider nitrogen, oxygen then we have translational degrees of freedom of the centre of mass that is three. Then you rotate like this you know in a molecule it can rotate like these I can rotate like that these rotation does not change anything. So we have two rotational degrees of freedom and we have this stretching vibration and the vibration degree.

So freedom the total number of degrees of freedom is six and then there is interesting things that come in which at the experimental observable things and gives us very important properties. So one of the reason we are so interested physical chemistry is so interested in vibration and rotation is that there is of through vibrational spectroscopy through rotational spectroscopy we these some of the things which we can access to like an annulmacy of vibrational frequencies experimentally we get through a expert vibrational spectroscopy.

Then the molecules are not harmonic, we will assume your harmonic but there are an harmonic otherwise they will not undergo a bond breaking even as all of you know that information about the anharmonicity. How when you puts them away how the bond weakens is very important quantity that we get through vibrational spectroscopy them rotation when molecule rotation they rotate very fast.

They get couples to vibration and called coroners coupling. That is a very important thing in the bond breaking event you know atmosphere high up in the atmosphere When molecules rotate very high temperature rotate very fast. So those are the things that the mandate of a physical chemistry and that is you know and so those very important information of the anomalies in or rotational coupling constants.

We get it from this study that I am going to tell you today. And these are the things I did not tell because I did not want to burden you but now we have to do these things and get what is called the layout of these real fruits of our study. Okay so we are talking about ideal gas, we are talking of molecules right now not interacting barely the kind of things I said here that they interact the coupling between that but we are going to ignore that now and we are going to do with a non-interacting.

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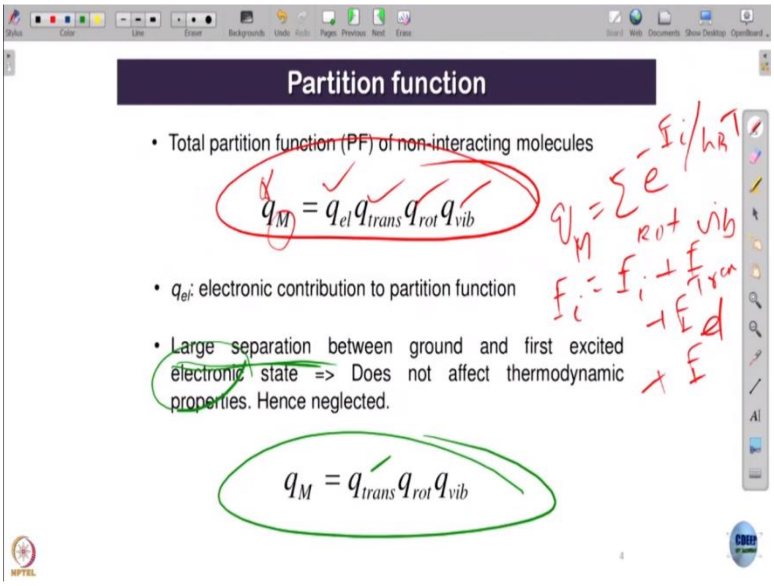

Partition function

- Total partition function (PF) of non-interacting molecules

$$q_M = q_{el} q_{trans} q_{rot} q_{vib}$$

- q_{el}: electronic contribution to partition function
- Large separation between ground and first excited electronic state => Does not affect thermodynamic properties. Hence neglected.

$$q_M = q_{trans} q_{rot} q_{vib}$$

So your ideal gas and the rotation translation vibration are not interacting with each other. And there are actually these interactions here become very important but we will do the later. So if I do not consider the coupling then I get a very nice very nice decoupling because energy levels are not coupled to each other. So we remembered my total partition function molecular partition function of a single particle.

That is why I use the notation q M stands for molecules then my qM sum over all the energy levels not energy states each individual energy level. We will we have to change that later as we go along and then the energy is some over-rotation vibration to energy is some over e – i – e - i- o + P vibration + e rotation vibration translation and plus electronic that is so then.

These are separates arms separates sums. So they go into a product. So, total molecular partition function is product of partition function of electronic the translation rotation vibration.

$$\boxed{q_M = q_{el} q_{trans} q_{rot} q_{vib}}$$

Now as I said much of these studies at room temperature ambient conditions the electron is in this ground state unless their electronic transition optically excited again a very huge branch of physical chemistry. If not, then we are we are looking at a large separation between ground and excited electronic states and that does not affect the thermodynamics most of the properties so we can ignore that.

So this we do not need to take top of electronic right now. Then my molecular partition functions become product of translation rotation vibration. We already have done translation now we go in to do rotational vibration and we will do the vibration first and then we will do the rotation and you will see a lot of very interesting things that I will talk to you today which I have not talked before and they are amazing particularly the amount of results we get and the natural phenomena we can directly access to by the vibration part just we translation I told you that it is very application but here you see even more dramatic things.

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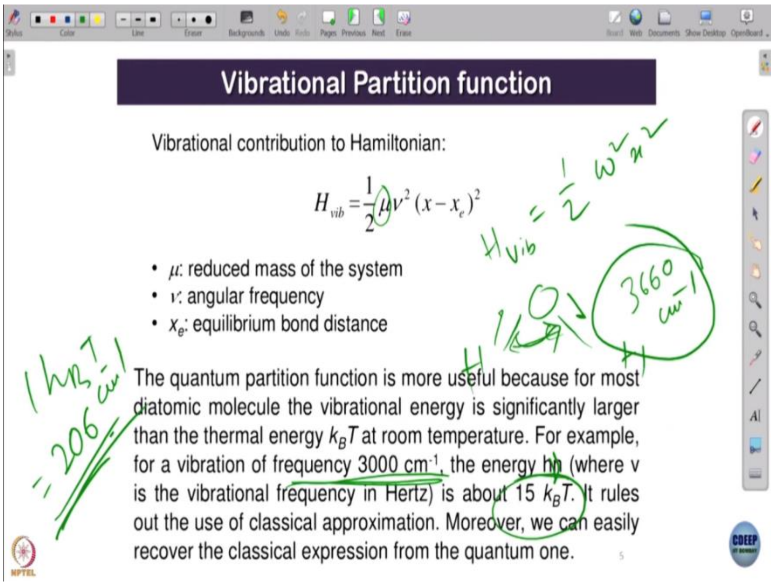

Vibrational Partition function

Vibrational contribution to Hamiltonian:

$$H_{vib} = \frac{1}{2}\mu\nu^2 (x - x_e)^2$$

- μ: reduced mass of the system
- ν: angular frequency
- x_e: equilibrium bond distance

The quantum partition function is more useful because for most diatomic molecule the vibrational energy is significantly larger than the thermal energy k_BT at room temperature. For example, for a vibration of frequency 3000 cm^{-1}, the energy $h\nu$ (where ν is the vibrational frequency in Hertz) is about 15 k_BT. It rules out the use of classical approximation. Moreover, we can easily recover the classical expression from the quantum one.

Okay so now we start we can write the vibrational Hamiltonian before you go to partition function we need the Hamiltonian and then we need the energy levels. So vibration is this 1/2µsquare you can write in many ways you know you can write how many times we are and we write up Omega square X square that is my favourite vibration and have not told you about this very accessible.

Okay so okay all right so now the quantum partition function is when you have almost a teeming molecules this is very important as I was taking that for example for a vibrational frequency 3000 centimetre inverse the energy H νH vis a vibrational frequency energy 15 k_BT and water oh h the symmetric vibration they are together going like these symmetric that is 3600 if I remember correctly centimetre and 1 k_BT 1k_B T 1 k_BT equal to 300 K in 206 cm^{-1}.

So we are talking of 36,000 cm^{-1} versus 206 cm^{-1}, so you are 18 k_BT. Then this bending is about 2,000 cm^{-1}. So we are talking of 10k_B T. So, these are very large numbers. That means right way by in vibration energy levels now vibration energy levels.

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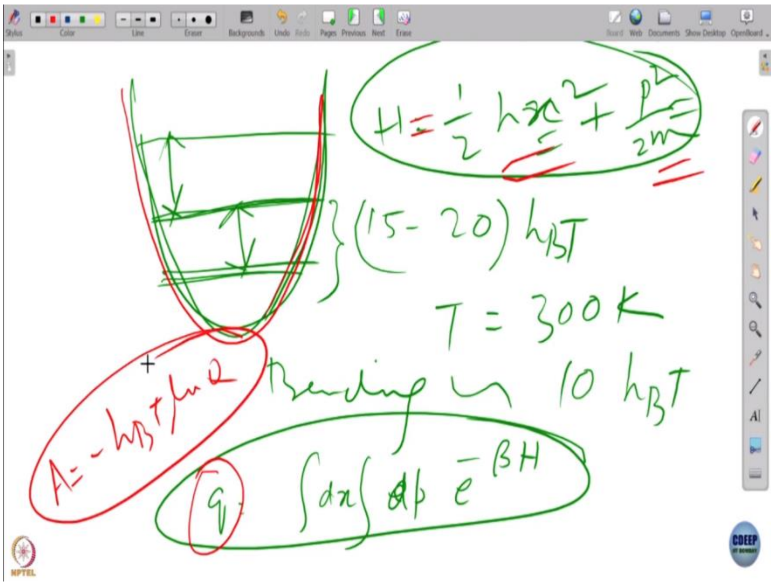

So if I talk of a vibrational potential energy surface then vibrational energy levels this gap is say 15 to 20 k_BT for water stretching and for bending it is bending it is you have about 10 K 10k_B T quite please 300 K. So this gap is large this gap is large, the zero point vibration energy vibration at the end easy first one. So this is the scenario we are looking at. And you have to we cannot do classical mechanics because classical mechanics what does not say mechanics a to say energy levels are continuous.

So I can go from one energy e to next one this small amount by 100 of k_BT 100 k_BT or something but that is not true that is true in translation where I have the next energy level just sitting next to each of the odd but not in a not in vibration and not even in rotation. Here the energy levels had spaced so wide that I cannot consider being continuum. So then I cannot do classical mechanics.

These prime case where I have to do quantum mechanics and the quantum mechanics aspect plays extremely important role and that we will see very quickly and most of the results that we do vibrational degrees of freedom even thermodynamics using classical mechanics by using half k x square. So I write half k x square then I write my having Toni on is vibration plus then p Square /2 m.

So and then I do the integration by dieting the partition function molecular partition function and doing integration there I am just do one dimension one particle and dx dp e to the power - beta H and then this double integral I do and I have both X and P as a Gaussian. I can do the integral that is a trivial actually two Gaussian integral. So, one again is half k x square no longer volume because the particle is now constrained.

Particle is constrained by this potential. So then I get root over pi by but pi m by k and then this is again 2 π mk_B T got 2 π k_BT 2 π k_BT /K from this term and 2 π mk_B T from this term. That is a classical partition function this trivial. And that I tell you it does not work it does not work in most of the cases. So we have to do the quantum mechanics. So this kind of classical approach which is trivial.

It is because my I am such a simple Hamiltonian and I can integrate and get the molecular partition function then go on and put the capital Q and then a equal to - k_BT ln K and I can go on doing my rest of the stuff but that does not work.

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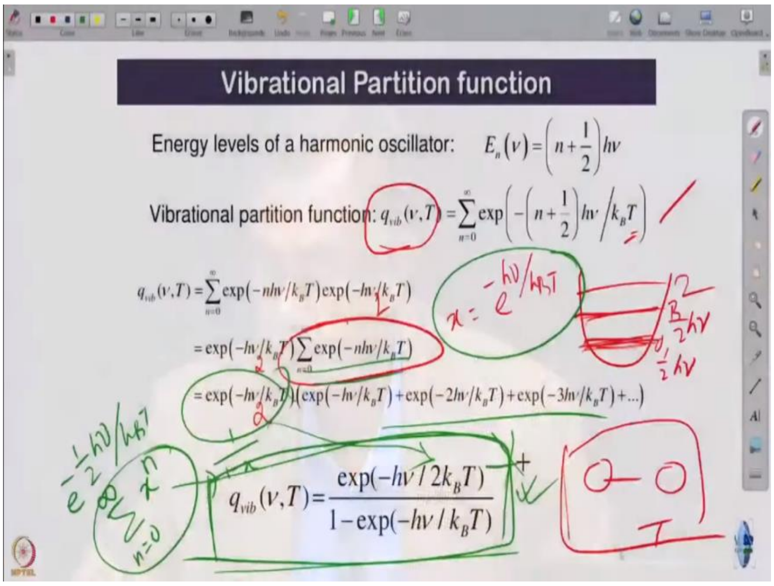

Vibrational Partition function

Energy levels of a harmonic oscillator: $E_n(v) = \left(n + \frac{1}{2}\right)hv$

Vibrational partition function: $q_{vib}(v,T) = \sum_{n=0}^{\infty} \exp\left(-\left(n+\frac{1}{2}\right)hv \Big/ k_BT\right)$

$$q_{vib}(v,T) = \sum_{n=0}^{\infty} \exp(-nhv/k_BT)\exp(-hv/k_BT)$$

$$= \exp(-hv/k_BT)\sum_{n=0} \exp(-nhv/k_BT)$$

$$= \exp(-hv/k_BT)(\exp(-hv/k_BT) + \exp(-2hv/k_BT) + \exp(-3hv/k_BT) + \dots)$$

$$q_{vib}(v,T) = \frac{\exp(-hv/2k_BT)}{1-\exp(-hv/k_BT)}$$

So now we have to do a little bit more so now in quantum occur you know the harmonic oscillator is, so these kind of energy levels that we have you know Schrödinger that solved the system for us that he also called particle in a box the one of the reason in quantum mechanics textbooks I told you before that you do not see any name. All the weight in hydrogen molecule because Schrödinger solved all of them.

There is very nice book collected works on quantum mechanics by Schrodinger and where you will see that he has solved if they taking particle in a formulation of writing an equation then solving it for particle in a box and solving for a harmonic oscillators one convenient rotated by hydrogen oxygen hydrogen molecule all the way is despite problems. I got that book very cheap in here. in Calcutta bookstore by paying couple of couple of rupees and there is a wonderful position that I had an old book somebody bound it.

There are some kind of notes here and there but that book was an eye opener for me that he goes and I feel much more much more understanding of the how quantum mechanics developed is very important historical statement. However now coming back we starting that is a result for statistical mechanics and here are the energy level so harmonic oscillator that energy levels this is zeroth energy level.

Zero one two and these in the energy of these is half h νand then and this is one plus half so is half h nu, this is 3 / 2 h nu. This why I would like that it goes I have to add it up now so the vibrational partition function we sum over these n zero to infinity up all the way, n plus half h νnekton by k_BT. This is my canonical single vibration partition function canonical partition function and I have this oblique that is why the temperature T is coming.

So that means my these harmonic oscillator which is oscillating here and these guy is oscillating but this is in a temperature bath with a temperature T and t plays a very important role because there allows the relative because of the energy gap ability weight of the different energy levels. You can easily see how why the many of the cases these particles zeroth order energy level plays such an important role.

That is in vibration such big deal to 0 vibrations there has been such a big deal for many other reasons but in thermodynamics that is very important. But even then even in zero vibrational level it plays a very important role. So now I can do this calculation because you know I take the half out so I am going to do that this h ν / 2 k_BT so q vibration is e to the power - H ν /T then I have a 2 k_BT here and missing here I have 2 T, then k_BI bring here.

This is correct in book but the when it was transferred from there it was this mistake was made. So, now e to the power - h ν / 2k_B T. So, this is the sum that I have to do and this is very easy right because if I put x equal to e to the power - h ν / k_B T if I make that into x this is my x then I have partition function becomes e to the power - half H ν /k_BT n equal to 0 to infinity x to the power n good that it starts from n equal to 0 to infinity and I know that this series when x is less than 1 this is nothing but 1 /1 over X all right and good. So, now this is become mine.

$$q_{vib}(V,T) = \sum_{n=0}^{\infty} \exp(-nh\nu/k_BT) \exp(-h\nu/2k_BT)$$

$$= \exp(-h\nu/2k_BT) \sum_{n=0}^{\infty} \exp(-nh\nu/k_BT)$$

$$= \exp(-h\nu/2k_BT)\,[1+ \exp(-h\nu/k_BT) + \exp(-2h\nu/k_BT) + \exp(-3h\nu/k_BT) +\ldots...]$$

So, this is h ν /2 k_BT that is in front that comes h ν /2k_B T and the sum this sum which the geometric series becomes 1 - x and x is e to the - 2 k_BT. So this is my partition function beautiful and neat expression and actually in this case Schrodinger did all the work giving us energy levels and now will have lot of fun with this expression. So, this is now by partition function and I am going to do some thermodynamics with that because I now know how to do, extract free energy from this.

I know how to extract entropy. I know how to extract specific heat terms of entropy which turns out to be excellent. We wrote a paper last year long paper and water and the whole thing of calculation of entropy of the vibrational mode. So, water but those are you inter molecular vibrational modes but low-temperature solid. This thing we will discuss and now and we will probably discuss more later but we will that is it sudden deafening to discuss it now. So now this beautiful expression that I have here I am going to use that.

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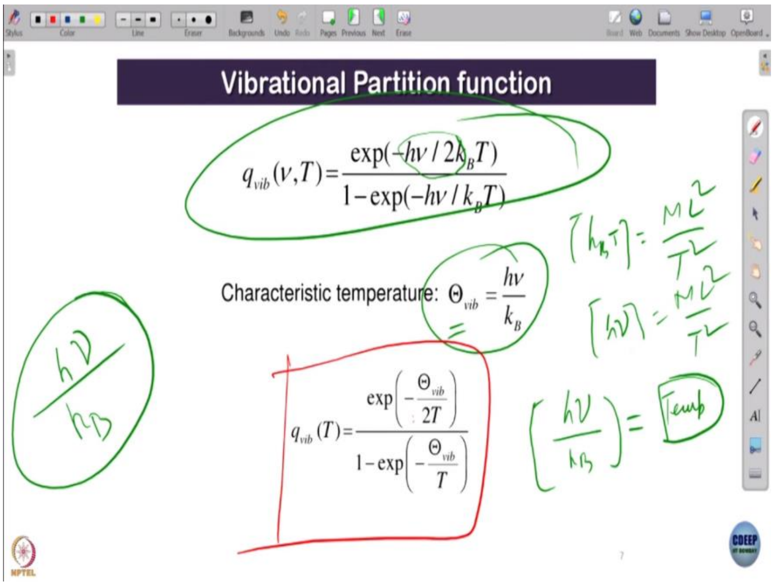

Vibrational Partition function

$$q_{vib}(\nu,T)=\frac{\exp(-h\nu/2k_BT)}{1-\exp(-h\nu/k_BT)}$$

Characteristic temperature: $\Theta_{vib}=\frac{h\nu}{k_B}$

$$q_{vib}(T)=\frac{\exp\left(-\frac{\Theta_{vib}}{2T}\right)}{1-\exp\left(-\frac{\Theta_{vib}}{T}\right)}$$

$\frac{h\nu}{k_B}$

$[k_BT]=\frac{ML^2}{T^2}$

$[h\nu]=\frac{ML^2}{T^2}$

$\left(\frac{h\nu}{k_B}\right)=\boxed{\text{Temp}}$

Okay, so again rewrite this expression because we love this expression beautiful p to the power - h ν / 2 k$_B$T 1 - h ν /2 k$_B$T so characteristic temperature. Now I introduce one thing I realize that that h ν /k$_B$ remember k$_B$T is energy the dimension of k$_B$T is energy and remember mr g ml square mass by t squared the dimension mass length and time.

k$_B$T is also energy h ν is also energy h ν is also energy, both are energy. So, now I realize then h ν /k$_B$ ν / k$_B$ has the dimension of temperature. This is the dimension of temperature that is now that because this must be dimensional temperature because it has to be dimension this because it is upstairs. Now, I define a temperature is very important characteristics things.

See, it is very interesting you have one universal constant Planck constant you have another universal constants k$_B$ and you multiply it by frequency and you get a temperature it is a beauty Planck's constant going to bank all state and the frequency. So, together define temperature and that temperature plays very important role. That temperature is denoted by theta vibration. You know vibrational temperature that the how hot a vibration is.

Now, I can rewrite introducing these notation that e to the power mivs theta by 2 t 1 - theta vibration by T. So, this is now my new my rewrite my partition function. Remember that is very beautiful thing but remember that to a factor of 2 is there. So, now I go and do the partitions function. So, these so this is the new vibration.

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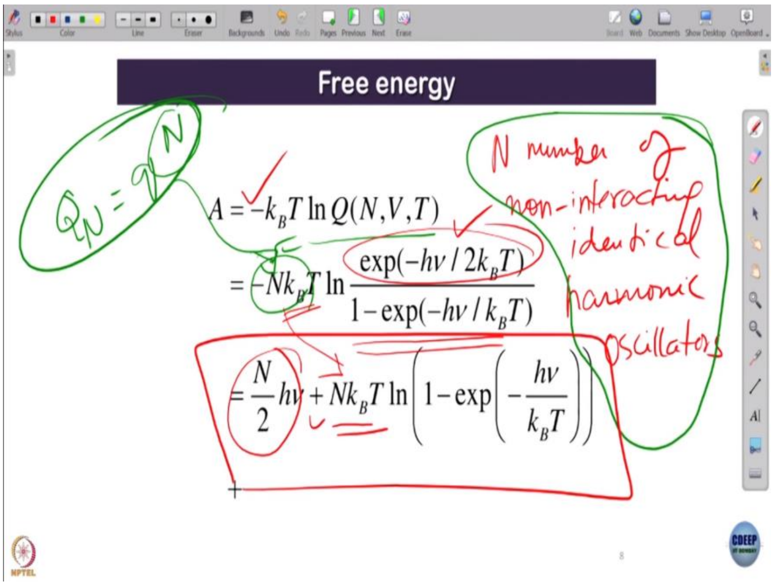

Free energy

$Q_N = q^N$

$$A = -k_BT\ln Q(N,V,T)$$

$$= -Nk_BT\ln\frac{\exp(-h\nu/2k_BT)}{1-\exp(-h\nu/k_BT)}$$

$$= \frac{N}{2}h\nu + Nk_BT\ln\left(1-\exp\left(-\frac{h\nu}{k_BT}\right)\right)$$

N number of non-interacting identical harmonic oscillators

Now, I want to go the free energy. So, free energy I know that there are n number of them. So, even n number of non interacting identical harmonic oscillators. So, that is the thing so then my Q n is q to the power n and then I write free energy equal to -k_B T ln Q and that n comes out this n comes out in front giving me pain here and then k_BT remains here so nk_B T and ln leave me ln e 2 divided /2 so this is just using the one previous slider clear speech.

So, now this is the I will go back to theta vibration again. So, free energy now is I can do something more. I note that remember we have to keep track of these -. So, this part has two parts. One part is the numerator part denominator part a numerical apart, then ln the exponential ln e to the power - x is l x. So, h ν comes out - and - becomes plus. k_BT comes denominator here that cancels this k_BT I get n /2hν so this is the first term that comes from there.

Now, these comes in the denominator the - sign that makes this - plus why get a plus here then I can in k_BT these m k_BT here and then ln 1 - h ν/ k_BT remember 2 is not here in the denominator. So, this is the free energy. So, free energy of n number of harmonic oscillator is given by this quantity. Okay, these well and good no need to go into much time here now.

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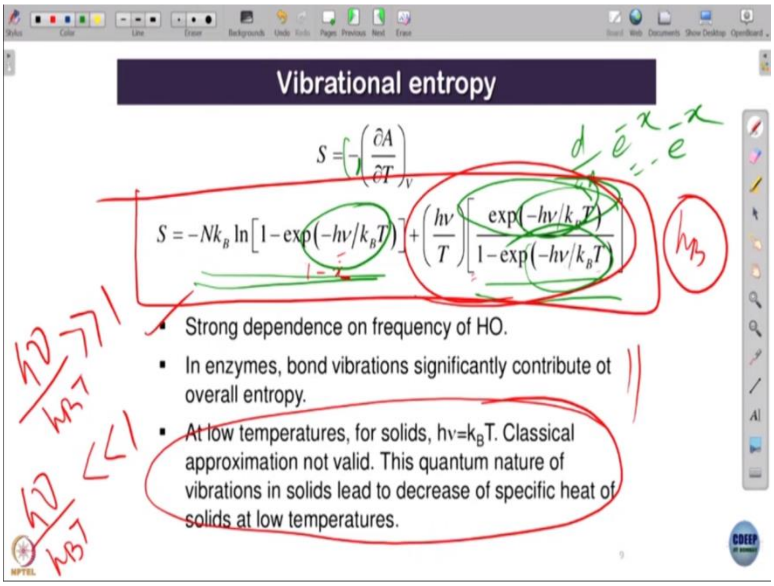

Vibrational entropy

$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

$$S = -Nk_B \ln\left[1-\exp\left(-h\nu/k_BT\right)\right] + \left(\frac{h\nu}{T}\right)\left[\frac{\exp\left(-h\nu/k_BT\right)}{1-\exp\left(-h\nu/k_BT\right)}\right]$$

- Strong dependence on frequency of HO.
- In enzymes, bond vibrations significantly contribute ot overall entropy.
- At low temperatures, for solids, $h\nu = k_BT$. Classical approximation not valid. This quantum nature of vibrations in solids lead to decrease of specific heat of solids at low temperatures.

$d\, e^{-x} = -e^{-x}$

$1-x$

k_B

$\frac{h\nu}{k_BT} >> 1$

$\frac{h\nu}{k_BT} << 1$

I want to calculate the entropy. This is where the fun starts. So, I do that. So, my free energy is here. I take derivative with respect to temperature. Remember that has no temperature, this term has no temperature. So, that goes to zero and then I have here I have two terms one is that one is this temperature and this temperature here so when I take the derivative I get two terms and that they are shown here.

One term is these so one term is just this term I take the derivative with respect temperature these disappears and I just get this term. Other term in KBT will remain. I go and take derivative respect to that is little complex because first ln x is 1 over x so that will go in the denominator. Then I have to go inside and take it derivative and I know when I take a derivative this term goes to 0 then these - comes with - but then I take derivative of that exponential comes down - - become plus.

However, I have t in denominator so, another - come then -t square. So, that - will be carried through - but that 1 over t Square 1 of the 1 over t square get cancelled by t, so I get 1 over t remain and Boltzmann constant gets cancelled. That what happened and then when I do all that I told you one term is the first term that comes and here because this is after taking derivative of exponential d / dx e to the power - x is - e to the power - x.

So, that remains from that term and as I told you one goes to be denominator and goes to denominator and there is one more negative sign here. So, what happens in that derivative if we have the in the derivative we have the following thing. There is one negative here and that get cancelled / these negative another negative comes from here third negative but then fourth negative comes from here so I get a positive term.

So, this is my definition of the entropy. This plays a very important role in many calculations. So let me mine so this is the entropy of the n number of harmonic oscillators. This Look at that is a very strong dependence on frequency νvery strong dependence. It is in e to the power – hν and this is over e to the - h nu. Now, when let us consider some things.

First a strong dependence on in there is one term then the enzymes and many molecules DNA and many cases the bond vibrations do this is something which is amazingly interesting but we will talk of it a little bit a little bit now this is this particular issue now. Before I do that let me consider the following thing that what happens when μ is small. There are some cases where μ can be small like you know in iodine. In iodine, vibration is about 500 cm^{-1}.

There are some vibrations which are even smaller in the molecular vibrations they can be smaller of the order hundred centimetres. So, even needs some collective vibration and now explain what the collective vibration is? Collective vibration, when you put many molecules together then the their translational modes they are constrained their translational modes forgot but number of degrees of freedom must be maintained, right.

So, say I have n number of molecules put together there three and vibration then we know that they will become three of n - 5 linear 3 and- 6 even nonlinear degrees of freedom that come. So, these degrees of freedom go over to the us, call them inter molecular vibrations. So, they could be rotation or with these are like consider. Then there are rotations of this kind or even long polymer chain there are many motions which are bound motions but there are very low vibration molecules.

And so then they can be low vibrational, low frequency modes and then you can start playing certain games. You can say ok if μ is small let me consider m is more when μ is large then we can easily see where μ is large temperature kept fixed then e to the power - h2 / k_BT goes to zero and I have a ln one and ln one goes to zero and then I say I am okay I go to new very large very large here is these quantity would go to zero and then I have these quantity goes to 0.

I have about only one compared to 1 this is small hv/ k_BT is large again hv / k_BT large means this term goes to 0. That means if I look at the limit large frequency limit that hv/ k_BT much later than 1 if I look at that limit then this quantity goes to 0 because of this small quantity in front but easy to do – hv/ k we can kill it. These will go to 0. So, this term will go to 0, hv/ k_BT will go to 0 will become very small I have left with 1 and as already escaped in.

It also Entropy's going to go to 0. So, entropic contribution of a large vibrational mode is negligible. That is why many times in molecular calculations we do not consider the contribution of entropy of additional modes; this is a very important very important statement that I am making. However, that is not the case in this case of collective modes that I said you know the collective modes now let us see that low frequency modes.

That mean what would happen in low frequency mode. Now, let me consider the other limit that hv. k_BT that is much lesser than 1 believe me there are cases like that in collective modes that in water in many cases that 10 centimetre inverse, 20 centimetre inverse and in solids you know and less than 10 cm^{-1} modes are there and they play very important role we do it amazingly nobody thought that they will play such an important role but they play a role and we shall come to that in a minute.

So, now when now μ becomes very long then I can expand that I now say hv/ k_B T small I can explain deliver - x and that e to the - x I can write as 1 - x. This one cancels this one and these become + x. So, I have n $k_B$hv/ k_BT, k_B k_B gets cancelled and I have hv/t sitting here which is nothing by my I have done it before. It isv/ t sitting in a come in front. Now, let us look at this quantity.

Now, hv/ k this is small so, again I can expand that I can expand that so this will become 1 - h 1 gets cancelled I have get hv/ k_B T coming out from here with a + sign in the denominator this h du / k_BT I said 1 – hv/k_BT but since hv/ k_BT must less than 1 I can neglect with next term. So, there were xv/ k_BT that so I have one on from numerator denominator.

I have hv/ k_B T and that now cancels hv/t and I am left with a k_B term here and that goes upstairs so it has I get adjust the k_B contribution from this entire things. And I get a contribution from here hv/2 from here. So, low frequencies have a very different contribution to entropy they come up with a significant contribution. So, while high temperature, high frequency modes make no contribution to entropy because h 2 by if they are all in exponential.

However, they are all in exponential like this term you like this term but in a low frequency as I just discussed a significant nonzero contribution comes and that play extremely important and that is where these seemingly trivial calculation that you are doing play the enormous the important role in understand in a very large a large important phenomena and that means nothing but the specific heat of solids now specific heat of Solid specific heat of solids low-temperature solids is an extremely interesting thing.