Introduction to Statistical Mechanics
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Lecture – 18
Theories of Specific Heat of Solids

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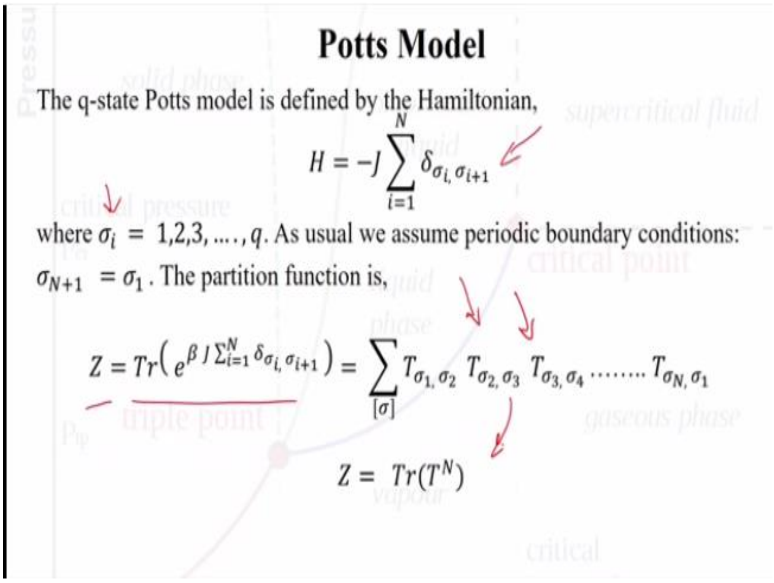

Potts Model

The q-state Potts model is defined by the Hamiltonian,

$$H = -J\sum_{i=1}^{N} \delta_{\sigma_i,\sigma_{i+1}}$$

where $\sigma_i = 1,2,3,\dots,q$. As usual we assume periodic boundary conditions: $\sigma_{N+1} = \sigma_1$. The partition function is,

$$Z = Tr\left(e^{\beta J\sum_{i=1}^{N}\delta_{\sigma_i,\sigma_{i+1}}}\right) = \sum_{[\sigma]} T_{\sigma_1,\sigma_2}\,T_{\sigma_2,\sigma_3}\,T_{\sigma_3,\sigma_4}\dots\dots T_{\sigma_N,\sigma_1}$$

$$Z = Tr(T^N)$$

Hello, so today I want to discuss a topic that I had somewhat ignored earlier but it is an extension of the 1 D ising model that I have been discussing and it is a slight variant of this but it is also interesting in its own right, it is called the q-state Potts model. So, basically the q -state Potts model is defined by this Hamiltonian which basically, states so in other words see inthe 1 D ising model this fundamental degrees of freedom are two folded; either up or down.

So, whereas here the fundamental degrees of freedom take q different values that means, the fundamental degrees of freedom say σ_i at site i, it can have one of few different values, I mean basically which give me 1, 2, 3, 4 or all the way up to q. So, the Potts model is defined by this Hamiltonian that says that the energy between neighbouring degrees of freedom like σ_i and σ_{i+1}, the energy is 0, unless the two numerical values coincide.

That means the degrees of freedom which can be labelled by 1, 2, 3, so if they are exactly equal, then the energy is lowered so, it becomes, the energy because -J, otherwise it is 0, so this is called the q-state Potts model and as usual we assume periodic boundary conditions, so now the goal is to calculate that partition function which is defined in this fashion.

So, as usual I am going to use the transfer matrix method to calculate the partition function and the way you do that is to invoke a certain 2 by 2 matrix and you say that it is going to be writable, so the partition function is; we kind of surmise that it could be written in this fashion that it is written as a string of the components of this transfer matrix in this fashion.

So but however, unlike the 1 D ising model where these σ's can only take 2 values now, it can have q values so, implying therefore that this transfer matrix T is a q by q matrix, so unlike in the 1 D ising model was a 2 by 2 matrix, so this is a q by q matrix, so this is writable as the Tr(T^N).

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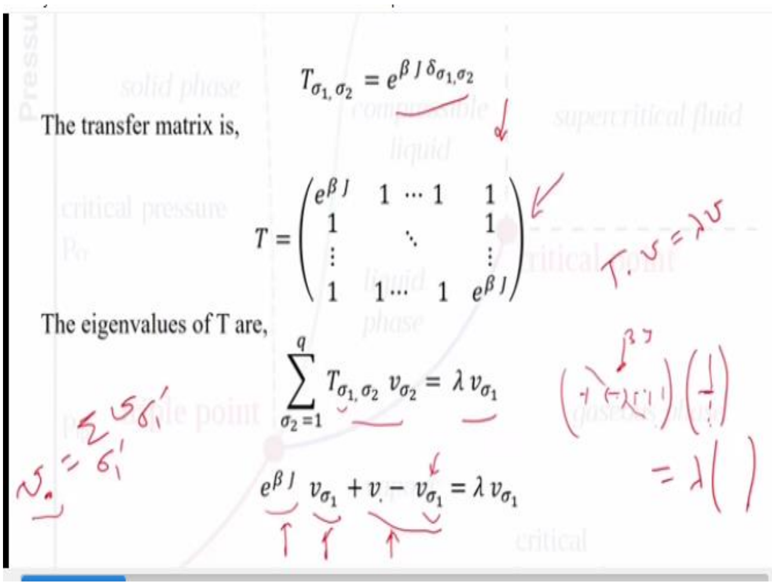

The transfer matrix is, $T_{\sigma_1,\sigma_2} = e^{\beta J \delta_{\sigma_1,\sigma_2}}$

$$T = \begin{pmatrix} e^{\beta J} & 1 \cdots 1 & 1 \\ 1 & \ddots & 1 \\ \vdots & & \vdots \\ 1 & 1 \cdots \; 1 & e^{\beta J} \end{pmatrix}$$

The eigenvalues of T are,

$$\sum_{\sigma_2=1}^{q} T_{\sigma_1,\sigma_2} v_{\sigma_2} = \lambda v_{\sigma_1}$$

$$e^{\beta J} v_{\sigma_1} + v_{.} - v_{\sigma_1} = \lambda v_{\sigma_1}$$

$T.v = \lambda v$

$v_{.} = \sum_{\sigma_1'} v_{\sigma_1'}$

$= \lambda (\;)$

So, as you can see it is easy to convince ourselves that the T that comes here in this formula is simply this given by this formula,

$$T_{\sigma_1,\sigma_2} = e^{\beta J \delta_{\sigma_1,\sigma_2}}$$

so written out in the matrix form, so these are the components of this matrix T which is a q by q matrix. So, written out in the matrix form it is going to be this so, in other words it is βJ when it is on the diagonal and it is 0, when it is not on the diagonal.

So, $e^0 = 1$, so all these other elements are populated by number 1, so now it looks like; it looks somewhat difficult to find the Eigenvalues but then recall that the eigenvalue equation is nothing but this so,

$$Tv = \lambda v$$

so this is the eigenvalue equation where v is your column vector. So, written out in components that is what it looks like.

Now, the point is that you can write, see remember that these are all 1's, so if you take any particular row, so you've got to multiply this by a column and it is going to be column, so you take any particular row and you multiply by this column, so somewhere here there is going to be $e^{\beta J}$ and the rest of it are all 1's. So, what I can do is; I can define a $v_{.}$ which is nothing but the sum over all the, v's okay, $v_{.} = \sum_{\sigma_1} v_{\sigma_1}$ sum over all the elements here.

So, this is $v_{.}$, so I just want to make sure that see the v_{σ_1} is going to be specifically multiplied by; so it is going to because this is a σ_1, the σ_1'th is going to be multiplied by $e^{\beta J}$ because that is on the diagonal here, so that is get; going to get multiplied by v_{σ_1}, so in other words plus the rest of it that is the rest of it are all multiplied by 1; 1, 1, 1, 1 times the rest of i.

So, the rest of it is basically all of them put together except v_{σ_1} that is what rest of it means other than v_{σ_1}, so that is what I have done here, so I have put $v_{.}$ means all of it minus v_{σ_1}, so except v_{σ_1}, so this is the rest of all the v's, so this is equal to λv_{σ_1}, so this is my equation.

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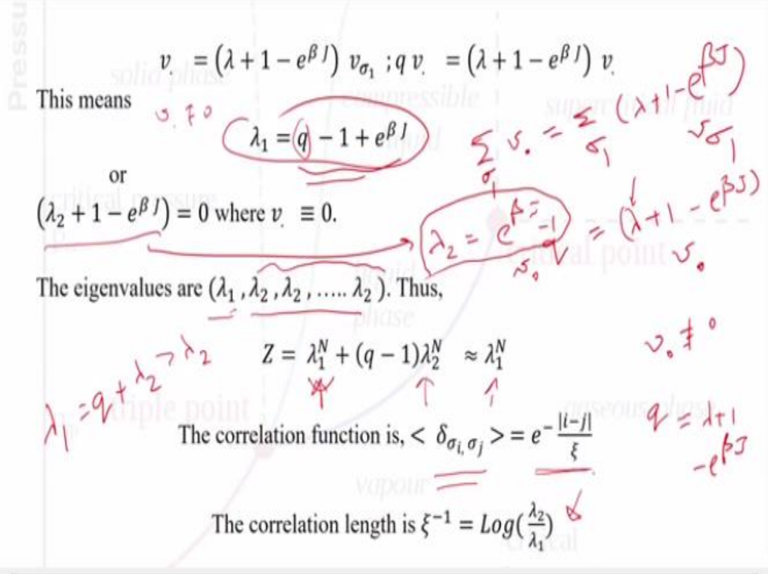

$$v_{.} = (\lambda + 1 - e^{\beta J})\, v_{\sigma_1} \;;\; q\, v_{.} = (\lambda + 1 - e^{\beta J})\, v_{.}$$

This means

$$v_{.} \neq 0$$

$$\boxed{\lambda_1 = q - 1 + e^{\beta J}}$$

$$\sum_{\sigma_1} v_{.} = \sum_{\sigma_1} (\lambda + 1 - e^{\beta J})\, v_{\sigma_1}$$

or

$$(\lambda_2 + 1 - e^{\beta J}) = 0 \text{ where } v_{.} \equiv 0.$$

$$\xrightarrow{} \boxed{\lambda_2 = e^{\beta J} - 1}$$

$$v_{.} = (\lambda + 1 - e^{\beta J})\, v_{.}$$

The eigenvalues are $(\lambda_1, \lambda_2, \lambda_2, \ldots\ldots \lambda_2)$. Thus,

$$v_{.} \neq 0$$

$$\lambda_1 = q + \lambda_2 > \lambda_2$$

$$Z = \lambda_1^N + (q-1)\lambda_2^N \approx \lambda_1^N$$

$$q = \lambda + 1 - e^{\beta J}$$

The correlation function is, $< \delta_{\sigma_i, \sigma_j} > = e^{-\frac{|i-j|}{\xi}}$

The correlation length is $\xi^{-1} = Log(\frac{\lambda_2}{\lambda_1})$

So, now I can solve for v_{σ_1} and in this fashion and then if I sum over all the σ_1's again, I end up with, so the sum over all the σ_1's is q, so I get; see, I just take all the v_σ to one side and the rest of it to the other side and I get this equation. Now, I sum over all the v_σ's so, I do

$$\sum_{\sigma_1} v. = \sum_{\sigma_1} (\lambda + 1 - e^{\beta J}) v_{\sigma_1}$$

$$v.q = \left(\lambda + 1 - e^{\beta J}\right) v.$$

, so now you see there are 2 possibilities; so if v dot is not 0, then the Eigenvalue is given by this equation, right. So, it is given by this equation which says that $q = \left(\lambda + 1 - e^{\beta J}\right)$, so that fixes one of the Eigenvalues.

So, all the other, so notice that it is a q by q matrix, so we expect q different Eigenvalues to be there because for 2 by 2 matrix, you have 2 different Eigen values, for a q by q matrix you have q Eigenvalues, some of them can be equal of course but in general, there be q Eigenvalues. So, now the point is that the point we are trying to make is that the largest Eigenvalue is actually this one already, okay.

So, it is given by λ_1 okay, so that is already the largest Eigenvalue here, so the rest of it we will have to calculate in this fashion. So and in fact the rest of them will all be equal because of the nature of that matrix, so the rest of it will all be equal and you can see from here that you can see what is happening here, so when v. = 0, so you will see what the Eigenvalue is.

So, if v. = 0, then if $v_{\sigma_1} \neq 0$, so then $\lambda_2 = e^{\beta J} - 1$, so that is what the Eigenvalue is okay, so that is what that is λ_2 , so λ_2; the second Eigenvalue is $e^{\beta J} - 1$. So, all the other Eigenvalues are equal, so they are all equal. So, when v.= 0, you will get the second, third, fourth etc., up to qth eigenvalue they are all equal.

But the first eigenvalue which is the largest is obtained when $v. \neq 0$, so when $v. \neq 0$, you get the largest Eigenvalue which is λ_1 and that is given by cancelling out the v. from both sides and you get this, so this is largest; this is larger than this for what reason because of this q, so it is basically $\lambda_1 = q + \lambda_2$, just by the identity here, okay.

So, just look at this; this is λ_2 and this is λ_1, so you just take λ_2, add q, you get λ_1 , so clearly this is larger than λ_2. So, now partition function will be just these Nth power of each of the eigenvalues added all together because that is the trace of the T^N. So that is basically, the largest eigenvalue raised to N + $\lambda_2{}^N \lambda_2{}^N + \lambda_2{}^N$.

And how many λ_2's are there; there are q - 1 λ_2's because the other one is λ_1, okay, so that put together there are q eigenvalues and one of them is λ_1, the other one is $(q – 1) \lambda_2$. So, you see since $\lambda_1 > \lambda_2$, so when in the thermodynamic limit, when N is very large the dominant contribution to Z comes from λ_1^N so this is going to be less important and this approximately λ_1^N .

So, now we can do the usual things; calculate susceptibility and all that but what is more interesting is the correlation function which is the average of this and which can be calculated because you know the second eigenvalue, so you can rewrite, so this I will leave to you as an exercise maybe, I will assign some home works for you I have to leave something for the tutorial for you to do during the evaluation process.

So, I am going to leave this as a homework so basically, what you have to show is that

$$< \delta_{\sigma_i,\sigma_j} > = e^{\frac{-|i-j|}{\xi}}$$

$$\xi^{-1} = Log(\frac{\lambda_2}{\lambda_1})$$

is nothing but this correlation function which tells you that it exponentially decays with a correlation length given by log of the smaller eigenvalue divided by the log of the larger eigenvalue, the reciprocal of that so that is the correlation length.

So, I will leave the other things for the exercises such as derivation of this and so on alright, so that was a very brief story of the Potts model which is basically just a variant of the 1 D ising model and both can be solved using transfer matrix method okay, all right. So, what I am going to do now is; I am going to discuss a topic which I had skipped to some extent and that is the Debye and Einstein's theories of specific heat of a solid.

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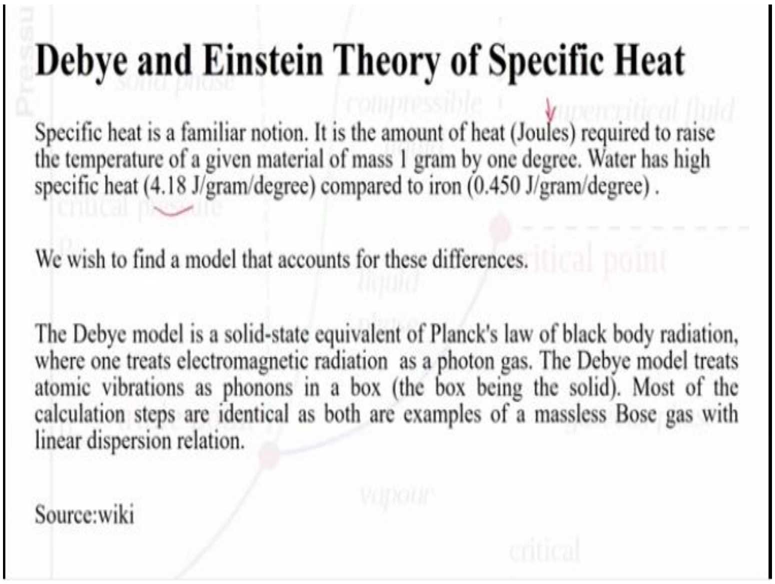

Debye and Einstein Theory of Specific Heat

Specific heat is a familiar notion. It is the amount of heat (Joules) required to raise the temperature of a given material of mass 1 gram by one degree. Water has high specific heat (4.18 J/gram/degree) compared to iron (0.450 J/gram/degree) .

We wish to find a model that accounts for these differences.

The Debye model is a solid-state equivalent of Planck's law of black body radiation, where one treats electromagnetic radiation as a photon gas. The Debye model treats atomic vibrations as phonons in a box (the box being the solid). Most of the calculation steps are identical as both are examples of a massless Bose gas with linear dispersion relation.

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So, basically a specific heat is a familiar concept, so the specific heat is basically the amount of heat that is measured in joules required to raise the temperature of a given material say of mass 1 gram by 1 degree, so this would be I mean this you could put kilogram here to make it consistent with the SI units, so but basically you get the idea; it is you take a mass of solid and you ask yourself how much heat I should input into that solid to raise its temperature by 1 degree.

So, different materials have different specific heat mainly because you know some materials quickly absorb the heat and become hot and other materials do not become so hot even though they absorb heat, so that is the sort of thing which that determines the specific heat. So, for example water has a high specific heat compared to iron, so for example water specific heat is 4.18 J/r gram/degree.

So, what does that mean? That means you take 1 gram of water and in order to raise the temperature by 1 degree, you have to supply 4.18 joules of energy or heat, so you have to supply 4.18 joules of heat to 1 gram of water, then you will be able to raise the temperature of water by 1 degree whereas, compare this to iron it is much easier to raise the temperature of iron by 1 degree, all you have to do is supply just 0.45 joules of heat to 1 gram of iron and you will be successful in raising the temperature of iron by 1 degree.

So, now the idea is that what Debye and Einstein both were trying is to find some kind of you know physical model which explained or somewhat roughly accounts for these differences to explain why there are; why materials have different specific heats. So, in particular we will find that basically the low temperature of course, this I have to specify at what temperature you have to raise by 1 degree, so it matters.

But in this so, specifically what Einstein and Debye were discussing is that they wanted to study the role played by quantum mechanics in determining the specific heats of solids at low temperatures, so at low temperatures you know that quantum mechanics is very important, so they wanted to see what are the roles played by quantum mechanics specifically.

So, we all know that if you pump in energy into a solid; 2 things are going to happen that when that energy is absorbed or the heat is absorbed by the solid, the lattice; it is going to set up lattice vibrations, so that means the heat content present in a solid just manifests itself as an increase in lattice vibrations but it also manifests itself in terms of the increased energy of the electrons.

So, the electrons in the solid also absorb a part of the energy and so it is important to distinguish between these 2 types of specific heat; one specific heat is called the lattice specific heat and the other is the electronic specific heat. So, remember that we already calculated the electronic contribution of specific heat when we were studying the Fermi gas, so the Fermi gas will tell you that the specific heat at low temperatures for a gas of fermions is as linear in temperature.

So, whereas, in this section we are trying to study the specific heat of a solid at low temperatures so, where we focus on the contribution due to lattice vibrations. So, the successful model which describes a specific heat of a solid is known as the Debye model, so that Debye model is the solid state equivalent of Planck's law of blackbody radiation where one treats electromagnetic radiation as a photon gas.

Whereas, the Debye model treats atomic vibrations which are known as phonons, see, sound analogue of light, so that means ‘phone’ means sound, so lattice vibration is actually are just they propagate a sound waves in the solid, so the quantized lattice vibrations are known as phonons whereas, photon; photo is light so, the photon is the quantized light waves which are called which are basically, the quanta of radiation.

But then there are a lot of similarities between photons and phonons, so even just as photons also do not conserve that number because photons can be absorbed and emitted by the walls of the container, so the quanta of vibrations can also be destroyed, they do not, they are not, their number is not conserved and they are also bosons because of the nature in; I mean they happen to be just excitations of just like harmonic oscillator I mean excitations of bosons, all these are just manifestations of that phenomenon.

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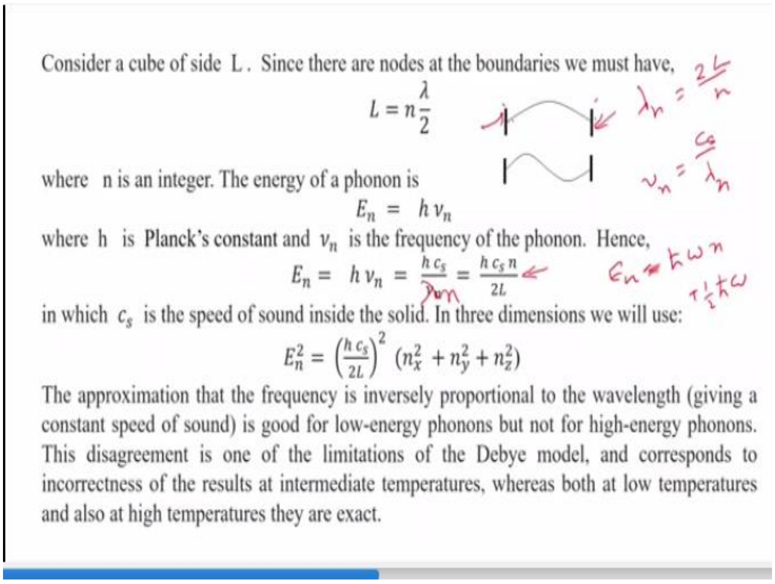

Consider a cube of side L. Since there are nodes at the boundaries we must have,

$$L = n\frac{\lambda}{2}$$

$\lambda_n = \frac{2L}{n}$

where n is an integer. The energy of a phonon is

$\nu_n = \frac{c_s}{\lambda_n}$

$$E_n = h\nu_n$$

where h is Planck's constant and ν_n is the frequency of the phonon. Hence,

$$E_n = h\nu_n = \frac{h c_s}{\lambda_n} = \frac{h c_s n}{2L}$$

$E_n = \hbar\omega n + \frac{1}{2}\hbar\omega$

in which c_s is the speed of sound inside the solid. In three dimensions we will use:

$$E_n^2 = \left(\frac{h c_s}{2L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

The approximation that the frequency is inversely proportional to the wavelength (giving a constant speed of sound) is good for low-energy phonons but not for high-energy phonons. This disagreement is one of the limitations of the Debye model, and corresponds to incorrectness of the results at intermediate temperatures, whereas both at low temperatures and also at high temperatures they are exact.

So, now so, let us understand how to study the quantized vibrations of a solid, so for that I am going to start with a 1 D solid, so it is kind of; it is the simplest starting point that you can imagine, where I imagine that these are the ends of the solid, okay and then imagine that I am setting up vibrations in this solid, so when I set up the vibrations in this solid then, I am necessarily going to find nodes at the end.

Because the ends of the solid are in movable, so they cannot move and when I set up solid, I mean when I set up the vibrations, the wavelength of the vibration will be such that the length of that solid will be integer multiples of the half wavelength because you know the longest wavelength is actually, twice the length of the solid because that is the way you can have nodes at the end here.

So, starting from the longest wavelength, you can get shorter and shorter wavelength as you increase the n value here, so it is 2L/ n is the formula for the wavelength of the vibration modes in the solid. So, according to Einstein the energy of these quanta are basically, hν, so where ν is the frequency of the vibration of these excitations.

So, if c_s is the sound velocity, we know that $\nu_n = \frac{c_s}{\lambda_n}$, so which is the relation between wavelength and frequency, so this is the sound velocity, so it is $E_n = \frac{h\,c_s}{\lambda_n}$ and what is λ_n; λ_n is nothing but from here we know that $\lambda_n = \frac{2L}{n}$. So, if I substitute that I get this relation that the energy is basically proportional to the quantum number n, okay.

So, this is in a 1 D situation and this should ring a bell because for example, a 1 D harmonic oscillator also is basically the energy is $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ so, apart from this zero point energy, the energy for the most part is proportional to the quantum number n. So, now if it is in 3 dimensions you have to work harder but you can easily convince yourself that it is basically $\frac{\hbar^2 k^2}{2\,mn}$, where k is you know related to λ and so on.

And then 1/λ is proportional to n, so there will be 3 kinds of n's corresponding to each direction, so remember that the particle in a box are also labelled by these quantum numbers, okay but there is one big difference between the photon gas and the phonon gas. So, you see the frequency of the photon gas is not limited, so it can be as large as it wants but then the frequency of the phonon gas is actually limited.

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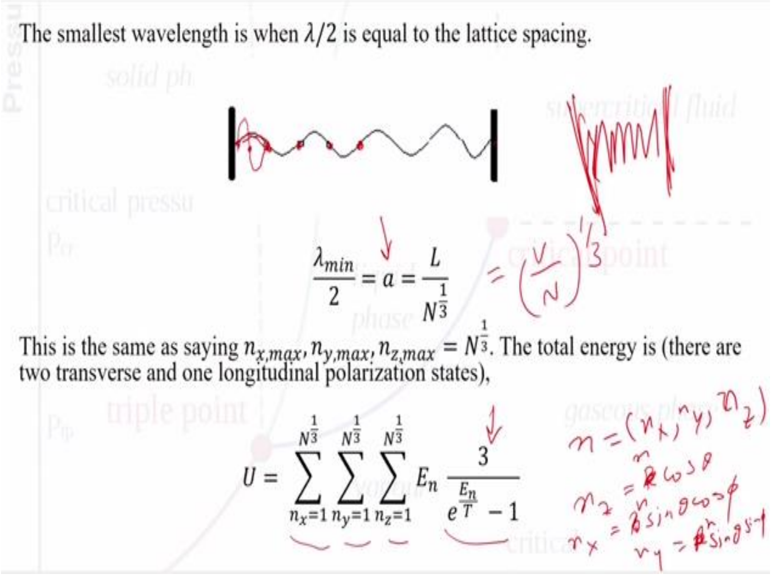

The smallest wavelength is when $\lambda/2$ is equal to the lattice spacing.

$$\frac{\lambda_{min}}{2} = a = \frac{L}{N^{\frac{1}{3}}} = \left(\frac{V}{N}\right)^{1/3}$$

This is the same as saying $n_{x,max}, n_{y,max}, n_{z,max} = N^{\frac{1}{3}}$. The total energy is (there are two transverse and one longitudinal polarization states),

$$U = \sum_{n_x=1}^{N^{\frac{1}{3}}} \sum_{n_y=1}^{N^{\frac{1}{3}}} \sum_{n_z=1}^{N^{\frac{1}{3}}} E_n \frac{3}{e^{\frac{E_n}{T}} - 1}$$

$n = (n_x, n_y, n_z)$

$n_z = n\cos\theta$

$n_x = n\sin\theta\cos\phi$

$n_y = n\sin\theta\sin\phi$

Because there is a smallest wavelength that is possible okay, so let us try to understand why. So, you see the reason is because for example, in this case so, if you want the smallest wavelength, so when you set up oscillations between these endpoints, so imagine this is a solid and you are setting up oscillations, right. So, then these are your atoms that are actually going up and down and creating these vibrations.

So, these wavelengths are they actually, they are not like photons, whereas just photons propagate in empty space, these are actually sound waves caused by the motion of; so here we are imagining this transverse motion of the atoms in the solid, so the point is that there is a smallest wavelength that is possible namely that if you try to make your wavelength, so if you try to do this okay, so this is your end point of the solid.

So, you will not be able to sustain with a very small wavelength smaller than this for example because you see you cannot sustain a wave smaller than this, so if you want to sustain a wave smaller than this, it has to be like this but then this is not going to happen because you need to have an atom here in order for that to be sustained. So, you see what is happening here, so if this wave has to be sustained you have to have an atom here also.

But there is no atom there by definition because this is the lattice spacing, so as a result the smallest wavelength so, this is $\lambda/2$, so the smallest $\lambda/2$ is basically given by the lattice spacing itself, so there is a smallest wavelength and that is possible and that is given by the lattice spacing and roughly speaking that is the length of this 1 D box or if you like basically, it is the volume per particle raised to one-third, so that is what the smallest wavelength is.

So, as a result, so that is the big difference between a phonon gas and a photon gas, so for a photon gas there is no limit to what these numbers can be; these quantum numbers n can be all the way from $n = 1$, all the way up to infinity because there is no limit to what is the largest frequency of photons that can be in the Planck blackbody radiation but for the phonon gas, there is a limit and this is very important.

Because it has very important practical consequences, so for a phonon gas it is limited by the lattice spacing of the solid which in turn is proportional to or inversely proportional to the one third power of the density of the solid. So, as a result the maximum value of the x component of this quantum number n is going to be one third the power of the total number of atoms in the solid.

So, using this idea I am going to now write the total energy of the solid, so notice that otherwise it is more or less the same, so here you have the Bose distribution function and notice that there is no chemical potential, so as a result the average number of phonons as a function of temperature is going to be this and you multiply it by the energy and that is you are going to be the average energy, so energy per mode times the; so here n means the triad of n_x, n_y and n_z.

But then what is this 3, you have to understand, this 3 is because there are 2 transverse and 1 longitudinal mode okay. So, you see for the photon gas there is no longitudinal mode because you know electromagnetic waves are always transverse but sound waves can be longitudinal as well as transverse, so as a result you have 3 there and then you have to sum over all these quantum numbers in this fashion.

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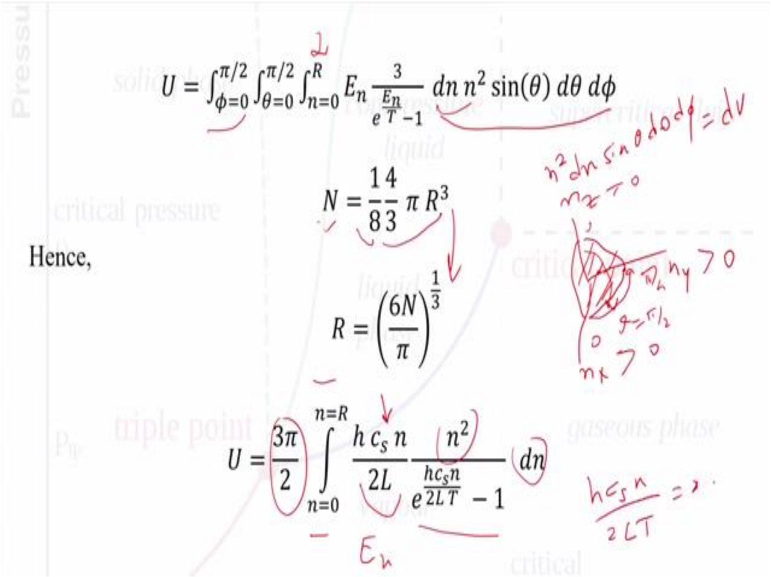

$$U = \int_{\phi=0}^{\pi/2}\int_{\theta=0}^{\pi/2}\int_{n=0}^{R} E_n \frac{3}{e^{\frac{E_n}{T}}-1}\, dn\, n^2 \sin(\theta)\, d\theta\, d\phi$$

Hence,

$$N = \frac{1}{8}\frac{4}{3}\pi R^3$$

$$R = \left(\frac{6N}{\pi}\right)^{\frac{1}{3}}$$

$$U = \left(\frac{3\pi}{2}\right)\int_{n=0}^{n=R} \frac{h c_s n}{2L} \frac{n^2}{e^{\frac{h c_s n}{2LT}} - 1}\, dn$$

So, I will give you the total energy as a function of temperature, so as usual I am going to assume a situation where these quantum numbers are sufficiently close to each other, so I can always integrate instead of; so the large number of these modes that are present, so I am going to be able to, there is no loss of generality in integrating rather than adding up. So, we have done this again and again if you recall from the point of view of Euler Maclaurin formula.

So, we actually showed how to convert a summation to an integration okay, so I am going to use that and so now how did I do this; so I am going to convert this into spherical polar coordinates, so I am going to call this $n_z = n\ \cos\theta$ and $n_x = n\ \sin\theta\ \cos\phi$ and $n_y = n\sin\theta\sin\phi$, okay. So, I am going to use that here .

So, now what is the volume; it is basically $dv =\ n^2 \sin\theta\ dn\ d\theta\ d\phi$ that is my volume and I am going to integrate from n equal to 1 to a maximum value of course, this maximum value is now going to be set by the total number of particles, so recall that I have to only integrate up to the maximum quantum number $n^{1/3}$ for each direction, so put together it is for n itself, it is of the order of the total number of particles, okay.

So and also it is , so remember that I am only restricting myself to the first octant, so it is actually so, the total number of particles only in this octant, so because this is n_x, n_y and n_z, so they are all positive numbers okay, so that is the one octant, so it is one eighth of the total volume there, it is the total number of particles, okay so that is how R is related to the number of atoms in the solid.

And these angles are of course and also because of the octant; see here φ cannot go from 0 to 2π, it has to go from 0 to π/2 only and this also the θ cannot go from 0 to π , it should stop at θ = π/2 again, 0 to π/2, so it is only then you will be covering just the octant okay; the first octant; φ goes from 0 to π/2 and θ also goes from 0 to π/2 , so you will be capturing the first octant.

So, as a result you will be able to write this R in terms of the number of atoms in the solid in this fashion and because of this I can now go ahead and rewrite this expression, so I write this formula for E_n in terms of n, so this is nothing but hc_s /2L, so in terms of n^2 and so then E_n itself is this okay, so then I can write it in terms of; so this is n^2 dn and all that so, the integration over θ and φ have been carried out and I get this prefactor after carrying out integration between θ and φ and this is my E_n okay.

And this is n^2 dn that was already present here and this is nothing but $e^{E_n/T}$, so now I have to integrate from 0 to n = R.

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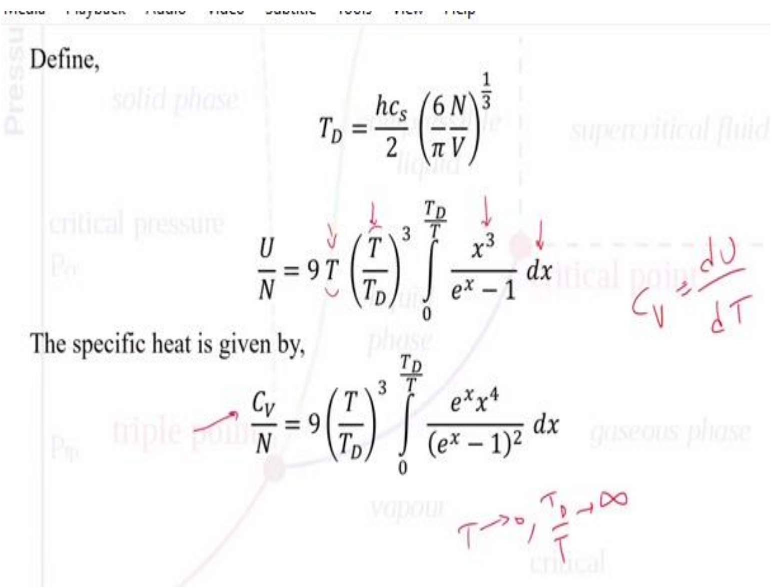

Define,

$$T_D = \frac{hc_s}{2}\left(\frac{6}{\pi}\frac{N}{V}\right)^{\frac{1}{3}}$$

$$\frac{U}{N} = 9\,T\left(\frac{T}{T_D}\right)^3\int_0^{\frac{T_D}{T}}\frac{x^3}{e^x-1}\,dx \qquad C_V = \frac{dU}{dT}$$

The specific heat is given by,

$$\frac{C_V}{N} = 9\left(\frac{T}{T_D}\right)^3\int_0^{\frac{T_D}{T}}\frac{e^x x^4}{(e^x-1)^2}\,dx$$

$$T \to 0,\ \frac{T_D}{T} \to \infty$$

So, now how do I do that, as usual I rescale my n in such a way that I will call $x = \frac{h\,c_S n}{2LT}$ but then I also have this energy scale T_D which is defined like this so, if I define this T_D in this fashion, then I will be able to write n so, I can rewrite n in terms of x okay and then if I define T_D like this, then you can convince yourself that so, remember that this is n^3 times n, so that is n^4 actually so, it is actually going to be like that only.

So, you will first get n^3 outside and so you can just do this algebra yourself and you will be able to show so, it is actually the T^4 is right here, so there is a T there, so remember there is n n^2 and dn, so put together it is n^4, so n^4 means x to the power; I mean dimensionally, it is; there should be 4x's and 4T's, so the 4T's are here, there is 1 T there and 3 T's here and the 4 x's are here.

So, there is 1 x there and 3 x there, so it is dimensionally consistent, so then you integrate over x all the way from 0 to the upper limit which is set by R but R in turn is this but because I have defined T_D in this fashion this upper limit is going for x is going to become T_D /T okay, so you please fill in the gaps yourselves okay. So, now once I know what is U; $C_V = \frac{dU}{dT}$ so C_V is nothing but the specific heat at constant volume.

So, I have to differentiate U with respect to T and this becomes a specific heat at constant volume becomes this, so now you can study the specific heat at constant volume in 2 different limits, so you can examine the low temperature limit as well as the high temperature limit, so let us do it now. So, at very low temperatures you can see that this T_D, so as T-> 0, $T_D/T \to \infty$.

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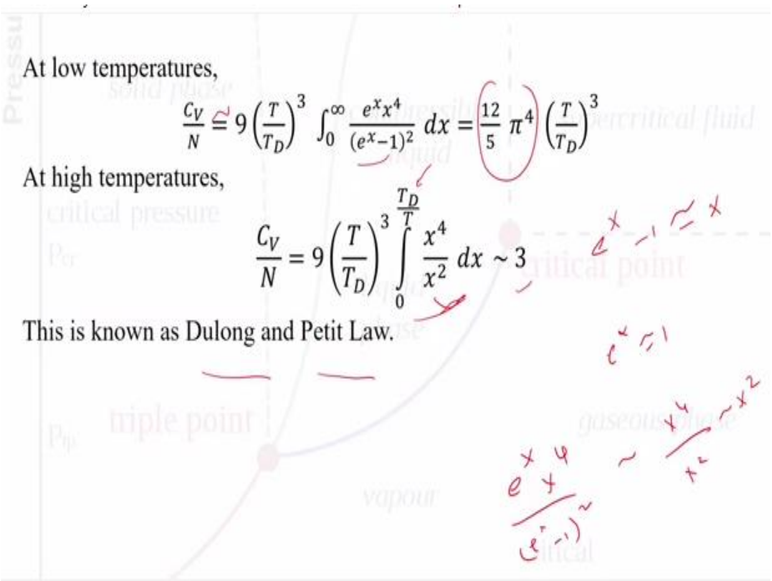

At low temperatures,

$$\frac{C_V}{N} \cong 9\left(\frac{T}{T_D}\right)^3 \int_0^\infty \frac{e^x x^4}{(e^x-1)^2}\, dx = \boxed{\frac{12}{5}\pi^4}\left(\frac{T}{T_D}\right)^3$$

At high temperatures,

$$\frac{C_V}{N} = 9\left(\frac{T}{T_D}\right)^3 \int_0^{\frac{T_D}{T}} \frac{x^4}{x^2}\, dx \sim 3$$

This is known as Dulong and Petit Law.

$$e^x - 1 \simeq x$$

$$e^x \simeq 1$$

$$\frac{e^x x^4}{(e^x-1)^2} \sim \frac{x^4}{x^2} \sim x^2$$

So, at very low temperatures, I am I entitled to pretend that this is actually approximately infinity and this is approximately going to become 9 $(T/T_D,)^3$ times some number and that number happens to be given by number times 9 happens to be given by this quantity okay, so in other words that is this quantity by 9, so this is just from you know your tables or your Mathematica or any of those symbolic packages will do this integration for you in case you do not know how to do it by hand.

So, it is not worth doing it by hand because the tables are already there, so the important point is that at low temperatures, the specific heat is proportional to the cube of the temperature, so remember that this contribution of the specific heat is due to the lattice vibrations and that is so Debye's theory of specific heat shows correctly that, this is consistent with observations that at low temperatures, the specific heat of a solid due to lattice vibration is proportional to the cube of the temperature.

So, at very high temperatures so, when I say high I have to explain high with respect to what; of course the scale is set by the Debye temperature itself, so this is the temperature, so when I say low temperatures I mean the temperature is small compared to the Debye temperature which is here and the high temperature means temperature is high compared to the Debye temperature.

So, now when T is very large, then this also is close to 0 and the lower limit is anyway 0, so x is being integrated between 0 and something which is very close to 0, so in other words, x is very small compared to 1, so I can Taylor expand this quantity and I will get, so I can write $e^{x-1} \approx x$ okay. So, as a result this becomes $e^x \approx 1$ in the numerator.

So,

$$\frac{e^x x^4}{(e^x - 1)^2} \approx \frac{x^4}{x^2} \approx x^2$$

so now if I integrate this with respect to x from 0 to T_D /T, you see I get a formula which basically the T cancels out there, there is a T^3 from outside and 1 / T^3 comes from this integration and when I; when it cancels out, I get a constant.

So, this is called the Dulong and Petit law which basically tells you that at temperatures high compared to the Debye temperature, the specific heat per particle is just equal to the number of degrees of polarization of the sound waves which is 3 in this case, so it just tells you that is equal to the 2 transverse plus 1 longitudinal, which is just a number equal to the number of degrees of polarization of the sound waves.

So, this is the story of the specific heat of a solid specifically, due to I mean the contribution due to lattice vibrations, so electronic contribution is something we have already calculated long ago in the context of the Fermi gas and there we showed that it is proportional to temperature, so put together the story is that at temperature is very low compared to the both the Fermi energy as well as the Debye temperature, there the dominant contribution is actually going to come from the electronic degrees of freedom.

Because T^3 is going to tend to 0 much faster than T, so the specific heat is dominated by the electronic degrees of freedom at very, very low temperatures but at moderately low temperatures, it is dominated by the phonons okay, so basically that is the story of the specific heat of the solid, okay.

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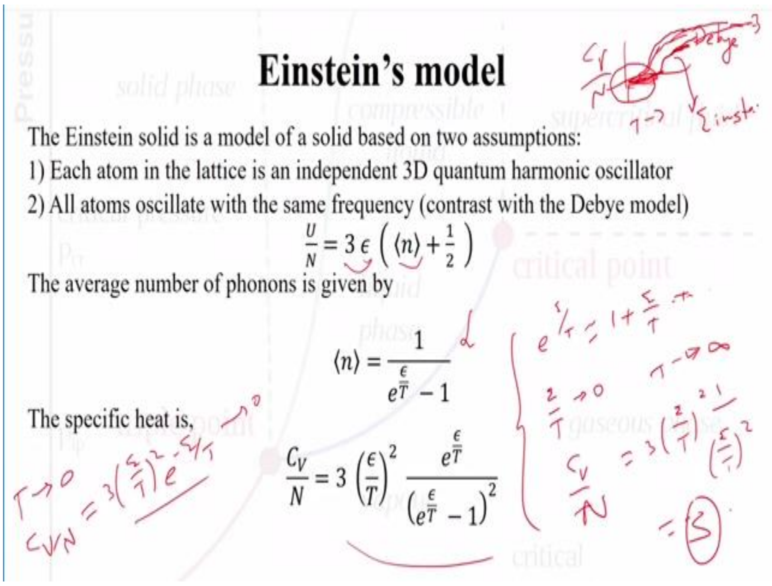

Einstein's model

The Einstein solid is a model of a solid based on two assumptions:

1) Each atom in the lattice is an independent 3D quantum harmonic oscillator

2) All atoms oscillate with the same frequency (contrast with the Debye model)

$$\frac{U}{N} = 3\,\epsilon\left(\langle n\rangle + \frac{1}{2}\right)$$

The average number of phonons is given by

$$\langle n\rangle = \frac{1}{e^{\frac{\epsilon}{T}} - 1}$$

The specific heat is,

$$\frac{C_V}{N} = 3\left(\frac{\epsilon}{T}\right)^2 \frac{e^{\frac{\epsilon}{T}}}{\left(e^{\frac{\epsilon}{T}} - 1\right)^2}$$

$T \to 0$

$C_V/N = 3\left(\frac{\epsilon}{T}\right)^2 e^{-\epsilon/T} \to 0$

$e^{\epsilon/T} \simeq 1 + \frac{\epsilon}{T} + \cdots$

$T \to \infty$

$\frac{\epsilon}{T} \to 0$

$\frac{C_V}{N} = 3\left(\frac{\epsilon}{T}\right)^2 \frac{1}{\left(\frac{\epsilon}{T}\right)^2} = \boxed{3}$

So, there is an unsuccessful attempt by Einstein which I have to mention, so this was the Debye's theory which is quite successful and this is the widely accepted account of the specific heat of a solid but Einstein made an unsuccessful attempt in the sense that finally is his result is incorrect but however, it is simpler than Debye's model so, I have to mention it.

So, instead of Debye correctly saying that it is there is a dispersion of the energy, so the energy depends on the wave vector and we have to take into account the dispersion relation the fact that you have all these modes propagating, Einstein said each atom in the lattice independently vibrates, so whereas Debye said that they all vibrate in unison, so in other words it is not the each atom that you have to look at but each mode that you have to count the modes that are propagating in the solid.

So, whereas Einstein said each atom independently vibrates, it is like a 3d harmonic oscillator and so if you assume that then you will get this idea that it is just 3 which represents again the polarization and the energy of each oscillator times the average probability that the quanta present and that is just given by this. So, if there is no dispersion relation, the energy per particle is as simple as this that is what Einstein thought it is.

Then he calculated the specific heat by differentiating with respect to temperature and it comes out to be this but then you see that at high temperatures this is okay because so, if you take ε/T -> 0, so that means high temperature, so at high temperatures this is acceptable because you see that this is going to be; so $\frac{C_V}{N} = 3\ (\frac{\varepsilon}{T})^2\ \frac{1}{(\frac{\varepsilon}{T})^2}$

so I can do a Taylor series; $e^{\frac{\varepsilon}{T}} \cong 1+\frac{\varepsilon}{T}+$..etc., etc., so that is at high temperatures. So, at high temperature so, this is going to be roughly 3 which is Dulong and Petit law, so at high temperatures both are Debye's theory and Einstein's theory give the same result namely Dulong and Petit law.

Whereas, at very low temperature so, if so that when T -> 0, then you see the C_V /N becomes something very different from what Debye predicts, so when T becomes very small you see that this is dominated by this quantity, so it is actually going to be

$$\frac{C_V}{N} = 3(\frac{\varepsilon}{T})^2 e^{-\varepsilon/T}$$

in other words that the specific heat goes to 0 in both cases of course, in Debye's case also.

So, in Debye's case the specific heat goes to 0 as cube of the temperature whereas, in the case of the Einstein model also it goes to 0 but it goes to 0 in this rather rapidly, so it goes to 0 exponentially fast, so Einstein's model predicts that at very low temperatures the; okay, so this is how it would look like, for this would be Debye model, so okay yeah, so whereas Einstein model will actually finally both of them will converge to 3, so this will be Einstein model, so this will be temperature.

So, the Einstein model will remain kind of 0 for a longer period here as temperature is very close to 0, it is more or less 0, whereas this will pick up faster and both will finally converge to 3 at large temperatures, so basically Einstein model and Debye model differ at low temperatures and experiments show that Einstein model is wrong because of the low temperature behaviour is correctly captured by Debye's model.

And also because naturally you know Einstein's model is too simplistic and Debye's model is more detailed, it takes into account the modes you know that modes should propagate in the solid because they are sound waves and Debye correctly modelled it, so this is one of those rare examples when Einstein got it wrong, when others got it right so okay, so I am going to stop here.

And so in the next couple of lectures maybe we will go ahead and discuss some tutorial problems we will try to do some problems to get some feeling for the subject, so I have been lecturing on and on, so I think and also the pace of my lectures might have been a little rapid and I might have skipped many intermediate steps which you may find a little bit uncomfortable, so I am going to try and remedy that by introducing them as tutorial problems which I am going to discuss subsequently.

And I hope that will benefit you in understanding the lectures themselves okay, thank you, so see you next time.