Basic Statistical Mechanics
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Lecture – 26
Ideals Gas of Diatomic Molecules: Microscopic Expression for Rotational and Vibrational Entropy and Specific Heat (Part 4)

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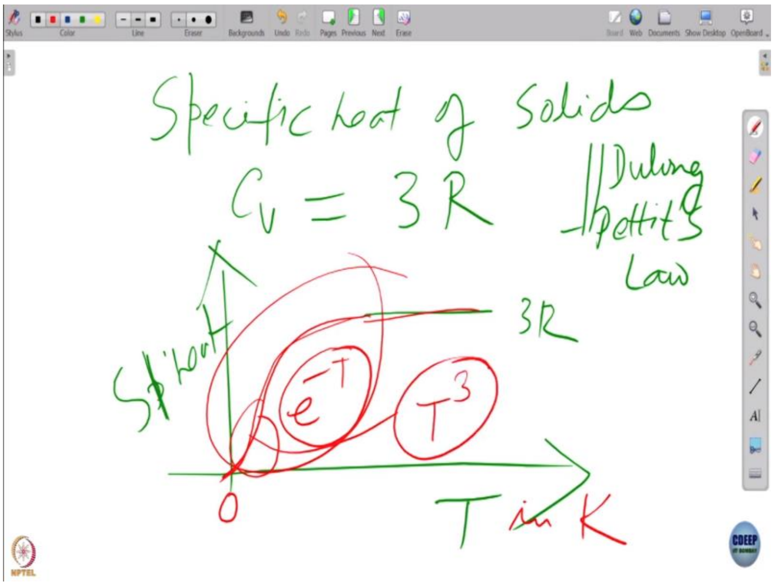

So, at high temperature specific heat of solids, all you have done in your high school and that you know that specific heat (C_v)goes as 3R. This is from classical vibrations, that was done in quantum mechanics and this is called do Dulong-Pettit law. However, when one measures the specific heat, here we plot against temperature, the one before people had up to this and that is Dulong-Pettit law (3R). But when you go to low temperature this starts goes like that.

That means these experimental results becomes available after low temperature studies in 1917-1920 and around that time this remarkable departure from classical statistical mechanics. These are just one of all those beautiful things happened starting with the blackbody radiation, photoelectric effect, Balmer series, quantum mechanics or all the other beautiful things. So, break down a specific heat at low temperature immediately drew huge amount of attention and people could not do, people could not solve because they did not have energy levels.

However, Schrodinger solution of the harmonic oscillator and energy $E = \left(n + \frac{1}{2}\right)h\nu$, they came available in 1926- 1927. And then at that time these beautiful departures from classical mechanics, it was done by Einstein. What did Einstein do and then corrected by Debye and that became to known as the Debye-Einstein or Einstein-Debye theory.

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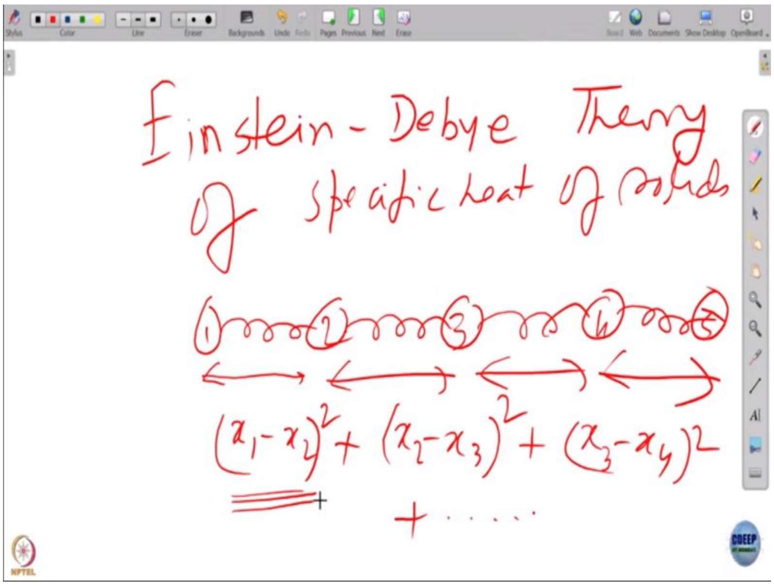

Einstein - Debye Theory of specific heat of solids

$(x_1 - x_2)^2 + (x_2 - x_3)^2 + (x_3 - x_4)^2 + \cdots$

So, what Einstein realized that the solids have many low-frequency modes. They are low frequency, in compared to, this is a very interesting, there are low frequency with respect to atomic vibration. But they are not that low frequency that you can treat them classical mechanics. So, there are frequencies which are normal modes. So, basically when I have a say once in a one-dimensional model.

So, we have this chain linear chain. Then the Hamiltonian is the vibration, this vibration, this vibration, this vibration, this vibration, n number of vibrations let us say. Now, these modes are: the position of these molecules $(x_1 - x_2)^2 + (x_2 - x_3)^2 \ldots\ldots.$, they are in terms of atomic position and goes like that. Now, I can make it so when I expand that the $(x_1 - x_2)^2 = x_1^2 + x_2^2 - 2x_1x_2$.

Now, I can make a coordinate transformation which the same as diagnosation where I go to representation where since $x_1.x_2$ is a linear coupling and this is a very important. And I do not need to go to it but nonlinear I cannot do that but linear coupling I can diagonalize this. And I go a new set of vibrations. Those vibrations are now is collective vibrations. That means it is like in water we have a collective symmetric stretching or asymmetric stretching where oxygen remaining the same but 2 hydrogen are moving together.

Okay, similarly, here all the molecules/atoms are moving together. That means there is a kind of these vibration, all of them moving together, they are like sound waves and their compression and their repulsion and their some of them are like these others are going like that. So just like symmetric-asymmetric stretching in water, there are many-many, you know if it is linear case (3n – 6) vibrations are coming in.

So, these are the collective modes when you get by diagonalizing the Hamiltonian and where collectively the molecules are moving together. And these are low frequency mode. Then these low frequency modes, as I told you, they are low enough frequency to contribute enormously significantly to entropy and to specific heat. But they are high enough such that you cannot contribute them through classical methods.

When you go to high temperature then these modes (low frequency modes) can be treated as quantum mechanically. But when you go to low temperature to low temperature, this is a temperature I am talking of 0 Kelvin (temperature in Kelvin). So, in this region, so maybe at 300 Kelvin or 200 Kelvin you can still have the Dulong-Pettit's law. But when you go to 10 Kelvin or 5 Kelvin, then those low frequency modes has to be treated quantum mechanically and they make a very important contribution.

That is now given by Einstein famous theory which first Einstein did it in it and has a $\exp(-T)$ dependence. What Einstein made, he did not do all these diagonalisation or anything. He just said all the frequencies, on this solid, you got the total number correct, all they have the same frequency i.e. constant frequency that is called Einstein frequency.

Then this is very easy, then I go to Einstein frequency and you can now calculate the specific heat from there. Debye did it tightly. Debye took care of what we called frequency dispersion i.e all these modes are of different frequency they have been lowest and the highest frequency. When he did that, he got the real value it is as T^3, the famous T^3 law but that came out essentially from just what you are doing here.

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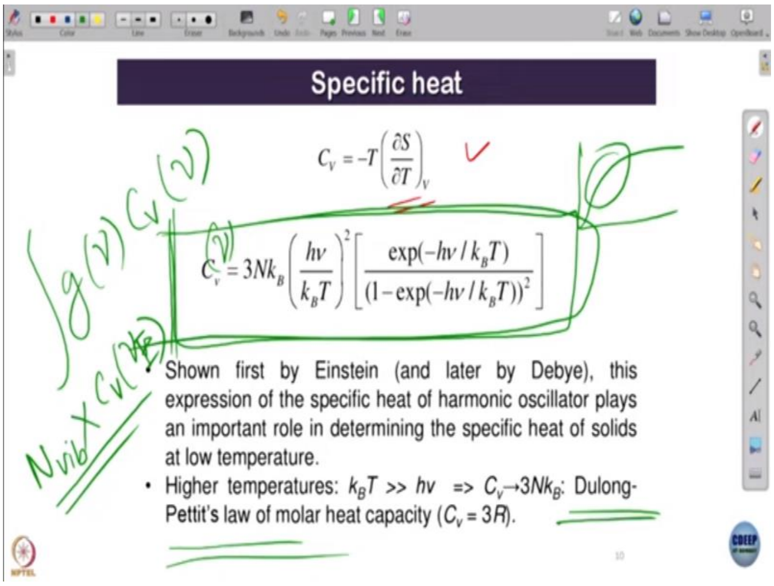

Specific heat

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

$$C_v = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2\left[\frac{\exp(-h\nu/k_BT)}{(1-\exp(-h\nu/k_BT))^2}\right]$$

- Shown first by Einstein (and later by Debye), this expression of the specific heat of harmonic oscillator plays an important role in determining the specific heat of solids at low temperature.
- Higher temperatures: $k_BT >> h\nu$ => $C_V \to 3Nk_B$: Dulong-Pettit's law of molar heat capacity ($C_v = 3R$).

Okay. So, this is specific heat,

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

Then when I do these from entropy then I get this expression,

$$\boxed{C_v = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2\left[\frac{\exp(-h\nu/k_BT)}{(1-\exp(-h\nu/k_BT))^2}\right]}.$$

So, this is the entropy,

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

I take derivative, I get one term from here, I get two terms from here, I can combine them and when I combine them you get this expression $\boxed{C_v = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2\left[\frac{\exp(-h\nu/k_BT)}{(1-\exp(-h\nu/k_BT))^2}\right]}$. You can check it out. It is trivial. From entropy this really trivial thing and I am not going to do it but believe me that this is the expression that comes in this is the specific heat of the one harmonic oscillator which frequency ν.

Now, as shown by Einstein and later on by Debye, these expressions plays an important role for specific heat of solids at low temperatures. So high temperature will go to Dulong-Pettit's law but at low temperature, we now in order to calculate make it as frequency dependency $C_v(\nu)$ and then we have to integrate with the density of states $\int g(\nu)C_v(\nu)$.

This is what Einstein did and Einstein said okay, I can have only one frequency i.e. all the frequencies are the same (identical). Then I have N number of vibration into $C_v(\nu_E)$ i.e $N_{vib} \times C_v(\nu_E)$ vibration, ν_E is Einstein frequency and I get an exponential dependence as Einstein showed in this region. However, all these vibrations do not have the same frequency. They have a maximum frequency because of the wave is acoustical they are essentially waves that you can accommodate within this thing.

For that extra consideration important becomes important that even at low-temperatures that gives T^3 law. So, this is a really interesting thing that happens in 1930 or 1932 or around that time that Einstein did and then Debye corrected Einstein. So, the statistical mechanics of a harmonic oscillator plays such an important role in doing this.

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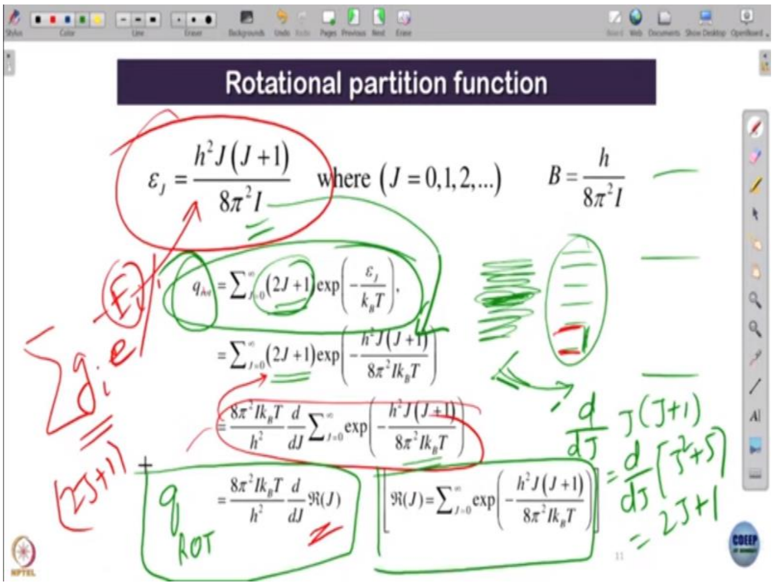

Rotational partition function

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

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)\exp\left(-\frac{\varepsilon_J}{k_B T}\right).$$

$$= \sum_{J=0}^{\infty} (2J+1)\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)$$

$$= \frac{8\pi^2 I k_B T}{h^2}\frac{d}{dJ}\sum_{J=0}^{\infty}\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)$$

$$q_{ROT} = \frac{8\pi^2 I k_B T}{h^2}\frac{d}{dJ}\Re(J) \qquad \Re(J) = \sum_{J=0}^{\infty}\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)$$

$$\sum g_i e^{-E_i} \qquad (2J+1)$$

$$\frac{d}{dJ} J(J+1) = \frac{d}{dJ}\left[J^2+J\right] = 2J+1$$

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So now continue. So, the next we will do the rational partition function. This is the vibration and as I said even very recently, even today many-many people are doing those entropy, those specific heat, you know, to consider amorphous solids and these low-temperature liquids. For example, we ourselves did a work last year with a collaborator Shinji Saito, a long paper came out in Journal of Chemical Physics. We used these things to calculate the specific and entropy of low temperature water and that simply explains several things.

So, many people are using this thing. So, just like quantum mechanics the vibrational spectra are given by the solution of Schrodinger equation and the harmonic oscillator plays a very important role, you know, is something really surprising that such a simple model and kind of artificial model play so important role. But that happens in physics again and again that is why harmonic oscillator model is very much cherished, that is very much loved and liked by scientist because they can use in many different situations.

Similarly, now it goes up like that translation, vibration also all these things are very important. Now, rotation. That is why we are repeating it. Now we do the statistical mechanics of rotational motion. With did translation, we did vibration, we said electronic is not important and but a rotation is important. Now rotation has a place which we do in vibration and translation.

In translation, we got away without doing quantum mechanics. In vibration we had to do quantum mechanics. But in case of rotation, it is in between. If translation energy level is facing like this, very continued continuous then and rotation will be like this, vibration is like this. So, this is where we are somewhere in between quantum and classical.

So, we will see that in low temperature, this energy discreetness, the quantum nature of the energy levels, the discreteness plays an important role but in a high temperature it can be like classical mechanics. So, let us do. Now again Schrodinger solved for a rigid rotated, the molecule is rotating with a moment of inertia I, moment of inertia plays the role of mass you know.

So, this is the energy levels that again Schrodinger gave us $\varepsilon_J = \frac{h^2 J\left(J+1\right)}{8\pi^2 I}$ where $\left(J = 0,1,2,...\right)$. But there is a very important thing now which we never faced before. That these energy levels are degenerate. So now before we are talking of individual energy level, they are not degenerate in particle in a box (one dimensional). For the particle in a box (three-dimensional box), they are degenerate in a different sense.

That means I can mix x, y, z. I can have (0,0,0), I can have (1,1,1) or I can have (1,1,2), (1,2,1), (2,1,1). But we just sum them up because as they are decoupled. Actually, if we take up that it becomes more complicated. But in rotation even for a single rotation we have the degeneracy which is (2J+1). Then partition function goes as sum over these energy states which are given by energy ε_j and then we have degeneracy g_i So, $q = \sum g_i \exp\left(\varepsilon_i / k_B T \right)$. So instead of each energy level, we count the energy states that means ok these energy states is ε_j but I have (2 J + 1) of them.

So, this thing is g_i = (2 J + 1) and this ε_j is this quantity $\varepsilon_J = \frac{h^2 J(J+1)}{8\pi^2 I}$ where $(J = 0,1,2,...)$. So, now my partition function now becomes this quantity. My partition function now become this quantity $q_{rot} = \sum_{J=0}^{\infty}(2J+1)\exp\left(-\frac{\varepsilon_J}{k_B T}\right)$. I tell you that again why it plays an important role in this case also. So now $q_{rot} = \sum_{J=0}^{\infty}(2J+1)\exp\left(-\frac{\varepsilon_J}{k_B T}\right)$ and then I put the ε_j here and then I get this $q_{rot} = \sum_{J=0}^{\infty}(2J+1)\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)$. Now I notice one something very interesting.

Till now I have been doing very simple substitution but now I can play little smart. I realize the (2J+1) is nothing but a derivative of J(J + 1). So, (2 J +1), if I take $\frac{d}{dJ}J(J+1) = \frac{d}{dJ}(J^2+J) = (2J+1)$. So these quantity is nothing but a derivative of the J(J+ 1). Okay be little smart. I do $\frac{d}{dJ}$ but however that brings how many other quantities and the partition function becomes, $q_{rot} = \frac{8\pi^2 I k_B T}{h^2}\frac{d}{dJ}\sum_{J=0}^{\infty}\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)$.

This is same as this quantity. But that is been now very nice. Okay I made some progress. I cannot evaluate this sum exactly which is a pity, really pity but we cannot do it many times. You will see some really simple things we cannot do. Maybe some of you can be smart and do a better approximation in this case. But we have not been able to do. So, then I can write

$$q_{rot} = \frac{8\pi^2 I k_B T}{h^2}\frac{d}{dJ}\Re(J), where$$

$$\Re(J) = \sum_{J=0}^{\infty}\exp\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_B T}\right)$$

As because it is not no point of writing it again and again so I find $\Re(J)$ as this quantity. So, this is my partition function rotational partition function.

That means then this is your rotational partition function. Let me see what I can do with it. So, as I said for many molecules, this is particularly important for physical chemists that where we have the rotation.

I remember when I was doing postdoc at University of Chicago with the James Frank Institute and there was some fantastic group of people there. There are some guys who made history and there are people like S. Rice, John Levy and they were doing spectroscopy in the gas and there was a lot of excitement to detect rotational level dependence of electronic and vibrational relaxation. This was the reason they have the partition function.

They know this thing is there. So, if a molecule rotates very fast then they will modify the coupling between different energy levels. Then we would be able to see if the temperature dependence of vibrational-relaxation, rotational level dependence that would not be otherwise, if the vibration rotation coupling is not there. Okay, so let us go ahead and do some little bit more of them down now.

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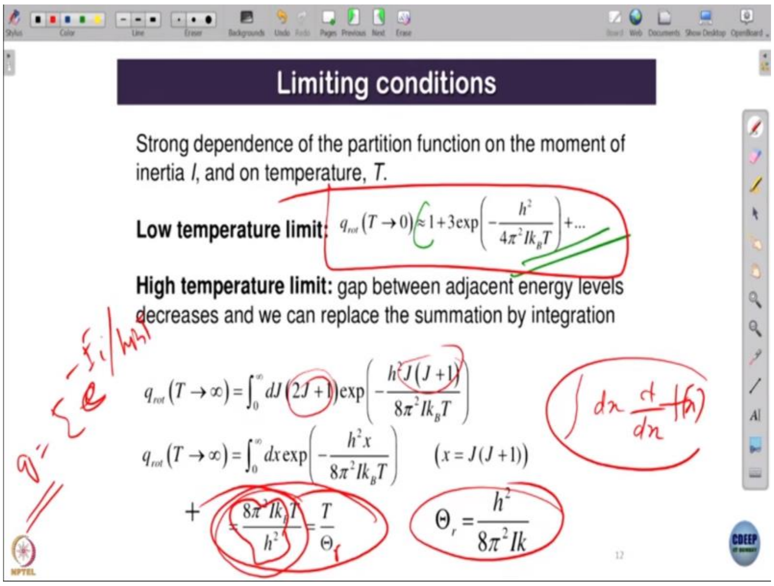

Limiting conditions

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

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

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

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

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

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

$q = \sum e^{-\varepsilon_i/k_B T}$

$\int dx \frac{d}{dx} f(x)$

Okay, so, important thing is that the very important comment here the strong dependence of partition function of moment of inertia. As I said, this plays a very important role in energy relaxation, in vibrational energy relaxation. So then low temperature we go to T going to 0 limits. Then this quantity if I go to low temperature then

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

Now the partition function is 1 + 3 by these things. A similar simplification happens in the high temperature also. High temperature energy levels are continuous like in classical mechanics that means J (J + 1)/k$_B$T when temperature is very large, they get squeezed. They are very close to each other. Now I can replace this sum by integral. If I replace this sum by integral, then I can do that integration because I already have the interesting thing that this guy (2J+1) is a derivative of this guy J (J + 1).

So, it is just an integration, $\int dx \frac{d}{dx} f(x)$. This is the integration $q_{rot}(T \to \infty) = \int_0^\infty dx \exp\left(-\frac{h^2 x}{8\pi^2 I k_B T}\right),$. I can do that integration and then it is trivial and I get this quantity, $\boxed{q_{rot}\,(high\ temperature) = \frac{8\pi^2 I k_B T}{h^2}}$.

So $q_{rot} = \frac{8\pi^2 I k_B T}{h^2} = \frac{T}{\Theta_r}, where, \Theta_r = \frac{h^2}{8\pi^2 I k}$. I have now a very nice partition function at high temperature. And, I define rotational temperature just like before that is $\Theta_r = \frac{h^2}{8\pi^2 I k}$ because the partition function must be dimensionless.

So, this quantity, Θ_r has units as inverse of temperature just like in vibration, I define rotation temperature. This is something one has to be careful. I said a very important thing here that partition function is dimensionless and that is q because it is sum over energy levels so this is number exponential is a number. So, q is a so when we did the translation or vibration function the quantity that makes this dimensionless is lambda.

So, we have to be very careful lambda is de Broglie wavelength and de Broglie wavelength comes again and again and that comes through this Planck's constant and all this combination plays very important role in the quantum-classical analogy. So, when Boltzmann and Gibbs did, they did not have the Planck's constant.

So, they left their partition function with a volume term and that then they that were reconciled as we see is the volume of the of the cell in the phase space and all these things but you do not need that really. You have to for bookkeeping you do not need the physical interpretation but because there is an exact expression well you can go. I do the physical interpretation like Richard Tolman did a lot of it and that probably helps in certain cases but you do not need that.

So now I have the beautiful expression of the rotational partition function which is $q_{rot} = \frac{8\pi^2 I k_B T}{h^2}$. This is my rotational partition function. So I have the translational partition function, the vibrational partition function and the rotational partition function.

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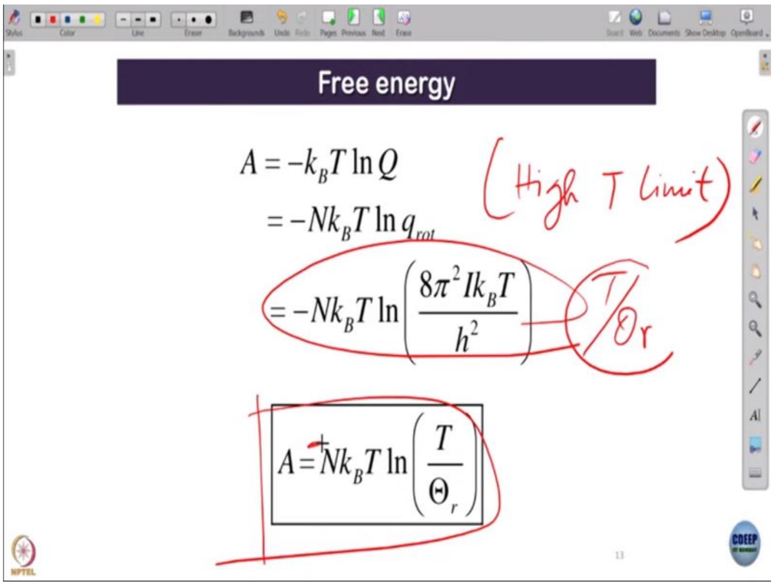

Free energy

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

Now I go the rotational partition function, calculate the free energy at in the particular high temperature limit. So, these the high temperature limit. In the high temperature limit, $A = -k_B T \ln Q$. Then I get this quantity and then I get the free energy as I look at that then it is T by T theta r and because the T is the numerator theta is the denominator theta it you can like that. That has to be careful about.

$$\begin{aligned} A &= -k_B T \ln Q \\ &= -Nk_B T \ln q_{rot} \\ &= -Nk_B T \ln\left(\frac{8\pi^2 I k_B T}{h^2}\right), \end{aligned}$$

$$or,$$

$$\boxed{A = Nk_B T \ln\left(\frac{T}{\Theta_r}\right)}$$

Okay so this is the free energy then we can calculate the other quantities like entropy.

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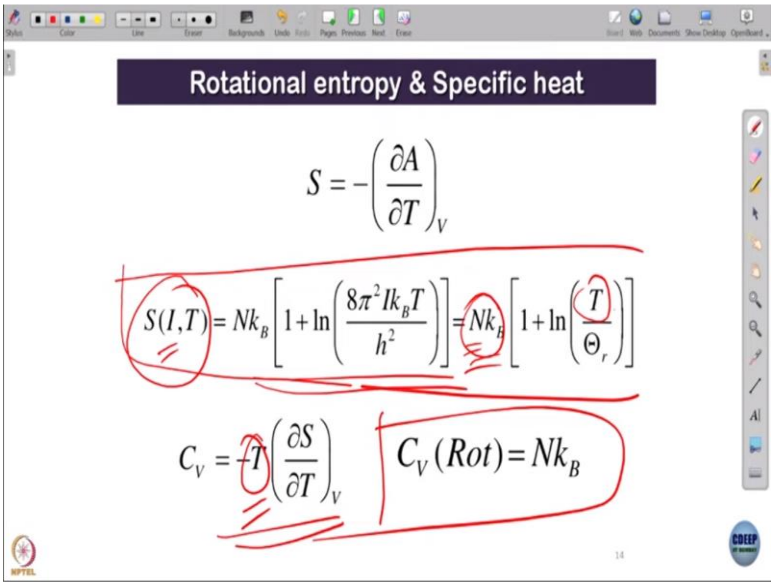

Rotational entropy & Specific heat

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

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

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

And this is important as I told you that when you are going to talk of low temperature and up in the cloud, the entropy of water molecules, entropy of a linear molecule; still now we are doing diatomic. We will do polyatomic very soon. But we get. These are the quantities we need. So entropy is now a function of moment of inertia. Entropy of molecule moment of inertia I.

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

$$or,$$

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

And the expression is by taking the derivative of the doing we get this quantity because these quantities before that and there is quantity there is a temperature here. There is a temperature here so two terms come out.

Now we get the specific heat, $C_r = -T\left(\frac{\partial S}{\partial T}\right)_V$. We take the derivative of entropy. There is no temperature here. There is only temperature here. When you do that, you get a beautiful expression just like an ideal gas that specific heat $C_V(Rotation) = Nk_B$. So, this is the thing that we really wanted to tell you that.

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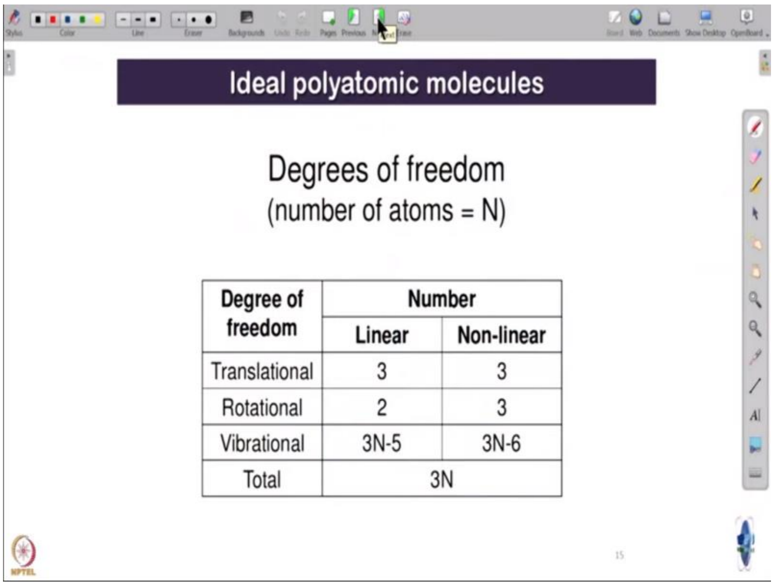

Ideal polyatomic molecules

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 next in the next lecture we will start with the polyatomic. Yes, we will finish the diatomic completely. We calculated entropy of rotation with vibration translation. So, but as I again and again telling these are very important things even though they are in non-interacting limit, they go on the backbone on each interaction is built in like variable equation. So, we start with Gay-Lussac's gas law. You add in the attraction and that the variable equation of state.

Okay then we start with the harmonic oscillator model. So, we add the correction term to that comes from ideal gas law. This is the way actual mechanics built up. Actually, there so a quantum mechanics also built up that your part of perturbation theory. That you want to talk of harmonic oscillator. But the transition vibration you need a perturbation. Otherwise, you know they are states. They do not talk with each other. So, the interacting system comes with a perturbation.

Sometimes when the perturbation does not work into where things are really interesting. So, the next lecture will start here in the polyatomic systems. And then we will go on doing some very interesting stuff so stay tuned. Thank you.