Basic Statistical Mechanics
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Lecture – 24
Ideal Gas of Diatomic Molecules: Microscopic Expression for Rotational and Vibrational Entropy and Specific Heat (Part 2)

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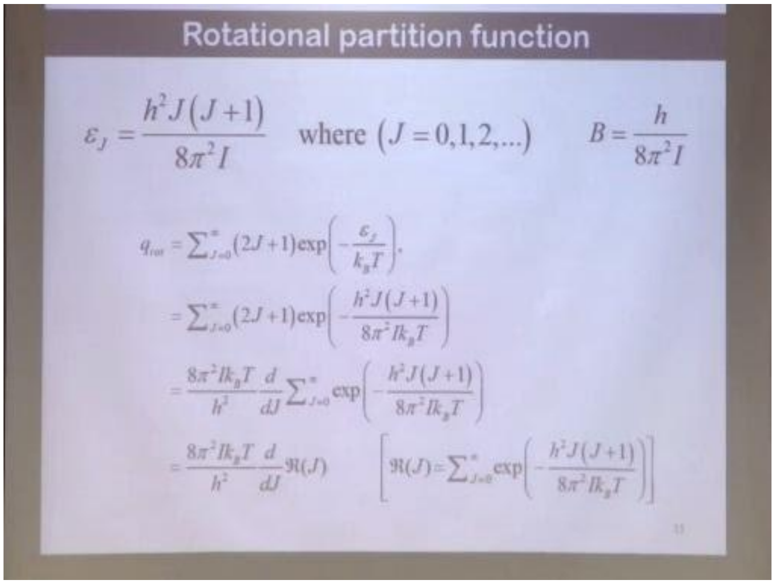

Rotational partition function

$$\varepsilon_J = \frac{h^2 J(J+1)}{8\pi^2 I} \quad \text{where } (J = 0,1,2,\ldots) \qquad B = \frac{h}{8\pi^2 I}$$

$$\begin{aligned} q_{rot} &= \sum_{J=0}^{\infty}(2J+1)\exp\left(-\frac{\varepsilon_J}{k_B T}\right). \\ &= \sum_{J=0}^{\infty}(2J+1)\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right) \\ &= \frac{8\pi^2 I k_B T}{h^2}\frac{d}{dJ}\sum_{J=0}^{\infty}\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right) \\ &= \frac{8\pi^2 I k_B T}{h^2}\frac{d}{dJ}\Re(J) \qquad \left[\Re(J) = \sum_{J=0}^{\infty}\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)\right] \end{aligned}$$

Vibration is done, we are now going to go to rotation. Again, what the game we play? We have a diatomic which is rotating and then we go and calculate the sort this Schrodinger equation assuming a rigid rotator. Remember rigid rotator of quantum mechanics, okay. And what are the energy levels? Important thing is that I is moment of inertia in the denominator just like in translation a would be in the denominator.

So in moment of inertia mode energy levels get watched together. Okay, so this is the we usually use this notation but we I do not see where I use this one, okay. So now important thing one very important thing in rigid rotator that given J is the quantum number like n there was the quantum number in harmonic oscillator, J is the quantum number. However, here it comes with the degeneracy. If you remember rotational levels come with degeneracy.

And here, any of anybody remembers raise hand. Who remembers the rotation has degeneracy? Okay, one guy remember, two guys remember these two does not three remember others do not that. So and when there is a degeneracy then it is trivially partition function is written trivially.

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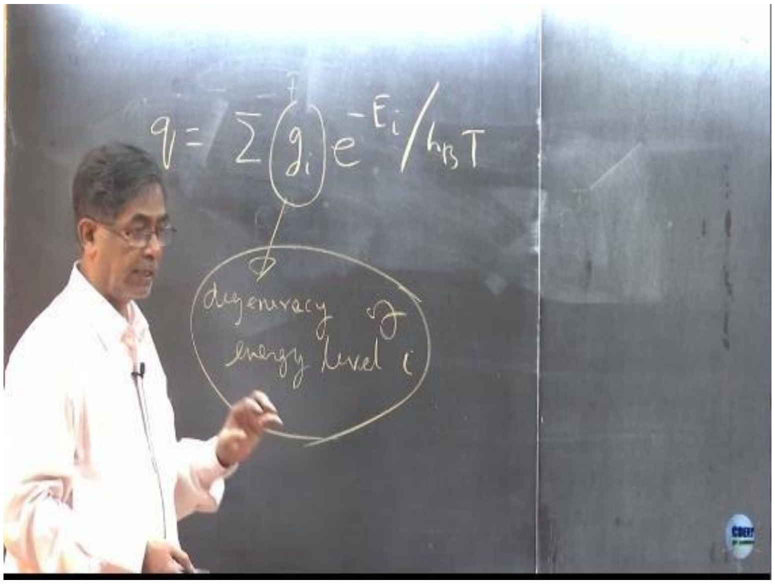

So this factor is the degeneracy factor, degeneracy of energy level, okay. So it is just a weight, you know g is the universally used as a weight factor; it is the density of states; g is used to the density of states and so it is essentially weight of that; like in the radial distribution function again g used so g comes we use g as a; is almost universal thing in a density of states and so this is the same thing.

So this is the density of states 2J + 1, so I put it there and this is the energy, so I put the energy x square J J+1. Now something very interesting here, did you notice that? That, if I take derivative of that, I get that quantity, there is one beauty. So then I write this quantity but if I take the derivative of that what happened J square + 1 become 2J+1 but I also get out h square / 8π I square I k_B which I should then compensate for and that is compensated here, okay.

So now I write the partition function in a very neat way in this in the following form. Looks pretty neat, very nice but unfortunately, we cannot evaluate it. Nobody has been able to evaluate this. So our rotational partition function remains little bit stuck. This has to but if they of course these days it is trivial; before people use to have tables and people tabulated tables for all rotation or different molecules; our times we use to have tables but now you do not need tables, tables have disappeared because you can put in one line in computer.

$$
\begin{aligned}
q_{rot} &= \sum\nolimits_{J=0}^{\infty} (2J+1)\exp\left(-\frac{\varepsilon_J}{k_B T}\right), \\
&= \sum\nolimits_{J=0}^{\infty} (2J+1)\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right) \\
&= \frac{8\pi^2 I k_B T}{h^2}\frac{d}{dJ}\sum\nolimits_{J=0}^{\infty} \exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right) \\
&= \frac{8\pi^2 I k_B T}{h^2}\frac{d}{dJ}\Re(J), \\
&\textit{where} \\
\Re(J) &= \sum\nolimits_{J=0}^{\infty} \exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)
\end{aligned}
$$

So you see now in this case there is a very strong dependence on moment of inertia I, okay very strong dependent on moment of inertia I as I told you it is very important. So low temperature but we can though we cannot evaluate this one we can evaluate a high and low temperature because at low temperature there is one case, high temperature one case, the high temperature this becomes small, low temperature this becomes very low temperature this becomes so large; these becomes large and so negative it goes to 0, so low temperature only first term would be enough, okay.

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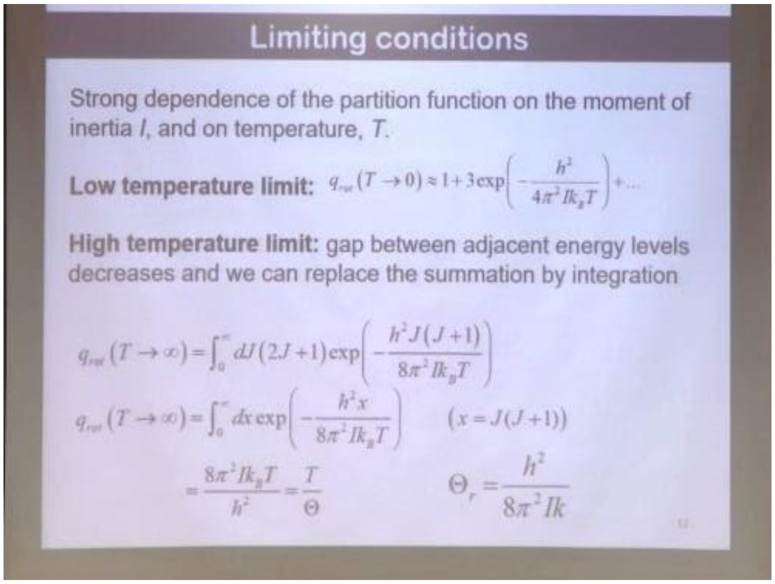

Limiting conditions

Strong dependence of the partition function on the moment of inertia *I*, and on temperature, *T*.

Low temperature limit: $q_{rot}(T \rightarrow 0) \approx 1 + 3\exp\left(-\frac{h^2}{4\pi^2 I k_B T}\right) + \ldots$

High temperature limit: gap between adjacent energy levels decreases and we can replace the summation by integration

$$q_{rot}(T \rightarrow \infty) = \int_0^{\infty} dJ(2J+1)\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)$$

$$q_{rot}(T \rightarrow \infty) = \int_0^{\infty} dx \exp\left(-\frac{h^2 x}{8\pi^2 I k_B T}\right) \qquad (x = J(J+1))$$

$$= \frac{8\pi^2 I k_B T}{h^2} = \frac{T}{\Theta} \qquad \Theta_r = \frac{h^2}{8\pi^2 I k}$$

So and then low temperature I can just evaluate this J = 1 becomes 1; J = 0 become 1 then I keep; I need to keep only one term J = 1 that is 3, okay and then I get this term and that is pretty good, okay. So this is the partition function at low temperature. High temperature now gap between energy levels become very small so I can now replace this sum by an integral, okay. Is that clear? One thing becomes very low like translational partition function.

I can replace the by an integration and this integration I can evaluate; anyway I know that this is d/dj and d/dj is trivial to integrate because you just evaluate in the two limits; this integration is done for you and then that is this quantity. So in the high temperature your rotational partition function is T 8 π square I/k_BT, now you define and since these quantity has a dimension 1 over temperature then I define these temperature as a rotational temperature.

$$q_{rot}\left(T \to \infty\right) = \int_0^\infty dx \exp\left(-\frac{h^2 x}{8\pi^2 I k_B T}\right),$$

$$or,$$

$$\boxed{q_{rot}\,(high\ temperature) = \frac{8\pi^2 I k_B T}{h^2}}$$

These things are important because these can tells you(rotational temperature tells you) below this temperature you have to be at low temperature limit; above the temperature you have to treat as high temperature. Similarly, in vibration, θ vibration tells you there is a crossover temperature; below that and above that things starts changes: of course it does not change at the temperature but it kind of goes through the swing, so it is gives a very good estimate of doing those quantities.

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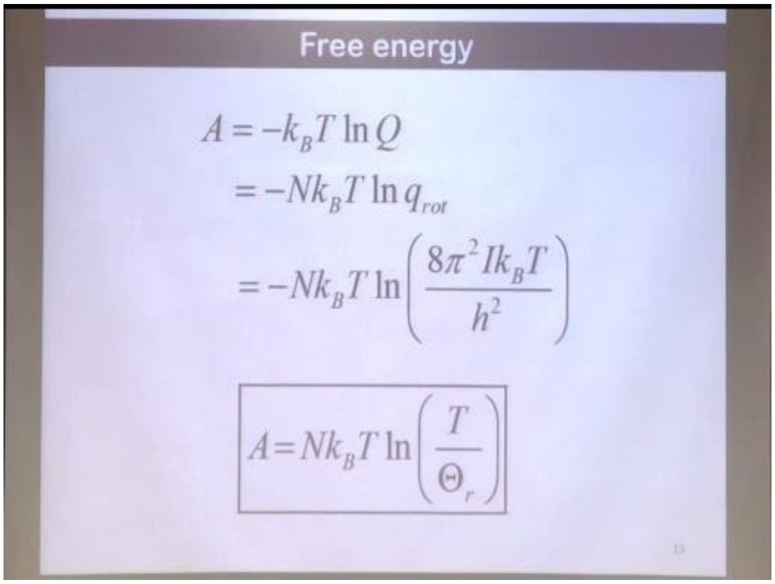

Free energy

$$A = -k_B T \ln Q$$
$$= -Nk_B T \ln q_{rot}$$
$$= -Nk_B T \ln\left(\frac{8\pi^2 I k_B T}{h^2}\right)$$
$$\boxed{A = Nk_B T \ln\left(\frac{T}{\Theta_r}\right)}$$

Now we go again and do the partition function –

$k_B T$ ln Q. Again now I have a bunch of rotators which are non-interacting; I have N $k_B T$ ln q rotation. Now this q rotation is ln 8п square / 8 $k_B T$. This is, I am doing now the high temperature. And as I told you many of the cases high temperatures is reasonably okay because it is 50-80 centimeter inverse, you totally say 300 Kelvin 200 centimeters you are not great leave but still you can get away; you are better than low temperature limit.

$$A = -k_B T \ln Q$$
$$= -Nk_B T \ln q_{rot}$$
$$= -Nk_B T \ln\left(\frac{8\pi^2 I k_B T}{h^2}\right),$$
$$or,$$
$$\boxed{A = Nk_B T \ln\left(\frac{T}{\Theta_r}\right)}$$

And then that is this quantity N comes out because q is q rotational to the power n that comes out – $Nk_B T$ ln 8п square Ik_B T / h square. And then I use my θ_r again, so I have this neat expression of free energy $Nk_B T$ ln / θ_r .

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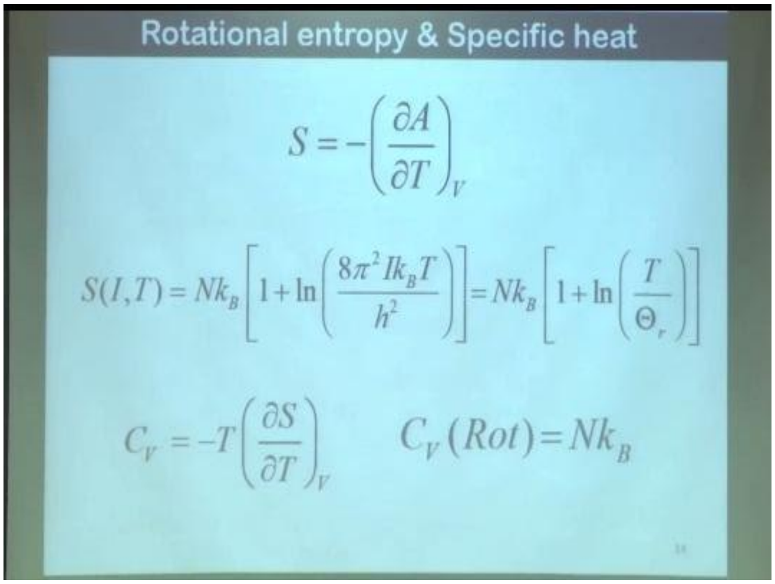

Rotational entropy & Specific heat

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

$$S(I,T)=Nk_B\left[1+\ln\left(\frac{8\pi^2 Ik_BT}{h^2}\right)\right]=Nk_B\left[1+\ln\left(\frac{T}{\Theta_r}\right)\right]$$

$$C_V=-T\left(\frac{\partial S}{\partial T}\right)_V \qquad C_V\,(Rot)=Nk_B$$

Okay, remember that now I play the game again. I find the rotational entropy, that said term turned out to be extremely important and modern days that what is the rotation entropy, it was not even in our time when we studied these things, we really thought Sackur – Tetrode equation by translational partition function only good for PV = k_BT beautiful derivation. Then vibration we liked it very much.

We knew because side by side solid state physics or solid state chemistry was taught so we knew that rotation we did not pay any attention to. However, it turns out I will tell you why it is so important. So this is the entropy. Now I take these derivatives from here, this quantity neat and clean and very simple so I can calculate the rotational entropy, right. I go there you take the derivative; one term comes from here and other term comes from here.

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

$$or,$$

$$S(I,T)=Nk_B\left[1+\ln\left(\frac{8\pi^2 Ik_BT}{h^2}\right)\right]=Nk_B\left[1+\ln\left(\frac{T}{\Theta_r}\right)\right]$$

And when I do that, I get this is the first term; this is the second term. So this is the beautiful expression for rotational entropy then I take the specific heat just like I did in vibration and then I get derivative of that, this term does not carry exactly parallel to vibration so then these ln become 1 over T / θ then a and it becomes one over T and that cancels the T cancels the one over T -, - and all these things will become Nk$_B$. Okay.

$$C_V(Rotation) = Nk_B$$

So rotation, since the beauty is that rotation; specific heat is Nk$_B$, vibration you already know, so it is become R, okay. Now we will just talk of some of the thermodynamics. So we have now derived all the things vibration; translation I did in the morning, we did vibration and rotation and have to come back and do little bit of monotony but that I will do in later because there is still some amount of way to go and as I told you that I wanted to start fresh and do this good job to diatomic because that is not done in a unified way. I have not seen; even the all these stat-mech books I have not done a good job in bringing the whole picture clearly to a, okay.

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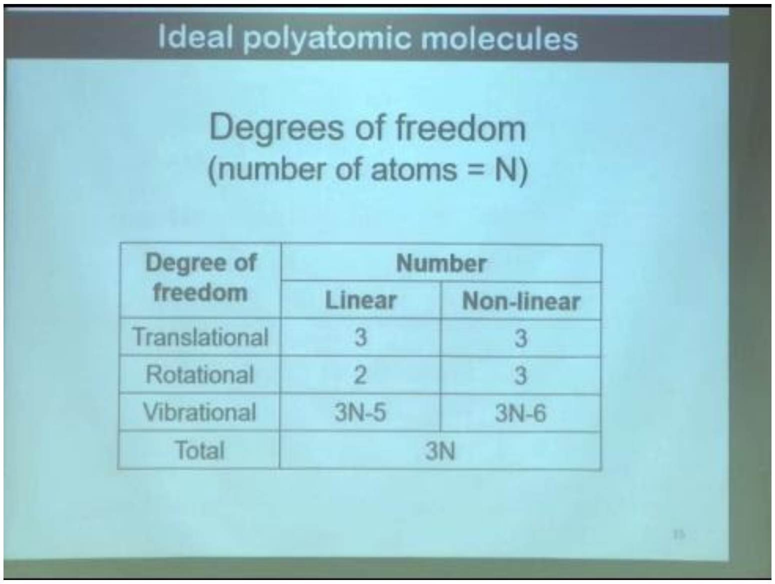

Ideal polyatomic molecules

Degrees of freedom
(number of atoms = N)

Degree of freedom	Number	
	Linear	Non-linear
Translational	3	3
Rotational	2	3
Vibrational	3N-5	3N-6
Total	3N	

Now let us see some examples again so ideal we go to now okay before you go to the ideal polyatomic molecules, we did ideal monatomic, ideal diatomic and polyatomic. For example, linear 3, translation 2, rotation, these are the vibration these are standard questions in oral. Sometimes even in PhD interview of course even in a job talk, even in job talk sometime we ask the suddenly, the faculty candidate also these questions.

So if the; we are nasty, we ask that and many times we find; by that time, they are giving a job talk they have forgotten these basic things, okay. So you know all of this that in a nonlinear 3 rotational degrees of freedom so 3N – 6, okay.

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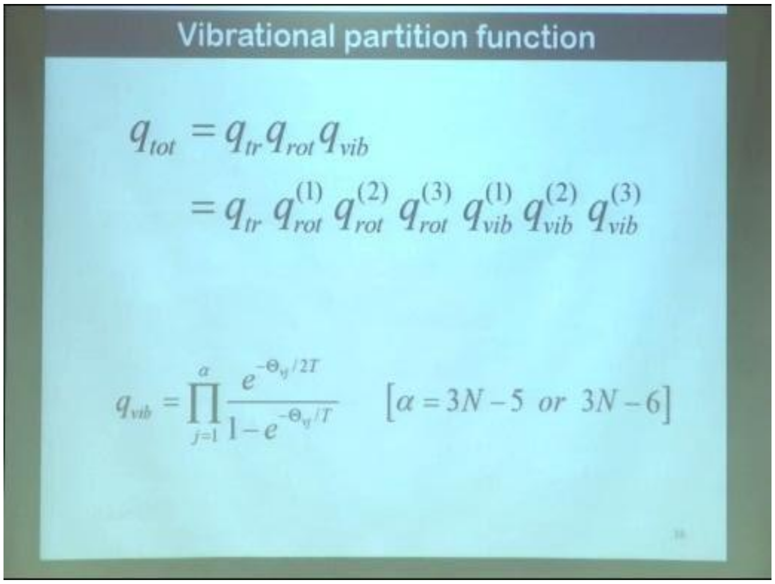

Vibrational partition function

$$q_{tot} = q_{tr} q_{rot} q_{vib}$$
$$= q_{tr}\, q_{rot}^{(1)}\, q_{rot}^{(2)}\, q_{rot}^{(3)}\, q_{vib}^{(1)}\, q_{vib}^{(2)}\, q_{vib}^{(3)}$$

$$q_{vib} = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{vj}/2T}}{1-e^{-\Theta_{vj}/T}} \qquad [\alpha = 3N-5 \;\; or \;\; 3N-6]$$

Vibrational partition function, total partition function, rotation, not vibration it is total partition function then this translation, nonlinear means three rotation then three vibration. So this is the total partition function, this should be total partition function, so this is the total partition function in all its glory so vibrational partition function is this quantity, rotational and translation we just described. The reason of writing it separately it was not written before.

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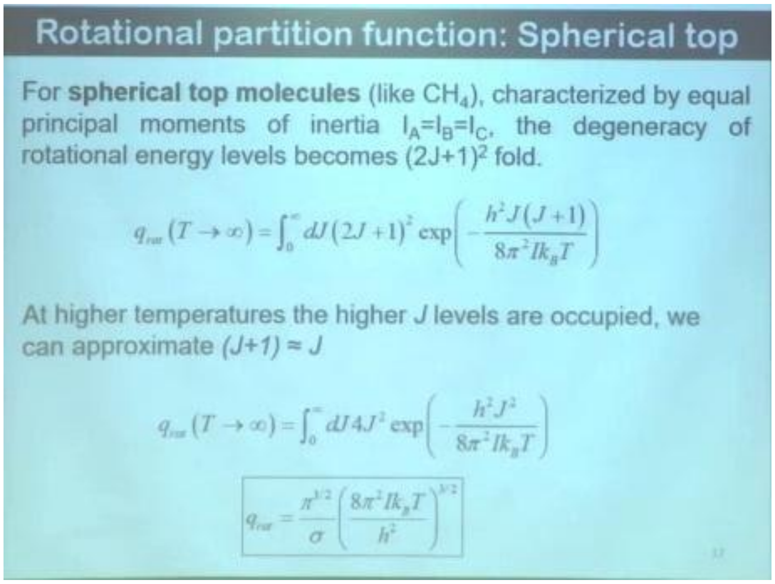

Rotational partition function: Spherical top

For **spherical top molecules** (like CH_4), characterized by equal principal moments of inertia $I_A=I_B=I_C$, the degeneracy of rotational energy levels becomes $(2J+1)^2$ fold.

$$q_{rot}(T \to \infty) = \int_0^{\infty} dJ\,(2J+1)^2 \exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)$$

At higher temperatures the higher *J* levels are occupied, we can approximate $(J+1) \approx J$

$$q_{rot}(T \to \infty) = \int_0^{\infty} dJ\,4J^2 \exp\left(-\frac{h^2 J^2}{8\pi^2 I k_B T}\right)$$

$$\boxed{q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I k_B T}{h^2}\right)^{3/2}}$$

Okay so this is the rotational partition function of a spherical top, spherical top is like a methane is we are now doing polyatomic, we have done one monatomic, diatomic, polyatomic and this is where much of the; well diatomic already lot of interesting things they are there like oxygen, nitrogen then you have carbon-monoxide, nitrous oxide, cyanide all these things are diatomic but polyatomic is where water, methane, ethane and ammonia all these things.

So but here is symmetric molecules then all the moment of inertia are the same that is the definition of a spherical top, then it is very easy. These things do not matter in vibration, but it matters in the rotation. Then there we can do these calculations here, then these integration as we did just before is the same thing again done.

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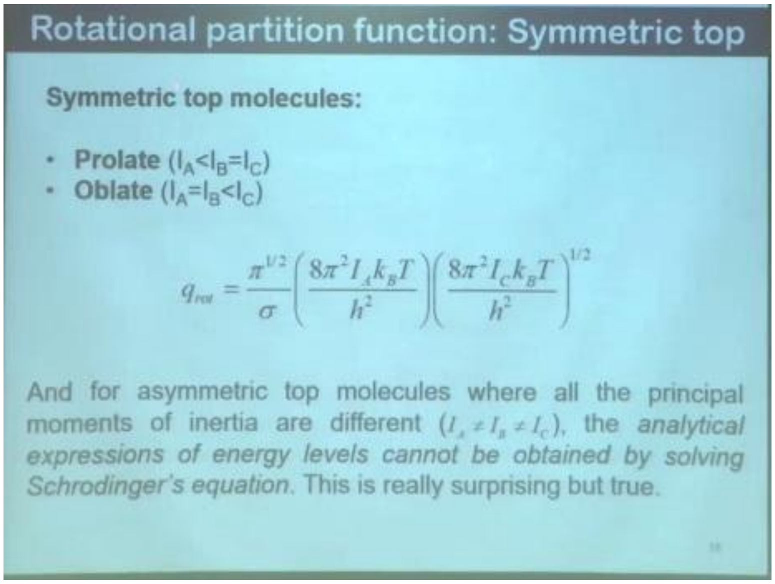

Rotational partition function: Symmetric top

Symmetric top molecules:

- **Prolate** ($I_A<I_B=I_C$)
- **Oblate** ($I_A=I_B<I_C$)

$$q_{rot}=\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A k_B T}{h^2}\right)\left(\frac{8\pi^2 I_C k_B T}{h^2}\right)^{1/2}$$

And for asymmetric top molecules where all the principal moments of inertia are different ($I_A \neq I_B \neq I_C$), the *analytical expressions of energy levels cannot be obtained by solving Schrodinger's equation*. This is really surprising but true.

However, if they are symmetric top not spherical top then the condition is that two are equal but third one not equal moment of inertia, in that case I write the rotational partition function in the following way, clear, two of them that is why half goes from here, third one the asymmetric one comes here the half, so this is the partition function of the rotation of asymmetric top molecules and that can again be calculated by the kind of approximation.

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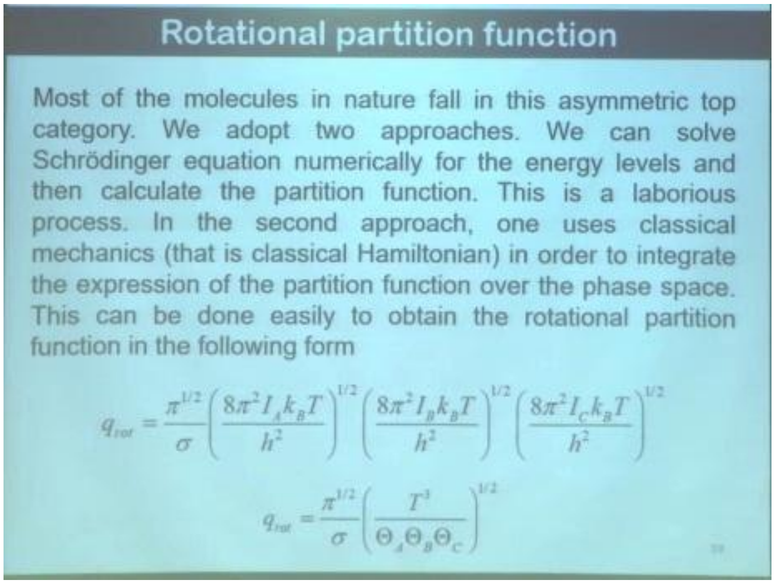

Rotational partition function

Most of the molecules in nature fall in this asymmetric top category. We adopt two approaches. We can solve Schrödinger equation numerically for the energy levels and then calculate the partition function. This is a laborious process. In the second approach, one uses classical mechanics (that is classical Hamiltonian) in order to integrate the expression of the partition function over the phase space. This can be done easily to obtain the rotational partition function in the following form

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_B k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_C k_B T}{h^2}\right)^{1/2}$$

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2}$$

Now if it is completely asymmetric then you have to be what much harder you have to write Ia, Ib, Ic a completely different from each other then you have to write them explicitly with their moment of inertia. There is a symmetry number that comes to take care of the symmetry of the Hamiltonian here which is typically two or three, but I forgot the exact origin of that, and anybody remembers? This is classical mechanics; otherwise you have to clarify in the next lecture, okay. In terms of θr this is the rotational partition function.

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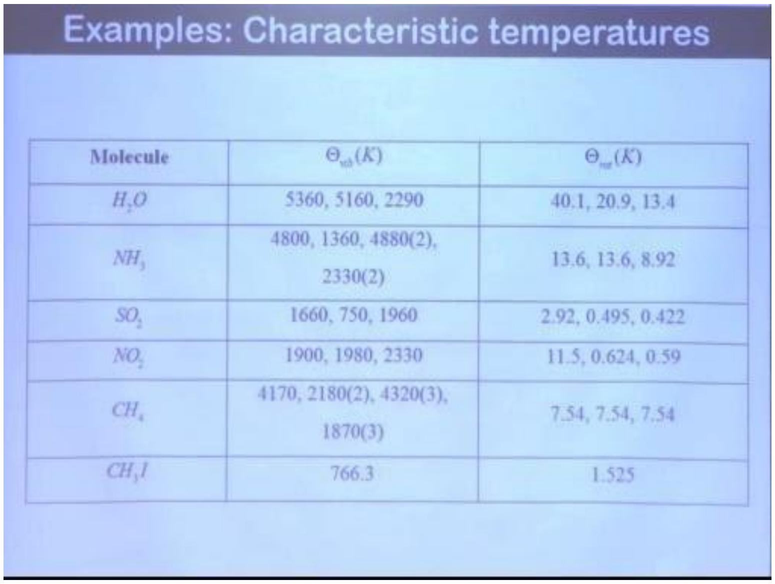

Examples: Characteristic temperatures

Molecule	$\Theta_{vib}(K)$	$\Theta_{rot}(K)$
H_2O	5360, 5160, 2290	40.1, 20.9, 13.4
NH_3	4800, 1360, 4880(2), 2330(2)	13.6, 13.6, 8.92
SO_2	1660, 750, 1960	2.92, 0.495, 0.422
NO_2	1900, 1980, 2330	11.5, 0.624, 0.59
CH_4	4170, 2180(2), 4320(3), 1870(3)	7.54, 7.54, 7.54
CH_3I	766.3	1.525

So all these things what done now leads through this is the table that I wanted to talk up that a characteristic temperatures and then and we now beginning to see what is the; why; what is it low temperature, high temperature approximation. Look here water, so this is; you remember with respect to k_BT, hv /k_B T and these similarly θ rotation is here is the θ rotation. So this is essentially the moment of inertia everything else is constant.

So then it look at here how high these things are in vibration, rotation they have come down drastically, water, there is no symmetry and all the three vibrations are different all the three rotations Ia, Ib, Ic, two of them are close to each other in vibration and but rotation all three are different. Here is the ammonia and these are the ammonia vibrations, and these are the rotations of vibration then sulfur dioxide all these things.

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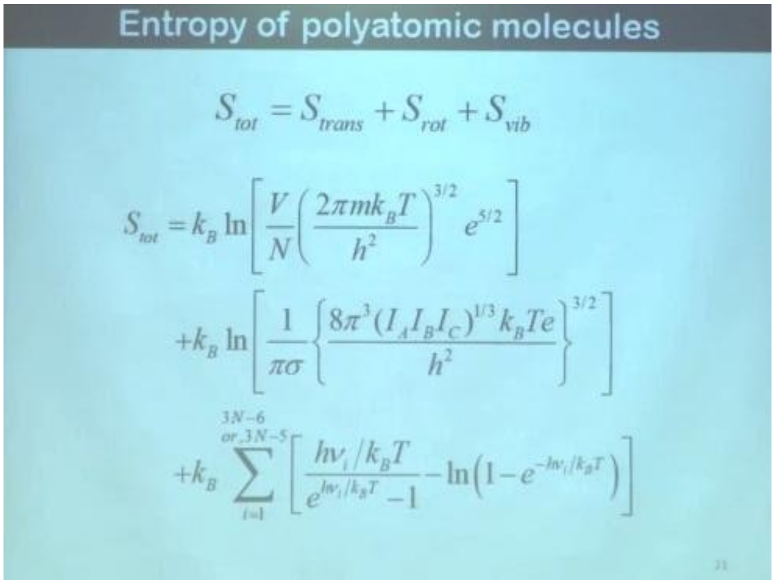

Entropy of polyatomic molecules

$$S_{tot} = S_{trans} + S_{rot} + S_{vib}$$

$$S_{tot} = k_B \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{5/2}\right]$$

$$+k_B \ln\left[\frac{1}{\pi\sigma}\left\{\frac{8\pi^3 (I_A I_B I_C)^{1/3} k_B T e}{h^2}\right\}^{3/2}\right]$$

$$+k_B \sum_{i=1}^{\substack{3N-6 \\ or, 3N-5}} \left[\frac{h\nu_i / k_B T}{e^{h\nu_i / k_B T} - 1} - \ln\left(1 - e^{-h\nu_i / k_B T}\right)\right]$$

Now these are given in my book and they have been one of the important things that is why all these things are taken from the book. Now this is entropy of polyatomic molecules. So this is trivial because they are not interacting, so entropy is the sum of the entropy, so you have the rotation; this is the translational entropy Sackur–Tetrode equation. There is a rotational entropy in the general form for an isotropic molecules and this is the vibrational entropy. So translation, rotation, vibration three things added. Now most of the time because of vibration water, this is so high that there is only one term that is important.

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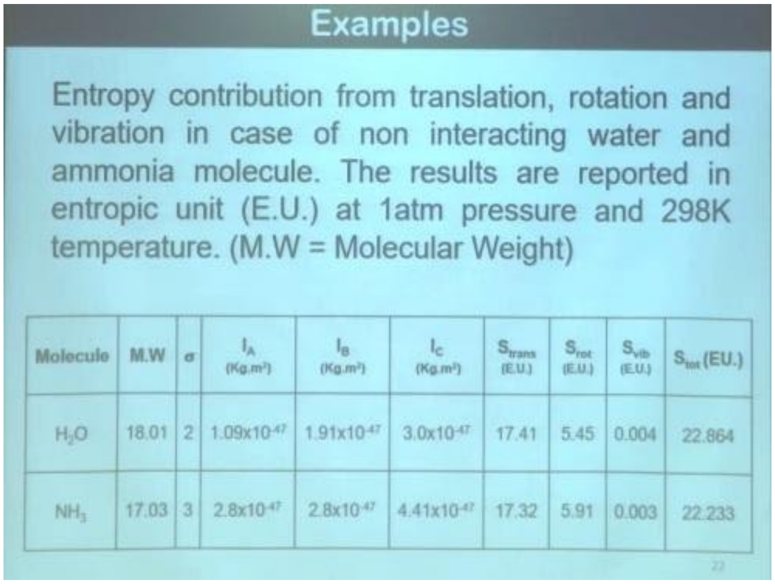

Examples

Entropy contribution from translation, rotation and vibration in case of non interacting water and ammonia molecule. The results are reported in entropic unit (E.U.) at 1atm pressure and 298K temperature. (M.W = Molecular Weight)

Molecule	M.W	σ	I_A (Kg.m^2)	I_B (Kg.m^2)	I_C (Kg.m^2)	S_{trans} (E.U.)	S_{rot} (E.U.)	S_{vib} (E.U.)	S_{tot} (EU.)
H_2O	18.01	2	1.09×10^{-47}	1.91×10^{-47}	3.0×10^{-47}	17.41	5.45	0.004	22.864
NH_3	17.03	3	2.8×10^{-47}	2.8×10^{-47}	4.41×10^{-47}	17.32	5.91	0.003	22.233

And here is these, the table for water and translation is this is the absolute value of entropy that it is 17; well look at rotation, rotation is 5.45, that is rotational entropy is about 30% of total entropy. This is an extremely important result. For ammonia is again; but look at vibration, vibration entropy is negligible. So if I think of water ideal entropy of water was, I told you is the significant; actually real entropy of water still these 22 makes a huge contribution.

Entropy goes down to maybe a value obtained of 12 but this still makes the lines contribution, so thermodynamic properties of water and ammonia lines contribution comes from the ideal, this is something I had no idea myself when I was taken away completely by these interaction and all these things but idea plays a very, very important role. So again repeat, in case of water rotation, vibrational entropy makes no contribution, rotational entropy is about 30% of total and this is the decomposition. But you can see though these are fairly different molecules there is a near constancy of.

"Professor - student conversation starts" That is correct. Yeah chemistry of the molecules will come through electronics and so that is the good question. So but the ammonia and water is different chemically because of the electronic properties, also there is a polarizability which is again electronic properties. And so we are doing; because of electronical polarizability and the shape of the molecules, interaction between two water molecules and two ammonia or between water ammonia they are very different.

Those things are not here. So we are not having any interactions, so when I am doing a thermodynamic properties ideal gas, but you should not be carried away you are right when it comes to chemical properties then the electronic features play an important role “**Professor - student conversation ends”**.

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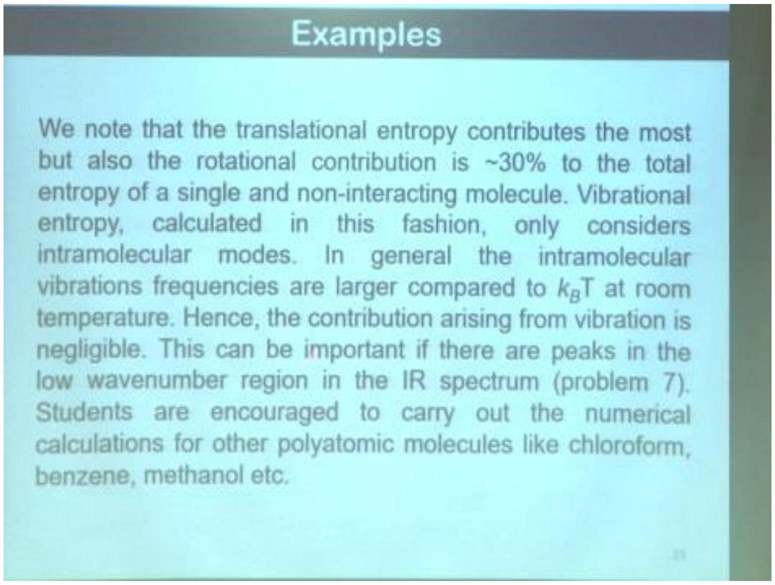

Examples

We note that the translational entropy contributes the most but also the rotational contribution is ~30% to the total entropy of a single and non-interacting molecule. Vibrational entropy, calculated in this fashion, only considers intramolecular modes. In general the intramolecular vibrations frequencies are larger compared to k_BT at room temperature. Hence, the contribution arising from vibration is negligible. This can be important if there are peaks in the low wavenumber region in the IR spectrum (problem 7). Students are encouraged to carry out the numerical calculations for other polyatomic molecules like chloroform, benzene, methanol etc.

Okay, so the translation entropy contributes the most but rotation is 30% of the total, actually very recently till about 5 to 10 years ago when you are calculating entropy of water, we are neglecting rotation contribution and we are writing a paper which will be submitted in the next few days I told you other; you are doing a ice water interface and ice water interface the ice goes into water in the ice neither translational not of much rotation.

But when it goes to liquid translational entropy you do not gain too much which is still highly constrained but rotational entropy is the one that dominates ice water interface for any molecular solid, rotational entropy is very easy to recover because rotation is not a concept quantity but translation is a concept of quantity; is a very important so I can destroy the rotational order very easily, you know. I can take one out of a rotational degree of freedom, but I cannot do in a real space.

"Professor - student conversation starts" (()) (19:00). Orientation is not a problem; orientation or density is not conserved. Conservation is a spatial density or number density. Yeah, but you see it can be anywhere in this sphere. So again it is a very fundamental concept coming from a little bit different field, but it is a number density. Okay if I do not I hate to do that whether I think most of you will not be able to follow it but let me let me try it do "**Professor - student conversation ends"**.

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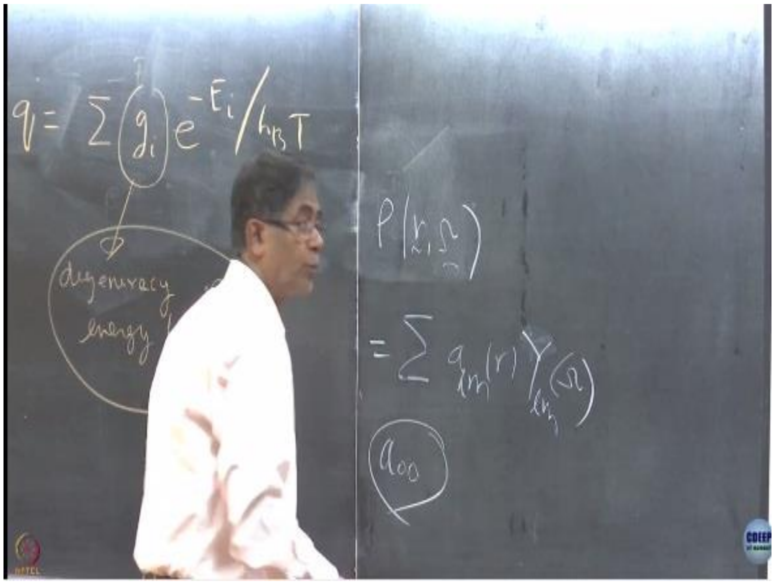

I have a density which is space dependent and I have a orientation dependent, okay. I write it as a spherical harmonic expansion that is what I did not want to. I should not have said what I said because it is just going to confuse you guys. Now this density is conserved. Where does the conservation come? They; if I integrate over and I say that is the conversed quantity, that will then this conservation will be constrained only on a00 isotropic part.

Orientation: this you have to think yourself; I think I should not have got into that and you do not want to get into that but that is a very interesting thing. I mentioned in the context of rotational entropy that many cases you will cover rotational entropy, but you do not recover translational entropy. Okay this is the path of; I now want to go back, and five minutes do the okay these we have done in the morning up to this; chemical potential, grand canonical take the derivative.

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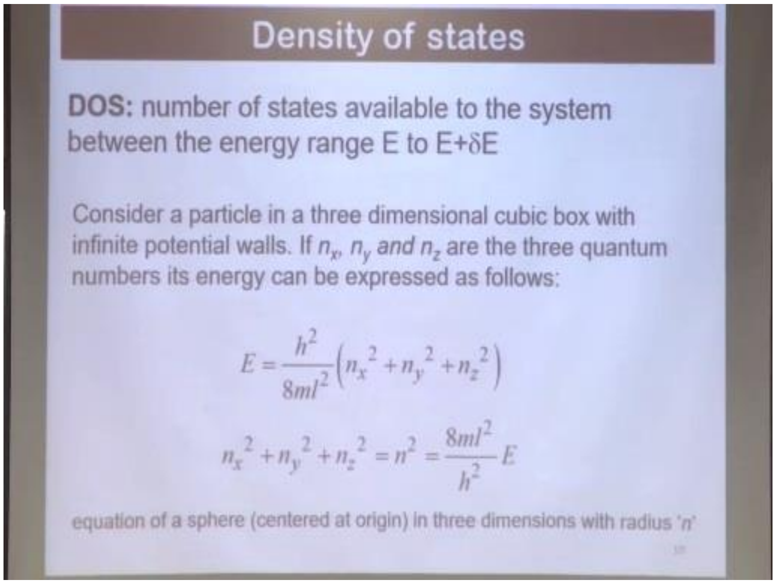

Density of states

DOS: number of states available to the system between the energy range E to E+δE

Consider a particle in a three dimensional cubic box with infinite potential walls. If n_x, n_y *and* n_z are the three quantum numbers its energy can be expressed as follows:

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

$$n_x^{\,2} + n_y^{\,2} + n_z^{\,2} = n^2 = \frac{8ml^2}{h^2}E$$

equation of a sphere (centered at origin) in three dimensions with radius '*n*'

Now we will do what the question you asked that what is the way to do the micro-canonical ensemble for ideal gas, right. And I said the following, it is very difficult in a classical, but it is trivial in quantum.

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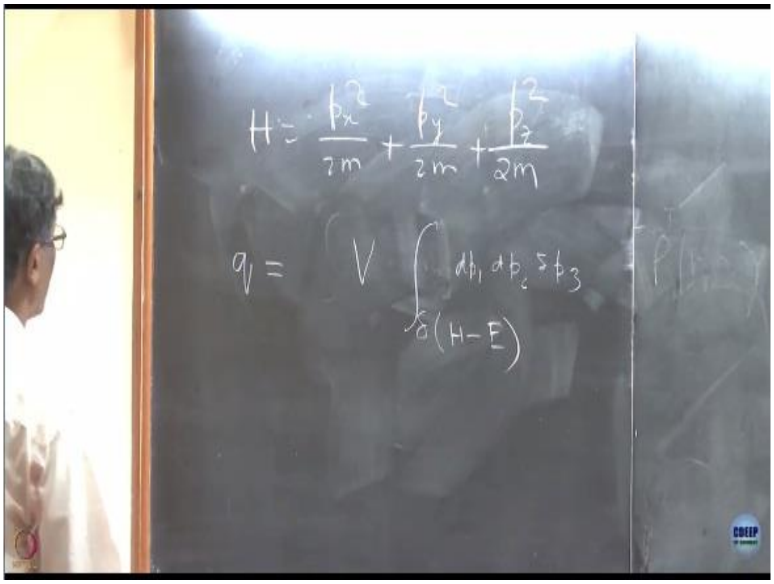

So if I want to do; if this is the ideal gas monatomic ideal gas this is Hamiltonian. So partition function should be dr1, I just do one particle dr3, dp1, dp2, dp3 then δ H – E, so NVE constant means Hamiltonian has to have constant energy. Okay. So you pick up a hyper surface, you pick up a hyper surface and these of course gives me just the volume as before, but this has to have this constraint. So I cannot have any momentum and any a.

So you see what they become trivial in the canonical partition function because I have just Gaussian integral because I allow energy fluctuations by bringing temperature, but in the constant energy surface this is you can do only numerically, okay. However, in quantum it becomes easy because quantum I have to sum over energy levels, and I can solve particle in a box, and this is my volume here write a length of the box; this is a cubic I can give a cubic box then it is like that. Okay.

Now this is nx, ny, nz all I introduce as n square then that n square here, if is constant imagine E is there, then I can go, there is a reason I am going to do that, this is very cumbersome way. I will first define the energy then I would say nx ny nz can be 0 to infinity and then it is amazing that students even after a 5th year PhD students they have no idea many times how to write equations. Of course that is the problem we come in chemistry.

I remember I worked with a very distinguished physicist who is now a chair professor of some university organization but very famous he has very famous book on statistical mechanics called Yoshi Oono, and I used to work with Yoshi in Chicago and Yoshi always used to tell me "Biman, why do you write equations in such cumbersome form?"

And a physicist has certain affection and love for mathematical equations which shows in their writing. Here also see how cumbersomely it is written. Okay, nx, ny, nz are all of them from 1, they are not from 0 remember, okay. If that is then; if I; now I should introduce that these quantity of the n squared because they come together remembering that nx, ny, nz can vary each of them independently then I put them equal to E.

$$n_x{}^2 + n_y{}^2 + n_z{}^2 = n^2 = \frac{8ml^2}{h^2}E$$

Now I am going to use something because I; these nx, ny, nz make a cubic system. I vary nx, along the x-axis, ny along y they are discrete points in a digit in a disk in a grid. So however, since mine is 1 to infinity I populate because of my energy levels one 1/8th of that, okay. So however, the n square I can write at as this quantity a vector in that space is n square and that is given by E, so that is this 8ml square by square E.

$$\Phi(E) = \frac{1}{8}\left(\frac{4}{3}\pi n^3\right)$$

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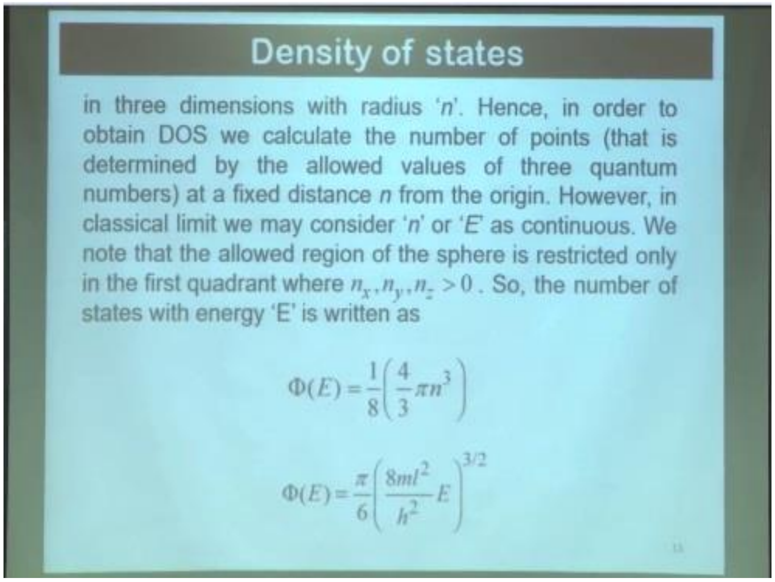

Density of states

in three dimensions with radius ‘*n*’. Hence, in order to obtain DOS we calculate the number of points (that is determined by the allowed values of three quantum numbers) at a fixed distance *n* from the origin. However, in classical limit we may consider ‘*n*’ or ‘*E*’ as continuous. We note that the allowed region of the sphere is restricted only in the first quadrant where $n_x, n_y, n_z > 0$. So, the number of states with energy ‘E’ is written as

$$\Phi(E) = \frac{1}{8}\left(\frac{4}{3}\pi n^3\right)$$

$$\Phi(E) = \frac{\pi}{6}\left(\frac{8ml^2}{h^2}E\right)^{3/2}$$

Now in three dimensions with the radius n, so I can calculate the density of states by calculating the number of points, is this clear?

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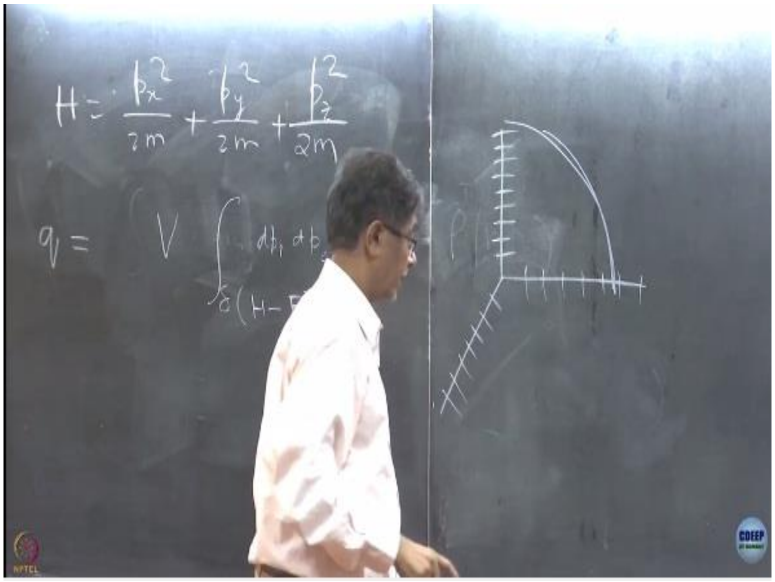

So these are all; so my total number now nx, ny, nz are all positive, okay. So there will be only one side of that, that will be I need to calculate, okay. It is not the whole space so if I do that then it is 1/8th of the whole average. So total number of points is in the radius, radius is nx, nx square, ny square, nz square this really lucky, so then it is 4π / 3π n cube. This is the volume. So 1/8 of the rain I know, and I know because that is connected to energy E.

I have NVE ensemble, ideal gas in NVE, they are non-interacting. So my volume of the box comes from l, energy comes through E, total n will be when I put them to the n because n number of them. So nve each play a role, it plays a role; it is a really very pretty, so this is your density of total number of states. Omega of that gives you the partition function. Sorry, this is your partition function ln of that gives you the entropy.

$$\Phi(E) = \frac{\pi}{6}\left(\frac{8ml^2}{h^2}E\right)^{3/2}$$

So this is the way, you know this goes on doing this what solid state physics is the density of states and all these things, but we do not need it right now for statistical mechanics. This used in some cases but if we need later, we will do, but this is where correspondence between quantum and classical statistical mechanics of a monatomic ideal gas. This is the capital Omega these total number of states. Capital Omega which depends on I should have put it in capital Omega again, so this is depends on E, this is depend on E.

Of course because n can be 1 to infinity; particle in a box remember the quantum numbers; quantum numbers from 1 to infinity. Do you remember that order or you forgotten? Okay, so then no between doing; so you are using source these that is why in many parts of statistical mechanics we cannot teach analyst quantum is done like we knew particle in a box, we need harmonic oscillator, we need rigid rotator. So that is why in every where statmech 1 starts in the second semester.

First semester quantum 1, quantum 1 and thermodynamics, so courses that I have taught in many places it was always the second semester which was very bad because every statmech used to be full winter when I taught in Harvard, taught in Wisconsin everywhere it was always the month of January, February, March, April which is horrible. Thermodynamics is the first semester, which is the called the fall here also in Indian Institute of Science SS201 our solid state, SS201 used to be thermodynamics. SS202 used to be statistical mechanics, same in physics everywhere.

But by the time, we are doing SS201 side by side SS204 or 5 is the quantum mechanics. So quantum is done parallel to thermodynamics then come to the statistical mechanics. Okay, but that is a different thing. So this is what completes; I said I will take 10-15 minutes more, it is done. So next in the book one usually goes doing Bose-Einstein condensation and Bose statistics I am not going to do that, that we will do later because this is a non-interacting system, I think next what we need to do is the interacting system, because that is where much of our applications are. But if you do not do the ideal gas or ideal case then you cannot do the interacting systems.

Sir, when you are calculating the translation partition **“Professor - student conversation starts” (())** (30:19) No you take the center of mass, center of mass is always well defined Yeah, the center of mass, total mass and then total mass then for rotation you will have mass of the moment of inertia along each axis, there are three principal axis, so in nonlinear molecules we get three moment of inertia I1, I2 and I3 “**Professor - student conversation ends”**.

Similarly, when you do vibration each vibration will have an effective mass. So translation we will have one mass, which is the central mass and then 3 masses for vibration, 3 masses moment of inertia for rotation. Anything else? Okay.