

Micro and Nanoscale Energy Transport
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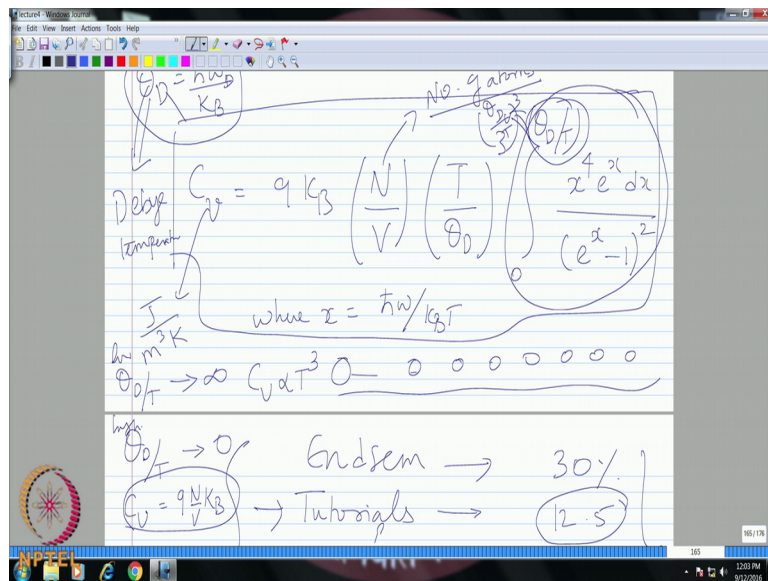
Lecture - 19
Fundamentals of Statistical Thermodynamics Part 4

This you can do it by the end of the semester.

Student: (Refer Time: 00:30).

Correct. By the last class or final exam you can do it. This all the three assignments, this two assignments, the computer assignment and the problem formulation, you turn it over at the end. Now, I think in the last class, we looked at the calculation of the heat capacities.

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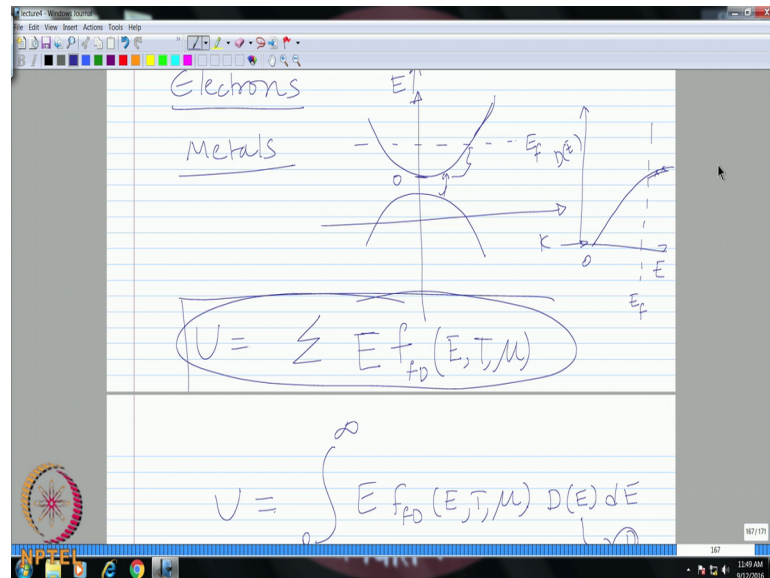
First we started off with heat capacity of gas molecules. We use the Maxwell Boltzmann distribution and we formulated it. Next we looked in to the phonons. We use the Bohr's Einstein distribution function, calculated the expression for the heat capacities. These are volumetric heat capacities.

So, the unit is for this is Joule per Student: meter cube. meter cube Kelvin and in this case I think towards the end we hurried up, but I ask you to check, we have the

expression for basically the heat capacity like this and then we also have an expression for the number of quantum states per unit volume by integrating the density of states and then we rewrote this expression in terms of N by V . We substituted for N by V and it looks like this. Why we are putting in this formulation is that here as you can know in the case of phonon crystal; this N number of quantum states with n atoms. There are with n number of atoms you have N number of quantum states. Therefore, these are nothing but number of atoms in the crystal structure. If you are therefore, looking at a particular crystal structure say monatomic; these are again valid for only monatomic once; the acoustic phonons considered. You have the Debye Approximation. So, I hope all of you can recollect that.

So, even this with now a chain of these atoms forming the crystal. If you know the count of this n number of atoms therefore, that can be directly substituted to get the heat capacity and this integral can be evaluated depending on the upper limit of the integration which is your Debye temperature and the Debye temperature we have defined here. It is an equivalent temperature equal to some $k_B T$ similar to the temperature that be replaced here with the Debye temperature for the crystal that is equal to $\hbar \omega_D$ equals to ω_D . This corresponds to actually ω_D . This is your Debye frequency which decides your Debye temperature. Once you know the value of Debye temperature we substitute this, calculate this integral and we also will know at a given temperature what is the ratio of θ_D by T we will know number of atoms. Therefore, we can evaluate what is the value metric heat capacity.

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The final energy carrier for which we need to evaluate the heat capacity is the electron. Now when it comes to electrons; phonons it is clear. Phonons in metals they do not play very vital role. They are mostly in semiconductors or dielectrics their contribution is significant but electrons are like everywhere. They can be important in a semiconductor also and predominantly in metals. Their contribution is there both in semiconductors dielectrics and also metals. Therefore, our analysis has to be slightly different when you look at metals and calculate the heat capacity compared to semiconductors; why because of the dispersion curve. We will right now focus mainly on the metals structure where if you recollect how you are dispersion curve was. That is your E versus K . Do you recollect? We have a conduction band approximated like this; we could also have a valance band like this and this was the band gap and where is the Fermi level located? Usually in the case of metals that is inside the conduction band. This is what it going to make the analysis different between metals and semiconductors the location of the reference the Fermi level.

Therefore, we start with the edge of the conduction band which is the reference 0 and from which we start our integration. Therefore, if you want to calculate the internal energy for the electrons; again we will apply our rule that you have a distribution function for the electrons occupying each and every quantum state or energy level and therefore, we multiplied with the corresponding energy of that quantum state; that is your electron energy E that is energy level of particular quantum states so this distribution

function will be your Fermi Dirac and the Fermi Dirac is a function of what? It is a function of the electron energy E , temperature and chemical potential μ . For sometimes the for reference sake we can take the chemical potential to be equal to the Fermi energy level E_f .

Now, therefore f is nothing but your volume metric distribution of electrons. Electrons occupying a particular quantum state per unit volume multiplied by the energy of that particular quantum state and when you sum this over all the energy levels that will give you the volumetric internal energy. Based on this we can calculate your heat capacity. What we are now going to do in this case unlike the phonon where we did again we use the summation over all the quantum states and then we converted this summation to continuous integral. The same way in this case we have dispersion relation which is continuous and so is our density of states. D of E as a function of E . If we plot the density of states; it will start from 0 at the edge of the conduction band and some where you have the Fermi level is a function $E - E_c$.

Therefore, to convert this into a continuous integral again we resort to using the density of states. This summation; discrete summation will be replaced by a continuous integral by introducing density of states. Density of states is nothing but the number of quantum states per unit volume and if you multiplied by the energy gap $D(E)$; that is nothing, but the number of quantum state per unit quantum. Therefore, this has to be multiplied by density of states dE . The discrete summation will now we replaced by a continuous integral and the limit is of this integration; now the density of states we have to go from 0 which is the starting of the conduction band and the electrons can move all around anywhere within the conduction band. It can actually go up to infinite and if I want to calculate the number of electrons per unit volume or number density of electrons; within the conduction band these are the free electrons.

(Refer Slide Time: 10:06)

The image shows a screenshot of a presentation slide with handwritten mathematical formulas. The top formula is $U = \int_0^{\infty} E f_{FD}(E, T, \mu) D(E) dE$, with a circled '1' next to it. Below this is the text "no. of electrons per unit volume." followed by a circled equation $n_e = \int_0^{\infty} f_{FD}(E, T, \mu) D(E) dE$, with a circled '2' next to it. At the bottom, there is another formula $U = \int_0^{\infty} (E - E_F)$. The slide also features a logo in the bottom left corner and a Windows taskbar at the bottom.

Electrons are there right from balance band and even before, but why we are interested in only this band? This is what is contributing to the actual internal energy because these are the free electrons which are actually moving about transferring the energy from one end to the other. So, these are the once which are free to move, these are the free electrons. Therefore we are interested in only accounting for electrons in the conduction band. If you want to therefore, whenever I say electrons do not think that these are the only electrons in the entire crystal. These are the free electrons. Number of electrons per unit volume; how do I calculate? I want all the free electrons in the conduction band; again look at this; if you remove E from here and just simply sum the distribution function what does it give you?

Particular quantum state these are the number of electrons per unit volume; next quantum state; number of electrons; so, the sum all these; totally it will give you Student: (Refer Time: 11:52) the number of electrons per unit volume. Therefore, how do we calculate now number of free electrons? Let us say n subscript e ; this is the number density of free electrons.

Student: (Refer Time: 12:11).

Replace sigma with integration; integral 0 to infinity what should come inside?

Student: (Refer Time: 12:35).

Student: D of E d E.

D of E d E; D of E d E gives you only quantum states. It does not give you how many electrons are actually occupying that.

Student: (Refer Time: 12:48).

f.

Student: (Refer Time: 12:52).

D of E; the actual number of electrons occupying each and every quantum state; you have to multiplied by the distribution function. Now for a given metal for example, this number of free electrons is constant. This value is a constant it can move around, but this number is a constant therefore, this is equal to a constant. Next what I am going to do let us say this is equation 1, this is equation 2; I am just going to do little bit of manipulation with equation 1. I will add and subtract my Fermi energy level to this. I can write this as E minus E f because Fermi energy level is a constant value because this is the value of chemical potential at 0 Kelvin or it tells me till what energy are the electrons occupying the conduction band at 0 Kelvin. That is my reference level so that is a constant value.

(Refer Slide Time: 14:20)

$$U = \int_0^{\infty} (E - E_f) f(E, T, \mu) D(E) dE \rightarrow E_f n_e$$

$$+ \int_0^{\infty} E_f f(E, T, \mu) D(E) dE$$

where E_f is the μ at 0K.

$$C_e = \frac{dU}{dT} = \int_0^{\infty} (E - E_f) \frac{df}{dT} D(E) dE$$

$$f = \frac{1}{\exp\left(\frac{E - \mu}{k_B T}\right) + 1}$$

I can simply add and subtract that μ D of E d E plus now I have to add E f f E T μ D of E t d E. I hope you understand what; Fermi level is the chemical potential act 0

Kelvin. Chemical potential means that is the potential up to which it is the energy level up to which the electrons are filling at Student: 0 Kelvin. 0 Kelvin; at different temperatures this level will be different of course, that higher temperature this level will keep moving down and down further down. So, that gives you the local chemical potential; that it is your electro chemical potential that is your electro chemical potential people call it.

But we are interested in the reference at 0 Kelvin. So, that value is fixed and therefore, now if you want to calculate the volumetric heat capacity of electrons; this is simply dU by dT . Therefore what happens to the second term?

Student: (Refer Time: 15:49).

This is 0 why?

Student: (Refer Time: 15:55).

f is a function of temperature.

Student: (Refer Time: 15:59).

Correct. Therefore, we have now defined n_e as integral this so therefore, this can be written as;

Student: (Refer Time: 16:12).

$E f$ into.

Student: n_e .

n_e ; $E f$ is a constant. Therefore, n_e is the constant $d f$ is the constant derivative of this will not change with the respective temperature. Therefore, we will have; so what will change out of this first term with the respective temperature? Only the distribution function is a function of temperature.

So, you have therefore, E minus $E f$ into $d f$ by $d T$ D of E $d E$. Can you calculate what is $d f$ by $d T$? You know your Fermi Dirac distribution function; 1 by exponential E minus μ by $K B T$ plus 1 .

(Refer Slide Time: 17:27)

$$\frac{df}{dT} = \frac{(E-\mu)}{k_B T^2} \cdot \frac{\exp\left(\frac{E-\mu}{k_B T}\right)}{\left(\exp\left(\frac{E-\mu}{k_B T}\right) + 1\right)^2}$$

$$C_e = \int_0^{\infty} (E-E_f) (E-\mu) \frac{\exp\left(\frac{E-\mu}{k_B T}\right)}{\left(\exp\left(\frac{E-\mu}{k_B T}\right) + 1\right)^2} D(E) dE$$

Therefore, calculate df by dT ; derivative with respect to temperature.

Student: (Refer Time: 18:29).

We have $E - \mu$ Student: (Refer Time: 18:35) correct upon $k_B T$ square Student: (Refer Time: 18:38) $E - \mu$ by $k_B T$ by Student: (Refer Time: 18:47) plus 1 the whole square. Therefore, your C_e ; $\int_0^{\infty} E - E_f$ we have $E - \mu$ by $k_B T$ square into exponential minus μ . Now we have to have that that is why here we have to understand the how the density of states behaves, how the distribution function behaves?

derived this I think there was plus E minus mu. I think probably in the table I must have made this.

Student: (Refer Time: 21:51).

Ok, but let us see.

Student: (Refer Time: 21:55).

Table we made this; here we have plus E minus mu. I think while we derived it; it was correct.

Student: (Refer Time: 22:08).

But I think after that I in the table I made the mistake. So, it should be plus please correct it.

So, that at very high energy level it should go back to the Boltzmann distribution function that is exponential minus E minus mu by K B T. So, at 0 Kelvin if I know my Fermi level as this E f at 0 Kelvin how will this distribution look?

Student: (Refer Time: 22:58).

This is 0, this is 1.

Student: (Refer Time: 23:06).

What is that?

Student: (Refer Time: 23:09).

Zero where?

Student: E f.

At E f; so, therefore, how does it look?

Student: It is symmetric about; the curve is symmetric.

Symmetric is; it will be anti symmetric.

Student: (Refer Time: 23:31).

It will be a step function. Everything below the Fermi energy level is occupied, above a Fermi energy level there are no electrons because why at 0 Kelvin the maximum till which energy level till where electrons are occupying is the Fermi level therefore, if you take Fermi level as the reference at 0 Kelvin; you have only electrons occupying till the a Fermi level. Therefore, the occupancy function is 1 up to the Fermi level above which there are no electrons; completely zero.

Slowly at higher temperatures this will start shifting from this Dirac delta function to a more continuous function. So, this then slowly it will become like this at may be 100 Kelvin. At even high temperature it will become more gradual and then finally, very high temperature it will be just some straight line. What does it mean? At higher and higher temperatures the electrons can move conduction band more freely. Therefore, there is a good amount of chance that also the lower energy levels and the energy levels beyond the Fermi levels are also occupied. If you look at again you go back to the dispersion curve here; if you are talking about 0 Kelvin; you have electrons occupying till here above which do not have anything. Now as you keep rising the temperature; the electrons can keep moving this way and therefore, there will be some possibility that electrons can fill all this higher states. So, very high temperatures you will have lot of electrons filling also the higher state it can freely move above.

And therefore, you will slowly see the shift from a sharp cut off like this at 0 Kelvin to more smoother and finally, nearly straight line; that means, you have equal probability of electrons occupying above Fermi level and below Fermi level. Therefore, if we look at the gradient $d f$ by $d T$; $d f$ by $d T$ is this particular value will be typically non zero only around this center that is above the Fermi level. So, this region and this region if you look at $d f$ by $d T$ in regions I mean which are typically close to the lower energy levels and higher energy levels they will not change much.

But primarily the maximum change will happen about the Fermi level. The gradient $d f$ by $d T$ will be mostly about this value and therefore, and about this value what happens to the density of states? It will usually taper off. We can assume that where the $d f$ by $d T$ maximum that is around the Fermi level; your density of states is nearly a constant. With this assumption we can therefore, pull this density of states outside the integral.

Therefore, we can rewrite this equation as $D(E_f)$. We will assume that this density of states is not going to change too much from your Fermi; the value at the Fermi level. The Fermi level already reaches somewhere close to the saturation point.

Now, the next $D(E_f)$ might be somewhere here, the next $D(E_f)$ might be somewhere here. But all these values are negligible change compared to $D(E_f)$. Therefore, we will assume that that is constant equal to $D(E_f)$. So, that we will pull this outside directly the integral and therefore, this integral now will become important only in a region about E_f . Therefore, we can write this 0 to infinity now as E_f minus some dE_f plus dE_f that is we take a band about this; Fermi level about which we are now doing this integral because that is where dN/dT is primarily non zero; the other places it will be negligible.

Therefore, we can write about this zone; we can replace this $E - \mu$ with $E - E_f$.

(Refer Slide Time: 29:26)

Handwritten derivation on a whiteboard:

$$C_e = D(E_f) \int_{E_f - dE_f}^{E_f + dE_f} \frac{(E - E_f)^2 \exp\left(\frac{E - E_f}{k_B T}\right)}{k_B T^2 \left[\exp\left(\frac{E - E_f}{k_B T}\right) + 1\right]^2} dE$$

$$C_e = k_B^2 T D(E_f) \int_{-\frac{E_f}{k_B T}}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx \quad \begin{aligned} x &= \frac{E - E_f}{k_B T} \\ dE &= dx \cdot k_B T \end{aligned}$$

$$\Downarrow \frac{\pi^2}{3}$$

Therefore we have $E - E_f$ the whole square by $k_B T$ square into exponential $E - E_f$ by $k_B T$ divided by exponential $E - E_f$ by $k_B T$ plus 1 the whole square dE . We can assume some dummy variable x is equal to $E - E_f$ by $k_B T$. Therefore, this can be written as $k_B^2 T$ some rewriting into T times $D(E_f)$ integral. So, my 0 to infinity for example, can be replaced with if I replace dE with dx as the dummy variable. This will become $x^2 e^x$ by $e^x + 1$ the

whole square. Please check this therefore, I will have an additional $K B$ square in the numerator and T .

I am replacing dE as dx times $K B T$. So, the original integration was from now zero to infinity; therefore, E equal to 0 means x equal to minus $E f$ by $K B T$. That is your modified over limit and E equal to infinity means x equal to infinity.

Student: sir already $K B T$ square. So, we have only multiply and divide by $K B T$ (Refer Time: 31:55).

$K B T$; that is $K B T$ square. Therefore, we multiply in K and divided by again $K B$ so that this will be x square

Student: (Refer Time: 32:06).

And therefore, we have $K B$ square.

Student: (Refer Time: 32:11).

From dE also we have a $K B$ and then we multiplied divided by $K B$. So, we have $K B$ square outside. So, $K B$ square $T D E f$ and this becomes x square.

This particular integral turns out to be if you evaluate equal to a constant π square by 3. Therefore, your; and also we can substitute for; so one more thing what we may have to do is the number of the number of electrons. So, we have written down the expression for calculating the number of electrons; that is your equation 2.

(Refer Slide Time: 33:22)

The image shows a digital whiteboard with handwritten mathematical derivations. At the top, the number density of electrons is given as $n_e = \int_0^{\infty} f^c D(E) dE$. Below this, a box labeled "At 0K" contains the equation $n_e = \frac{2}{3} E_f D(E_f)$. An arrow points from this box to a circled number 3. Below that, another box contains the equation $\Rightarrow C_e = \frac{1}{2} \pi^2 n_e K_B \cdot \frac{T}{T_f}$. At the bottom, it says "where $T_f = E_f$ ".

Therefore if you substitute for the Fermi Dirac distribution function zero to infinity f D of E dE ; if you substitute for f and then also the density of states.

I will just give you only the final expression that comes out will be; $\frac{2}{3} E_f D$ of E_f . This is your number density of electrons expression; you can actually just try it out as a home work substitute for f and D of E and then you evaluate this at 0 Kelvin. That means, you will be integrating only it in the Fermi energy level E_f . Therefore, you can rewrite our expression for heat capacity you can replace $D E_f$ in terms of you know n_e and E_f and therefore, your C_e turns out to be $\frac{1}{2} \pi^2 n_e K_B$ into T by T_f .

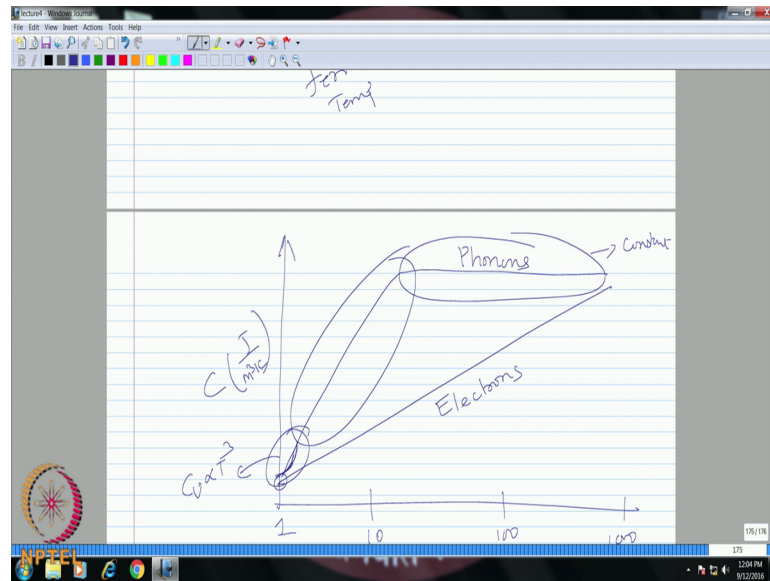
(Refer Slide Time: 35:05)

The image shows a screenshot of a presentation slide with a white background and a blue border. At the top, there is a menu bar with options like 'File', 'Edit', 'View', 'Insert', 'Actions', 'Tools', and 'Help'. Below the menu bar is a toolbar with various drawing tools. The main content of the slide is handwritten in blue ink. It starts with an arrow pointing to a boxed equation:
$$C_e = \frac{1}{2} \pi^2 n_e K_B \frac{T}{T_F}$$
 Below this, the word 'where' is written, followed by another boxed equation:
$$T_f = \frac{E_f}{K_B}$$
 An arrow points from the word 'where' to the boxed equation. Below the boxed equation, the words 'fermi Temp' are written in a cursive style. In the bottom left corner, there is a small circular logo with a red and white pattern. In the bottom right corner, there is a small rectangular box containing the text '174' and '11:59 AM 9/22/2016'.

Where; T_f is equal to E_f by K_B . This is another temperature this is called the Fermi temperature just like we have the Debye temperature in phonons we are defining, introducing these are not physical temperatures; some kind of conceptual temperature based on the value of the Fermi energy level. Similar to the Debye temperature which is based on the phonon energy level at ω_D ; the same way we are now introducing another temperature and we are substituting for E_f in terms of T_f as K_B times T_f and therefore, this is our final expression let us say 3.

Therefore, according to this expression once you know the number density of electrons, free electrons you know the Fermi temperature; based on the value of the Fermi energy level for that metal and the actual temperature room temperature or high elevated temperature you can calculate the heat capacity.

(Refer Slide Time: 36:20)



And therefore, if you have plot it how does it look with respect to temperature. We have heat capacity volumetric heat capacity joule per meter cube Kelvin and we have a log scale in the temperature 1, 10, 100, 1000; how does it look for the case of electrons? This is the constant, this is the constant and this is the constant for a given metal. It will be a straight line.

It will start from some value at 1 Kelvin and then go up like this where as for phonons we have our expression which is given by this once you know the number of atom per unit is value you know the Debye temperature; substitute this we can plot this has a function of temperature. So, how does look if you plotted it? It will be like this, it will go on and then finally, it will saturate. This is for phonons. In fact, for the two limits for phonons; I have not actually discussed this so let me quickly complete that for the case of very low temperatures. So, that is one (Refer Time: 38:06). That is the case where θ_D by T going to low temperature limit, infinity, very small values of t may be order of 1 Kelvin, 2 Kelvin cryogenic temperatures.

θ_D by T going to infinity then C_V will actually go as if you evaluate it cubic power of temperature where as for the other case where your t is very large θ_D by T going to 0; if you evaluate C_V this terms out to be a constant equivalent to $9N$ by VKB . This integral will exactly turn out to be θ_D by T the whole cube so this will cancel of and then you will exactly have a constant value this is for the high temperature limit and this

is for the low temperature limit. Therefore, at the low temperature case your heat capacity if you look at really zoom in this will be cubic variation of temperature here to be like this it will not be a straight line. This is your C_V going as T^3 and for the high temperature case this will be a constant and in between you have some kind of linear variation. This is the nature of the heat capacity variation for phonons and electrons.

So, we will stop here. I think now you must have a good understanding of what you know Statistical thermodynamics can tell us. It has helped us to define internal energy from all the micro states based on which we can calculate a very important property of the material which is the heat capacity and depending on whether we have dealing with gas molecules, whether we have dealing with semiconductors, dielectrics or with metals we know how to evaluate heat capacity, what is the contribution to heat capacity in each case and how it behave it is temperature. So, the next problem is to look at transport of heat.

If you want to solve the diffusion equation; one parameter, one property is heat capacities which we have obtain from this. The other is your thermal conductivity. Thermal conductivity we cannot obtain from just assumption of equilibrium because it is the transport property. We have to look at transport of heat by the energy carriers only under that situation we can evaluate the second most important thermo physical property. Once you understand how to evaluate that then we can directly evaluate the thermo physical properties from a very fundamental understanding and solve the macro scale equations.

So, the next class we will start with a hand waving argument of evaluating your thermal conductivity for heat conduction and in the case of hydrodynamics viscosity that is your transport property that; is also physical property. These two will evaluate in a hand waving argument using what we call kinetic theory before we go to the rigorous method using the Boltzmann transport equation.

So, this kind of this class completes the equilibrium; the so called equilibrium part. This Statistical thermodynamics can only give this much of information, but if you want to go calculate the transport properties such as conductivity viscosity and so on then we have to look in to also the transport of heat flow and so on. So tomorrow's the next class we will start looking at evaluating these other thermo physical properties also.

Student: (Refer Time: 42:47).

OK.

Student: (Refer Time: 42:49).

For which case.

Student: (Refer Time: 42:54).

Electron case.

I think this.

Student: t minus $d f$ (Refer Time: 43:02).

This one; it goes from minus $E f$ by $K B T$ to infinity. This turns out to be a constant; that means, the value of $E f$ is kind of frozen here so this should be a constant the lower limit

Student: (Refer Time: 43:23).

I mean the reason why I have you know involve that is to only tell you the $D E$ can be pulled out inside the integral. You can actually do the integration from 0 to infinity, but I wanted to pull $D E f$ outside the integral by telling you that $d f$ by $d T$ is very strong gradient only about $D E f$ about which your density of states is invariant.

So, I involved that approximation to pull $D E f$, but you can actually do the integral right from 0 to infinity. Therefore, your integral will have in this case after you transform into dummy variable will be minus $E f$ by $K B T$ to infinity. What was your question; that was your question right we were actually looking at $d f$ minus $D E f$.

Student: (Refer Time: 44:30).

So, that is at $e a$ is equal to 0; at E equal to 0 x is equal to minus $K f$ by $E f$ by $K B T$ and at E equal to infinity it is infinity.

So, we will stop here.