Electronic Properties of the Materials

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Lecture - 12
Quantum Free Electrons: Sommerfeld Theory (Part 2)

Hello friends, in this lecture, we continue our discussion on quantum free electrons and Sommerfeld theory.

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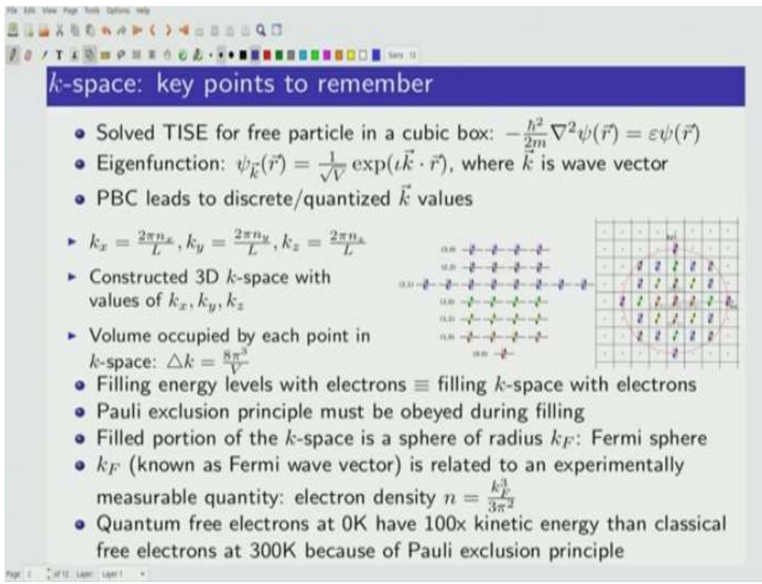

Let us briefly revise what we have done so for. So, we have solved time independent Schrodinger equation for free particle in a cubic box. And then we had bounded Eigenfunctions in this form exponential ik dot r where k is the wave vector. Now, we applied periodic boundary conditions and that gave us these discrete or quantized k values where k x =2 pi n x by L and so on here nx, ny, nz these are integers.

Now, using these discrete or quantize k values, we constructed a 3D k space with allowed values of k x k y and k z. Volume occupied by each of these discrete points is given by delta k = 8 pi cube divided by V, then we fill the energy levels and then we found that filling of energy levels with electrons is same as filling of k space k electrons. During the filling Pauli exclusion principle must be obeyed that means, we cannot put more than 2 electrons per energy level or per k point. Filled portion of the k space is a sphere of radius k F.

And this is known as the Fermi sphere k F is known as the Fermi wave vector. And this is related to an experimentally measurable quantity that is the electron density. Electron density n = k F cube divided by 3 pi square. We also found that one term free electrons at 0 Kelvin have 100 times more kinetic energy than classical free electrons at 300 Kelvin and this happens because of the Pauli exclusion principle.

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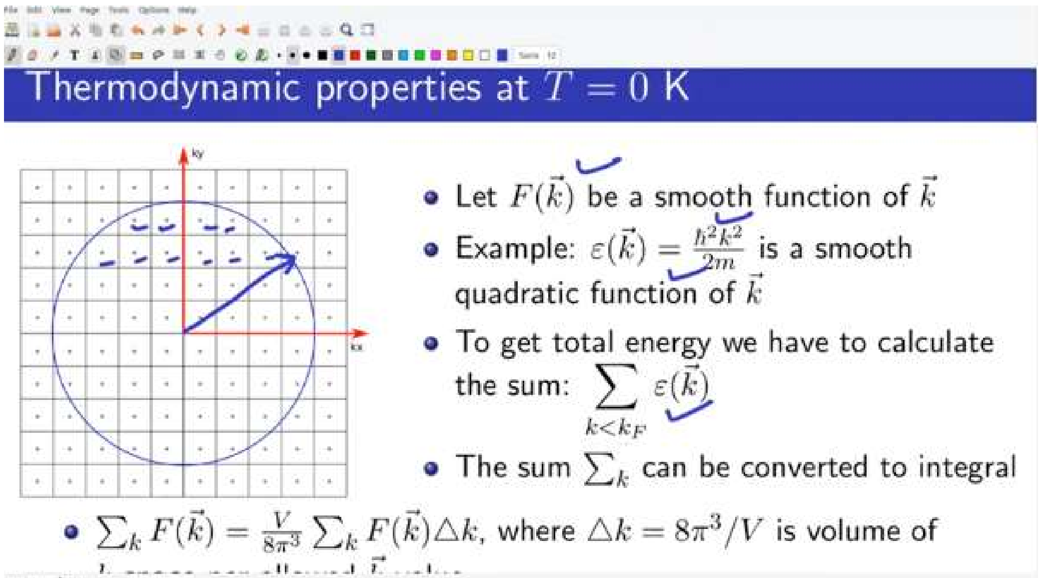

Let us calculate some thermodynamic properties at ground state. Say we know some property as a function of k and we have a smooth function of k. For example, energy = h cross square k square divided by 2m is a smooth function of k. Now, we want to calculate the total energy of the system. Now, this is the Fermi sphere with radius k F and the value of k F is given to us. To calculate the total energy, we have to add up the energies of all the k states line inside the Fermi sphere. For example, we know that all these steps, these are lying inside the Fermi sphere.

So, we have to add the energy of all the steps inside the Fermi sphere and then we can get the total energy. So, we have to calculate this sum. Let us convince ourselves that the sum can be converted to an integral under certain condition.

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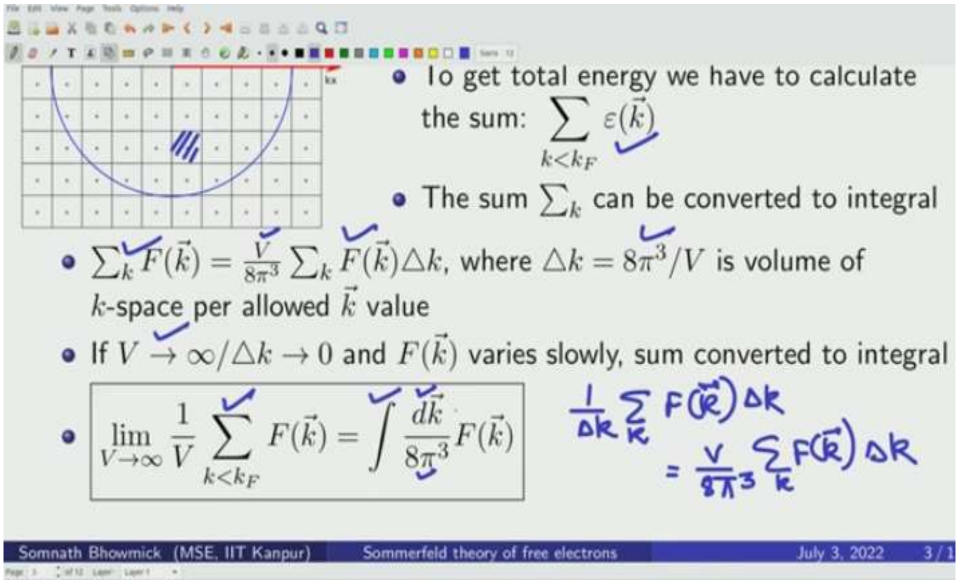

So, we have to calculate this sum for all the allowed values of k. Now, we can take this so sum over k F of k we want to calculate the sum. So

$$\frac{1}{\Delta k}\sum_k F(\vec{k})\Delta k = \frac{V}{8\pi^3}\sum_k F(\vec{k})\Delta k$$

Now, we use some limit V goes to infinity, then you see that this box they become delta k becomes very small.

So, each of these boxes it will become very small as V goes to infinity and then this discrete K points they will become almost continuous and that is why in this limit we get convert this sum to an integral so, what we do that in this equation correct being V to the left hand side so, that means, this left hand side will become 1 by V sum over k less than k F of k. and then the right hand side we have 1 by 8 pi cube. So, we have this term and we have delta k is now, we just write it as dk dk and then we have this function F of k and then as I said that this discrete space becomes almost continuous in the limit delta V going to infinity or delta k goes to 0. So, that means, we just we can do this calculate this integral.

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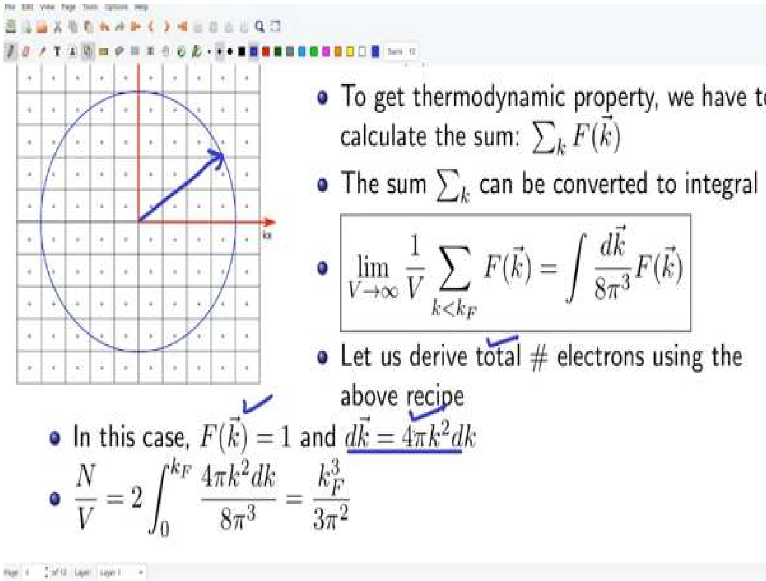

Let us derive total number of electrons using the above method; we have to find out how many states are there within the Fermi sphere. And then we have to multiply with 2 as there are 2 electrons per state according to the Pauli's exclusion principle that will give us the total number of electrons in the system. In this case, the function the smooth function is F of k this is equal to 1 and then we write the volume element in the case space dk as 4 pi k square dk we can write it in this form, because we have spherical symmetry. Now, let us calculate this.

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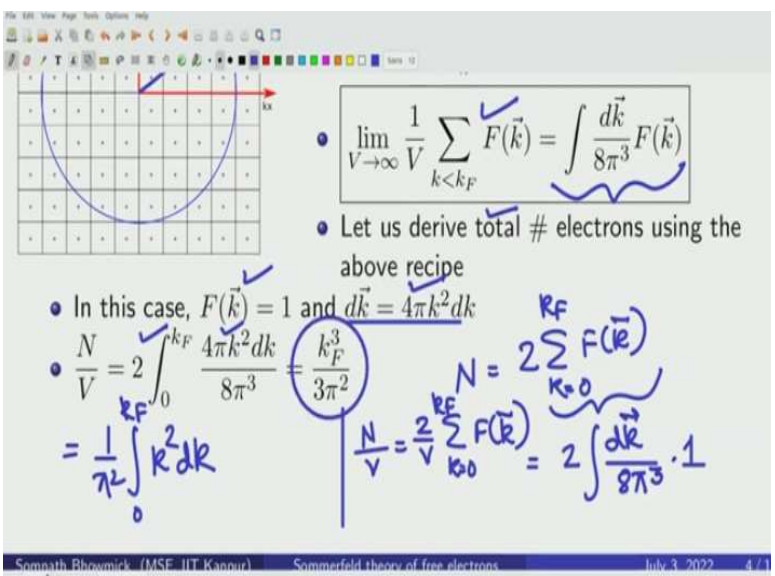

So, total number of electrons $N = 2\sum_{k=0}^{k_F} F(\vec{k})$. Now, we multiply to because of Pauli's exclusion principle. So, this sum will give you the total number of steps within the Fermi sphere and then we have to multiply with 2 because each state can have 2 electrons and now, we divided by volume such that $\frac{N}{V} = \frac{2}{V}\sum_{k=0}^{k_F} F(\vec{k})$ and I know that 1 by V sum over k less then F of k this is given by this integral. So, that means, N by V can be better than in this form.

So, I just replaced this sum with the $2\int \frac{d\vec{k}}{8\pi^3}$ and then I know that this f of k=1 and then in place of begin I just replaced 4 pi k square dk. So, this is the integral that we have to evaluate and this is not so, difficult to evaluate. So, if we just do this, so, this is like 1 over pi square integral 0 to k F k square dk and in that case, we see that N by V = k cube F divided by 3 pi square.

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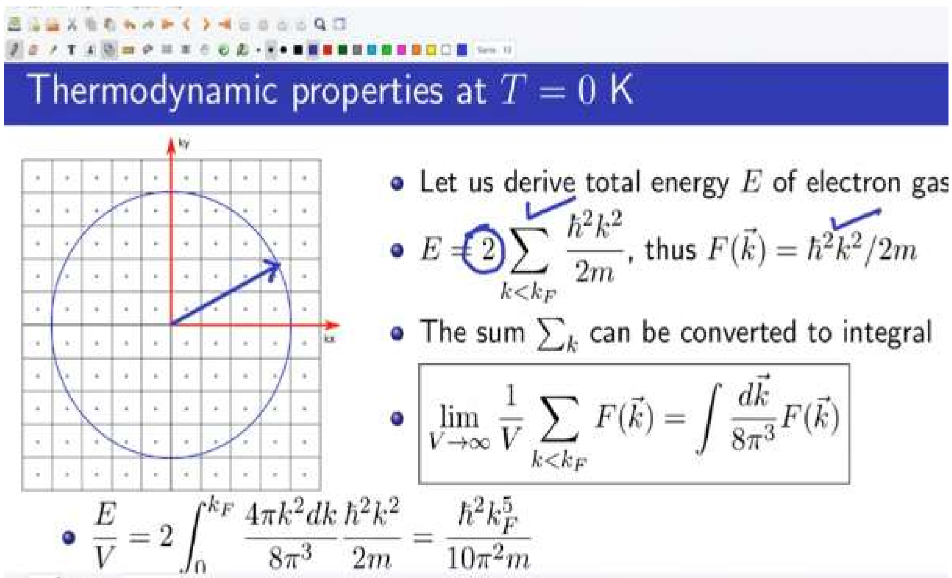

Let us derive total energy of the electron gas again the Fermi sphere is given to us the radius of the sphere. So, what we have to do is that, we have to find all the states lying within this Fermi sphere and then we have to add the energy of every state to get the total energy. So, that means we have to calculate this sum. And then we have F of k the function that we have to integrate is h cross square k square divided by 2m known that this factor to these accounts for the Pauli exclusion principle that means we have 2 electrons, but state now, let us calculate this.

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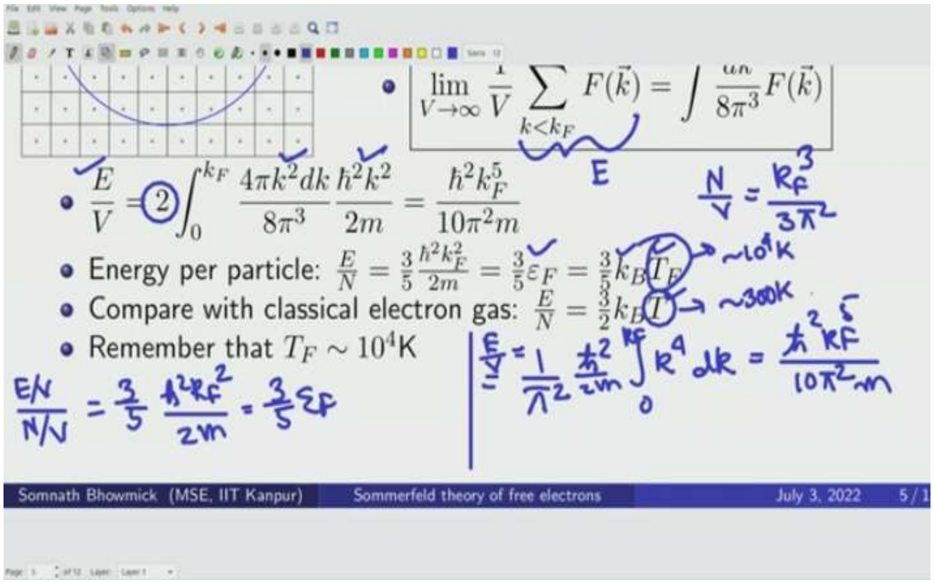

So, we know that the sum can be converted to some integral of this form and then we also know that this is equal to E. So, this is where we are just adding the energies of all the states. So, this will give E. So, that means, this factor on the left-hand side that is equal to E by V and then we have this factor of 2 which accounts for that Pauli exclusion principle and in the right-hand side we have this integral and then we know that dk = 4 pi k square. So, 4 pi k square dk and this is because of the spherical symmetry and then we have this function f of k = h cross square k square by 2m.

So, you have to calculate this integral and then this integral will be equal to

$$\frac{1}{\pi^2}\frac{\hbar^2}{2m}\int_0^{k_F} k^4\, dk = \frac{\hbar^2 k_F^5}{10\pi^2 m}$$

So, now, what we know is we know that N by V = k F cube divided by 3 pi square and we know that this term is equals to E by V. E by V is equals to this term.

So, that means, we can also write this ratio of E by V and then N by V and that will turn out to be 3 5th of h cross square k F square divided by 2 m and then we know that this h gross square k F square by 2m = E F square And the Fermi of the square 3 by 5 of E F and then E F we can convert it to some temperature scale we can just write E F is equals to Boltzmann constant k B times T F where T F is some temperature scale.

$$\frac{E/V}{N/V} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m} = \frac{3}{5}\varepsilon_F$$

Now, we can compare this with classical the energy of the classical electron gas and that turns out to be 3 by 2 times K B T whereas, this is of the order of 10 power for Kelvin and the room temperature T this is of the order of 300 Kelvin. Thus, we again see that the quantum free electron gas has almost 100 times more energy than the classical free electron gas.

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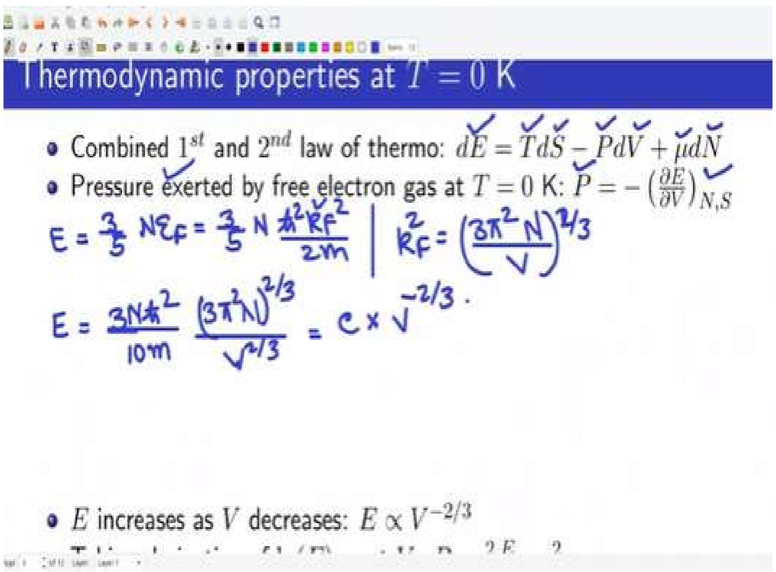

We already have calculated the internal energy of free electron gas, let us calculate few more thermodynamic properties combining first and second law of thermodynamics we can write dE so, this is the E is the internal energy equal to TdS, T is the temperature, S is the entropy minus PdV the P is pressure, V is volume plus mu dN mean is chemical potential and N is the total number of particles. Now, if we take this equation, then we can calculate the pressure exerted by the free electron gas that T = 0 Kelvin.

So, by calculating this partial derivative del E del V that constant N and S that is equal to pressure. Let us calculate this term. So, we already know that $E = \frac{3}{5} N \varepsilon_F$where N is the total number of particles, total number of electrons and E F is the Fermi energy. Now, we know that the Fermi energy can further written as $\frac{3}{5} N \frac{\hbar^2 k_F^2}{2m}$ .Now, we also know that

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

So, that means,

$$E = \frac{3N\hbar^2}{10m}\frac{(3\pi N)^{2/3}}{V^{2/3}} = cV^{-2/3}$$

so, thus energy increases as V decreases. So, energy is proportional to V power -2 by 3.

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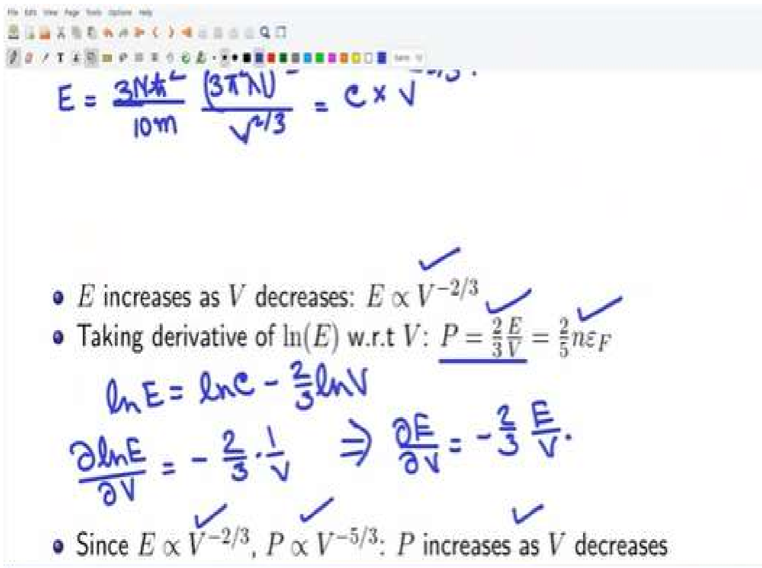

Now, we can take log of this equation and then we can write log of E = log of C - 2 third log of V and then we calculate this derivative, del we calculate the partial derivative del log E divided by del V = -2 by 3 into 1 by V. So, this implies that we can further write del E by del V = -2 by 3 E by V. So, this is what we have and then we can further write this term like this. Since, energy goes as V power minus 2 by 3 then from this equation write from this equation.

We can see that all we can find out that pressure goes as V power -5 by 3. So, pressure increases as volume decreases thus, as one tries to compress a metal free electron pressure is going to resist.

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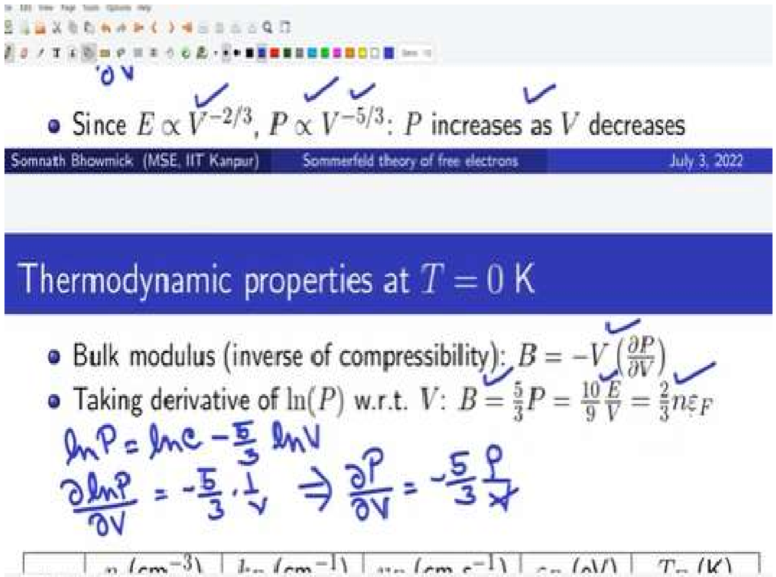

The resistance to compression is known as the bulk modulus. It is defined as the ratio of infinitesimal pressure increase due to the decrease of volume. Let us calculate these all. So, again we get log such that we can write log of P is equals to, so, we are just taking log of this equation so, log of P = log of some constant minus 5 by 3 log of V and again we calculate the derivative points which is equal to -5 by 3 into 1 by V and then we can write this in this form del P by del V = -5 by 3 P by V.

Thus we can write bulk modulus B is equals to -V. So, minus V will cancel this V and then del P del V. So, it is like 5 by 3 of P. So, that means bulk modulus will be 5 by 3 times P and then we can further express it in terms of energy as well as Fermi energy.

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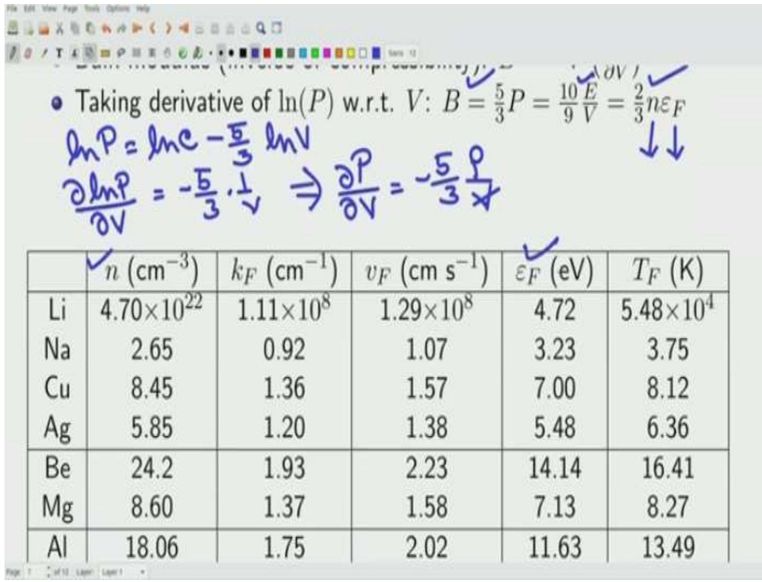

	n (cm^{-3})	k_F (cm^{-1})	v_F (cm s^{-1})	ε_F (eV)	T_F (K)
Li	4.70×10^{22}	1.11×10^{8}	1.29×10^{8}	4.72	5.48×10^{4}
Na	2.65	0.92	1.07	3.23	3.75
Cu	8.45	1.36	1.57	7.00	8.12
Ag	5.85	1.20	1.38	5.48	6.36
Be	24.2	1.93	2.23	14.14	16.41
Mg	8.60	1.37	1.58	7.13	8.27
Al	18.06	1.75	2.02	11.63	13.49

So, that means, you see the bulk modulus can be expressed in terms of the electron density as well as the Fermi energy, but now, note that we already have estimated the value of n electron density and the value of the Fermi energy thus, we can compare the calculated value with the experimental value.

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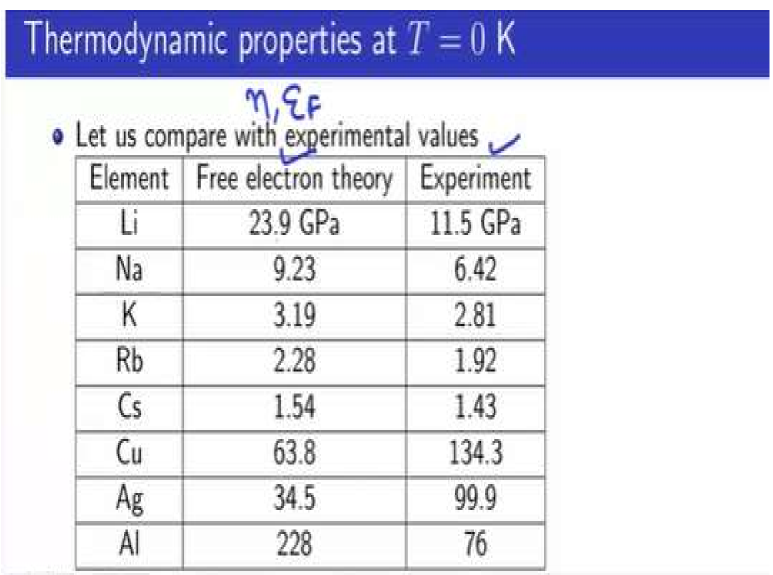

Element	Free electron theory	Experiment
Li	23.9 GPa	11.5 GPa
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76

In this column, we have the experimental values of bulk modulus for different metals and then in this column we have the values calculated from free electron theory. So, what we did is that we calculated the value of an electron density we calculated the value of E F and from that, we can find the value of bulk modulus.

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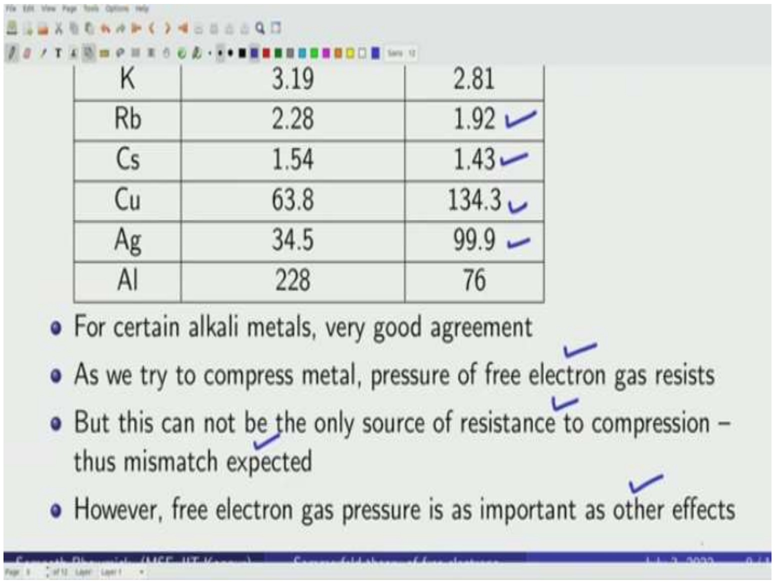

And then you will see that the values for certain alkali metals like rubidium and cesium the agreement is really good. It is not so, good for say like copper or silver and so on. So, what we can conclude from this as we try to compress a metal the pressure of free electron gas will resist, but this cannot be the only source of resistance to compression. So, the mismatch that we find here is expected.

But you see that the filling on gas pressure is as important as other effects because, if you at least look at the order of magnitude, these numbers they are of the same order of magnitude. So, that leads to the conclusion that that free electronic gas pressure is as important as other effects.

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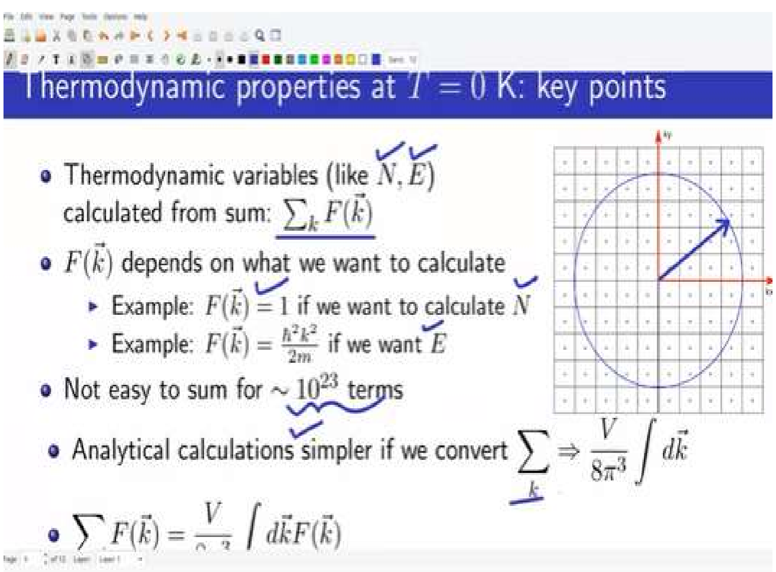

Before we go further, let us review what we have done so, far. So, we have found that thermodynamic variables like the total number of electrons or the energy of the electrons can be calculated from this sum and this sum needs to be calculated up to the Fermi sphere. Now, F of k depends on what do you want to calculate for example, F of k =1 if we want to calculate the total number of electrons, F of k is h cross square k square by 2m if we want to calculate the total energy and so, on.

Now, note that this is not an easy solve to calculate, because the number of electrons that we have in the system is huge it is of the order of 10 power 23. Analytical calculation it becomes simpler if we convert the sum to the integral

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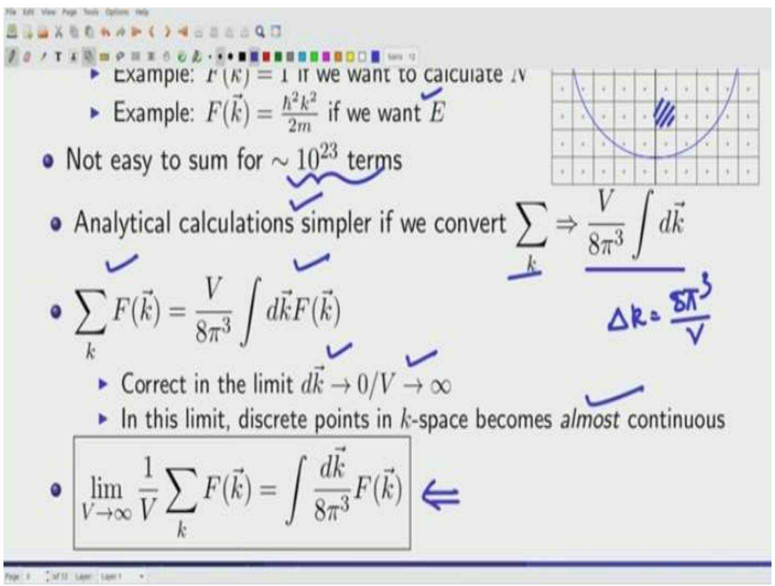

And then this is how the sum can be written as an integral and this conversion is correct in the limit delta k dk goes to 0 or that means in the limit V is going to infinity. So, that means, so, this is like delta k right the point and occupied other volume occupied by one point. So, we see that as V goes to 0. So, delta k = 8 pi cube by 3. So, as V goes to infinity, the volume occupied by each point this will go to almost 0.

So, that means the discrete space now can be looked at as some almost continuous space and then we can convert the sum to this integral and then we can write it in this form. And we have used this to evaluate the total number of electrons as well as the total energy of the electrons.

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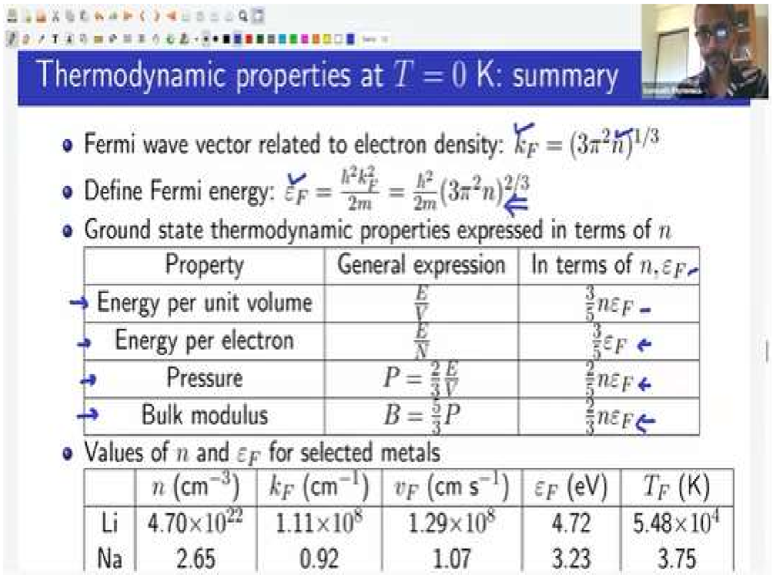

Let me summarize some of the thermodynamic properties of free electron gas at ground state. The beauty of free electron gas model is its simplicity, we need only one parameter in the electron density and from that we can calculate k F the Fermi wave vector and from Fermi wave vector we can calculate E F the Fermi energy and once we have this n and E F, we can express all the thermodynamic properties.

For example, energy per unit volume, this is given by 3 5th n times E F, energy per electron this is given by 3 5th F, pressure is given by 3 5th n times F, bulk modulus is given by 2 3rd n times F. Now, although we are using both n and E F, actually we have only one independent variable and because E F is related to n by this equation.

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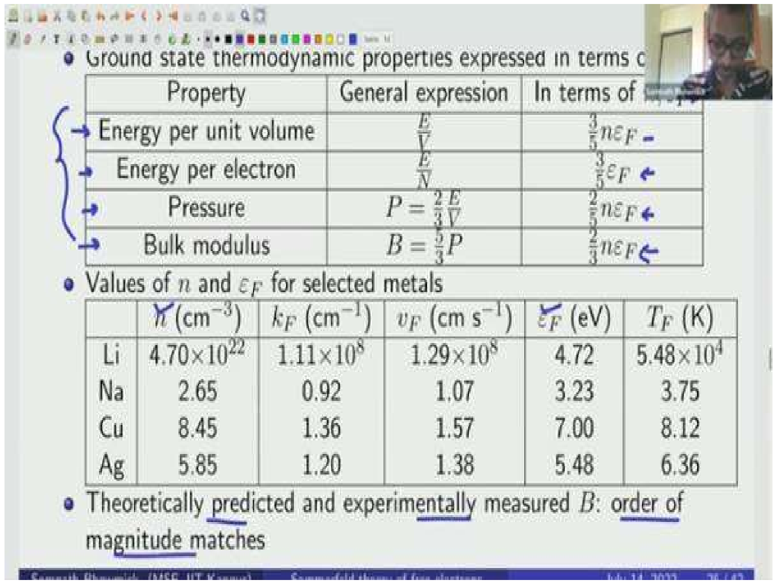

So, now, if you look at this table, once we have found the value of n, we can find the value of F and from that we can calculate all the ground state properties listed in this table. Among all the properties, we can actually compare with experimental result in case of bulk modulus. And then, we already have seen that the theoretical predicted and experimentally measured value of bulk modulus for most of the metals the order of magnitude matches. This provides us some kind of validation of quantum free electron gas model.