

Last time:

Finished with phonons, optical and thermal properties.

Today: Start with electronic properties of metals.

Free electron model.

Fermi energy.

Density of states.

Electronic heat capacity

Lecture 7



Electrons in metals: free electron model

- Simplest way to represent the electronic structure of metals
- Although great simplification, works pretty well in many cases, describes many important properties of metals
- In this model, the valence electrons of free atoms become conduction electrons in crystal and travel freely
- Neglect the interaction of conduction electrons with ions of the lattice and the interaction between the conduction electrons – a *free electron gas*
- Fundamental difference between the free electron gas and ordinary gas of molecules:

- 1) electrons are charged particles \Rightarrow to maintain the *charge neutrality* of the whole crystal, we need to include positive ions. This is done within the *jelly model*: the positive charge of ions is smeared out uniformly throughout the crystal - charge neutrality is maintained, no field on the electrons exerted
- 2) Free electron gas must satisfy the Pauli exclusion principle, which leads to important consequences.

Free electron gas in one dimension

Assume an electron of mass m is confined to a length L by infinite barriers

Schrödinger equation for electron wave function $\psi_n(x)$: $H\psi_n(x) = E_n\psi_n(x)$
 E_n - the energy of electron orbital

assume the potential lies at zero $\Rightarrow H$ includes only the kinetic energy \Rightarrow

$$H\psi_n(x) = \frac{p^2}{2m}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n(x) = E_n\psi_n(x)$$

$U(x) = 0$ ($0 \leq x \leq L$), ∞ otherwise



Note: this is a one-electron equation – neglected electron-electron interactions

General solution: $A\sin q_n x + B\cos q_n x$

boundary conditions for the wave function:

$$\Rightarrow B = 0; q_n = \pi n/L; n - \text{integer} \quad \psi_n(0) = \psi_n(L) = 0$$

$$\psi_n(x) = A \sin\left(\frac{\pi n}{L}x\right) \quad \text{Substitute, obtain the eigenvalues:}$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2$$

❖ What is Hamiltonian?

- For particles confined to this box, there is only a kinetic energy term to the Hamiltonian H

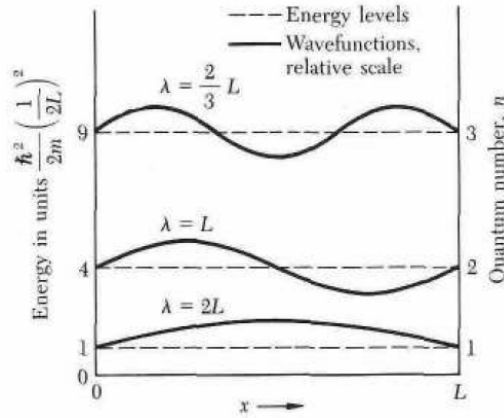
$$H = \frac{p^2}{2m} = \frac{1}{2m}(-i\hbar \frac{d}{dx})(-i\hbar \frac{d}{dx}) \quad \leftarrow \text{Quantum mechanical operator}$$

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad \xrightarrow{\text{so we have to solve}} \quad H\psi_n = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n = \varepsilon_n \psi_n$$

First three energy levels and wave-functions of a free electron of mass m confined to a line of length L :

$$\psi_n(x) = A \sin\left(\frac{\pi n}{L}x\right)$$

$$E_n = \frac{\hbar^2}{2m} \left(\frac{\pi n}{L}\right)^2$$



picture from Kittel

Fermi energy

We need to accommodate N valence electrons in these quantum states.

Pauli principle: no two electrons can have identical quantum numbers.

Electronic state in a 1D solid is characterized by quantum numbers n and m_s , where n describes the orbital $\psi_n(x)$, and m_s - the projection of the spin: $m_s = \pm 1/2$.

\Rightarrow each orbital labeled by the quantum number n can accommodate two electrons, one with spin up and one with spin down orientation.

Let n_F - the highest filled energy level. Start filling the levels from the bottom ($n = 1$) and continue until all N electrons are accommodated.

Condition $2n_F = N$ determines n_F

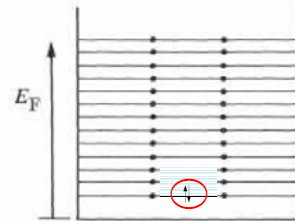
The energy of the highest occupied level is called the **Fermi energy E_F**

For the one-dimensional system of N electrons
$$E_F = \frac{\hbar^2}{2m} \left(\frac{\pi N}{2L}\right)^2$$

Finite temperature: the Fermi - Dirac distribution

The ground state of the N electron system at zero temperature: all the electronic levels are filled up to the Fermi energy.

All the levels above are empty.



What happens if the temperature is increased?

The kinetic energy of the electron gas increases with temperature

\Rightarrow some energy levels become occupied which were vacant at 0 K; some levels become vacant which were occupied at 0 K.

The distribution of electrons among the levels is described by the *distribution function*, $f(E)$ - the probability that the level E is occupied

Fermi - Dirac distribution:
$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

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μ - the *chemical potential*.

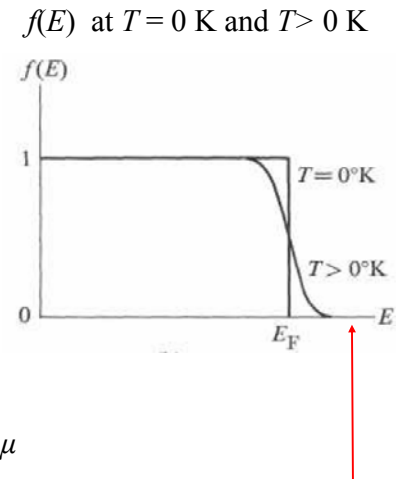
It can be determined in a way that the total number of electrons in the system is equal to N .

At $T = 0$ K $\mu = E_F$

At any T if $f(E) = 1/2$ when $E = \mu$

High energy tail of $f(E)$, when $E - \mu \gg k_B T$:
$$f(E) = e^{(\mu-E)/k_B T}$$

called *Maxwell - Boltzmann distribution*

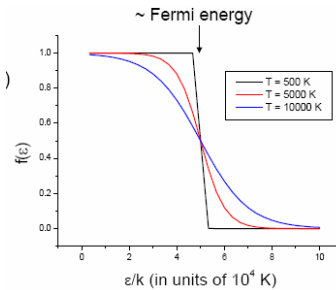


Effect of temperature on Fermi-Dirac distribution

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu)/kT] + 1}$$

Probability that an orbital of energy ε will be occupied

Chemical potential
(~ amount of energy needed to add an electron to the system)



Free electron gas in three dimensions

The Schrödinger equation in the three dimensions:

$$H\psi(\mathbf{r}) = \frac{p^2}{2m}\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

If the electrons are confined to a cube of edge L , the solution is

$$\psi(\mathbf{r}) = A \sin\left(\frac{\pi n_x}{L}x\right) \sin\left(\frac{\pi n_y}{L}y\right) \sin\left(\frac{\pi n_z}{L}z\right)$$

introduce periodic boundary conditions, as we did for lattice vibrations

– assume that our crystal is infinite and disregard the influence of the outer boundaries of the crystal on the solution

– require that our wave function is periodic in x , y , and z directions with period L , so that $\psi(x+L, y, z) = \psi(x, y, z)$

and similarly for the y and z coordinates.

The solution of the Schrödinger equation satisfying these boundary conditions has the form of the traveling plane wave:

$$\psi_{\mathbf{k}}(\mathbf{r}) = Ae^{i\mathbf{k}\cdot\mathbf{r}}$$

provided that the component of the wave vector \mathbf{k} satisfy

$$k_x = \frac{2\pi n_x}{L}; \quad k_y = \frac{2\pi n_y}{L}; \quad k_z = \frac{2\pi n_z}{L} \quad \text{where } n_x, n_y, \text{ and } n_z - \text{integers}$$

substitute this to the Schrödinger equation, obtain the energy of the orbital with the wavevector \mathbf{k} :

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

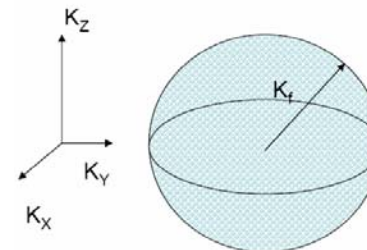
Wave functions $\psi_{\mathbf{k}}$ – the eigenfunctions of the momentum operator

$\mathbf{p} = -i\hbar\nabla$ The eigenvalue of the momentum is $\hbar\mathbf{k}$.

The velocity of the electron is defined by $\mathbf{v} = \mathbf{p}/m = \hbar\mathbf{k}/m$

Back to k-space

- Each value of \mathbf{k} occupies a volume of $(2\pi/L)^3$ in \mathbf{k} -space



How many \mathbf{k} states (orbitals) are in a sphere of radius k_f ?

Total no. of states Unit of \mathbf{k} -space

$$(N/2) = (\text{Volume of sphere}) / (2\pi/L)^3$$

$$(N/2) = (4\pi k_f^3/3) / (2\pi/L)^3$$

$$\text{So : } k_f = (3\pi^2 N/V)^{1/3}$$

(each dot is separated by $2\pi/L$, and represents a wave with wavevectors (K_x, K_y, K_z))

We can also define a Fermi temperature to be $T_f = E_F / k_B$
(Boltzmann's constant)

Meaning of the Fermi Temperature

- The Fermi temperature is not the temperature of the electron gas!
- It is a measure of where the Fermi energy is at (typically on the order of ~ 10000 K)
- So, for most metals say at room temperature, not many electrons are excited above the Fermi energy.

Fermi energy and Fermi momentum

In the ground state a system of N electrons occupies states with lowest possible energies \Rightarrow all the occupied states lie inside the sphere of radius k_F .

The energy at the surface of this sphere is the *Fermi energy* E_F .

The magnitude of the Fermi wave vector k_F and the Fermi energy are related by the equation: $E_F = \frac{\hbar^2 k_F^2}{2m}$

The Fermi energy and the Fermi momentum are determined by the number of valence electrons in the system N .

We need to count the total number of energy orbitals in a sphere of radius k_F which should be equal to N .

The volume element in the \mathbf{k} space (volume per single set of $k_x, k_y,$ and k_z) is equal to $\left(\frac{2\pi}{L}\right)^3$

Thus in the sphere of $V_F = \frac{4\pi k_F^3}{3}$ the total number of states is

$$2 \frac{4\pi k_F^3 / 3}{(2\pi/L)^3} = \frac{V}{3\pi^2} k_F^3 = N \quad \text{where does the factor 2 come from?}$$

$$\Rightarrow k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad \text{- depends only of the electron concentration}$$

Obtain then for the Fermi energy:

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

and the Fermi velocity:

$$v_F = \frac{\hbar}{m} \left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad (\sim 10^6 \text{ m/s!})$$

Density of states

Defined as the number of electronic states per unit energy range – an important characteristic of electronic properties of a solid

To find it, write the total number of orbitals of energy $< E$.

$$\text{We had } E = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N(E)}{V}\right)^{2/3} \Rightarrow N(E) = \frac{V}{3\pi^2} \left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

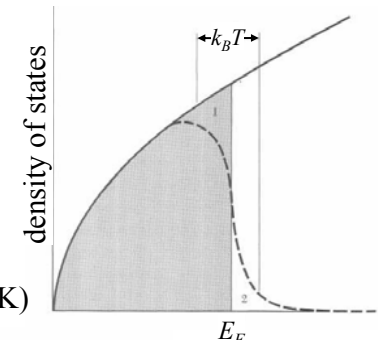
So, the *density of states* $D(E)$ is

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} = \frac{3N(E)}{2E}$$

$$\text{the integral } N = \int_0^{E_F} D(E) dE$$

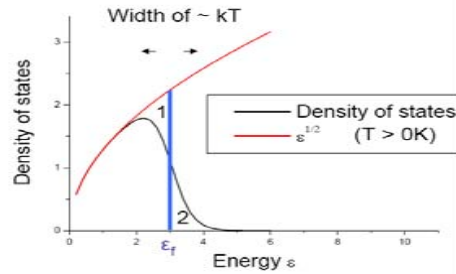
- total number of electrons in system (at 0K)

At $T \neq 0$ should take into account the Fermi distribution: $N = \int_0^{\infty} D(E) f(E) dE$



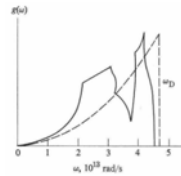
3D Density of States

- What does this look like?
- This represents how many energy values are occupied as a function of energy in the 3D k-space
- Why does this look differently than the FD distribution function?
- There can be many states occupied at the same energy, but they have different k-values.
- The larger your sphere is in k-space, the more k-values you have (and therefore, the more degenerate energy states you have)

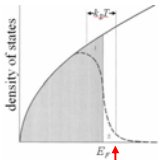


The red curve is the $\epsilon^{1/2}$ function
The black is the $\epsilon^{1/2} \times$ FD distribution.
Note that the electrons that were once in section 1 at $T = 0$ K are now in section 2 at some higher temperature

⇒ Density of states For phonons $D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq}$



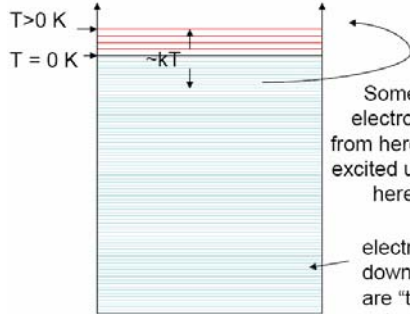
Heat capacity of the electron gas



- Classical statistical mechanics - a free particle should have $3k_B/2$; N atoms each give one valence electron and the electrons are freely mobile \Rightarrow the heat capacity of the electron gas should be $3Nk_B/2$
- Observed electronic contribution at room T is usually < 0.01 of this value
- The discrepancy is resolved by taking into account the Pauli principle and the Fermi distribution function.
- When we heat the crystal from 0 K, not every electron gains an energy $\sim k_B T$ as expected classically, but only the electrons within an energy range $k_B T$ of the Fermi level can be excited thermally.
- These electrons gain an energy, which is itself of the order of $k_B T$

“Ripples in the Fermi Sea”

Energy levels fill up until $N/2$ at $T = 0$ K, and at $T > 0$ K, we have some higher levels occupied



- One way of looking at this is like a “sea” of electrons, but only those electrons near the surface (at the highest energies) can absorb energy as heat
- So, it is the “ripples” in the Fermi sea that determine electronic properties
- The higher the T, the more ripples we have, and the more electrons we can excite to higher levels

Some electrons from here are excited up to here

electrons down here are “trapped”: only electrons within $\sim kT$ of the Fermi Surface can absorb energy

Qualitative solution to the problem of the heat capacity of free electron gas

If N is the total number of electrons, only a fraction of the order of $k_B T/E_F$ can be excited thermally at temperature T - only these lie within an energy range of the order of $k_B T$ of the top of the energy distribution

Each of these $Nk_B T/E_F$ electrons has a thermal energy of the order of $k_B T \Rightarrow$ The total electronic thermal kinetic energy U is of the order of $U \approx (Nk_B T/E_F)k_B T$.

The electronic heat capacity is then $C_{el} = dU/dT \approx Nk_B(k_B T/E_F)$ - directly proportional to T , in agreement with the experiment

At room T C_{el} is smaller than the classical value $\approx Nk_B$ by a factor $k_B T/E_F$, which is 0.01 or less.

Quantitative expression for the electronic heat capacity at low temperatures

$k_B T \ll E_F$. E.g. for room T $k_B T \approx 26$ meV ; $E_F \sim$ few eV.

The total energy of a system of N electrons at temperature T is

$$U = \int_0^{\infty} E D(E) f(E, T) dE \quad \text{where } f(E, T) \text{ is the Fermi distribution function and } D(E) \text{ is the density of states}$$

heat capacity is $C_{el} = \frac{dU}{dT} = \int_0^{\infty} E D(E) \frac{df(E, T)}{dT} dE$ - only $f(E, T)$ depends on T

little trick: rewrite $C_{el} = \int_0^{\infty} (E - E_F) D(E) \frac{df(E, T)}{dT} dE$

using the fact that $0 = E_F \frac{dN}{dT} = E_F \int_0^{\infty} D(E) \frac{df(E, T)}{dT} dE$

We are interested only in temperatures for which $k_B T \ll E_F \Rightarrow df/dT$ is large only at the energies very close to the Fermi energy \Rightarrow can ignore the variation of $D(E)$ under the integral

so
$$C_{el} = D(E_F) \int_0^{\infty} (E - E_F) \frac{df(E, T)}{dT} dE$$

Also ignore the variation of the chemical potential with temperature and assume that $\mu = E_F$ (good approximation at room T and below).

Then $\frac{df(E, T)}{dT} = \frac{E - E_F}{k_B T^2} \frac{e^{(E-E_F)/k_B T}}{[e^{(E-E_F)/k_B T} + 1]^2}$ and

$$C_{el} = D(E_F) \int_0^{\infty} \frac{(E - E_F)^2}{k_B T^2} \frac{e^{(E-E_F)/k_B T}}{[e^{(E-E_F)/k_B T} + 1]^2} dE = D(E_F) \int_{-E_F/k_B T}^{\infty} \frac{x^2 (k_B T)^3}{k_B T^2} \frac{e^x}{(e^x + 1)^2} dx$$

Taking into account that $E_F \gg k_B T$, we can put the low integration limit to $-\infty$ and obtain

$$C_{el} = D(E_F) k_B^2 T \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3} D(E_F) k_B^2 T$$

For a free electron gas use $D(E) = \frac{3N}{2E}$ for the density of states

Obtain $C_{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$ where the Fermi temperature is defined as $T_F = E_F/k_B$

Result is similar to what we obtained from qualitative arguments

The heat capacity at temperatures much below both the Debye temperature and the Fermi temperature can be represented as:

$$C = C_{el} + C_{ph} = \gamma T + \beta T^3 \quad \text{Electronic term dominates at sufficiently low } T$$

γ and β can be by fitting the experimental data.

Meaning of the Sommerfeld Constant

- So, the Sommerfeld constant is \sim density of states at the Fermi energy ($\gamma = 1/3 \pi^2 k^2 D(\epsilon_f)$)
- This makes sense – it is only these electron states that can absorb energy
- The Sommerfeld constant is also related to an “effective mass” of the conduction electrons (which should be \sim mass of an electron)
- How? Mass of conduction electron
- The Fermi Energy is $\epsilon_f = \hbar^2 k_f^2 / 2m = (\hbar^2 / 2m) (3\pi^2 N/V)^{2/3}$
- So, rearranging our terms we have:

$$\Rightarrow \gamma = \frac{1}{3} \pi^2 \frac{N k^2}{\epsilon_f} = \frac{1}{3} \pi^2 N k^2 \left(\frac{2m}{\hbar^2} \right) \left(3\pi^2 \frac{N}{V} \right)^{-2/3}$$

- And therefore, $\gamma \sim m$

Electrical conductivity

Drude model: the simplest treatment of the electrical conductivity.

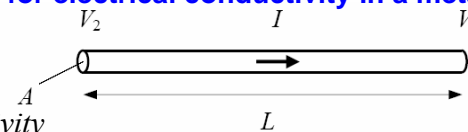
Four major assumptions:

1. Electrons are treated as classical particles within a free-electron approximation: neglect the interactions with other electrons and ions; no external electromagnetic fields - move uniformly in a straight line. In the presence of fields - move according to Newton's laws
2. Electrons move free only between collisions with scattering centers. Collisions, are instantaneous - abruptly alter the electron velocity.
A particular type of scattering centers does not matter in the Drude model. Simply assume that there is *some* scattering mechanism.
3. Electron experiences a collision with a probability per unit time $1/\tau$. The time τ - an average time between the two consecutive scattering events - known as, the *collision time (relaxation time)*. The relaxation time τ is taken to be independent of electron's position and velocity.
4. Electrons achieve thermal equilibrium with their surroundings only through collisions. These collisions are assumed to occur in a simple way: immediately after each collision an electron emerges with a velocity that is not related to its velocity before the collision, but randomly directed and with a speed corresponding to the temperature at the place where the collision occurred.

Application of the Drude model for electrical conductivity in a metal

Ohm's law: $\mathbf{j} = \sigma \mathbf{E}$

σ - conductivity; $\rho = 1/\sigma$ - resistivity



$$\mathbf{j} = I/A; V_2 - V_1 = EL, R = L/\sigma A = \rho L/A \Rightarrow I = (V_2 - V_1)/R$$

n electrons per unit volume all move with velocity $\mathbf{v} \Rightarrow \mathbf{j} \parallel \mathbf{v}$

in a time dt $n(vdt)A$ electrons will cross an area A perpendicular to the direction of flow \Rightarrow charge crossing A in dt will be $-nevAdt \Rightarrow$

$\mathbf{j} = -nev$ \mathbf{v} is the average electronic velocity or *drift velocity*

Let t - time elapsed since electron's last collision.

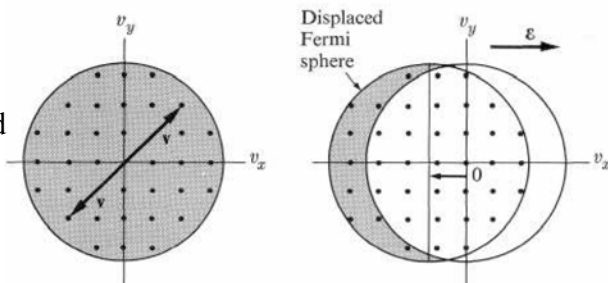
Its velocity will be $\mathbf{v}_0 - eEt/m$ (\mathbf{v}_0 is velocity immediately after the last collision - random \rightarrow no contribution to drift velocity)

average of t is the relaxation time $\tau \Rightarrow \mathbf{v} = -\frac{e\mathbf{E}\tau}{m} \Rightarrow \mathbf{j} = -\frac{ne^2\mathbf{E}\tau}{m} \Rightarrow \sigma = \frac{ne^2\tau}{m}$

In the above discussion we treated electrons on a classical basis.

How are the results modified when the quantum mechanics is taken into account?

No electric field - the Fermi sphere is centered at the origin. The total current of the system is zero.



Applied field \rightarrow each electron acquires a drift velocity \rightarrow the whole Fermi sphere is displaced

displacement is very small: $v \ll v_F$ e.g. 0.1 V/cm causes $v \sim 1\text{cm/s}$
 $v_F \sim 10^8\text{ cm/s}$

\Rightarrow the great majority of the electrons still cancel each other

some electrons (shaded area) remain uncompensated - produce current

Estimate the current density: the fraction of electrons which remain uncompensated is $\approx v/v_F \Rightarrow$ concentration of these electrons is $n(v/v_F)$

Each electron has a velocity $\approx v_F \Rightarrow \mathbf{j} = -en(v/v_F)v_F = -nev$

- Same result as before \Rightarrow the same formula for conductivity

Actual picture of conduction is quite different from the classical one:

- In the classical picture, the current is carried equally by all electrons, each moving with a very small drift velocity v .
- In the quantum-mechanical picture the current is carried only by very small fraction of electrons, all moving with the Fermi velocity.
- Relaxation time is determined only by electrons at the Fermi surface, because only these electrons can contribute to the transport properties.
- The latter approach is conceptually more accurate.

Since only electrons at the Fermi surface contribute to conductivity, we can define the mean free path of electrons as $l = \tau v_F$.

Can estimate the mean free path for metal at room temperature: $\sim 100\text{\AA}$.

On the origin of collision time

We see that between two collisions, the electron travels a distance of more than 20 times the interatomic distance - much larger than one would expect if the electron really *did* collide with the ions

This can be explained only using quantum mechanical concepts of wave character of electron.

Well known from the theory of wave propagation in periodic structures: wave passes through a periodic lattice without scattering

Atoms in the lattice is to absorb energy from the wave and radiate it back, → the wave continues without modification in either direction or intensity, but the speed of wave changes

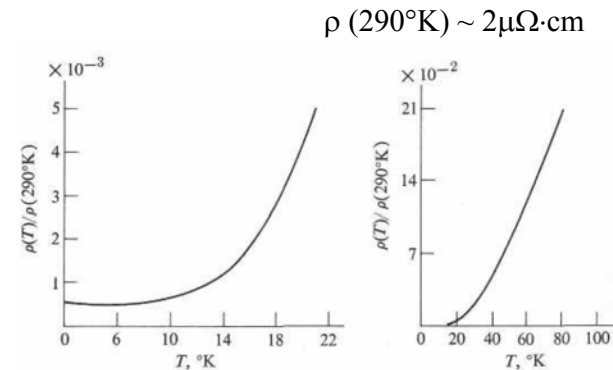
Effect of periodic lattice: free electron mass m_0 is replaced by *effective mass* m^* : Drift velocity is then
$$\mathbf{v} = -\frac{e\mathbf{E}\tau}{m^*}$$

We see that, if the ions form a perfect lattice, there is no collision at all - that is, $l = \infty \Rightarrow \tau = \infty$ - infinite conductivity.

Finiteness of σ - due to the deviation of the lattice from perfect periodicity; (1) thermal vibration of the ions (2) the presence of defects or impurities.

Temperature dependence of the electrical conductivity

Characteristic temperature dependence of resistivity of a metal: normalized resistivity $\rho(T)/\rho(290\text{K})$ versus T for Na



low-temperature region
 $T \sim 0\text{K}$: ρ has
a small *constant* value

At higher temperatures ρ increases with T , slowly at first, but afterward ρ increases linearly with T .

The linear behavior continues essentially until the melting point.

Observed in most metals, and usually room temperature falls into the linear range.

We want to explain this behavior of in terms of the Drude model.

Have
$$\rho = \frac{1}{\sigma} = -\frac{m^*}{ne^2\tau}$$

Two types of the deviations from a perfect lattice:

- Lattice vibrations (phonons) of the ions around their equilibrium position due to thermal excitation of the ions.
- All static imperfections, such as impurities or crystal defects. Of this latter group we shall take impurities as an example.

The total probability for an electron to be scattered in a unit time is the sum of the probabilities of scattering by phonons and by impurities:

$$\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_{ph}} \Rightarrow \rho = \rho_i + \rho_{ph} = \frac{m^*}{ne^2\tau_i} + \frac{m^*}{ne^2\tau_{ph}}$$

residual resistivity *lattice resistivity*

The scattering by impurities is essentially independent of temperature

The number of phonons increases with temperature
⇒ the scattering by phonons is temperature dependent

Very low T : scattering by phonons is negligible $\Rightarrow \tau_{ph} \rightarrow \infty, \rho_{ph} \rightarrow 0$
⇒ $\rho = \rho_i = \text{constant}$ - in agreement with experiment

As T increases, scattering by phonons becomes more effective
⇒ $\rho_{ph}(T)$ increases ⇒ ρ increases

When T becomes sufficiently large, scattering by phonons dominates
⇒ $\rho \approx \rho_{ph}(T)$

The statement $\rho = \rho_i + \rho_{ph}$ is known as the *Matthiessen rule*.
(not always valid)

Now let's derive approximate expressions for τ_i and τ_{ph} from the kinetic theory. Consider first the collision of electrons with impurities.

Expect that ρ_i should increase with impurity concentration n_i

Write
$$\tau_i = \frac{l_i}{v_F}$$

where l_i is the mean free path for collision with impurities.

In order to find the mean free path, introduce the *scattering cross section* of an impurity σ_i - the area an impurity atom presents to the incident electron.

Then, can argue that $l_i \sigma_i = 1/n_i$ - average volume per impurity

$$\Rightarrow l_i = \frac{1}{n_i \sigma_i}$$

Expect the scattering cross section σ_i to be of the same magnitude as the actual geometrical area of the impurity atom, i.e. $\sigma_i \sim 1\text{\AA}^2$.

Accurate calculations require quantum scattering theory

substitute l_i into formula for ρ_i :
$$\rho_i = \frac{m^* v_F}{ne^2} n_i \sigma_i$$

As expected, $\rho_i \propto n_i$

For phonons, calculating ρ_{ph} involves electron-phonon interaction.

However, we can still write
$$l_{ph} = \frac{1}{n_a \sigma_a}$$

where n_a is the concentration of the host atoms in the lattice, σ_a - the scattering cross section per atom.

σ_a has no relation to the geometrical cross section of the atom. Rather it is the area presented by the thermally fluctuating atom to the electron

Suppose that the distance of deviation from equilibrium is x

\Rightarrow the average scattering cross section is $\sigma_a \propto \langle x^2 \rangle$ - average of $\langle x^2 \rangle$

Atom is a harmonic oscillator $\Rightarrow \langle x^2 \rangle \propto$ the average of its potential energy = half the total energy:

$$\sigma_a \propto \langle x^2 \rangle \propto \frac{2k_B T}{C} \quad \text{where } C \text{ is interatomic force constant}$$

\Rightarrow see that at high T the resistivity is linear in T :
$$\rho_{ph} = \frac{m^* v_F n_a}{ne^2} \frac{2k_B}{C} T$$

Electronic thermal conductivity

Heat current density, j_Q , i.e. the amount of thermal energy crossing a unit area per unit time is proportional to the temperature gradient:

$$j_Q = -K \frac{dT}{dx} \quad \text{where } K \text{ is the thermal conductivity}$$

Already know that in insulators, heat is carried entirely by phonons, but in metals heat may be transported by both electrons and phonons.

The thermal conductivity K is therefore
$$K = K_e + K_{ph}$$

In most metals, $K_e \gg K_{ph}$, because of high concentration of electrons. Typically $K_e \sim 10^2 K_{ph}$.

Heat is transported by electrons having the Fermi energy, because those well below this energy cancel each other's contributions

Evaluate the thermal conductivity K quantitatively, use
$$K = \frac{1}{3} C_{el} v_F l$$
 here C_{el} - electronic specific heat per unit volume, v_F - Fermi velocity; l is the mean free path of electrons at the Fermi energy.

Use expression for the heat capacity derived earlier:
$$C_{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

Then
$$K = \frac{1}{3} \left(\frac{\pi^2}{2} n \frac{k_B^2 T}{E_F} \right) v_F l \quad \text{Note that } E_F = \frac{1}{2} m v_F^2 \text{ and } l/v_F = \tau$$

obtain
$$K = \frac{\pi^2 n k_B^2 \tau T}{3m}$$
 - expression for thermal conductivity in terms of the electronic properties of the metal

Recall that electrical conductivity $\sigma = -\frac{ne^2 \tau}{m}$ find that

$$\frac{K}{\sigma} = \frac{1}{3} \left(\frac{\pi k_B}{e} \right)^2 T = LT \quad \text{- Wiedemann-Franz law}$$

$L = 2.45 \cdot 10^{-8} \text{ W}\Omega/\text{K}^2$ - Lorentz number - independent of the particular metal (depends only on k_B and e)

Summary (continued)

- ❖ Free electron model – simplest way to describe electronic properties of metals: the valence electrons of free atoms become conduction electrons in crystal and move freely throughout the crystal.

1D case.

$$\psi_n(x) = A \sin\left(\frac{\pi n}{L}x\right) \quad E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2$$

Fermi energy for the 1D system of N electrons:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{\pi N}{2L}\right)^2$$

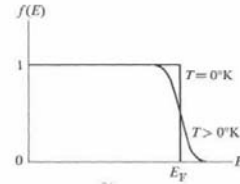
Finite temperature:

the Fermi - Dirac distribution:

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

High energy tail of $f(E)$, when $E = \mu \gg k_B T$

$$f(E) = e^{-(\mu-E)/k_B T} \quad \text{Maxwell - Boltzmann distribution}$$



Summary

- ❖ Fermi energy - energy of the highest occupied electronic level at $T = 0$ K;
3D case:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \quad k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad v_F = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

- ❖ Density of states of 3D free electron gas:

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} = \frac{3N}{2E}$$

- ❖ Heat capacity of free electron gas at low temperatures $k_B T \ll E_F$:

$$C_{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

- ❖ Electrical conductivity:

$$\sigma = -\frac{ne^2\tau}{m^*}$$

$$\rho = \rho_i + \rho_{ph}(T)$$

- ❖ Thermal conductivity:
Wiedemann-Franz law

$$K = L\sigma T \quad L = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2$$