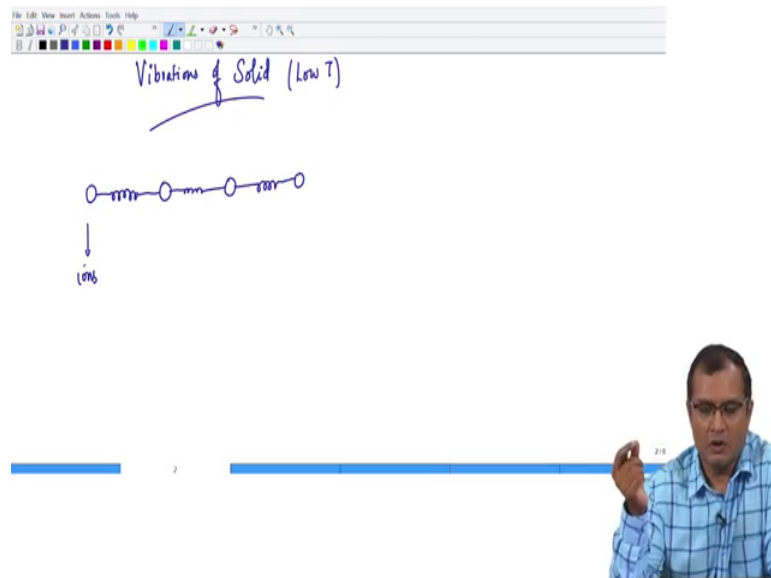


**Statistical Mechanics**  
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**Indian Institute of Technology, Madras**

**Lecture –30**  
**Vibrations of Solid (Low Temperature)**

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So, good afternoon students, today we will take another example of a system of bosons, which is vibrations of a solid at low temperatures and I am going to take low temperatures. So, how is this system of phonons this is because we can think of solid at low temperature as a network of ions and this is basically to simplify the whole picture I am showing ions in one dimension.

So, let us say the interaction is modeled in terms of a hooking spring and whose, spring constant is given by the second derivative of the interaction energy, we will discuss all that, but just to illustrate the point I am showing ions here in one dimension. So, at low temperature these ions would be sitting at equilibrium mechanical equilibrium, which would be like the potential energy minimum of their nearest neighbors.

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A screenshot of a presentation slide showing a handwritten diagram of a diatomic molecule. The molecule is represented by two small circles connected by a horizontal line with a central dot. Below the diagram, the text reads: "ions sitting at mechanical equilibrium at  $T=0$ ". Below that, it says: "At low  $T \neq 0$ , there are displacements from mean positions." The slide also shows a software toolbar at the top and a presenter's headshot in the bottom right corner.

So, you know, they are sitting at mechanical equilibrium at  $T$  tending to 0 or  $T$  equal to 0. Now suppose I lift the temperature from 0 to some non zero values. So, at low, but non zero temperatures you know, I will take some low temperatures you expect these ions to undergo some displacement.

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A screenshot of a presentation slide. The top part shows the same handwritten text as the previous slide: "At low  $T \neq 0$ , there are displacements from mean positions." Below this, there is a small diagram of a diatomic molecule with a double-headed arrow between the two ions, and the text "Writing the potential energy: ( $T \neq 0$ )". The slide also shows a software toolbar at the top and a presenter's headshot in the bottom right corner.

So, there are displacements from mean positions, which means you can think of an ion that has displaced in by some in one dimension an ion could have been displaced by some displacement let us called as  $dx$ .

And in 3 dimensions you would expect this displacement to be a vector having 3 components ok. So, for n ions in 3 dimensions, you expect that the total potential energy is now a function of these displacement from the origin ok, because the interaction has been taken to be sufficiently harmonic in nature. So, I can write down the, potential energy at non zero temperatures.

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Handwritten equations on the slide:

$$U = U_0 + \sum_{\substack{i,j; \alpha, \beta \\ (i,j) \neq (1,1)}} \frac{\partial^2 U}{\partial \vec{r}_{i,\alpha} \partial \vec{r}_{j,\beta}} \vec{d}_{i,\alpha} \cdot \vec{d}_{j,\beta} + O(d^3)$$

Additional notes on the slide:

- "Low T" Close to mechanical equilibrium
- $\frac{\partial U}{\partial \vec{r}_{i,\alpha}} = -F_{i,\alpha} = 0$

So, we can write down the potential energy as some potential energy that was at T equal to 0. And now you are going to expand it in powers of the displacement. So,  $U_0$  is the leading term, which was the potential energy at the equilibrium and now, you can expand it. So, the leading term of course, would be you have to take the derivative of the potential and keep in mind that there are n particles in the system and you have to, accommodate that each particle has 3 degrees of freedom. So, this derivative is gradient of the potential energy will be running over all particles and for each particle you will run over all components.

So, let me just write it in the way that makes things much more clear. So, I am going to sum over all particles. So,  $r_i$  such that i belongs to N and I am going to sum over all alpha, which belongs to 1 to 3 ok and this is nothing, but the leading term fine. So, it has du by dx of first particle, du by dy first particle, du by dz of second particle and so on and so forth.

Let us write down 1 more term, which is due to the second order displacements or what we have taken is nothing, but the first order displacement. So, because this is a Taylor expansion I have to multiply it by a displacement ok. So, this completes the first order term. Then I am going to write down the second order term and due to the limitations of the space, I am going to write the second order term below this. So, the second order term is summation over all, i js and alpha betas of the second derivative.

So, by taking all combinations of i alpha and j beta, you are taking the second derivatives of all types. So, if there will be d square u by dx square for first particles, there could be d square u by dx 1 dx 2 and so on and so forth. So, basically all possible second or second order derivatives have to be taken here, naturally I have to this is nothing, but the derivative I have to take the order of the displacement which is just quadratic it displacement. So, you can say that the strength of the displacement is quadratic here.

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$$U = U_0 + \sum_{\vec{r}_i, \vec{r}_j; \alpha, \beta} \frac{\partial^2 U}{\partial \vec{r}_{i,\alpha} \partial \vec{r}_{j,\beta}} d\vec{r}_{i,\alpha} d\vec{r}_{j,\beta} + O(d^3)$$

low T

And then naturally the high order terms are being dropped here, because they are of the order d r cube ok, we are considering displacements that are very close to 0 or displacements that keeps very close to the mechanical equilibrium. So, this is basically the low temperature approximation, that my terms of the order 3 are going to be 0.

Not only that if you look at the first term, first sub leading term here which is proportional to the derivative of the gradient of the potential energy this will also be 0. Because again, we are at low temperatures which means that we are close to mechanical

equilibrium and if that is the case then this term negative gradient of this term which is gradient of potential energy has to be seen with negative of the force. So, the term that I have taken to 0 is due to the fact that I am close to mechanical equilibrium. So, this  $\frac{\partial u}{\partial r_i}$ , which is the gradient of the potential energy it is nothing, but negative of the force acting on the  $i$ th ion and the  $\alpha$  component of it ok.

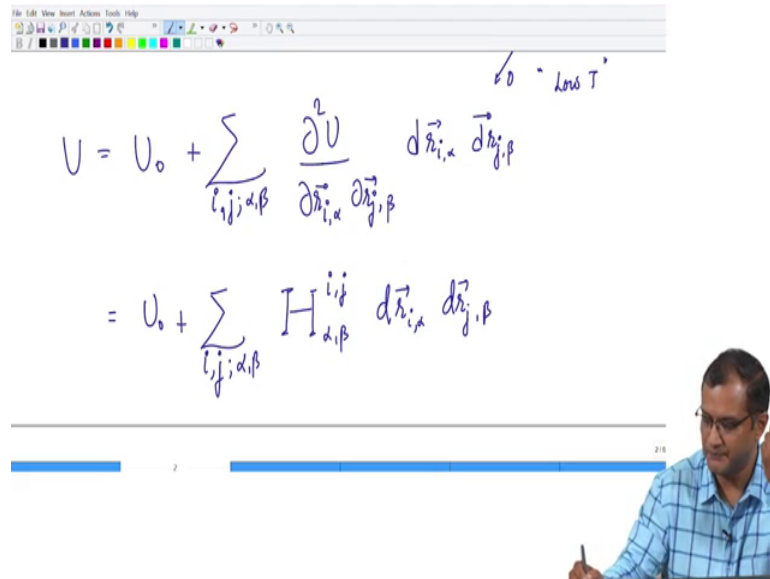
So, here as you can see I have taken a gradient of the potential energy, with respect to the  $i$ th particle I have taken of the  $\alpha$  component of it. So, it is the negative of the force acting on the  $i$ th particle and the  $\alpha$  component of it and that has to be 0, because we are close to mechanical equilibrium. So, all first order derivatives would be 0 and we have taken the higher order derivatives to 0, because they are anyway negligible.

So, our potential energy is basically now nothing, but some reference which is arbitrary the energy is a state function its a reference arbitrary or you measure any process is the change in energy. So, you know it does not pose any issue to me, but this is actually added to a more meaningful and interesting term, which is the Hessian. So, I have to sum over all  $i$  in  $j$ s and  $\alpha$  and  $\beta$  and the better way to write this is not  $r_i r_j$ , but just  $i j$  because we are summing over  $i$  and  $j$ .

So, let me just write it as  $i$  comma  $j$  and  $\alpha$   $\beta$  and the same here, I am going to just write this as a summation over  $i$   $\alpha$ . So, here  $i$  belongs to 1 to  $N$  and  $\alpha$  belongs to, 1 to 3, this belongs from 1 to  $N$  ok. So, now, we know that the potential energy is now reduced to a reference  $U$  naught plus a second derivative of potential energy with respect to the coordinates ok and this second derivative of potential energy. If you see can be written as some kind of a matrix element, because there are 4 indices here and you can take each direction to be a combination of 2 indices.

So, eventually this will be a matrix of if you take,  $n$  particles in 3 dimensions then this turns out to be a matrix of size  $3 N$  by  $3 N$ .

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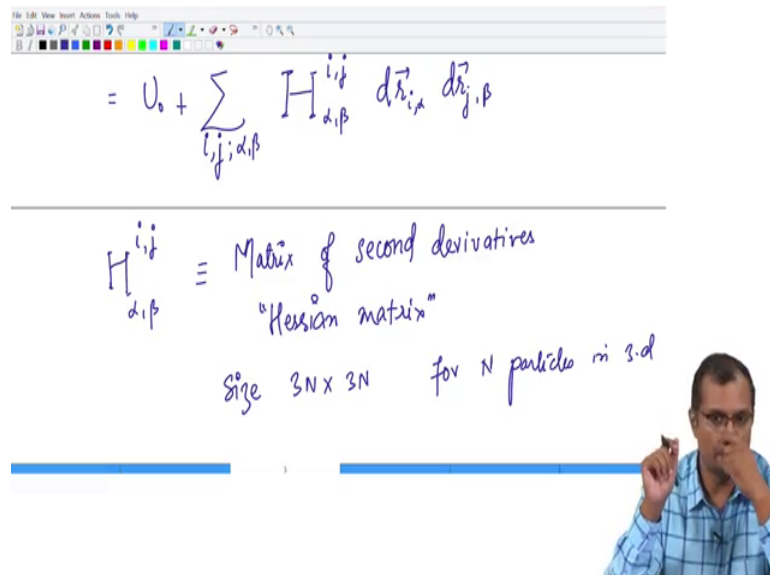
The image shows a whiteboard with handwritten mathematical equations. At the top right, there is a handwritten note:  $\rightarrow \text{Low } T$ . The main equation is:

$$U = U_0 + \sum_{i,j;\alpha,\beta} \frac{\partial^2 U}{\partial \vec{r}_{i,\alpha} \partial \vec{r}_{j,\beta}} d\vec{r}_{i,\alpha} d\vec{r}_{j,\beta}$$
$$= U_0 + \sum_{i,j;\alpha,\beta} H_{\alpha,\beta}^{i,j} d\vec{r}_{i,\alpha} d\vec{r}_{j,\beta}$$

A presenter is visible in the bottom right corner of the slide.

So, I can write this  $U$  as this, I can write down this second derivative has matrix of rank 2 or tensor of rank 2 and I can write this as, some  $H$  and  $H$  here is basically nothing, but a Hessian matrix. So, I am going to write it as sum  $i, j$  alpha beta  $dr_i$  and  $dr_j$  comma beta.

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The image shows a whiteboard with handwritten text defining the Hessian matrix. The equation from the previous slide is repeated at the top:

$$= U_0 + \sum_{i,j;\alpha,\beta} H_{\alpha,\beta}^{i,j} d\vec{r}_{i,\alpha} d\vec{r}_{j,\beta}$$

Below this, the text reads:

$H_{\alpha,\beta}^{i,j} \equiv$  Matrix of second derivatives  
"Hessian matrix"  
Size  $3N \times 3N$  for  $N$  particles in 3-d

A presenter is visible in the bottom right corner of the slide.

So, here the matrix of second derivatives, is basically it is also called as a Hessian matrix and if you take  $n$  particles in 3 dimensions, then this matrix has a size of  $3N$  by  $3N$  ok. So, you can write down this matrix of second derivatives in the form of a array or a 2

dimensional matrix and if you look at the form of this matrix, it does not matter if I change the location of alpha and beta, because this matrix is symmetric in its indices.

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Size  $3N \times 3N$

Being symmetric in nature,  
It is diagonalizable.  $\Rightarrow U H U^T = \Lambda$   
 $= (\lambda_1, \lambda_2, \dots, \lambda_{3N})$

$\lambda_i$ 's are normal modes of vibration

So, being symmetric in nature ok. I can it is diagonalizable, which means there exists a unitary matrix  $U$  that can readily diagonalize it. So, if I construct a unitary matrix  $U$ , then  $U$  a  $U$  transpose can diagonalize this into a matrix of only diagonal values. So, this matrix would be nothing, but a matrix of all the eigenvalues, which are nothing, but your normal modes ok. So, here these lambda is are nothing, but normal modes of vibration. So, this is a matrix of size  $3N$  by  $3N$ , when you diagnose it you will get  $3N$  eigenvalues which are nothing, but the modes of vibration of a solid.

So, this would be like, there are  $n$  particles in the solid and this is a 3dimensional system. So, if you ask, the following question that how many different frequencies? One has to consider then there are precisely  $3N$  frequencies one for each direction and  $n$  for each particle total  $3N$ . So, these are  $3N$  fundamental I would say  $3N$  fundamental frequencies of the oscillator. So, I can now expect that the system has  $3N$  oscillators ok.

(Refer Slide Time: 16:12)

The slide shows a whiteboard with handwritten text and a mathematical equation. At the top, it says " $\lambda_i$ 's are normal modes of vibrations." Below that, it says "Hamiltonian due to these 3N oscillators!" followed by the equation 
$$H = \sum_{\alpha=1}^{3N} \left( n_{\alpha} + \frac{1}{2} \right) \hbar \omega_{\alpha}$$
 To the right of the equation, it says "Zero point energy:  $\frac{1}{2} \hbar \omega_{\alpha}$  of  $\alpha^{\text{th}}$  oscillator". In the bottom right corner, there is a small video inset of a man in a blue checkered shirt speaking.

And we can now think of the Hamiltonian, due to these 3 N oscillators. So, our system has you know each particle has now oscillations in 3 directions. So, it is like, there are 3 oscillators for each particle and now, you have N particles being that the system can be represented by 3 N oscillators and these oscillators can be attributed some energy, which is our Hamiltonian ok.

So, we can write down the Hamiltonian in the form of you know, the summation over all the oscillators where alpha will go from 1 to 3 N and we will write down the energy of this oscillator as some excitation plus, one half h cut omega ok. So, here the half h cut omega is the zero point energy of the oscillator and this is zero point energy of the alpha th oscillator ok.

Now, what is alpha here? Now each alpha each oscillator can be in a state of excitation ok.



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$\alpha = 1$

of  $\alpha$  oscillator

$n_\alpha$  is the excitation of  $\alpha$  oscillator.

Microstate:  $\{n_i\} i \in (1, N)$

$\nu_1: (n_1, n_2, \dots, n_N)$

$\nu_2: (n'_1, n'_2, \dots, n'_N)$

So,  $n_\alpha$  represents the state of excitation of the  $\alpha$ th oscillator, in some sense  $n_\alpha$  tells us basically the occupation number of the  $\alpha$ th oscillator. So, how many phonons are there that in how many quantum of energy which is the number of phonons, in that energy level  $\alpha$  or in that oscillator.

So,  $n_\alpha$  represents in some sense the excitation of the  $\alpha$ th oscillator and  $\omega_\alpha$  in some sense tells us the vibrational frequency of that oscillator fundamental frequency of that oscillator.

Student: Frequencies are not necessarily in this statement.

So, we have it for this reason we in this discussions we allow different frequencies for each oscillator and  $n_\alpha$  simply represents and some sense the excitation of an oscillator, having a fundamental frequency  $\omega_\alpha$  right. So, now you can the fact, that we are dealing with the system of bosons there is no upper limit on the maximum number of bosons I can accommodate in a level. So,  $n_\alpha$  here in principle can be 0 to infinity what this means is that there could be infinite number of phonons up to sitting in any oscillating mode ok.

So, or any oscillator which would simply make the total energy of the  $\alpha$ th oscillator. Now there are  $3N$  oscillators. So, you simply take, what is the energy of each oscillator? And sum over all oscillators that will give you the total Hamilton in the system. So,

now, I can write down the I can imagine or a microstate of my system. now this is where the question of what is  $n$  alpha becomes more clear.

So, the microstate here is nothing, but the set of these excitations you know, where these  $i$  belongs to. So, what is the suppose you take the  $i$  th oscillator you know to be an excitation  $n_1$ ,  $j$  th oscillator to be an excitation  $n_j$ , these are numbers. So, different set of numbers for each oscillator is nothing, but the microstate of a system. So, if you specify 1 microstate as  $n_1, n_2$ , all the way to  $n_N$  some specified values.

This is one microstate you can take another microstate as  $n_1$  bar,  $n_2$  bar all the way to  $n_N$  bar, this is another microstate, the set of excitations of each oscillator is 1 microstate for you.

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The slide shows handwritten notes in blue ink on a white background. At the top, there is a menu bar with options like 'File', 'Edit', 'View', 'Insert', 'Actions', 'Tools', and 'Help'. Below the menu bar, the text reads: 'Microstate:  $\{n_i\} i \in (1, 3N)$ '. This is followed by two examples:  $\nu_1: (n_1, n_2, \dots, n_{3N})$  and  $\nu_2: (n'_1, n'_2, \dots, n'_{3N})$ . A vertical ellipsis follows. Below that, it says 'Large no. of micro-states'. At the bottom, it says 'No restriction as  $\sum_{i=1}^{3N} n_i \neq 3N$ '. To the right of the text is a video inset showing a man in a blue checkered shirt speaking.

This way you can construct a large number of microstates for your system.

Student: Some of the small  $n$  is should be total  $n$ .

No that is not  $n$ ,  $n$  is cannot sum up to a conserved quantity, because you can have any number of bosons you have only  $3N$  oscillators. So, here I think I should take the last object to  $3N$  or  $dn$ , here the particle number is not conserved we do not have as  $k$  these are not real particles, there is no restriction here that my there is no restriction here, if your question is that if I sum over all is going from 1 to  $3N$   $n$  is this will be  $3N$ .

There is no such restriction like this first of all  $n$  is are excitations of  $i$  th oscillator, it could be in any state. In fact, I will take  $n$  is in the following this discussion from 0 to infinity it could be in any excited state ok. So, we do not have to conserve the number of these virtual bosons in this case the phonons to something their number is not conserved and so, this number does not is not fixed ok.

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Large no. of micro-states

Partition function:  $Z = \sum_{\{n_i\}} e^{-\beta H\{\{n_i\}\}}$

$= \sum_{\{n_i\}} e^{-\beta \sum_{\alpha=1}^{3N} (n_{\alpha} + 1/2) \hbar \omega_{\alpha}}$

So, how would we write down the partition function? So, the partition function can be written as, summation over all microstates. So, I am going to sum over all possible excitations.

So, the first oscillator may have an excitation  $n_1$ , second oscillator may have an excitation  $n_2$ , third oscillator may have an excitation  $n_3$ ,  $n_1$   $n_2$   $n_3$  are some values, some of these  $n$  is not conserved you do not have the conservation here. So, then we can simply say that our partition function here is a summation over all the microstates of the Boltzmann factor that is written as  $e$  raise to minus beta and the Hamiltonian.

Now, our Hamiltonian itself is function of all the excitations, but the way in which it depends on the excitations is nice. So, it is written as, summation over all the excitations  $e$  to the power minus beta and our Hamiltonian is nothing, but we have to now add up the energy of all oscillators. So, the energy of each oscillator Hamiltonian is the total energy of  $3N$  oscillator. So, the energy each of oscillator is  $n_{\alpha} + 1/2 \hbar \omega_{\alpha}$  this is one oscillator.

You sum over all alphas there are  $3N$  oscillators. Now the  $n$  alphas that you take here in the Hamiltonian correspond to the microstate that you have taken here ok. So, you keep changing that microstate compute the total energy and compute the Boltzmann factor that is how you will compute this sum ok.

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$\{n_j\}$

$$= \sum_{\{n_j\}} e^{-\beta(n_1 + 1/2)\hbar\omega_1} e^{-\beta(n_2 + 1/2)\hbar\omega_2} \dots e^{-\beta(n_{3N} + 1/2)\hbar\omega_{3N}}$$

$$= \prod_{j=1}^{3N} \sum_{n_j=0}^{\infty} e^{-\beta(n_j + 1/2)\hbar\omega_j}$$

So, then this would simply become if you think of it this way it is nothing, but I can write it as summation over all possible microstates,  $e$  to the power minus beta I can take it as  $n_1 + 1/2 \hbar \omega_1$  into  $e$  raised to minus beta  $n_2 + 1/2 \hbar \omega_2$  all the way to  $e$  raised to minus beta  $n_{3N} + 1/2 \hbar \omega_{3N}$ .

Fine. So, this is like I can take this as a product and I will take this product outside. So, this would be a product of  $j$  going from 1 to  $3N$ . So, I am going to write it as since I have taken this product on over all the exponents outside. So, the inside is just summation over  $n_j$ , that will go from 0 to infinity  $e$  raised to minus beta  $n_j + 1/2 \hbar \omega_j$  ok.

So, the  $3N$  products are outside, for each product you take  $n_j$  going from 0 to infinity.

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$$\begin{aligned}
 &= \prod_{j=1}^{3N} \sum_{n_j=0}^{\infty} e^{-\beta n_j h \omega_j} \\
 &= \prod_{j=1}^{3N} e^{-\beta h \omega_j / 2} \sum_{n_j=0}^{\infty} e^{-\beta n_j h \omega_j} \\
 &= \prod_{j=1}^{3N} e^{-\beta h \omega_j / 2} \left[ 1 + e^{-\beta h \omega_j} + e^{-2\beta h \omega_j} + \dots \right]
 \end{aligned}$$

And then you can think of it this way that the I can do it this way, that the submission does not operate on omega j it only operates on n j. So, what I will do is, I will take the omega j is operated on only by the product. So, I can take e to the power minus beta, h cut omega j outside and I will say that the summation operates only on n js, the summation variable is n j only and this is e to the power minus beta n j h cut omega j ok. So, the for the summation the omega j is a constant here.

Student: That e power minus beta h plus omega j by 2.

Correct. So, there should be omega j by 2 fine ok. So, this summation is only on the n j not on omega j, for which is constant inside the summation. So, I can write it as product over all 3 N modes e to the power of minus beta h cut omega j by 2 and this would be nothing, but if you do the summation write down the first few terms. So, for n j equal to 0 you get 1 then, for n j equal to 1 you get minus you got e to the power minus beta h cut omega j, plus e to the power minus 2 beta h cut omega j and so on. You have been finite terms.

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$$j=1$$

$$= \prod_{j=1}^{3N} \frac{e^{-\beta \hbar \omega_j / 2}}{1 - e^{-\beta \hbar \omega_j}}$$

$$= \prod_{j=1}^{3N} \frac{1}{e^{\beta \hbar \omega_j / 2} - e^{-\beta \hbar \omega_j / 2}}$$

Geometric series  
 Common ratio =  $e^{-\beta \hbar \omega_j}$   
 $= \frac{1}{1 - e^{-\beta \hbar \omega_j}}$

So, if you look at this, this is a geometric series and it converges for a common ratio which is  $e$  to the power  $e$  to the power minus  $\beta \hbar \omega_j$ , that is a common ratio and I know as you know the summation goes towards larger and larger end this with common ratio will go to 0. So, this series is uniformly convergent for this common ratio and so, I can write down this as, product over  $j$  going from 1 to  $3N$   $e$  raised to minus  $\beta \hbar \omega_j$  by 2 and the product has been the geometric series has been reduced to this sum, which is 1 upon 1 minus the common ratio which is  $e$  raise to minus  $\beta \hbar \omega_j$ .

So, this is equal to the sum 1 upon 1 minus ok. So, this is common ratio fine. So, now, you can see that I can reduce it further by just multiplying the numerator and denominator with  $e$  to the power  $\beta \hbar \omega_j$ . So, this will give me 1 upon  $e$  to the power  $\beta \hbar \omega_j$  by 2 minus  $e$  to the power minus  $\beta \hbar \omega_j$  by 2 ok.

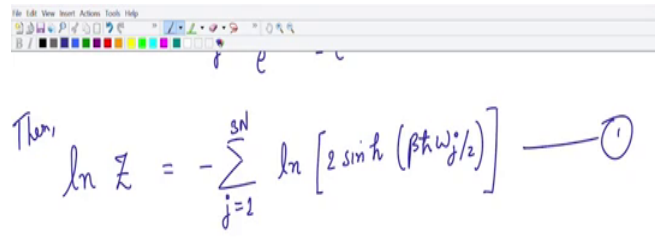
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$$Z = \prod_{j=1}^{3N} \frac{1}{e^{\beta \hbar \omega_j / 2} - e^{-\beta \hbar \omega_j / 2}} = \prod_{j=1}^{3N} \frac{1}{2 \sinh(\beta \hbar \omega_j / 2)}$$
$$\text{Then, } \ln Z = - \sum_{j=1}^{3N} \ln [2 \sinh(\beta \hbar \omega_j / 2)]$$

And this can be visualized to be as nothing, but product of  $3N$  I can write it as, 1 upon I can write it as twice sin hyperbolic of beta h cut omega j by 2 fine. So, this is nothing, but our partition function. So, I can write down my logarithm of the partition function, that sort of builds connection with thermodynamics.

So, I can write down my  $\ln Z$  as nothing, but the logarithm of products becomes summation of logarithms and the fact that you have inverse for each term, it simply gives me a negative sign outside and it becomes a summation over all  $3N$  oscillators of logarithm twice sin hyperbolic beta h cut, omega j by 2 that is the expression for your partition function for our  $3N$  dimensional solid ok.


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Then,

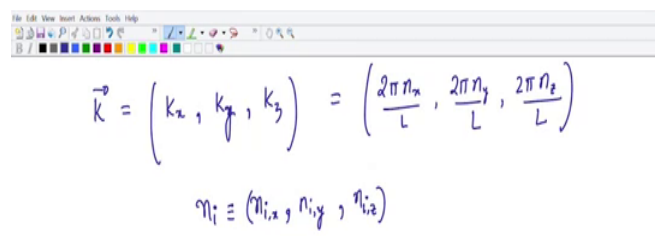
$$\ln Z = - \sum_{j=1}^{SN} \ln \left[ 2 \sinh \left( \beta \hbar \omega_j / 2 \right) \right] \quad \text{--- (1)}$$

We know that,  $N \rightarrow \infty$        $N/V \rightarrow \text{finite}$   
 $V \rightarrow \infty$



So, now you can build thermodynamics from here. So, what you want to do from it is onwards is we know that. So, I am just going to as you take the your system to be very large. So, as N goes to infinity and your volume goes to infinity such that, your number of particles becomes finite and you have a well defined homogenous density, in this limit you can think of your wave vectors to be tightly spaced in the box.

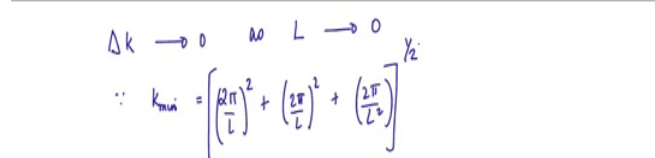
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$$\vec{k} = (k_x, k_y, k_z) = \left( \frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L} \right)$$

$$\eta_i \equiv (\eta_{i,x}, \eta_{i,y}, \eta_{i,z})$$


---



$\Delta k \rightarrow 0$       as  $L \rightarrow \infty$

$$\therefore k_{min} = \left[ \left( \frac{2\pi}{L} \right)^2 + \left( \frac{2\pi}{L} \right)^2 + \left( \frac{2\pi}{L} \right)^2 \right]^{1/2}$$


In the sense that, any wave vector k that you take for your system would be nothing, but a collection of these components of the wave vector and I can call these components of



the wave vector as  $2\pi n_x$  over  $l$ ,  $2\pi n_y$  over  $l$ , assuming you have a cubic box and now, what are these  $n_x n_y n_z$ s?

$n_x n_y n_z$  nothing, but the excitation of each oscillator that you have taken. So, each oscillator that you said is an excitation of  $n_i$  I can actually write down that  $n_i$ , as a combination of you know  $n_{ix}$ ,  $n_{iy}$  and  $n_{iz}$ . So, the  $n_x n_y n_z$  are basically, the components of the excitation of any oscillator in the system. So, if you take this  $L$  to be very large, then you can think of your wave vectors  $k$  to be very closely spaced because the minimum wave vector that you can have is basically  $2\pi$  by  $L$  into  $n_x$ .

$2\pi$  by  $L$  into  $n_y$   $2\pi$  by  $L$  into  $n_z$ . So, if  $L$  goes to very large the  $\Delta k$  that is the separation between your wave vectors goes to 0 ok, since you can write down the  $k$  minimum is nothing, but in some sense the you can take  $n_x n_y n_z$  to be 1, that is the minimum value of. So, this  $k$  minimum would be nothing, but  $2\pi$  by  $L$  of the order of  $2\pi$  by  $L$ . So, it is basically  $2\pi$  by  $L$  square plus  $2\pi$  by  $L$  square, plus  $2\pi$  by  $L$  square and the whole thing.

So, this would be the minimum from  $k$  minimum you can construct the magnitude of  $k$  minimum. So, you know its would be of the order  $2\pi$  by  $L$  ok, because some of these threes the same order.

(Refer Slide Time: 36:36)

Handwritten mathematical derivation on a whiteboard:

$$\Delta k \rightarrow 0 \quad \text{as } L \rightarrow \infty$$

$$\therefore k_{\min} = \left[ \left( \frac{2\pi}{L} \right)^2 + \left( \frac{2\pi}{L} \right)^2 + \left( \frac{2\pi}{L} \right)^2 \right]^{1/2} \sim \frac{1}{L}$$

$$\omega \sim k \quad (\omega = ck)$$



If we take the square root is of the order  $1/L$ . So, as  $L$  goes to infinity our separation between the modes goes to 0. So, you can think of the summation here, in  $1$  it will turn into an integral ok.

Now, we are as modes are coming close since  $\omega$  is proportional to  $k$ ,  $\omega$  is actually  $c$  times  $k$  the actual relationship is. So, if  $k$ s are coming very close to each other, we expect  $\omega$ s to be also very closely. In fact, the  $c$  is not the velocity of light this is a acoustic speed ok, please make the distinction here my  $c$  is the acoustic speed. We are talking about vibrations of in a solid. So, basically we are talking about the speed of sound in the solid.

So,  $c$  here corresponds to the acoustic speed and is as  $k$  becomes tighter and tighter in the system as we have just seen, we expect the  $\omega$  is also to be very close and close to each other. Now if you have large number of these  $\omega$ s and they are all very close to each other and it makes no sense to continue with this summation that is very painful ok. So, you what you will have in this instead of this is that as  $N$  goes to infinity, the our upper limit of summation also go to infinity and your  $\omega$ s are very close tight now. So, I am going to convert this summation into an integral in the thermodynamic limit.

(Refer Slide Time: 38:19)

The image shows a whiteboard with handwritten mathematical notes and an integral equation. At the top, it says  $\omega \sim k$  ( $\omega = ck$ ). Below that, it says "In the thermodynamic limit, modes are tightly spaced,". The main equation is  $\ln Z = - \int_{\omega=0}^{\infty} \ln \left[ 2 \sinh \left( \frac{\beta \hbar \omega}{2} \right) \right] g(\omega) d\omega$ , with a circled 2 next to it. An arrow points from  $g(\omega)$  to the text "dim( $1/\omega$ )". In the bottom right corner, there is a small video inset of a man in a blue checkered shirt.

So, in the thermodynamic limit as modes are more and more and they are tightly spaced, because of the arguments that just preceded it makes a good it makes good sense if I

write down my  $\ln Z$  as an integral. So, I am going to write down my  $\ln Z$  as an integral. So, this would be like 0 to  $\omega$  we will go from 0 to infinity.

And I will have to integrate  $\ln$  of twice, sin hyperbolic into  $\beta \hbar \omega$  cut  $\omega$  0 by 2, correct and there shall not be any. In fact, just  $\omega$  the subscript on  $\omega$  will not disappear because, we are integrating over all  $\omega$   $d\omega$ . Now as you can see this integration is not correct unless I take into account certain density of states, because otherwise this integration is not dimensionally consistent.

You see this quantity  $g$  of  $\omega$  should have the dimensions of 1 over  $\omega$ , only then this integration is dimensionless and becomes our  $\ln Z$ , but what should be this  $g$  of  $\omega$  and why should we have  $g$  of  $\omega$ ? Well the simple reason is we have  $g$  1 from summation over all  $\omega$ s to integral over all  $\omega$ s.

(Refer Slide Time: 40:24)

The slide contains the following handwritten text:

$$\sum_{\omega} \rightarrow \int d\omega g(\omega) = \Omega_{modes}$$

$$g(\omega) \equiv \frac{d\Omega}{d\omega}$$

Einstein's proposal :  $g(\omega) = \delta(\omega - \omega_0)$

Now this integration only makes sense, if you are multiplying your integrand with the density of states. So, in some sense the density of states is required to basically, say that your if you have number of states in some frequency interval ok. Then if you integrate over the entire frequency interval, then the summation of overall  $g$  of  $\omega$  is simply unity or number of modes, if you have not normalized your density of states.

So, this should simply give me all the number of modes in the system ok, all the modes in the system. Because number of modes per unit energy range, if you integrate over all the range should give you the total number of modes.

So, depending upon what density of states we choose we can get different answers and in this, the first case that I am going to take here today, is the case proposed by Einstein who said that all  $3N$  oscillators are oscillating with the same frequency. So, that was the most simple quantum mechanical description given by Einstein we said that, let us not worry about let us say question asked in the beginning was are all  $\omega_j$  is the same. So, I said that let us start with all the frequencies different.

But now here, here we are with a nice expression in the continuum limit the first solution was given by Einstein who said that instead of taking all  $\omega$ s to be different why not take them all to be the same. So, Einstein proposed. So, Einstein's proposal was to take all oscillators with the same frequency. So, in some sense Einstein was saying that the density of states here, is like a Dirac delta distribution what does this mean? He was saying that all oscillators having the same frequencies.

Now, if you ask question, what is the number of oscillators per frequency? This has to be infinity, because his frequency width is 0 everything is in 1 frequency and you have got  $N$  or  $3N$  oscillators all of them oscillating with  $\omega_0$  which means, if you considered  $dN$  by  $d\omega$  its got to be infinity because number of oscillators in your unit frequency width the width is 0 everything is in 1 oscillator, everything is on 1 frequency. So, this is got to be a Dirac delta distribution.

(Refer Slide Time: 43:24)

Handwritten notes on a whiteboard:

$g(\omega) = \frac{dN}{d\omega}$

Einstein's proposal :  $g(\omega) = SN \delta(\omega - \omega_0)$  "All oscillators with same frequency"

$\int_0^{\infty} g(\omega) d\omega = \int_0^{\infty} SN \delta(\omega - \omega_0) d\omega = SN$

So, you can think of these  $\omega$  here as the Einstein's frequency,  $\omega_0$  is the frequency of all the oscillators, it is like saying that you know. So, if each oscillator's frequency is the same and you ask me, what is the density of states? It's got to be a delta function, ok, because if you integrate this over all the frequency space then there is got to be simply 1, it's got to be simply you know, if you take it as  $N$  times  $3N$  times delta. So, then this simply gives me the number of oscillators, ok.

So, we are going to take this example of the Einstein's oscillator of Einstein's model and proceed with the calculation.

(Refer Slide Time: 45:02)

Einstein's proposal :  $g(\omega) = 3N \delta(\omega - \omega_0)$  "All oscillators with same frequency"

Q: What is heat capacity in this model?

$$\ln Z = - \int_{\omega=0}^{\infty} 3N \delta(\omega - \omega_0) \ln \left[ 2 \sinh \left( \frac{\beta \hbar \omega}{2} \right) \right] d\omega$$

So, I am going to take the example of the Einstein's model and compute the partition function. So, the question is what is the heat capacity in this model ok? So, let us first compute the partition function, because from there we compute all the quantities. So, what partition function is basically  $\ln Z$  or logarithm of the partition function has been already computed to be negative of the derivative of  $g$  omega, which is  $3N$  times this there are delta distribution into the logarithm of  $2 \sinh$  beta  $\hbar$  cut omega  $0$  by  $2$ , just omega of course,  $d$  omega correct.

(Refer Slide Time: 46:30)

$$\ln Z = - \int_{\omega=0}^{\infty} 3N \delta(\omega - \omega_0) \ln \left[ 2 \sinh \left( \frac{\beta \hbar \omega}{2} \right) \right] d\omega$$
$$= -3N \ln \left[ 2 \sinh \left( \frac{\beta \hbar \omega_0}{2} \right) \right]$$

Compute  $E = \langle H \rangle = - \frac{\partial}{\partial \beta} (\ln Z) = 3N \coth \left( \frac{\beta \hbar \omega_0}{2} \right) \cdot \frac{\hbar \omega_0}{2}$

Now you can see that by the property of delta function distribution, the entire integral picks up the contribution from the function where the delta function has its source. So, the source is at  $\omega = 0$ . So, in the entire integrand comes from that source. So, it is becoming  $\ln$  of twice  $\sin$  hyperbolic  $\beta \hbar \omega_0$  by 2 ok.

Now, which means that I can compute the thermodynamic quantities, because this is my bridge that can I start my to thermodynamics. So, computing total internal energy which is nothing, but the expectation value of the Hamiltonian is now cakewalk. So, this is nothing, but what we have seen in the last chapter is negative derivative of logarithm  $Z$  ok. If you recall the results of the canonical ensemble and this is the ensemble in constant  $N, V, T$  conditions.

The number of particles temperature and the volume of the solid does not change. So, this is the canonical partition function and whose derivative in this form, gives you the internal energy. So, negative  $\ln Z$  is already given to me. So, I am just going to copy the previous expression and write this as thrice  $N$  and the derivation of logarithm is just its just going to give me tangent, not tangent its going to give me cot hyperbolic  $\beta \hbar \omega_0$  by 2 into  $\hbar \omega_0$  by 2.

(Refer Slide Time: 48:51)

The image shows a digital whiteboard with handwritten mathematical derivations. At the top, there is a toolbar with various drawing tools. Below the toolbar, the following equations are written in blue ink:

$$E = 3N \frac{\hbar \omega_0}{2} \cot \hbar \left( \frac{\beta \hbar \omega_0}{2} \right)$$

$$\text{Heat capacity } C_V = \left. \frac{\partial E}{\partial T} \right|_{N,V} = \frac{3N \hbar \omega_0}{2} \frac{\partial}{\partial T} \cot \hbar \left( \frac{\beta \hbar \omega_0}{2} \right)$$

$$\text{Noting: } \frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T} \Rightarrow \frac{\partial}{\partial T} = -\beta^2 k_B \frac{\partial}{\partial \beta}$$

At the bottom right of the whiteboard, there is a small inset video of a man in a blue checkered shirt, who appears to be the lecturer.

And I can now write it as  $3 N \hbar \omega_0$  by 2 into cot hyperbolic,  $\beta \hbar \omega_0$  by 2 all right, but this is my total energy I want heat capacity ok. So, the heat capacity at

constant volume, is given as the temperature derivative of the total energy at constant number of particles and volume we are in  $N, V, T$  on symbol.

So, I am going to write it as  $\frac{3}{2} N \hbar \omega_0$ , into  $\frac{d}{dT}$  of  $\coth$  hyperbolic  $\beta \hbar \omega_0 / 2$ , let us do it carefully it is natural to do this derivative in terms of  $\beta$  ok. So, what I am going to do here is basically note that. So, noting that  $\frac{d}{d\beta}$  can be transformed into a temperature derivative which means, my temperature derivative can be written as,  $-\frac{1}{k_B T^2} \frac{d}{d\beta}$  and that would be nothing, but  $-\beta^2 k_B$  into  $\frac{d}{d\beta}$  because  $\beta$  itself is  $1/k_B T$ . So, one  $k$  will cancel right.

(Refer Slide Time: 50:59)

$$C_V = \frac{3}{2} N \hbar \omega_0 (-\beta^2 k_B) \frac{\partial}{\partial \beta} \coth\left(\frac{\beta \hbar \omega_0}{2}\right)$$

$$= -\frac{3}{2} N \hbar \omega_0 \frac{(\hbar \omega_0)}{k_B T^2} \frac{\partial}{\partial (\hbar \omega_0 \beta)} \coth\left(\frac{\beta \hbar \omega_0}{2}\right)$$

$$= -\frac{3}{4} N k_B \left(\frac{\hbar \omega_0}{k_B T}\right)^2 \frac{\partial}{\partial (\hbar \omega_0)}$$

So, I am going to substitute this change of derivatives. So, my heat capacity at constant volume will become  $\frac{3}{2} N \hbar \omega_0$  and I get a  $-\beta^2 k_B$ , into  $\frac{d}{d\beta}$  of  $\coth$  hyperbolic  $\beta \hbar \omega_0 / 2$ . And let me make some more substitution. So, I am going to write it as. So,  $\beta^2 k_B$  can be written as  $1/k_B T^2$  and I will have a  $1/k_B$ , with a negative sign.

Student: (Refer Time: 51:59) square.

No just a second. So, I am going to write it as. So, that would be correct. So, this will be  $k_B T^2$  ok.

Student: (Refer Time: 52:50)  $k_B T$ .



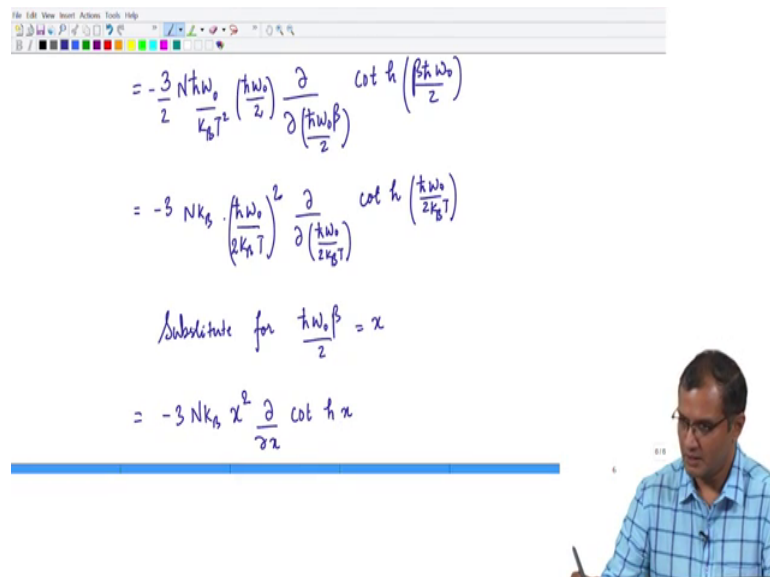
So, beta is 1 upon kt. So, beta square is k square T square in the denominator. So, then I should.

Student: (Refer Time: 53:00).

So, I am going to write it as just with the minus sign here and what I am going to do next is multiply and divided by h cut omega 0 by 2 and then write this as minus 3 by 2, into N k B into so in fact, I am going to write it as minus 3 by 4.

Because there is there are 2 factors of 2 there in to h cut omega 0 by k BT, the whole square ok, into d by d of h cut omega 0 by. In fact, I can take the 2 inside here fine.

(Refer Slide Time: 54:45)



The image shows a whiteboard with handwritten mathematical steps. The top part of the whiteboard has a toolbar with various drawing tools. The equations are as follows:

$$= -\frac{3}{2} N k_B \frac{(\hbar \omega_0)}{k_B T} \frac{\partial}{\partial (\frac{\hbar \omega_0 \beta}{2})} \cot \hbar \left( \frac{\beta \hbar \omega_0}{2} \right)$$

$$= -3 N k_B \left( \frac{\hbar \omega_0}{2 k_B T} \right)^2 \frac{\partial}{\partial (\frac{\hbar \omega_0}{2 k_B T})} \cot \hbar \left( \frac{\hbar \omega_0}{2 k_B T} \right)$$

Substitute for  $\frac{\hbar \omega_0}{2} = x$

$$= -3 N k_B x^2 \frac{\partial}{\partial x} \cot \hbar x$$

In the bottom right corner, there is a small video inset of a man with glasses and a blue checkered shirt, who appears to be the lecturer.

So, I can substitute for h cut omega 0 beta by 2 as x. So, this becomes nothing, but minus 3 N k B, into x square. So, these are substitutions which I believe will make life easy for us del by del x square, del by del x of cot hyperbolic h cut or cot hyperbolic x. So, I think it has already made life easy ok.

(Refer Slide Time: 55:59)

Use the fact,  $\frac{d}{dx} \cot hx = \frac{-1}{\sinh^2 x} = \frac{d}{dx} \left( \frac{e^x + e^{-x}}{e^x - e^{-x}} \right)$

$$C_V = \frac{3 N k_B x^2}{\sinh^2 x} = \frac{3 N k_B x^2 \cdot 4}{(e^x - e^{-x})^2}$$

$$= 12 N k_B x^2 \frac{1}{(e^x (e^{-x} - 1))^2}$$

And it is known I am just going to use the fact, that the derivative of cot hyperbolic x is nothing, but minus 1 upon sin hyperbolic square x its known. So, you can work it out very simple by simply saying that I will write down my cot hyperbolic x, you just use the simple chain rule as cos hyperbolic x divided by sin hyperbolic x, which is nothing, but do this derivative up by yourself.

So, it would be e to the power x plus e to the power minus x, upon e to the power x minus e to the power minus. So, this is cot hyperbolic x do this derivative you will get minus 1 upon sin hyperbolic x square. Anyway I am not going to do that derivative here. So, I am going to just write down my internal energy as minus 3 N k B.

Student: This is heat capacity.

This is heat capacity, I am sorry its already taken derivative minus 3 N k B into x square and into minus 1 by sin x square. So, minus turns into positive. Now, sin hyperbolic square x ok. So, this is nothing, but this is 3 times N k B, into x square ok. So, you can write it as sin hyperbolic square x would be nothing, but 1 upon e to the power x minus e to the power minus x by 2 the whole square. So, there will be a 4 in the numerator ok. So, this will be if I call this as this becomes 12 times N k B, into x square and I am simply going to take 1 e raise to minus x from the denominator.

So, this becomes e raise to x upon. So, this becomes if i. So, let me just; so, let me just. So, I am going to write down 1 upon, I will take e raise to x by 2. So, that will be e raise to minus x and so, I am going to take e raise to x outside. So, this becomes 1 sorry e raise to minus x outside. So, this becomes correct all right.

So, if I write under this square root under the square, then it simply becomes e raise to x minus e raise to minus x ok. So, if you want to understand this, you can say that I am going to write it without the square here and then this is the overall square ok, then this goes inside becomes e raise to x minus e raise square and the entire square is outside.

(Refer Slide Time: 61:31)

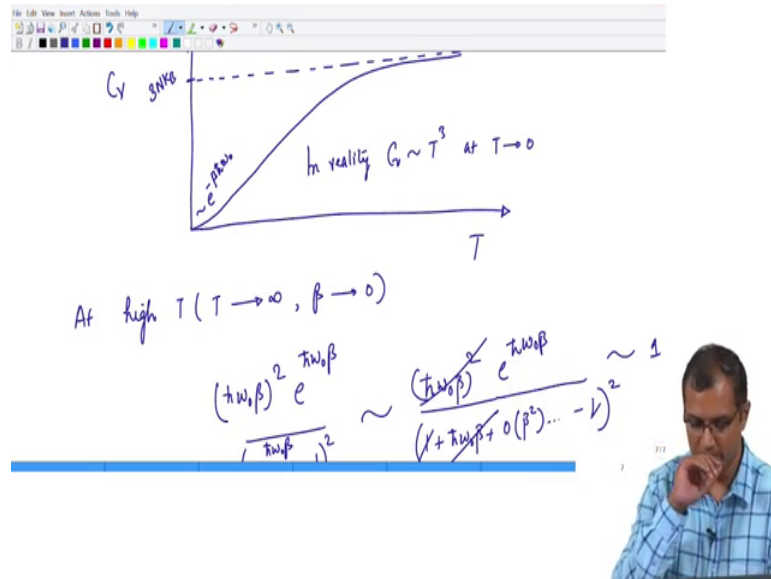
$$= 12 N k_B x^2 \frac{1}{e^{-2x} (e^{2x} - 1)^2}$$

$$= 12 N k_B x^2 \frac{e^{2x}}{(e^{2x} - 1)^2}$$
 Substituting for  $x = \hbar \omega_0 / 2$   

$$C_v = 3 N k_B \left( \frac{\hbar \omega_0}{k_B T} \right)^2 \frac{e^{\hbar \omega_0 / k_B T}}{(e^{\hbar \omega_0 / k_B T} - 1)^2}$$

So, now I am saying that I want to write it as e raise to minus, if I ok. So, this simply becomes twice N k B into x square e raise to 2 x, over e raised to 2 x minus 1 the whole square and substituting for x, as h cut mega 0 beta by 2. I can write down my heat capacity as thrice N k B, h cut omega 0 by k B T whole square, e raise to h cut omega 0 beta divided by e raise to h cut omega 0 beta minus 1 the whole square fine. So, this tells you something about heat capacity and that is a very important message here.

(Refer Slide Time: 61:23)



So, if you try to sketch the heat capacity you know, what is going on, but there is one thing definitely that there is a high temperature limit and there is a low temperature limit. So, at  $t$  tending to infinity that is tending to infinity your beta will go to 0 because beta is 1 over  $kT$ .

So, the limit beta tending to infinity beta tending to 0 is very clear. So, the denominator here becomes it can be very easily seen. So, if your beta goes to 0, then I can write down my I will write down, let me write down everything. So, there is  $h$  cut  $\omega_0$  beta right.

(Refer Slide Time: 64:18)

T

At high T ( $T \rightarrow \infty, \beta \rightarrow 0$ )

$$\frac{(h\nu_0\beta)^2 e^{h\nu_0\beta}}{(e^{h\nu_0\beta} - 1)^2} \sim \frac{\cancel{(h\nu_0\beta)^2} e^{h\nu_0\beta}}{(1 + \cancel{h\nu_0\beta} + o(\beta^2) \dots - 1)^2} \sim 1$$

$C_V \sim 3Nk_B$

So, I have got an  $h \nu_0 \beta$  the whole square ok, which is this term  $h \nu_0 \beta$  the whole square, into  $e$  raised to  $h \nu_0 \beta$  and I have division by  $e$  raised to  $h \nu_0 \beta$  minus 1 the whole square.

So, this will if you look at the denominator this is 1 plus  $h \nu_0 \beta$ , plus order  $\beta^2$  then minus 1. So, I am going to drop this to 0. So, this one cancels off and what you have is just denominator is going to be  $h \nu_0 \beta$ , the whole square and you go to numerator  $h \nu_0 \beta$  the whole square and you have got  $h \nu_0 \beta$ . So, this will knock off with this and as the  $\beta$  goes to 0 or this will go as 1 ok.

Now, the prefactor here is just  $3/2 N k_B$ . So, the high temperature limit or  $\beta$  going to 0 limit is just  $3/2 N k_B$  ok. So, this is the high temperature limit also called Dulong petit law. So, that is the high temperature limit. So, becomes constant at the high T heat capacity becomes  $3 N k_B$  ok. Now what happens to low temperature.

(Refer Slide Time: 66:25)

At low  $T$  ( $T \rightarrow 0$ ,  $\beta \rightarrow \infty$ )

$$\frac{(\hbar\omega_0\beta)^2 e^{\hbar\omega_0\beta}}{(e^{\hbar\omega_0\beta} - 1)^2} \sim \frac{(\hbar\omega_0\beta)^2 e^{\hbar\omega_0\beta}}{e^{2\hbar\omega_0\beta}} \sim (\hbar\omega_0\beta)^2 e^{-\hbar\omega_0\beta}$$

$\sim e^{-\hbar\omega_0\beta}$   
 $T \rightarrow 0$   
 $\beta \rightarrow \infty$

So, this is the high temperature limit, at low temperatures where this when  $t$  going to 0 or beta tending to infinity in this limit, if you look at this expression. So, as beta goes to infinity you see that, the denominator here. So, I am going to just use the same thing. So, just copy it.

So, as beta goes to infinity. So, I can say that my denominator here becomes. So, large that I am going to drop 1. So, it goes as  $\hbar$  cut  $\omega_0$  beta square  $e$  raise to  $\hbar$  cut  $\omega_0$  beta, divided by  $e$  raised to twice  $\hbar$  cut  $\omega_0$  beta, because beta is infinity. So, I can drop 1 and so, the square becomes twice. Now this will go as  $\hbar$  cut  $\omega_0$  beta square, into  $e$  raised to minus  $\hbar$  cut  $\omega_0$  beta and this I will argue that it goes as  $e$  raise to minus  $\hbar$  cut  $\omega_0$  beta as  $T$  goes to 0 or beta goes to infinity.

For the simple reason being, beta square  $e$  raised to minus  $\hbar$  cut beta will go as  $e$  raise to minus  $\hbar$  cut beta by L Hopitals rule.

(Refer Slide Time: 68:12)

Handwritten mathematical derivations on a whiteboard:

$$\frac{(\hbar\omega_0\beta)^2 e^{\hbar\omega_0\beta}}{(e^{\hbar\omega_0\beta} - 1)^2} \sim \frac{(\hbar\omega_0\beta)^2 e^{\hbar\omega_0\beta}}{e^{2\hbar\omega_0\beta}} \sim (\hbar\omega_0\beta)^2 e^{-\hbar\omega_0\beta}$$

$$\lim_{\beta \rightarrow \infty} f(\beta) = \lim_{\beta \rightarrow \infty} \frac{\beta^2}{e^{\hbar\omega_0\beta}} = \frac{\infty}{\infty} \xrightarrow{\text{L'Hopital}} \frac{2}{(\hbar\omega_0)^2 e^{\beta\hbar\omega_0}} \rightarrow 0$$

Annotations on the right side of the whiteboard:

$$\sim e^{-\hbar\omega_0\beta} \xrightarrow{\begin{matrix} T \rightarrow 0 \\ \beta \rightarrow \infty \end{matrix}}$$

So, you can see my function is basically I can drop  $h$  cut  $\omega$ . So, just raise  $\beta$  square over  $e$  raise to  $h$  cut  $\omega$  0  $\beta$ . So, its low temp  $\beta$  infinity limit would simply be the  $\beta$  infinity limit here and this becomes infinity by infinity. So, you invoke L Hopitals rules.

And so, what you get here is nothing, but invoke it twice. So, it gives you just 2 by  $h$  cut  $\omega$  0 the whole square,  $e$  raise to  $\beta h$  cut  $\omega$  and that will go to 0 exponentially. So, its low temperature behavior is exponential and high temperature limit is getting to the  $d$  along spurted law or saturation.

So, here it will go as  $e$  raised to minus  $\beta h$  cut  $\omega$  0 and high temperature limit becomes a constant. So, in reality what is basically obtained is a  $dk$  to 0 which is much lower than the exponential  $dk$ . So, in reality heat capacity is seen to be third power of temperature at low temperatures. So, this is called as in some sense, the  $t$  cube law which is universally shown by most metals and while Einstein's law is fairly accurate at overall temperature region, it does not show  $t$  cube universality at low temperatures.

And so, in the next class, I will show why this  $t$  cube universality cannot be recovered in Einstein's law and what 1 has to do in how to recover the  $t$  cube universality. In this class we stop here and when we meet again tomorrow, we will talk about corrections to Einstein's law which goes by the name of  $d$  by corrections. So,  $d$  by proposed some corrections in terms of the density of states of these lattice oscillators to recover the  $t$

cube behavior of heat capacity at low temperatures. So, we meet again in the next class and take it up from there.

Thank you.