

Lecture 2

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In the last lecture we found out the equation -

$$\frac{d\vec{P}(t)}{dt} = -\frac{\vec{P}(t)}{\tau} + \vec{f}(t) \quad \text{--- (i)}$$

From here using the steady state condition we found a relationship between resistivity ρ and relaxation time τ . We also saw that the scattering introduces the resistivity in the metal with the first term on the right hand side of equation (i). The relation between τ and ρ was found to be,

$$\tau = \frac{m}{\rho n e^2}$$

Here, ρ is a function of temperature and increases with temperature (one can measure ρ using experimental set ups).

Conversely, τ decreases as temperature increases. Using the equipartition of energy the electron velocity comes out to be in the order of 10^5 ms^{-1} at room temperature, which is temperature dependent. However, electrons are not really classical particles, and Maxwell-Boltzmann statistic does not apply to them. If the correct Fermi-Dirac statistics is applied considering the quantum nature, the velocity

comes out to be an order above, and temperature independent. At very low temperatures, thus, τ is high and the mean free path $l_0 = \tau v_0$ can even become 10^3 or

more Angstroms, which is about a thousand times

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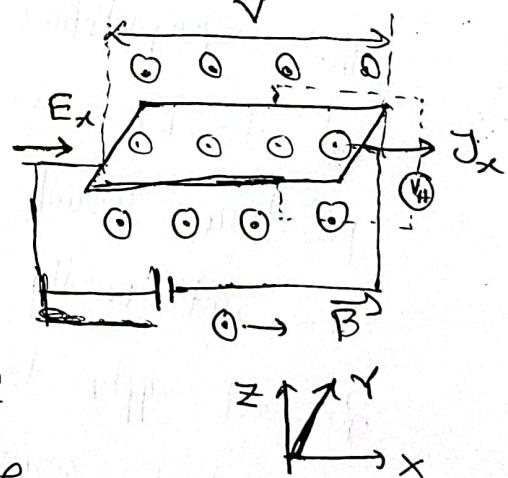
the interatomic spacing. This actually discredits Drude theory that electrons bump off of positive ion cores with random orientation.

However, Drude's model successfully describes another phenomenon - Hall effect.

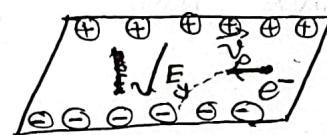
Hall effect (first conceived by E.H. Hall in 1879)

Consider a very thin sheet of metal (so thin it can basically be considered as 2D). Say, you apply a voltage difference by using a battery between the sides of the metal, which introduces a current, say I_x and a surface current density J_x . However, now, we introduce a magnetic field perpendicular to the plane of the metal.

Now one finds, apart from the voltage drop along x -direction, if there is another voltage introduced in the y -direction, the Hall voltage. If the magnetic field is switched off, the Hall voltage also diminishes. One then expects Hall voltage to be a function of magnetic field, which indeed is.



Say, the electron velocity is given by, $\vec{v} = v_0 (-\hat{i})$ and the magnetic field is given by $\vec{B} = B_0 \hat{k}$.



The Lorentz force on the electron is given by,

$$\vec{F} = -e \vec{v} \times \vec{B} = -e (v_0 \hat{i} \times B_0 \hat{k}) = -ev_0 B_0 \hat{j}$$

Due to the force on the charges, they will be deflected towards the $-\hat{j}$ edge of the metal, and move till they hit the boundary of the metal. However, as the negative charges starts building on $-\hat{j}$ edge side, we are left out with a net positive charges on the $+\hat{j}$ end. This will in turn introduce an electric field E_j . As more and more building up of charges occurs, E_j increases. This E_j will induce a force on the electrons given by,

$$\vec{F}_e = -e \vec{E}_j = -e E_j (-\hat{j}) = +e E_j \hat{j}$$

In the case of equilibrium situation, this force will balance out the Lorentz force and current will only flow in the x -direction.

Now, let's introduce Drude's theory in this scenario. We will apply Drude's theory when there are both electric and magnetic field present.

We had,

$$\frac{d\vec{P}}{dt} = -\frac{\vec{P}}{\zeta} + \vec{f}(t)$$

$$\Rightarrow \frac{d\vec{P}}{dt} = -\frac{\vec{P}}{\zeta} + \left[-e \left[\vec{E}_0 + \vec{V} \times \vec{B} \right] \right]$$

$$\rightarrow \frac{d\vec{P}}{dt} = -\frac{\vec{P}}{\zeta} - e\vec{E} - e\vec{V} \times \vec{B}$$

Current is independent of time

In the steady state, $\frac{d\vec{P}}{dt} = \vec{0}$, when $\vec{f}(t) = -e[\vec{E}_0 + \vec{V} \times \vec{B}]$ balances the drag term $-\frac{\vec{P}}{\zeta}$.

In this case, we then have,

$$\vec{0} = -\frac{\vec{P}}{\zeta} - e\vec{E} - e\vec{V} \times \vec{B}$$

$$\Rightarrow \vec{0} = -\frac{-m}{ne\zeta} \vec{J} - e\vec{E} - \left(\frac{-\vec{J}}{ne} \times \vec{B} \right)$$

$$\Rightarrow e\vec{E} = \vec{J} \frac{m}{ne\zeta} + \frac{\vec{J} \times \vec{B}}{n}$$

We had,

$$\vec{J} = -ne\vec{V}$$

$$\Rightarrow \vec{V} = -\frac{\vec{J}}{ne}$$

$$\text{Also, } \vec{J} = -\frac{ne}{m} \vec{P}$$

$$\therefore \vec{P} = -\frac{m}{ne} \vec{J}$$

$$\therefore \vec{E} = \frac{m}{ne^2\zeta} \vec{J} + \frac{1}{ne} \vec{J} \times \vec{B}$$

In our case, $\vec{J} = J_x \hat{i}$

Let's write, $\vec{J} = J_x \hat{i} + J_y \hat{j}$ and $\vec{B} = B_0 \hat{k}$.

$$\therefore \vec{E} = \frac{m}{ne^2\zeta} (J_x \hat{i} + J_y \hat{j}) + \frac{1}{ne} (J_x \hat{i} + J_y \hat{j}) \times B_0 \hat{k}$$

$$\therefore \vec{E} = \left(\frac{m}{ne^2\zeta} J_x + \frac{1}{ne} J_y B_0 \right) \hat{i} + \left(\frac{m}{ne^2\zeta} J_y - \frac{1}{ne} J_x B_0 \right) \hat{j}$$

$$\boxed{\begin{aligned} E_x &= \frac{1}{\rho} J_x + \frac{B_0}{ne} J_y \\ E_y &= \frac{1}{\rho} J_y - \frac{B_0}{ne} J_x \end{aligned}}$$

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Once the electric force nullifies the Lorentz force, we can calculate the Hall field E_y by just putting $J_y = 0$ in the above equations.

$$\boxed{E_x = \frac{J_x}{\rho}} \quad \text{--- (1)}$$

and

$$\boxed{E_y = -\frac{B_0}{ne} J_x} \quad \text{--- (2)}$$

Now, the first equation describes the usual relation of elec. electric field and current density. You can write the equation as, $E_x = \rho J_x$ and define the ρ as the magnetoresistance. Hall found out that the ~~resistivity~~ resistivity is independent of the applied magnetic field, since equation (1) describes the relation ~~with~~ which is valid for zero magnetic field as well. However, just a passing note: careful experiments reveal that this resistivity indeed depends on the magnetic field, and one needs the introduction of quantum theory of solids to explain this.

However, equation (2) gives us another relation between the transverse electric field E_y and the current density J_x , and hence we may define the Hall resistivity

by S_H , given by the equation, $E_y = S_H J_x$ with

$$S_H = -\frac{B_0}{ne} = R_H B_0$$

One can then plot a graph S_H vs B_0 (with an experimental set up), the slope immediately gives what we call the Hall coefficient,

$$R_H = -\frac{1}{ne}$$

So, Hall coefficient depends only on the electron density n , and nothing else! So, the Hall coefficient is a constant for a particular metal. Also, if you measure R_H experimentally, the above equation immediately gives you n , by just conducting an experiment!

However, experiments suggest that, the Hall coefficient varies with the strength of magnetic field. Furthermore, it depends on the temperature. Although Drude model explains the Hall phenomena nicely, it can't account for these inconsistencies. Also, in calculating the Hall coefficient, we assumed the sign of the charge carrier to be negative. If, instead the charge carrier was positive, you can work out in the

same way to find,

$$R_H = + \frac{1}{ne}$$

Calculated from
real experiment

Metal	$\frac{1}{R_H ne}$
Li	-0.8
Na	-1.2
K	-1.1
Cu	-1.5
Ag	-1.3
Be	0.2
Mg	0.4
Al	0.3

The value of $\frac{R_H}{ne}$ for different metals with a very high magnetic field ($\sim 10^4$ G) and low temperature is shown in the table. n is the density for which Drude form of $R_H = -\frac{1}{ne}$ is satisfied, that is $n = \frac{1}{TR_H}$.

Although the alkali metals obey the Drude result reasonably well, there are deviations in other cases. For Be, Mg and Al, it even follows that $R_H = + \frac{1}{ne}$ instead of $R_H = - \frac{1}{ne}$, as if the charge carriers are positive! This can't be explained by Drude theory. So, along with some successos, Drude theory of electrical conduction faces incomiciencies which can't be resolved.

Note: The specific choice of high magnetic field and low temperature is that, in these ~~cases~~ circumstances, the value approaches to a limiting value.

Thermal conductivity of a metal

The most impressive success of Drude theory at that time was the explanation of empirical law of Wiedemann and Franz. They found that, the ratio of electrical thermal to electrical conductivity, $\frac{\kappa}{\sigma}$ is directly proportional to temperature T , and the proportionality constant is the same for all metals with more or less a fair accuracy. The proportionality constant is given by $\frac{\kappa}{\sigma T}$, known as the Lorentz number. The table shows the values for 273 K temperature.

To explain the thermal conduction in metals, Drude assumed that the thermal current is carried out by conduction electrons. This was motivated by the fact that, insulators were bad conductor of heat, and the main difference between insulators and metals were the free electrons.

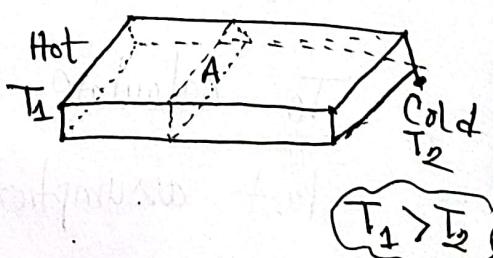
To define and calculate thermal conductivity, consider a metal bar where temperature varies slowly

Element	κ (W/cm-K)	$\kappa/\sigma T$ (W-Ω/K)
Li	0.71	2.82
Na	1.38	2.12
K	1.0	2.42
Ag	4.18	2.31
Fe	0.80	2.61
Sb	0.18	2.57

If there are no sources or sinks at the ends of the bar, to maintain the temperature gradient, then heat will flow from the hot end to the cool end and the hot end will cool and cold end will get warm. So, thermal energy (heat) will flow in the opposite to the temperature gradient (gradient would have a direction from cool to hot, and heat would flow in opposite). If we supply heat at the hot end as fast as it dissipates, we can produce a steady state in which both the temperature gradient and the flow of thermal energy is present.

Just like the ~~thermal~~ electric current density, we define the thermal current ~~density~~ \vec{J}^q as a vector parallel to the direction of heat flow, with a magnitude of thermal energy (heat) per unit time crossing a unit area perpendicular to the heat flow. In terms of magnitude then,

$$\vec{J}^q = \frac{1}{A} \frac{dQ}{dt}$$



Now, Fourier's law (which is an empirical law based on experiments) states that, for small temperature

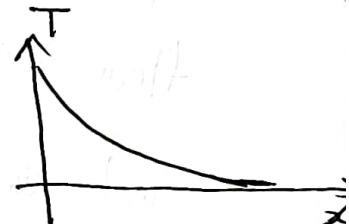
gradients, the thermal current is proportional to the temperature gradient, which can be written as,

$$\vec{J}^q = -K \vec{\nabla} T$$

where K is the proportionality constant and is called the thermal conductivity. The negative sign should make sense according to our discussion before.

For example, you can think of this in one dimensional case. The equation will be reduced to

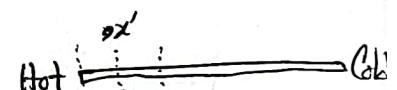
$J^q = -K \frac{dT}{dx}$. If you consider $T(x)$ such that it's a rapidly decreasing function of x , then the gradient is high, and thermal current is also high. If $T(x) = \text{constant}$, the gradient is zero and no current should flow, as expected. You can also then understand what would happen if temperature falls very slowly as a function of x .



To calculate the thermal current, we resort to the last assumption of Drude, that after a collision, the electron emerges with a speed appropriate to the local temperature. Consequently, even though

net electric current
 is just mean non-electric current
 moving in \vec{v}_T direction
 the mean electronic velocity at a point may
 vanish, electrons arriving at that point from a
 high temperature side will be more energetic
 compared to the electron arriving at that point
 from the low temperature side, which leads to
 a net flow of thermal energy to the low
 temperature side.

Let's first consider an oversimplified one-dimensional scenario, where electrons only moves in the x -direction. So, at a point x , our assumption will be that electrons will be coming from both hot and cold side. We will also assume, at point x , half of the electrons are coming from the hot end and half coming from the cold end so that the density of electron is preserved. This is important since we don't want any net electric charge to flow in this direction, that is no electric current. If $\epsilon(T)$ is the thermal energy per electron in equilibrium temperature T inside the metal, then the electron which had its



last collision at x' will, on average have thermal energy of $\epsilon(T[x'])$. Now, electrons coming from the hotter side will have, on average their collision a $\frac{1}{2}$ time before, and so, the position of last collision will be at $x-v\frac{1}{2}$. So, these electrons will carry a thermal energy of $\epsilon(T[x-v\frac{1}{2}])$ per electron. Similarly, the electrons coming from the cold end will carry a thermal energy of $\epsilon(T[x+v\frac{1}{2}])$ per electron.

Now, if n is the density of electrons inside the metal, $\frac{n}{2}$ will be the density of electrons coming from the hot end and $\frac{n}{2}$ will be the density of electrons coming from the cold end. Now, the ~~thermal~~ current density corresponding to this electron flow will be given by,

$$\vec{j}_+ = \frac{n}{2} v \epsilon(T[x-v\frac{1}{2}]) \hat{i} \quad \left| \begin{array}{l} \text{Like the case} \\ \text{of electron current} \\ \text{density, } \vec{j} = -n\vec{v}\epsilon \end{array} \right.$$

$$\vec{j}_- = -\frac{n}{2} v \epsilon(T[x+v\frac{1}{2}]) \hat{i}$$

So, net thermal current flow at x is,

$$j^2 = \frac{n}{2} v [\epsilon(T[x-v\frac{1}{2}]) - \epsilon(T[x+v\frac{1}{2}])]$$

If the variation of temperature is very small over the mean free path ($l_0 = v\frac{1}{2}$), we can expand j^2 about the point x by using Taylor's series expansion.

$$\begin{aligned} \mathcal{E}\{T[x-vz]\} &= T(x) - \frac{dT}{dx}(vz) + \frac{1}{2!} \frac{d^2T}{dz^2} (vz)^2 + \dots \\ &\approx T(x) - \frac{dT}{dx}(vz) = T(x) - \Delta T \\ T[x+vz] &= T(x) + \frac{dT}{dx}(vz) + \frac{1}{2!} \frac{d^2T}{dz^2} (vz)^2 + \dots \\ &\approx T(x) + \frac{dT}{dx}(vz) = T(x) + \Delta T \end{aligned}$$

with $\Delta T = \frac{dT}{dx}(vz)$

Then again, $\mathcal{E}(T[x-vz]) \approx \mathcal{E}(T(x) - \Delta T) \approx \mathcal{E}(T(x)) - \frac{d\mathcal{E}}{dT} \Delta T$
 $\mathcal{E}(T[x+vz]) \approx \mathcal{E}(T(x) + \Delta T) \approx \mathcal{E}(T(x)) + \frac{d\mathcal{E}}{dT} \Delta T$

$$\therefore J^q = \frac{1}{2} n v \left[\mathcal{E}(T(x)) - \frac{d\mathcal{E}}{dT} \Delta T - \mathcal{E}(T(x)) - \frac{d\mathcal{E}}{dT} \Delta T \right]$$

$$\Rightarrow J^q = \frac{1}{2} n v \left(-2 \frac{d\mathcal{E}}{dT} \times \frac{dT}{dx} vz \right)$$

$$\boxed{\therefore J^q = n v^2 z \frac{d\mathcal{E}}{dT} \left(-\frac{dT}{dx} \right)}$$

Comparing with $J^q = K \frac{dT}{dx}$ we get the thermal conductivity to be,

$$\boxed{K = n v^2 z \frac{d\mathcal{E}}{dT}}$$

Now, for going to three dimensional scenario, we will have to replace v with v_x , the x -component of velocity \vec{v} .

$$\therefore J_x^q = n v_x^2 z \left(\frac{d\mathcal{E}}{dT} \right) \left(-\frac{dT}{dx} \right)$$

However, we have to remember that this $\langle v_x^2 \rangle$ is the average of the x-component ~~speeds~~ of velocities of all the electrons. Since there should be no preference of x, y or z-direction of electron velocity, that is the velocity distribution is isotropic.

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

Here, we are using $\langle v^2 \rangle$ as just v^2 while keeping in mind that this is actually the average.

$$\therefore \vec{j}^q = n v^2 \sum \left(\frac{dE}{dT} \right) \left(-\frac{\partial T}{\partial x} \right) \hat{i} + n v^2 \sum \left(\frac{dE}{dT} \right) \left(-\frac{\partial T}{\partial y} \right) \hat{j} + n v^2 \sum \left(\frac{dE}{dT} \right) \left(-\frac{\partial T}{\partial z} \right) \hat{k}$$

$$\therefore \vec{j}^q = \frac{1}{3} n v^2 \sum \left(-\vec{\nabla} T \right) \frac{dE}{dT}$$

Now, $n \frac{dE}{dT} = \frac{N}{V} \frac{dE}{dT} = \frac{1}{V} \left(\frac{dE}{dT} \right) = C_v$ where

$E = N\epsilon$ is total thermal energy of the metal.

$$\therefore \vec{j}^q = \frac{1}{3} C_v v^2 \sum (-\vec{\nabla} T)$$

and so, thermal conductivity,

$$K = \frac{1}{3} C_v v^2 \sum$$

$$= \frac{1}{3} C_v l_0 v^2$$

Now, ~~Lorentz~~ now

Now, the ratio of thermal to electric conductivity

$$\text{is, } \frac{\kappa}{\sigma} = \frac{\frac{1}{3} C_v v^2 z}{n e^2 \gamma m}$$

$$\therefore \frac{\kappa}{\sigma} = \frac{C_v v^2 m}{3 n e^2}$$

For finding the electronic specific heat and ~~average~~ mean square speed, Drude applied the classical ideal gas law, meaning the Maxwell-Boltzmann distribution, which gives,

$$f(\vec{v}) d\vec{v} = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} \quad d\vec{v} \text{ as Velocity distribution}$$

$$\text{and } f(v) dv = \frac{4\pi}{\sqrt{\pi}} \left(\frac{m}{2\pi k_B T} \right)^{3/2} v e^{-\frac{mv^2}{2k_B T}} \quad dv \text{ as Speed distribution}$$

One ~~can~~ can calculate to find that the mean square speed given by, $\langle v^2 \rangle = \int v^2 f(v) dv$ is equal to $\frac{3k_B T}{m}$, where k_B is the Boltzmann constant.

$$\therefore m \langle v^2 \rangle = \frac{3}{2} k_B T$$

Also, according to kinetic theory of gases if you calculate the specific heat, it will be given by,

$$C_v = \frac{1}{V} \left(\frac{dE}{dT} \right)_V = \frac{1}{V} \frac{d}{dT} \left(N \times \frac{3}{2} k_B T \right) = \frac{3}{2} n k_B$$

$$\therefore \frac{\kappa}{\sigma} = \frac{\frac{3}{2} n k_B \times \frac{3k_B T}{m} \times m}{3 n e^2}$$

$$\therefore \frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T$$

$$\therefore \frac{k}{\alpha T} = 1.11 \times 10^{-8} \text{ W-ohm/K}^2$$

The Lorentz number $\frac{k}{\alpha T}$ is indeed found to be a constant according to Drude model. However, the number is half the value of Wiedemann and Franz law. But this is not the whole story! In Drude's original paper, in Annalen der Physik, 1, 566, Drude found mistakenly calculated the speed to be $\frac{1}{2} \frac{eE}{m}$ and hence calculated the electric conductivity of half the original calculation. This in turn gave the value of $\frac{k}{\alpha T}$ to be twice as our calculation, that is $2.22 \times 10^{-8} \text{ W-ohm/K}^2$. This was a huge success, although erroneous. However, the electronic contribution to the specific heat was not verified later, as, for example at room temperature there is no contribution to the specific heat was measured. The room temperature specific heat electronic contribution was later found to be 100 times smaller, and mean square electronic speed is about 100 times higher than the classical calculation. This has contributed to the apparent success of Drude's theory at that time apart from the factor of two mistake.

There are some roughness in the calculation that one can talk about. One might object, that the thermal energy per electron should depend on the direction from where they are coming, so will their average speed, since this too depends on the temperature at the place of their last collision. If electrons emerging from a collision has higher energies because the temperature was higher, they should have higher speeds. So, we should really consider the electron speed to be position dependent, that is we should write the velocities of left and right side electrons as $v(x-v_2)$ and $v(x+v_2)$. Immediately after the temperature gradient is applied, there will be a non-vanishing mean electronic velocity in the opposite direction of temperature gradient. It means there will be a net flow of charge and hence a ~~non-zero~~ non-zero electric current. However, thermal conductivity measurements are performed in open circuit conditions, that is no current can flow. Here, the ~~non-zero~~ electric current flows until there are enough electric charge accumulation at the ends. If we could set up a temperature gradient in a closed circuit, a current would flow up the gradient (since electrons would flow in the opposite direction). However, in an open circuit, this electric current gives rise to a net building up of charges at the end, which then induces an

electric field, \vec{E} . Steady state is obtained when field is sufficient to cancel out the drift velocity. The existence of such a field is called the thermoelectric field and the effect is known as Seebeck effect. The field is conventionally written as -

$$\vec{E} = \varrho \vec{\nabla} T$$

The proportionality constant ϱ is called the thermopower.

In one dimensional model, the mean electronic velocity

at a point x due to the temperature gradient is,

$$v_g = \frac{v(x-vz) - v(x+vx)}{2} = \frac{v(x) - \frac{dv}{dx} v^2 - v(x) + \frac{dv}{dx} v^2}{2}$$

$$= -v^2 \frac{dv}{dx} = -\frac{d}{dx} \left(\frac{v^2}{2} \right) = -\frac{d}{dT} \left(\frac{v^2}{2} \right) \frac{dT}{dx}$$

We will again generalize to three dimension by letting $v \rightarrow v^2$

and $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} v^2$, so that,

$$\vec{v}_g = -\frac{1}{6} \vec{\nabla} v^2$$

$$= -\frac{1}{6} \frac{\partial v^2}{\partial T} \vec{\nabla} T$$

$$|\vec{\nabla} T \parallel \vec{\nabla} v^2$$

Now, the mean velocity due to the electric field produced

will be,

$$\vec{v}_E = -\frac{e\vec{E}}{m}$$

At steady state, $\vec{v}_g + \vec{v}_E = \vec{0}$

$$\Rightarrow -\frac{1}{6} \frac{\partial v^2}{\partial T} \vec{\nabla} T + \frac{e\vec{E}}{m} \times \varrho \vec{\nabla} T = \vec{0}$$

$$\begin{aligned} \therefore \vartheta &= -\frac{m}{6e} \frac{d}{dT} (v^2) = -\frac{1}{3e} \frac{d}{dT} \left(\frac{1}{2} m v^2 \right) \\ &= -\frac{1}{3e} \frac{d}{dT} \left(\frac{3}{2} k_B T \right) = -\frac{k_B}{2e} = -\frac{\frac{3}{2} n k_B}{2 \times \frac{3}{2} n e} = -\frac{C_V}{3ne} \end{aligned}$$

$$\boxed{\therefore \vartheta = -\frac{k_B}{2e} = -0.43 \times 10^{-4} \text{ Volt/K}}$$

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However, the measured thermopowers were in the order of microvolts per Kelvin, meaning a factor of 100 smaller. The same factor was also emerging in Drude's derivation of Wiedemann-Franz law. Although that was compensated by another factor, this one didn't. This phenomenon also indicates that we can't treat electron as classical particles. All these have motivated treating electron as quantum particle and replace classical statistical mechanics by quantum statistical mechanics, where one ~~studies~~ studies electron dynamics using the proper Fermi-Dirac statistic rather than Maxwell-Boltzmann statistics.

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