

PHYS 342/555

Condensed Matter in a Nutshell

Instructor: Dr. Pengcheng Dai
Professor of Physics
The University of Tennessee
(Room 407A, Nielsen, 974-1509)
(Office hours: TR 1:10PM-2:00 PM)
Lecture 2, room 314 Nielsen
Chapter 5: Free electron metals

Lecture in pdf format will be available at:

<http://www.phys.utk.edu>

Under quantum theory and the Pauli exclusion principle, we consider N noninteracting electrons confined to a volume $V(L^3)$. If the wave function of single electron is $\psi(\vec{r})$, then

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = \varepsilon \psi(\vec{r}).$$

Applying boundary condition

$$\psi(x, y, z + L) = \psi(x, y, z); \psi(x, y + L, z) = \psi(x, y, z);$$

$$\psi(x + L, y, z + L) = \psi(x, y, z). \text{ The solutions are}$$

$$\psi_K(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}, \varepsilon(k) = \frac{\hbar^2 k^2}{2m}. \text{ Note the probability of}$$

$$\text{finding the electron somewhere in the volume is } 1 = \int d\vec{r} |\psi(\vec{r})|^2.$$

Note that $\psi_K(\vec{r})$ is an eigenstate of the momentum operator,

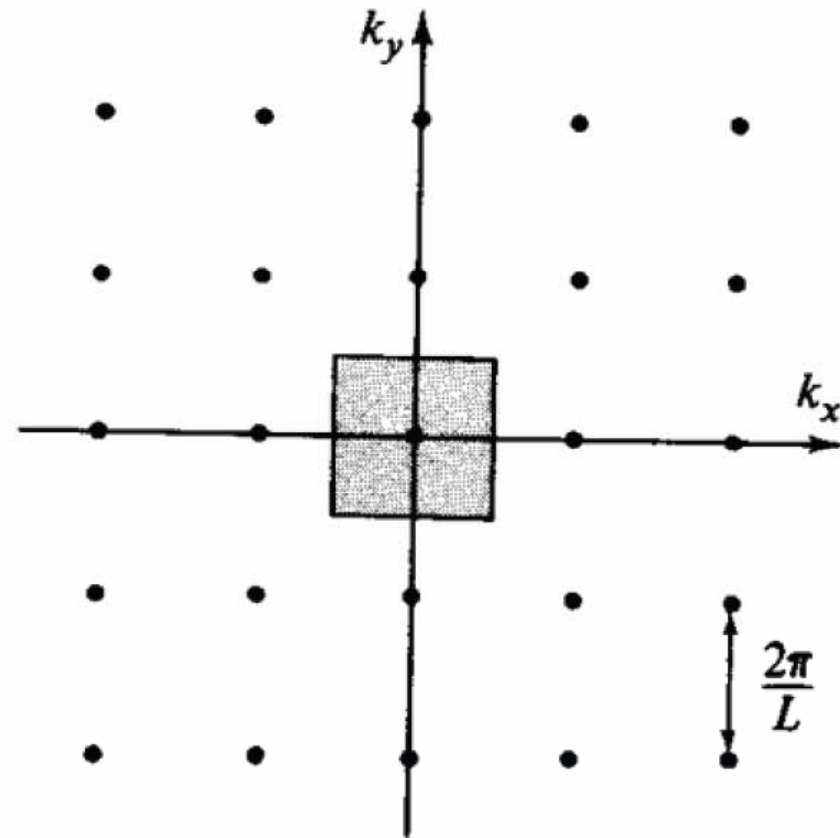
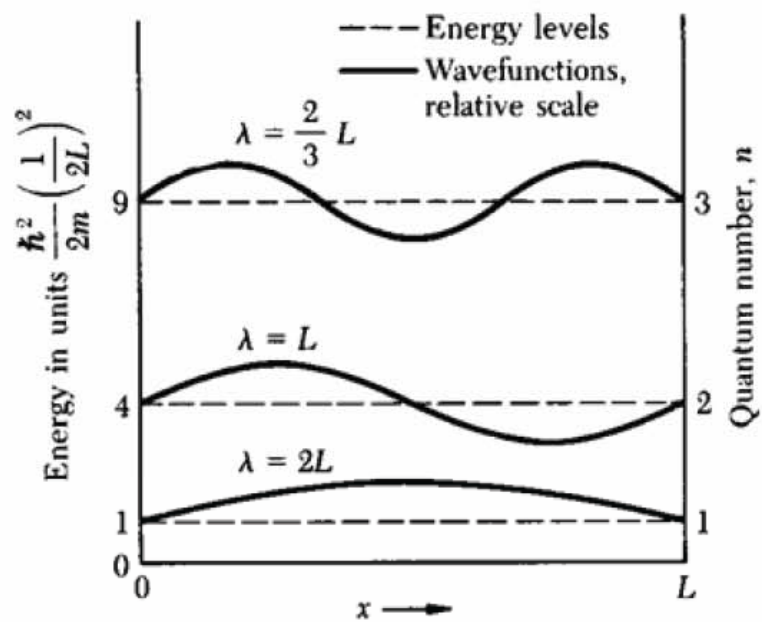
$$\vec{p} = \frac{\hbar}{i} \frac{\partial}{\partial \vec{r}} = \frac{\hbar}{i} \nabla, \frac{\hbar}{i} \frac{\partial}{\partial \vec{r}} e^{i\vec{k} \cdot \vec{r}} = \hbar \vec{k} e^{i\vec{k} \cdot \vec{r}}$$

an electron in the level $\psi_K(\vec{r})$ has a momentum $\vec{p} = \hbar \vec{k}$ and a velocity $\vec{v} = \vec{p} / m = \hbar \vec{k} / m$, where $\lambda = 2\pi / k$.

Periodic boundary condition requires

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1 \text{ or } k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{2\pi n_z}{L}$$

Thus in a 3-D k -space, the allowed wavevectors are those along the three axes given integer multiples of $\frac{2\pi}{L}$.



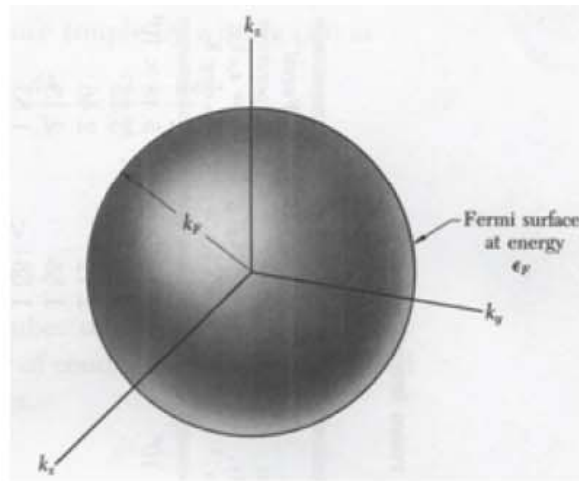
To calculate the allowed states in a region of k -space volume Ω ,

$$\frac{\Omega}{(2\pi/L)^3} = \frac{\Omega V}{(2\pi)^3}$$
 or the number of allowed k -values per unit

volume of k -space (known as the k -space density of levels) is

$$\frac{V}{(2\pi)^3}.$$
 Because the electrons are noninteracting we can build up

the N -electron ground state by placing electrons into the allowed one-electron levels. Pauli exclusion principle allows each wavevector to have 2 electronic levels with spins up and down.



Since the energy of a one-electron level is directly proportional to k^2 , when N is enormous the occupied region will be indistinguishable from a sphere. The radius of this sphere is called k_F (F for Fermi), and its volume Ω is $4\pi k_F^3 / 3$. The # of allowed \vec{k} within the sphere is:

$$\left(\frac{4\pi k_F^3}{3} \right) \left(\frac{V}{8\pi^3} \right) = \frac{k_F^3}{6\pi^2} V. \text{ Since each allowed } k\text{-value leads to two}$$

one-electron levels, we must have $N = 2 \frac{k_F^3}{6\pi^2} V = \frac{k_F^3}{3\pi^2} V$.

If electron density is $n = N/V$, then we have $n = k_F^3 / 3\pi^2$.

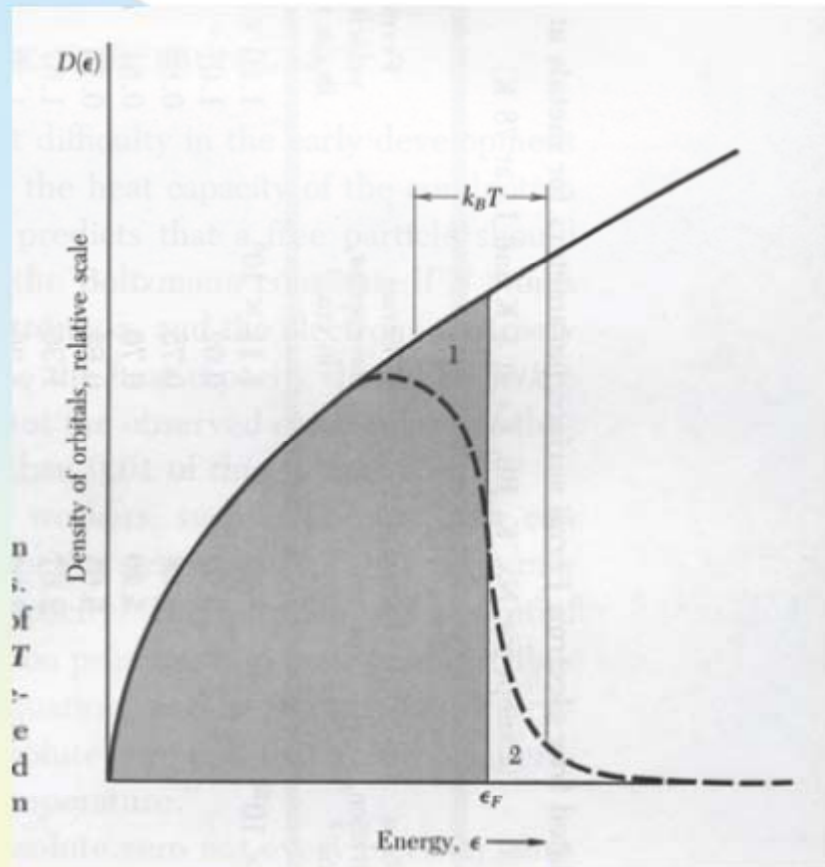
The sphere of radius k_F containing the occupied one electron levels is called the Fermi sphere.

The Surface of the Fermi sphere, which separate the occupied from the unoccupied levels is called the Fermi surface.

The momentum $p_F = \hbar k_F = \hbar \left(\frac{3\pi^2 N}{V} \right)^{1/3}$ of the occupied one-electron levels of highest energy is the Fermi momentum.

$\varepsilon_F = \hbar^2 k_F^2 / 2m = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$ is the Fermi energy;

$v_F = p_F / m = \left(\frac{\hbar}{m} \right) \left(\frac{3\pi^2 N}{V} \right)^{1/3}$ is the Fermi velocity.



To find an expression for the number of allowed electron states per unit energy, $D(\epsilon)$, we use

$$N = \frac{V}{3\pi^2} \left(\frac{2m\epsilon}{\hbar^2} \right)^{3/2}, \text{ and}$$

$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}.$$

$$\ln N = \frac{3}{2} \ln \epsilon + \text{const};$$

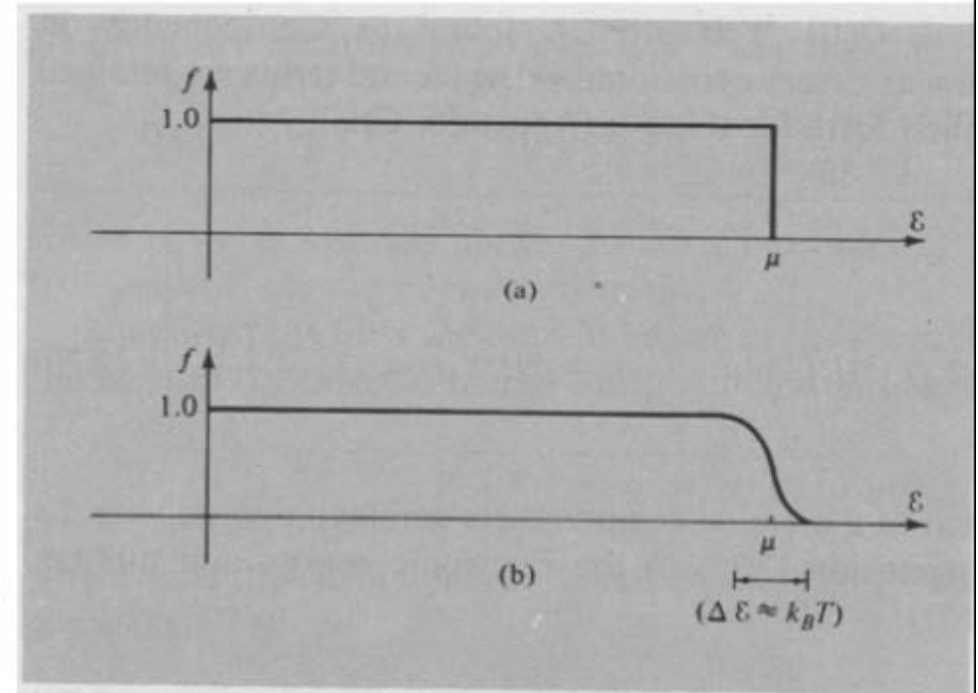
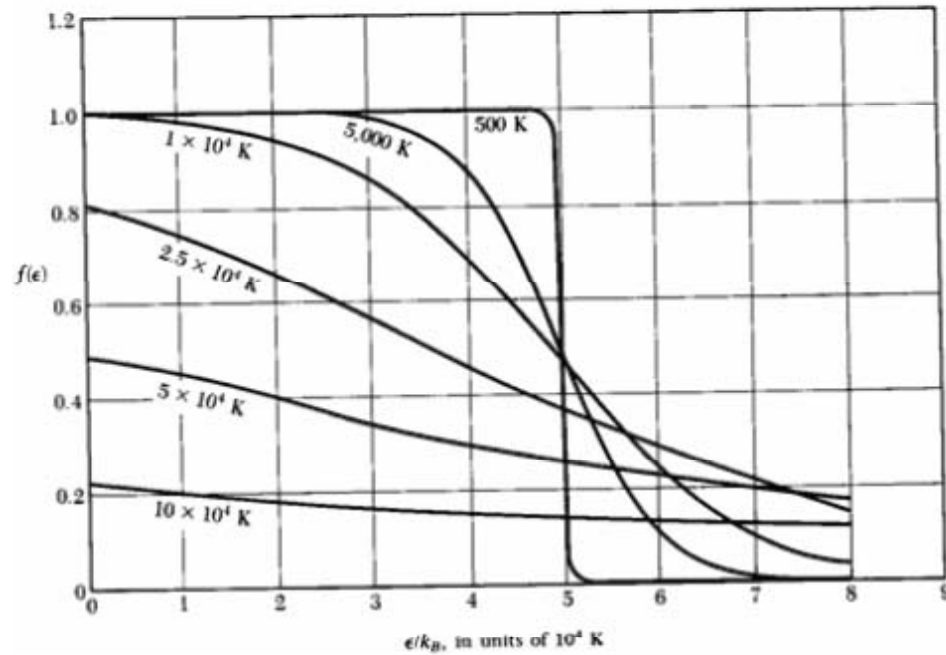
$$\frac{dN}{N} = \frac{3}{2} \frac{d\epsilon}{\epsilon}, \text{ where } D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{3N}{2\epsilon}.$$

Table 1 Calculated free electron Fermi surface parameters for metals at room temperature
(Except for Na, K, Rb, Cs at 5 K and Li at 78 K)

Valency	Metal	Electron concentration, in cm^{-3}	Radius ^a parameter r_s	Fermi wavevector, in cm^{-1}	Fermi velocity, in cm s^{-1}	Fermi energy, in eV	Fermi temperature $T_F = \epsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^8	1.29×10^8	4.72	5.48×10^4
	Na	2.65	3.93	0.92	1.07	3.23	3.75
	K	1.40	4.86	0.75	0.86	2.12	2.46
	Rb	1.15	5.20	0.70	0.81	1.85	2.15
	Cs	0.91	5.63	0.64	0.75	1.58	1.83
	Cu	8.45	2.67	1.36	1.57	7.00	8.12
	Ag	5.85	3.02	1.20	1.39	5.48	6.36
	Au	5.90	3.01	1.20	1.39	5.51	6.39
2	Be	24.2	1.88	1.93	2.23	14.14	16.41
	Mg	8.60	2.65	1.37	1.58	7.13	8.27
	Ca	4.60	3.27	1.11	1.28	4.68	5.43
	Sr	3.56	3.56	1.02	1.18	3.95	4.58
	Ba	3.20	3.69	0.98	1.13	3.65	4.24
	Zn	13.10	2.31	1.57	1.82	9.39	10.90
	Cd	9.28	2.59	1.40	1.62	7.46	8.66
3	Al	18.06	2.07	1.75	2.02	11.63	13.49
	Ga	15.30	2.19	1.65	1.91	10.35	12.01
	In	11.49	2.41	1.50	1.74	8.60	9.98
4	Pb	13.20	2.30	1.57	1.82	9.37	10.87
	Sn(w)	14.48	2.23	1.62	1.88	10.03	11.64

^aThe dimensionless radius parameter is defined as $r_s = r_0/a_H$, where a_H is the first Bohr radius and r_0 is the radius of a sphere that contains one electron.

Effect of temperature on the Fermi-Dirac distribution



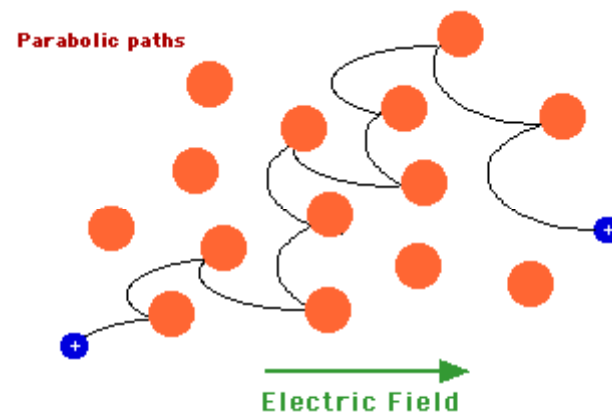
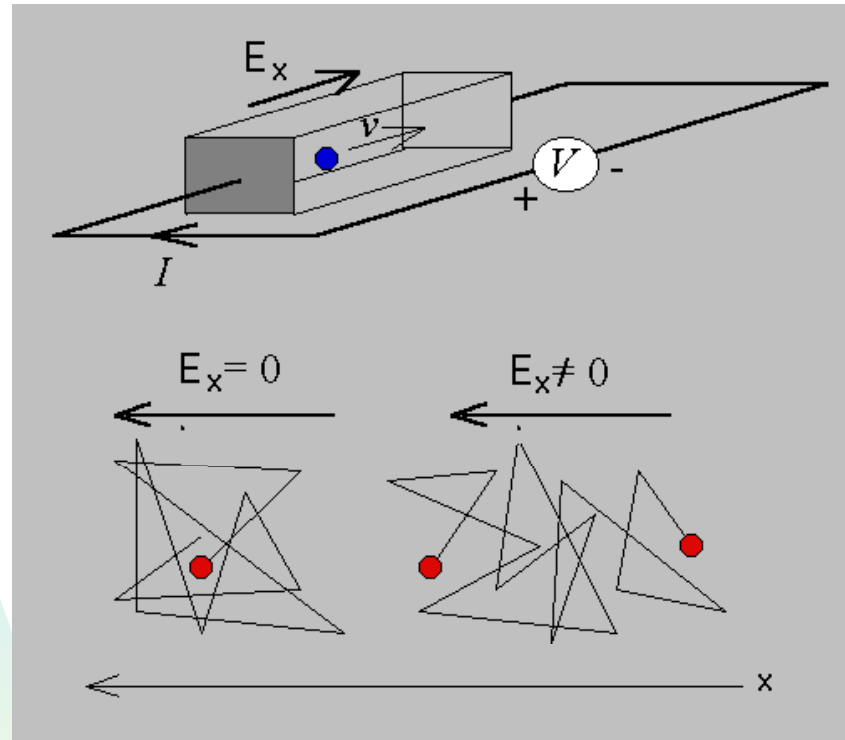
$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}$$

μ is chemical potential,
 $f(\epsilon) = 1/2$ when $\epsilon = \mu$.

3.1 Drude Model

The most important characteristic of a metal is its high electrical conductivity. Around 1900, shortly after J. J. Thompson's discovery of the electron, people became interested in understanding more about the mechanism of metallic conduction. The first work by E. Riecke in 1898 was quickly superseded by that of Drude in 1900. Drude¹ proposed an exceedingly simple model that explained a well-known empirical law, the Wiedermann–Franz law (1853). This law stated that at a given temperature the ratio of the thermal conductivity to the electrical conductivity was the same for all metals. The assumptions of the **Drude model** are:

- (i) a metal contains free electrons which form an electron gas.
- (ii) the electrons have some average thermal energy $\langle \frac{1}{2}mv_T^2 \rangle$, but they pursue random motions through the metal so that $\langle \mathbf{v}_T \rangle = 0$ even though $\langle v_T^2 \rangle \neq 0$. The random motions result from collisions with the ions.
- (iii) because the ions have a very large mass, they are essentially immovable.



Microscopic Model of Waves in Metals

- What will we need to include in a microscopic model of a metal?
- Simplest model of electrons in a metal is the Drude or free electron model
 - ▶ Metal behaves like an empty box containing a free electron gas
 - ▶ The free electron gas consists of the outer conduction electrons - a monovalent metal such as copper contributes one electron per atom

Drude Model of Metals

- What will we need to include in a microscopic model of a metal?
- Simplest model of electrons in a metal is the Drude or free electron model
 - ▶ Between collisions, other interactions are neglected
 - ▶ The mean free time between collisions is τ and is independent of the electron's position or velocity

Drude Model of Metals

- What effect does an applied electric field have on the motions of the electrons?
 - ▶ There are also interactions with the lattice ions (scattering) which leads to resistance
 - ▶ This drag force means that electrons do not accelerate indefinitely in the field an electric field \underline{E}

$$m \frac{d\underline{v}}{dt} = e\underline{E} - \gamma m \underline{v} = \underline{F}$$

Drude Model of Metals

- What effect does an applied electric field have on the motions of the electrons?
 - ▶ As a consequence of these opposing forces the electrons reach a final drift velocity v_f
 - ▶ In which case the forces add to zero

$$m \frac{d\mathbf{v}}{dt} = e\mathbf{E} - m\mathbf{v}_f = 0$$

Drude Model of Metals

- Rearrangement gives the coefficient gamma a
- μ is known as the mobility of the electron

$$\gamma = \frac{eE}{mv_f} = \frac{e}{m\mu}$$

Drude Model of Metals

- The velocity can be determined from the equation of motion

$$m \frac{d \underline{v}}{dt} + \frac{e \underline{E}}{\underline{v}_f} \underline{v} = e \underline{E}$$

- with a solution

$$\underline{v} = \underline{v}_f \left(1 - e^{-\frac{e \underline{E}}{m \underline{v}_f} t} \right)$$

Drude Model of Metals

- We define a relaxation time τ

$$\underline{v} = \underline{v}_f \left(1 - e^{-\frac{e \underline{E}}{m \underline{v}_f} t} \right)$$

$$\underline{\tau} = \frac{m \underline{v}_f}{e E} = \frac{1}{\gamma}$$

Drude Model of Metals

- Current density \underline{J} (N_f = number of free electrons)

$$\underline{J} = N_f e \underline{v}_f$$

$$\underline{J} = \frac{N_f e^2 \tau}{m} \underline{E}$$

3.5 Criticisms of Drude Model

1. If $\langle \frac{1}{2}mv_{\text{T}}^2 \rangle = \frac{3}{2}k_{\text{B}}T$, then the electronic contribution to C_{v} had to be $C_{\text{v}} = \frac{3}{2}Nk_{\text{B}} = \frac{3}{2}R$. This is half as big as the lattice contribution and was simply not observed.
2. Experimentally σ varies as T^{-1} . This implies that $n_0\tau \propto T^{-1}$ since e^2 and m are constants. In Drude's picture, the mean free path $l \simeq v_{\text{T}}\tau$ was thought to be of the order of the atomic spacing and therefore independent of T . Since $v_{\text{T}} \propto T^{1/2}$ this would imply that $\tau \propto T^{-1/2}$ and, to satisfy $n_0\tau \propto T^{-1}$, that $n_0 \propto T^{-1/2}$. This did not make any sense.

3.6 Lorentz Theory

Since Drude's simple model gave some results that agree fairly well with experiment, Lorentz³ decided to use the full apparatus of kinetic theory to investigate the model more carefully. He did not succeed in improving on Drude's model, but he did make use of the Boltzmann distribution function and Boltzmann equation which we would like to describe.

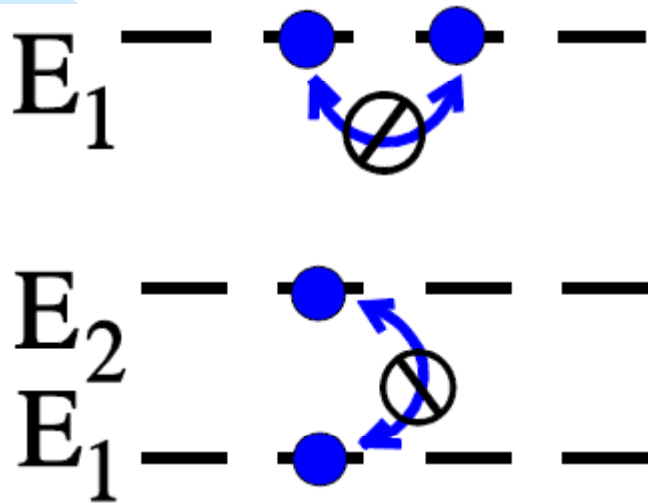


Figure 8.5.3: Switching electrons does not produce a new microstate.

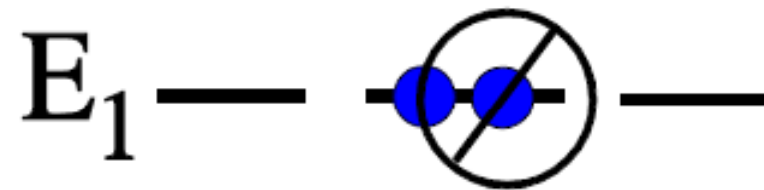


Figure 8.5.4: Two Fermions cannot occupy the same state at the same time.

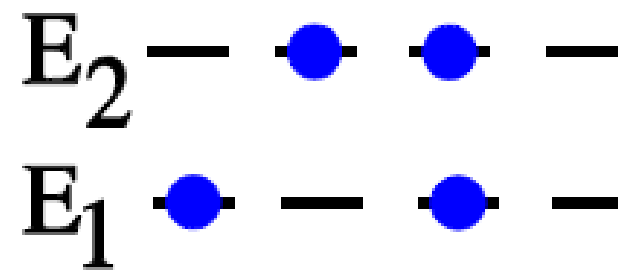


Figure 8.5.5: The simple system.

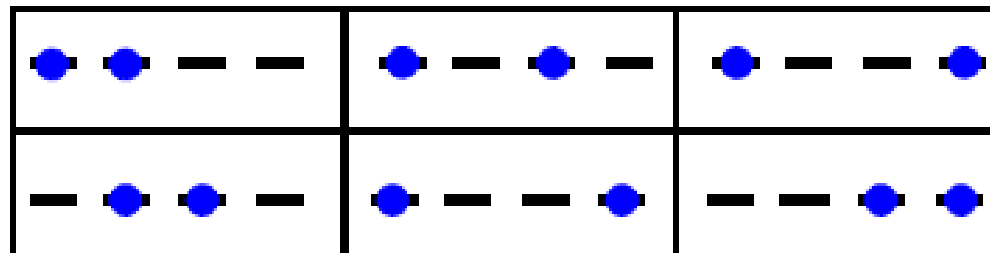


Figure 8.5.6: Six distinct arrangements for the first level.

Heat capacity of the electron gas

In a gas of free and independent electrons, the one electron levels are specified by wavevector \vec{k} and spin quantum # \vec{s} with

$$\varepsilon(\vec{k}) = \hbar^2 k^2 / 2m$$

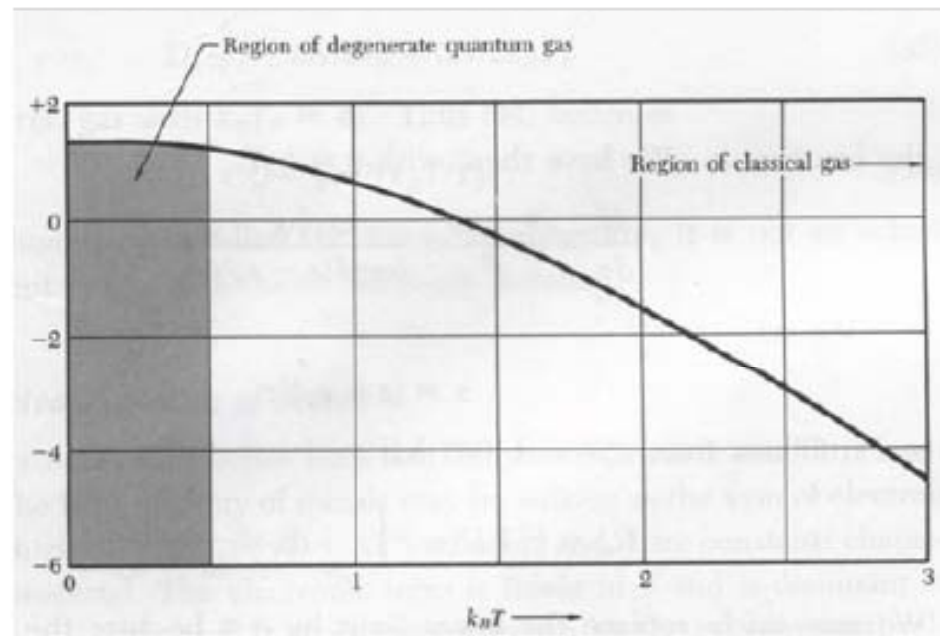
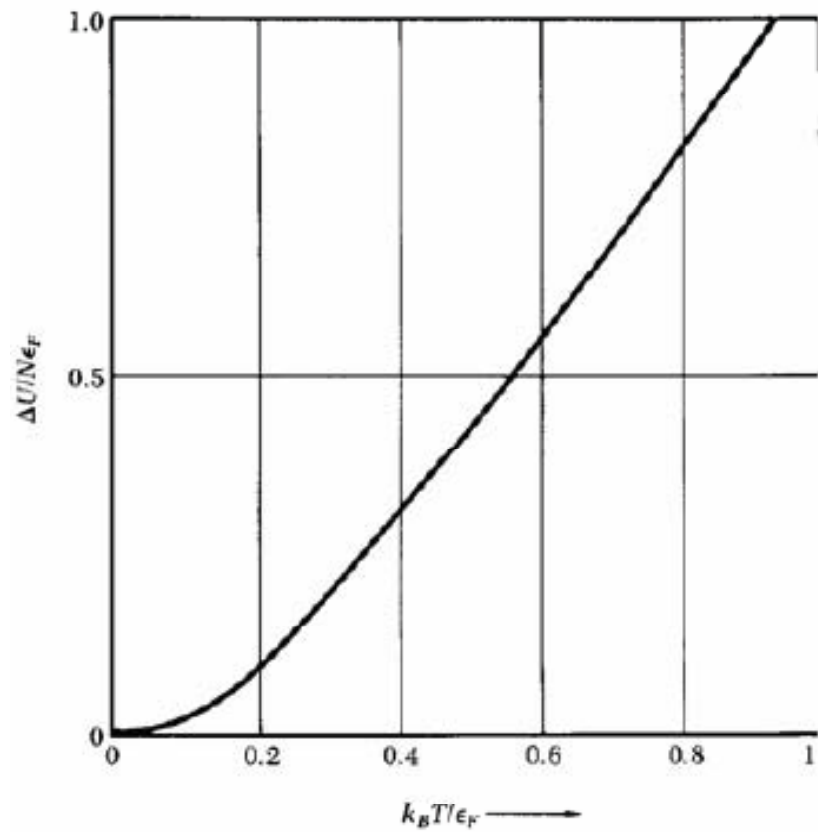
As $T \rightarrow 0$, we have $\lim_{T \rightarrow 0} f = 1$, for $\varepsilon(\vec{k}) < \mu$ and zero for $\varepsilon(\vec{k}) > \mu$.

$$c_V = \left(\frac{\partial u}{\partial T} \right)_V, u = \frac{U}{V}.$$

$U = 2 \sum_{\vec{k}} \varepsilon(\vec{k}) f(\varepsilon(\vec{k}))$. As $V \rightarrow \infty$, we have

$$u = \lim_{V \rightarrow \infty} \frac{1}{V} 2 \sum_{\vec{k}} \varepsilon(\vec{k}) f(\varepsilon(\vec{k})) = 2 \int \frac{d\vec{k}}{8\pi^3} \varepsilon(\vec{k}) f(\varepsilon(\vec{k}))$$

If the electron density $n = N/V$, $n = \int \frac{d\vec{k}}{4\pi^3} f(\varepsilon(\vec{k}))$.



At low temperature $k_B T \ll \varepsilon_F$, the increase in energy when heated

to a temperature T is $\Delta U = \int_0^\infty d\varepsilon D(\varepsilon) \varepsilon f(\varepsilon) - \int_0^\infty d\varepsilon D(\varepsilon) \varepsilon$.

$$\left(\int_0^{\varepsilon_F} + \int_{\varepsilon_F}^\infty \right) d\varepsilon D(\varepsilon) \varepsilon_F f(\varepsilon) = \int_0^{\varepsilon_F} d\varepsilon D(\varepsilon) \varepsilon_F.$$

$$\Delta U = \int_{\varepsilon_F}^\infty d\varepsilon D(\varepsilon) (\varepsilon - \varepsilon_F) f(\varepsilon) + \int_0^{\varepsilon_F} d\varepsilon D(\varepsilon) (\varepsilon_F - \varepsilon) [1 - f(\varepsilon)].$$

$$C_{el} = \frac{dU}{dT} = \int_0^\infty d\varepsilon D(\varepsilon) (\varepsilon - \varepsilon_F) \frac{df}{dT} \approx D(\varepsilon_F) \int_0^\infty d\varepsilon (\varepsilon - \varepsilon_F) \frac{df}{dT}$$

$$\frac{df}{dT} = \frac{\varepsilon - \varepsilon_F}{\tau^2} \cdot \frac{\exp[(\varepsilon - \varepsilon_F)/\tau]}{\{\exp[(\varepsilon - \varepsilon_F)/\tau] + 1\}^2}$$

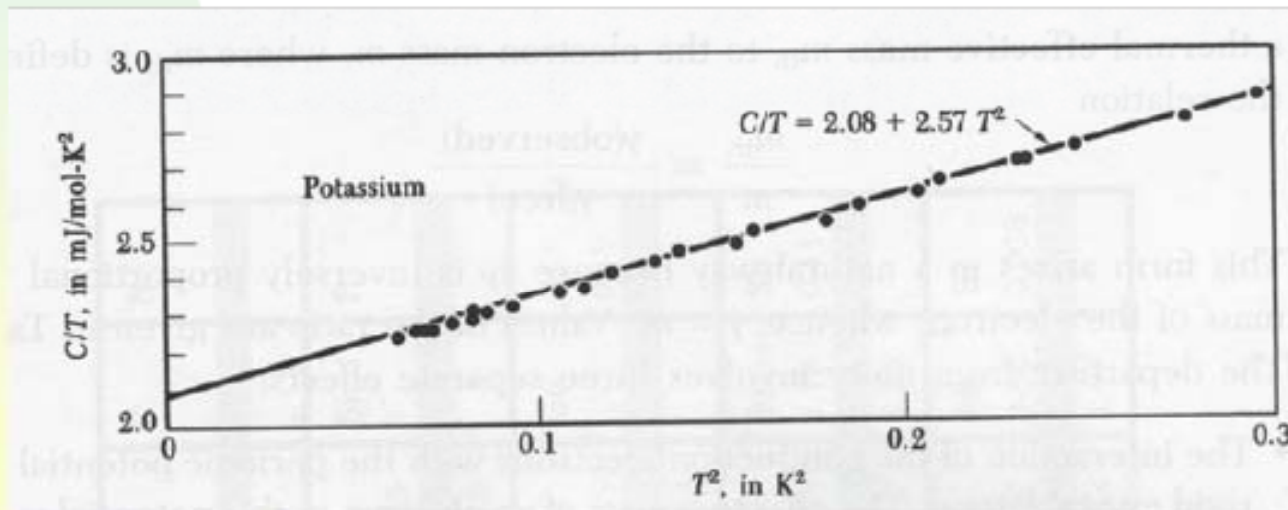
Define $x \equiv (\varepsilon - \varepsilon_F)/\tau$, we have

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

Experimental heat capacity of metals

At sufficient low temperatures, $C_V = \gamma T + AT^3$. Where γ is the Sommerfeld parameter. The ratio of the observed to the free electron values of the electronic heat capacity is related to thermal effective mass as:

$$\frac{m_{th}}{m} \equiv \frac{\gamma(\text{observed})}{\gamma(\text{free})}$$



5.2.5 Fermi Surfaces

The energy bands of free electron metals are $\mathcal{E}(k) = \hbar^2 k^2 / 2m_e$ except near to symmetry points in the BZ. At those points the energy bands developed band gaps. This behavior is found in one, two, and three dimensions. The energy bands are parabolic except near to the edges and other symmetry points.

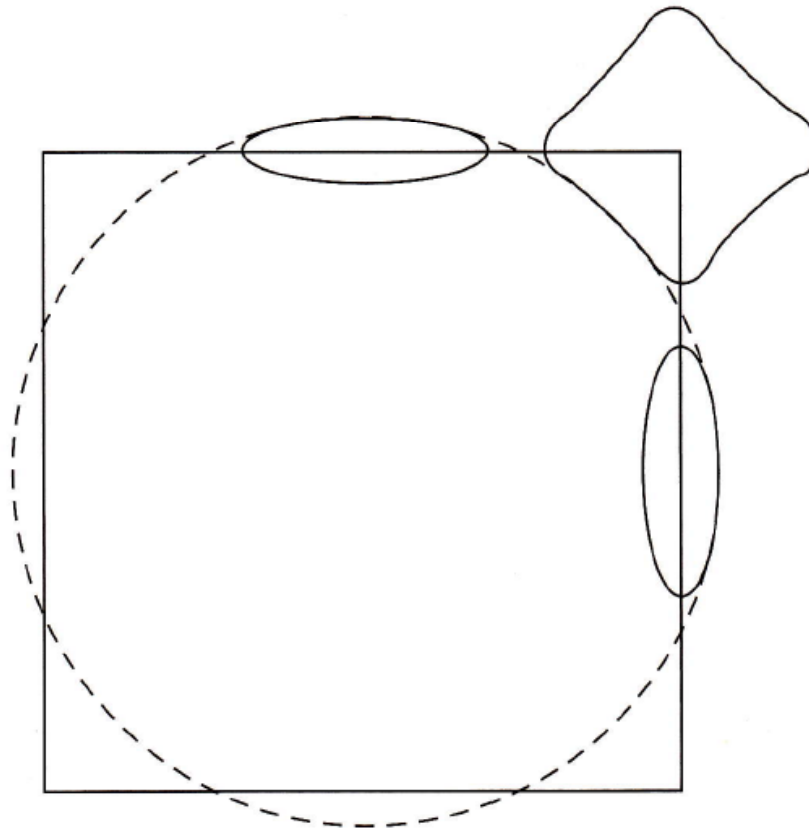
The Fermi surface is the line of points at zero temperature that divides the occupied from the empty electron states.

- In one dimension, the free electron Fermi surface is two points in the BZ, at $\pm k_F$, where $n_e = 2k_F/\pi$.
- In two dimensions, the free electron Fermi surface is a circle of radius k_F , where $n_e = k_F^2/2\pi$.
- In three dimensions, the free electron Fermi surface is a sphere of radius k_F , where $n_e = k_F^3/3\pi^2$.

Figure 5.1 shows an example in two dimensions. It shows the BZ of a square lattice. The circle is Fermi surface with two electrons per unit cell ($n_e = 2/a^2$). Write the density of electrons on the sq lattice as $n_0 = n/a^2$, where n_0 is the density, and n is the number of valence electrons per atom. The Fermi wave vector is

$$k_F = \sqrt{2\pi n_0} = \frac{\sqrt{2\pi n}}{a} \quad (5.55)$$

Some values are shown in table 5.2. The edge of the BZ is at $G_0/2 = \pi/a$. If $n = 1$, the circle is entirely within the first BZ since $2.507 < \pi$, and the material is a conductor.



Electrical conductivity and Ohm's law

Considering Newton's second law, we have

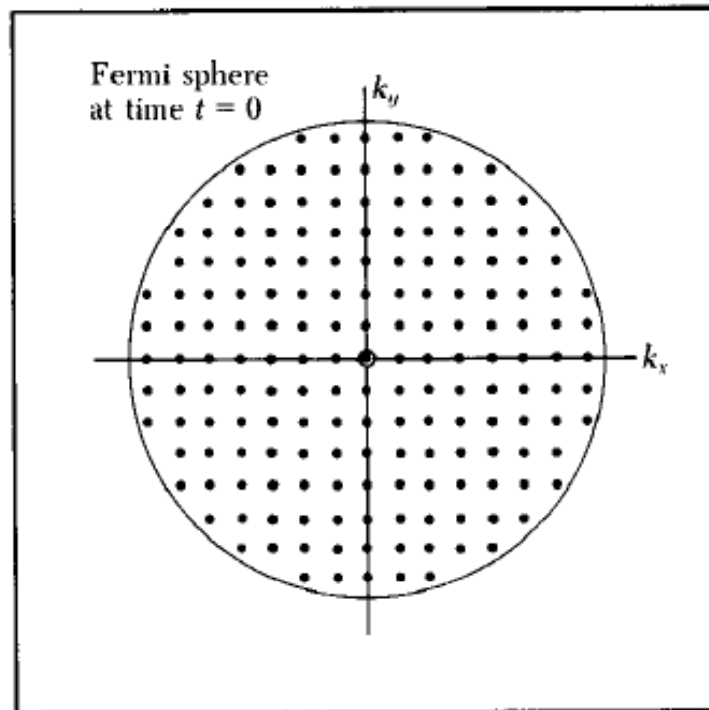
$$\vec{F} = m \frac{d\vec{v}}{dt} = \hbar \frac{d\vec{k}}{dt} = -e(\vec{E} + \frac{1}{c} \vec{v} \times \vec{B})$$

The displacement of the Fermi sphere, $\delta\vec{k} = -e\vec{E}t / \hbar$.

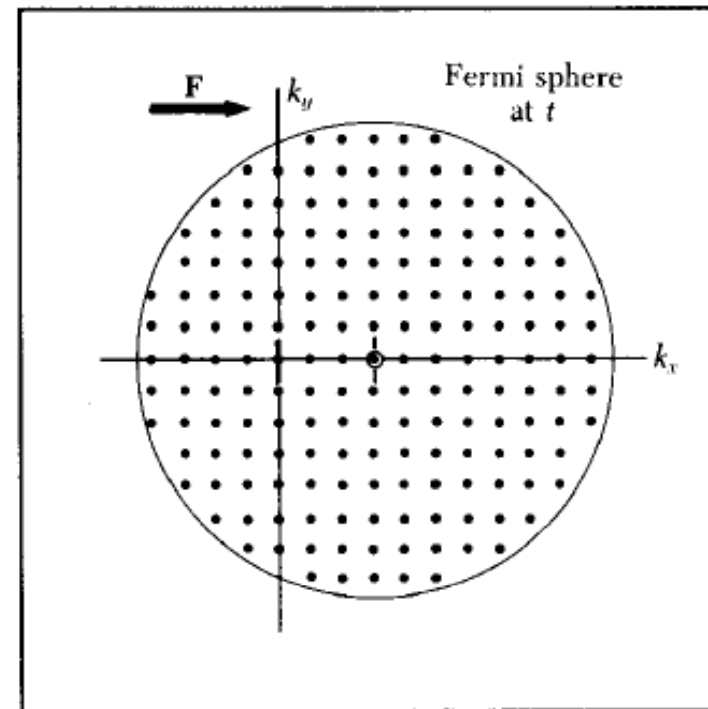
If collision time is τ , the incremental velocity is $\vec{v} = -e\vec{E}\tau / m$.

In a constant electric field \vec{E} and n electrons per volume, the electric current density is $\vec{j} = nq\vec{v} = ne^2\vec{E}\tau / m = \sigma\vec{E}$.

The electrical conductivity $\sigma = ne^2\tau / m$.

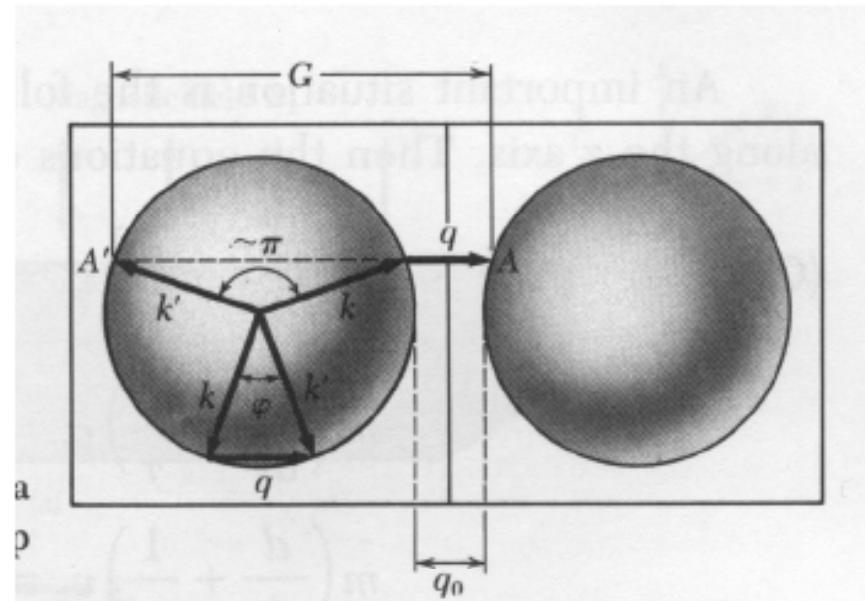
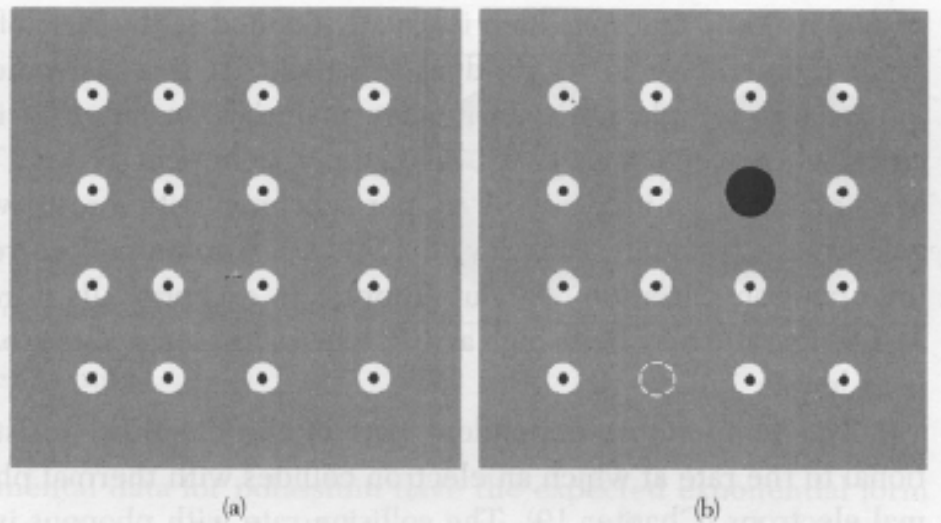


(a)



(b)

Experimental electrical resistivity of metals and Umklapp scattering



Motion in magnetic fields

The Lorentz force on an electron is

$$\vec{F} = m \frac{d\vec{v}}{dt} = \hbar \frac{d\vec{k}}{dt} = -e(\vec{E} + \frac{1}{c} \vec{v} \times \vec{B})$$

For a static magnetic field \vec{B} lie along the \vec{z} axis, we have

$$m(\frac{d}{dt} + \frac{1}{\tau})v_x = -e(E_x + \frac{B}{c}v_y)$$

$$m(\frac{d}{dt} + \frac{1}{\tau})v_y = -e(E_y - \frac{B}{c}v_x)$$

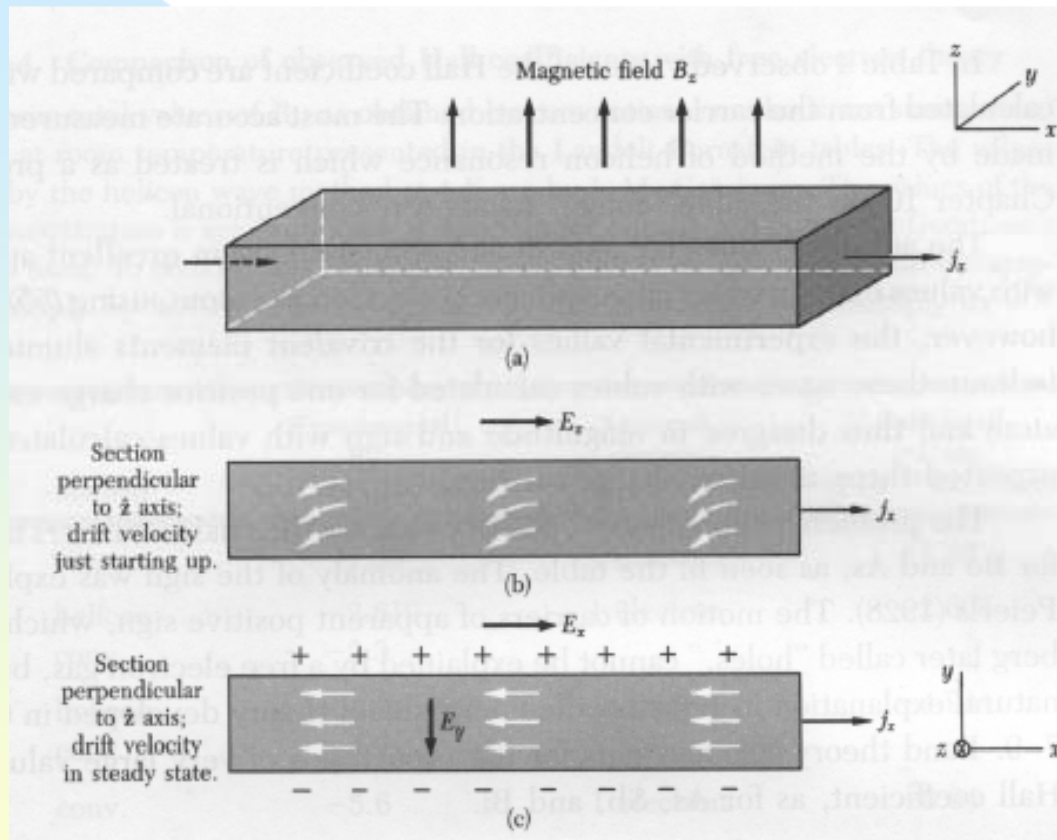
$$m(\frac{d}{dt} + \frac{1}{\tau})v_z = -eE_z$$

In the steady state in a static electric field, the drift velocity is

$$v_x = -\frac{e\tau}{m}E_x - \omega_c\tau v_y; v_y = -\frac{e\tau}{m}E_y + \omega_c\tau v_x; v_z = -\frac{e\tau}{m}E_z$$

$\omega_c \equiv eB/mc$ is the cyclotron frequency.

Hall effect



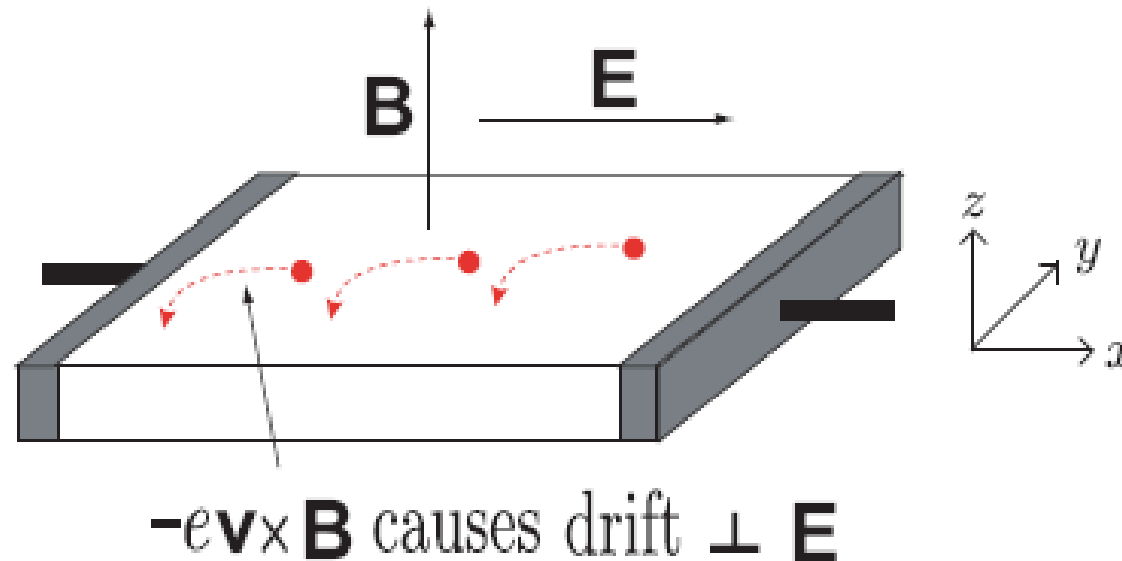
$$E_y = -\omega_c \tau E_x = -\frac{eB\tau}{mc} E_x$$

$$R_H = \frac{E_y}{j_x B} \text{ is called Hall coefficient}$$

3.16 Hall Effect and Magnetoresistance

If we apply an electric field \mathbf{E} in the x -direction, the Lorentz force, $-\frac{e}{c}\mathbf{v} \times \mathbf{B}$ causes a drift velocity in the y -direction. If $\omega = 0$ charge will accumulate on the surfaces normal to the y -direction until a field E_y builds up that exactly cancels the Lorentz force. (See Figure 3.5.) The condition $j_y = 0$ gives

$$j_y = \sigma_{xx}E_y - \sigma_{xy}E_x = 0,$$



Thermal conductivity

The thermal conductivity coefficient K of a solid is defined as,

$j_U = -K \frac{dT}{dx}$, where j_U is the flux of thermal energy, and

x is distance. From the kinetic theory of gases we find

$K = \frac{1}{3} C v l = \frac{1}{3} C v^2 \tau$, where C is the heat capacity per volume,

v is the average particle velocity, and l is the mean free path of a particle between collisions, τ^{-1} is the phonon collision rate.

Thermal conductivity of metals Wiedemann-Franz law

Thermal conductivity for a Fermi gas

$$K_{el} = \frac{1}{3} C v l = \frac{\pi^2}{3} \cdot \frac{n k_B^2 T}{m v_F^2} \cdot v_F \cdot l = \frac{\pi^2 n k_B^2 T \tau}{3m}$$

The Wiedemann-Franz law states that for metals at not too low temperatures the ratio of the thermal conductivity to the electrical conductivity is directly proportional to the temperature, independent of the particular metal.

$$\frac{K_{el}}{\sigma} = \frac{\pi^2 n k_B^2 T \tau / 3m}{n e^2 \tau / m} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T \equiv L T.$$

Lorenz number $L = 2.45 \times 10^{-8}$ watt-ohm/deg²

Table 5 Experimental Lorenz numbers

$L \times 10^8$ watt-ohm/deg ²			$L \times 10^8$ watt-ohm/deg ²		
Metal	0°C	100°C	Metal	0°C	100°C
Ag	2.31	2.37	Pb	2.47	2.56
Au	2.35	2.40	Pt	2.51	2.60
Cd	2.42	2.43	Sn	2.52	2.49
Cu	2.23	2.33	W	3.04	3.20
Mo	2.61	2.79	Zn	2.31	2.33