Dept of Phys

M.C. Chang

Free electron Fermi gas (Sommerfeld, 1928)

- counting of states
    - Fermi energy, Fermi surface
- thermal property: heat capacity
- transport property
    - electrical conductivity
    - Hall effect
    - thermal conductivity

• In the free electron model, there is no lattice, and no electron-electron interaction, but it gives nice result on electron heat capacity, electric/ thermal conductivity… etc.

• Free electron model is most accurate for alkali metals.

Early history of solid state physics

(Ref: Chap 4 of 半導體的故事, by 李雅明)

Atomic crystal

1878 – Crookes, Cathode ray

1895 – Rontgen, x-ray

1908 – Einstein model of specific heat

1910 – Debye model, T^3 law

1912 – von Laue, x-ray diffraction by crystal

Electron

1897 – Thomson discovered electron

1899 – Drude theory of classical electron gas, explained Wiedemann-Franz law

1924 – Bose-Einstein statistics, de Broglie wave

1925 – Pauli exclusion principle

1926 – Fermi-Dirac statistics

(1925,6 – Heisenberg/Schrodinger theory)

1927 – Electron diffraction by crystal (Davisson and Germer; G.P. Thomson)

1927 – Sommerfeld's quantum theory of metal

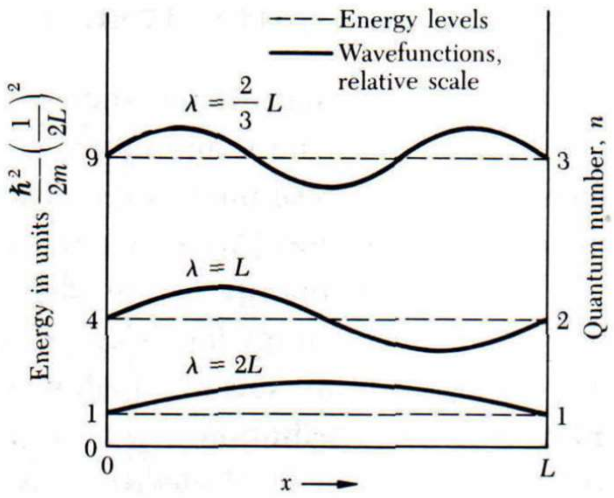
… Sommerfeld does not seem to have asked why the ions did not influence the electrons between collisions, or why the effects arising from motion of the ions could be neglected. As Bethe recalls, "he didn't even care terribly much why the electrons were free, which I thought was a very important thing to know."[89] Neglect of the ions also disturbed other physicists, including Heisenberg and Frenkel;[90] Schottky wrote to Sommerfeld that "to assume a field free condition inside a metal appears to me to be too specialized for the problem."[91] Sommerfeld was aware of these problems, but, as Peierls reflected recently, he was optimistic that in one way or another they would be resolved.[92]

L. Hoddeson et al, Out of the crystal maze, p.104

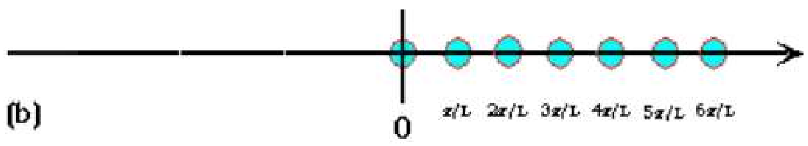
Counting of states: Quantization of *k* in a 1-dim box

- Free electron, plane wave: $\psi(x) = Ae^{ikx} + Be^{-ikx}, \ \varepsilon(k) = \hbar^2 k^2 / 2m$

(1) "Box" BC

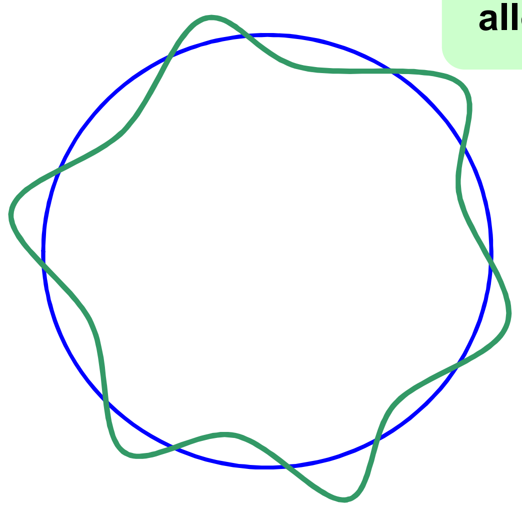


$k = \pi/L, 2\pi/L, 3\pi/L\ldots$

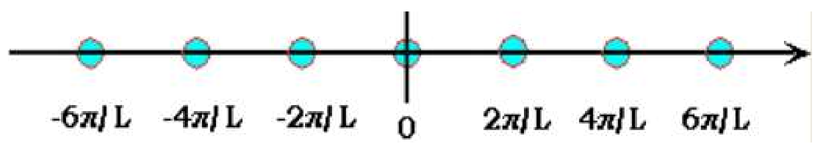


(2) Periodic BC (PBC)

Advantage: allows travelling waves



$k = \pm 2\pi/L, \pm 4\pi/L, \pm 6\pi/L\ldots$



Free electron in a 3-dim box

$$\left(-\frac{\hbar^2}{2m}\nabla^2+0\right)\psi(\vec{r})=\varepsilon\psi(\vec{r})$$

separable, assume

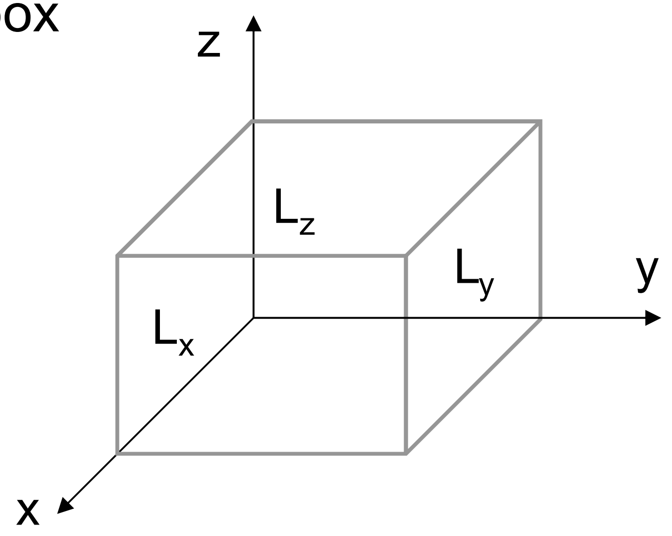
$$\psi(\vec{r})=\phi_x(x)\phi_y(y)\phi_z(z)$$

then

$$\begin{cases}\dfrac{d^2}{dx^2}\phi_x(x)+k_x^2\phi_x(x)=0,\\[2mm] \dfrac{d^2}{dy^2}\phi_y(y)+k_y^2\phi_y(y)=0,\\[2mm] \dfrac{d^2}{dz^2}\phi_z(z)+k_z^2\phi_z(z)=0,\end{cases}$$

$$k_x^2+k_y^2+k_z^2=\frac{2m\varepsilon}{\hbar^2}$$

$$\Rightarrow\quad \phi(\vec{r})=\frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}$$



Periodic Boundary Condition:

$$\phi_x(L_x)=\phi_x(0);\ \phi_y(L_y)=\phi_y(0);\ \phi_z(L_z)=\phi_z(0)$$

$$\Rightarrow\quad k_x=\frac{2\pi}{L_x}n_x,\quad n_x\in Z$$

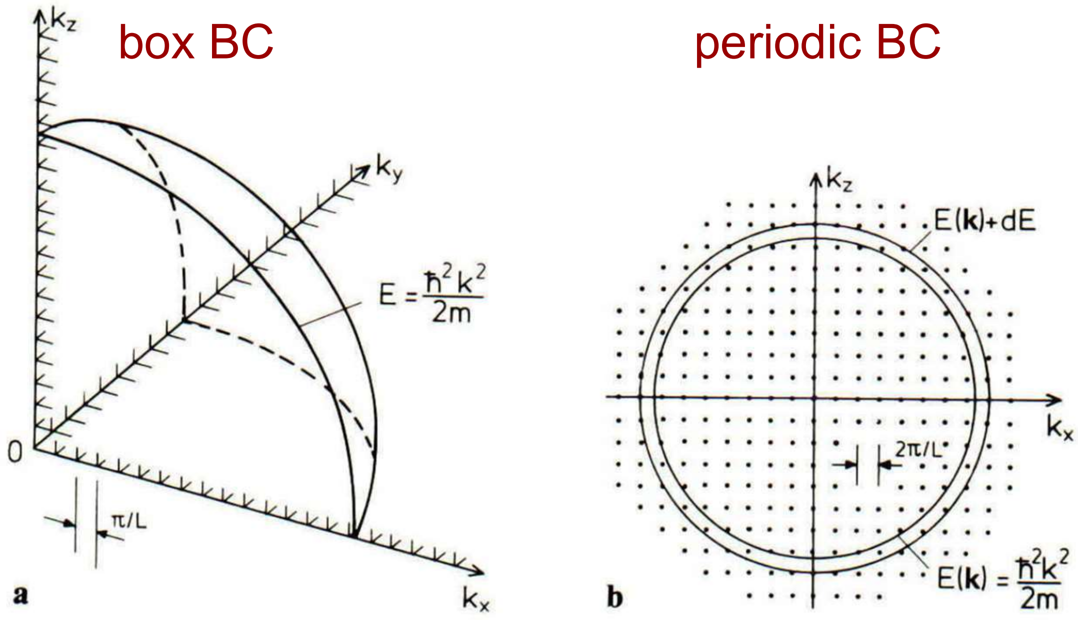
$$k_y=\frac{2\pi}{L_y}n_y,\quad n_y\in Z$$

$$k_z=\frac{2\pi}{L_z}n_z,\quad n_z\in Z$$

$$\Delta^3 k=\left(\frac{2\pi}{L}\right)^3$$

Quantization of *k* in a 3-dim box

box BC periodic BC



• Each point can have 2 electrons (because of spin). After filling in *N* electrons, the result is a spherical sea of electrons called the Fermi sphere. Its radius is called the Fermi wave vector, and the energy of the outermost electron is called the Fermi energy.

• Different BCs give the same Fermi wave vector and Fermi energy

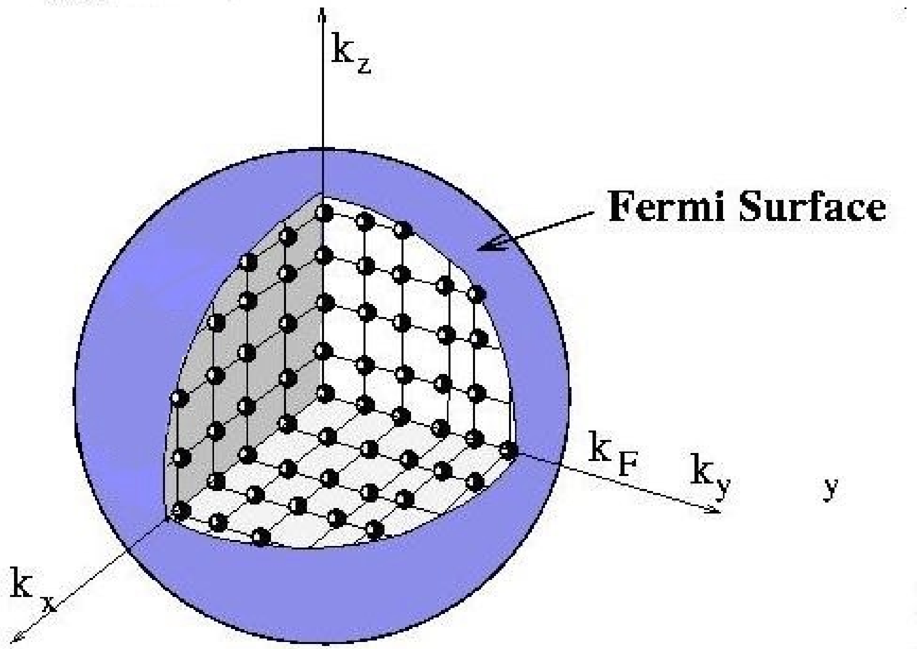
box BC $N = 2\frac{1}{8}\frac{(4\pi/3)k_F^3}{(\pi/L)^3}$ periodic BC $N = 2\frac{(4\pi/3)k_F^3}{(2\pi/L)^3}$

Connection between electron density and Fermi energy

$$N = 2\frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{k_F^3}{3\pi^2}V$$

$$\Rightarrow k_F = \left(3\pi^2 n\right)^{1/3}$$

$$\Rightarrow \varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$



- For K, the electron density n=1.4×10^{28} m^{-3}, therefore

$$k_F = 0.746\ A^{-1} \qquad \varepsilon_F = 3.40\times10^{-19}\,J = 2.12\ \text{eV}$$

- k_F is of the order of a^{-1}.
- ε_F is of the order of the atomic energy levels.

Fig from Baggioli's paper

Fermi temperature and Fermi velocity

$$\varepsilon_F = k_B T_F = \frac{m}{2} v_F^2$$

$$\text{also,}\ \hbar k_F = m v_F$$

- The Fermi temperature is of the order of 10^4 K

ELEMENT	r_s/a_0	ε_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	$1.12 \times 10^8\ \mathrm{cm}^{-1}$	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40

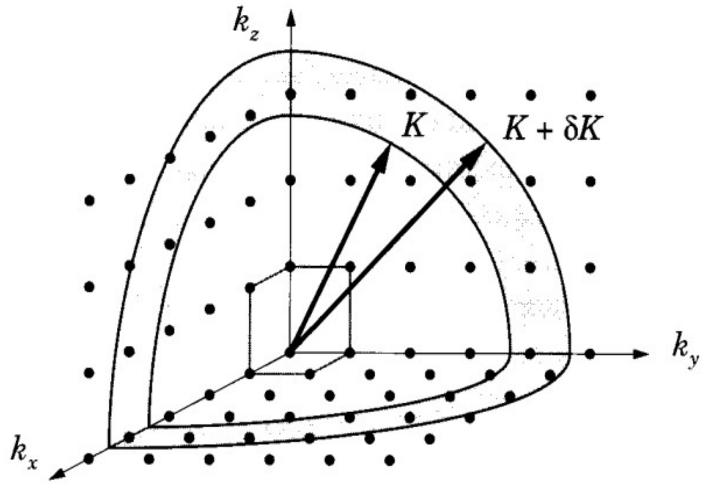
important

Density of states $D(\varepsilon)$ (DOS, 態密度)

- $D(\varepsilon)d\varepsilon$ is the number of states within the energy surfaces of ε and ε+dε

$$D(\varepsilon)d\varepsilon = \frac{2\int_{shell} d^3k}{\Delta^3 k}, \quad \Delta^3 k = \left(\frac{2\pi}{L}\right)^3$$

$$2\int \frac{d^3k}{\Delta^3 k} h(\varepsilon_{\vec{k}}) = \int d\varepsilon D(\varepsilon) h(\varepsilon)$$



- For a 3D Fermi sphere,

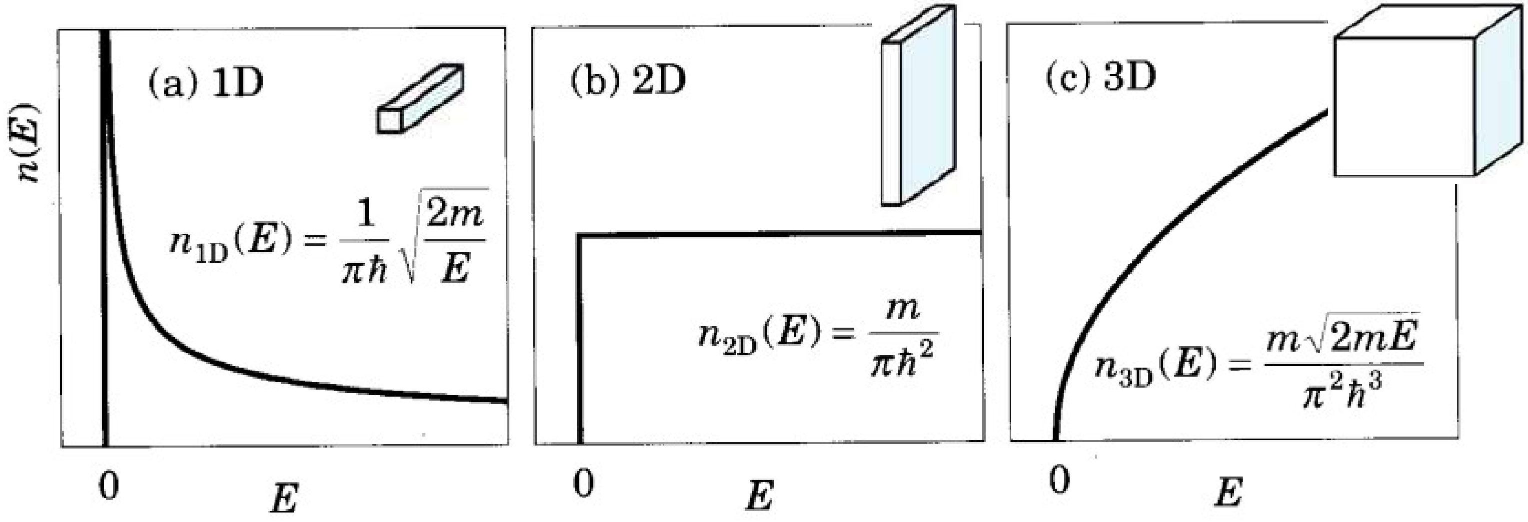
$$D(\varepsilon)d\varepsilon = 2\int_{shell} \frac{d^3k}{(2\pi/L)^3}$$

$$= 2\frac{4\pi k^2 dk}{(2\pi/L)^3}$$

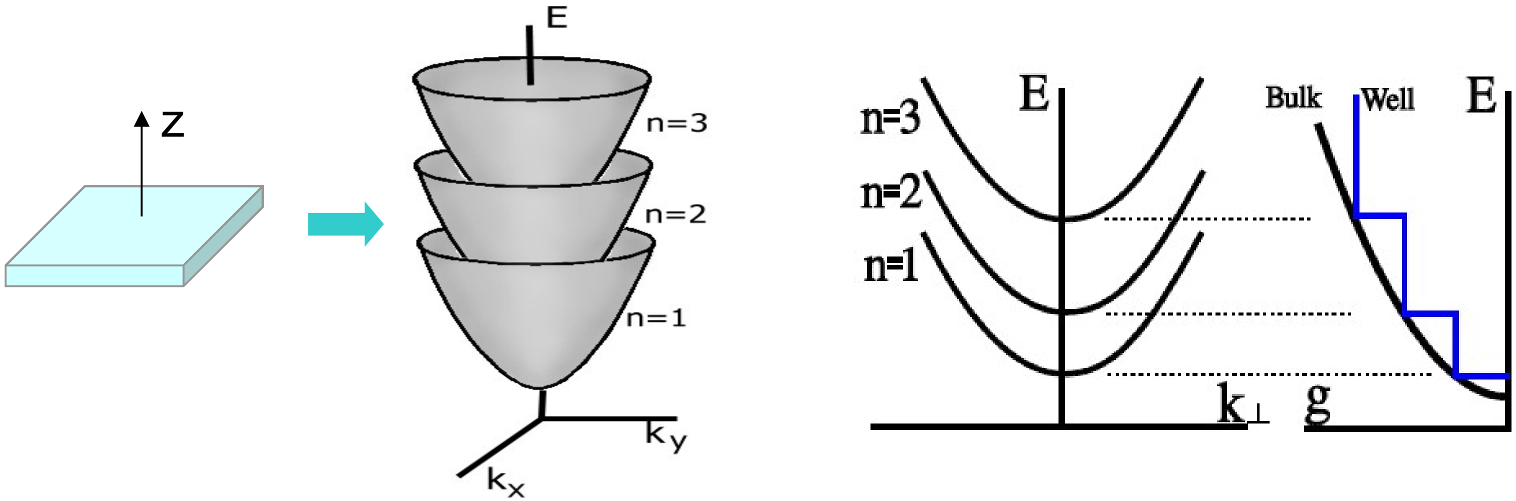
$$\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$

$$\Rightarrow D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$$

- Free electron DOS (per unit volume) in 1D, 2D, and 3D

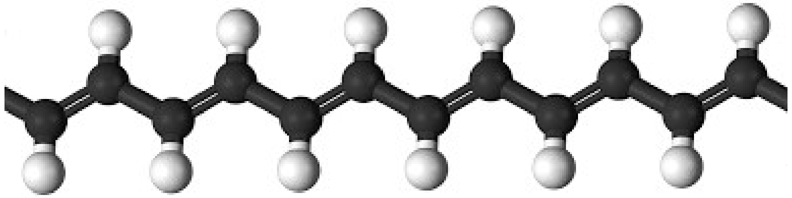


- Multiple bound states in a 2D box with finite thickness

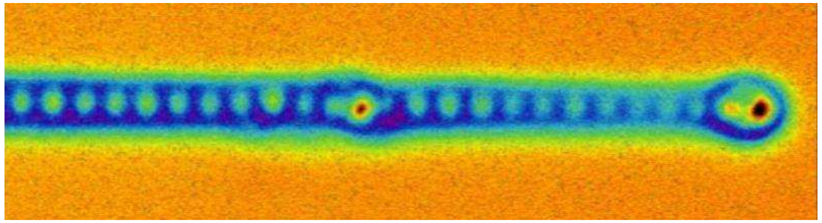


Examples of low-dimensional electron system

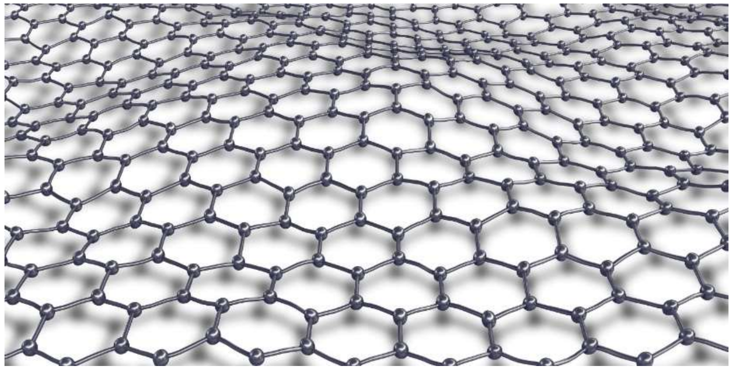
Poly-
acetylene



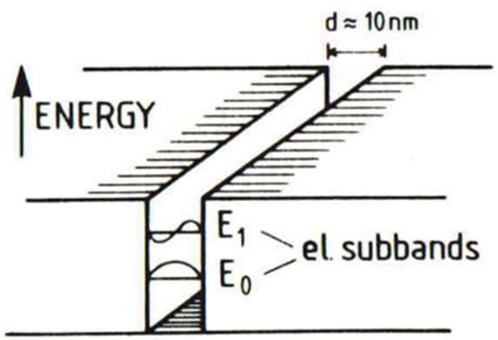
Fe chains on
Pb surface

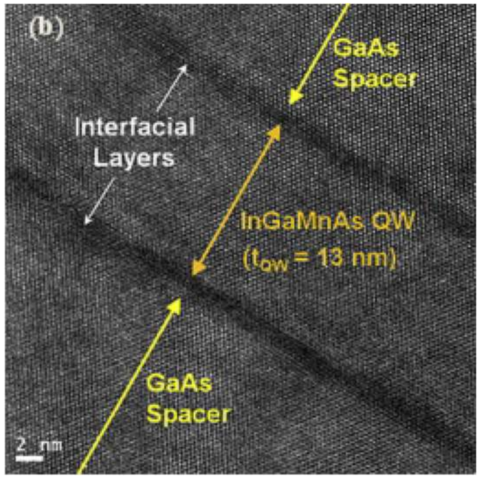


Graphene



Quantum well





- counting of states
  - Fermi energy, Fermi surface
- thermal property: heat capacity
- transport property
  - electrical conductivity
  - Hall effect
  - thermal conductivity

To calculate internal energy, we need to know the following:

- Electron number

T=0 $\quad N = 2 \sum_{\text{filled } \vec{k}} 1$ $\qquad$ $T \neq 0$ $\quad N = 2 \sum_{\vec{k}} f(E_k)$

- Electron energy

T=0 $\quad U(0) = 2 \sum_{\text{fill } \vec{k}} E_k$ $\qquad$ $T \neq 0$ $\quad U(T) = 2 \sum_{\vec{k}} f(E_k) E_k$

- From summation to integral

$$\sum_{\vec{k}} f(\vec{k}) \cong \int \frac{d^3k}{\Delta^3 k} f(\vec{k}) \quad \text{in solid state} \qquad \Delta^3 k = \left(\frac{2\pi}{L}\right)^3$$

- From *k*-integral to *E*-integral

$$2\int \frac{d^3k}{\Delta^3 k} f(\varepsilon_{\vec{k}}) = \int d\varepsilon D(\varepsilon) f(\varepsilon)$$

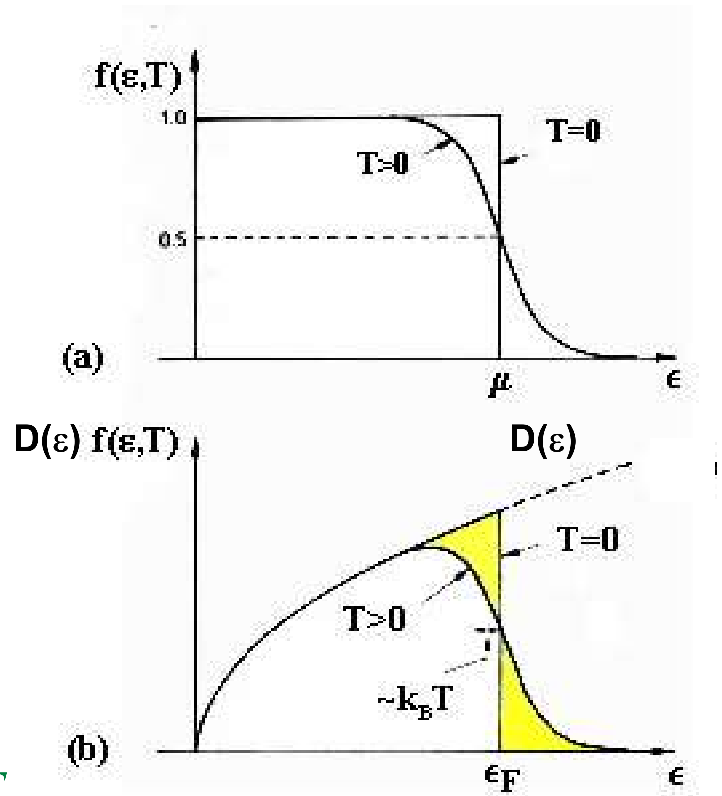
important

Therefore, $2\sum_{\vec{k}} f(E_{\vec{k}}) = 2\int \frac{d^3k}{\Delta^3\vec{k}} f(E_{\vec{k}}) = \int dE D(E) f(E)$

where $f(E) = \dfrac{1}{e^{(E-\mu)/kT}+1}$

μ : chemical potential $\left(f(\mu) = 1/2 \right)$

$$\begin{cases} \mu(T=0K) = E_F \\ \mu(T>0K) < E_F \text{ in 3-dim} \end{cases}$$



總電子數

Hotel rooms

$$N = 2\int \frac{d^3k}{(2\pi/L)^3} \xrightarrow{T\neq 0} \int dE D(E) f(E,T)$$

occupation

內能

$$U(T) = 2\int \frac{d^3k}{(2\pi/L)^3} E(\vec{k}) \xrightarrow{T\neq 0} \int dE D(E) f(E,T) E$$

money

Electronic heat capacity, a heuristic argument

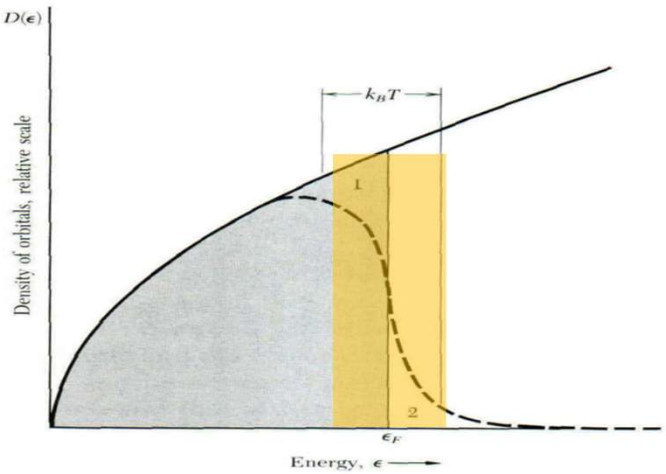
- Only the electrons near Fermi surface are excited by thermal energy k_BT.

Number of excited electrons is roughly

$$\Delta N = N\,(k_BT / E_F)$$

- Energy absorbed by the electrons,

$$U(T) - U(0) \sim \Delta N\,(k_BT)$$
$$= N\,(k_BT)^2/E_F$$



- Heat capacity $C_e = dU/dT$

(per mole) $\sim 2R\,k_BT/E_F$

$= 2R\,T/T_F$

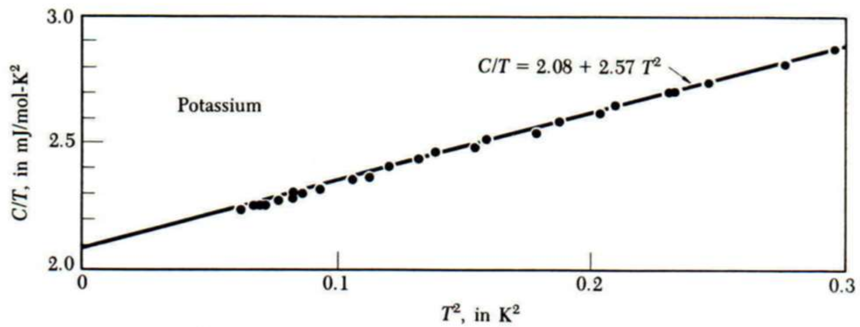
A factor of T/T_F smaller than classical result 3R/2.

A better result, $$C_e = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$ (see Kittel p.142)

- $T/T_F \sim 0.01$: Electron heat capacity is negligible compared to phonon's.

- In general $C = C_e + C_p$
  $= \gamma T + aT^3$

C_e is important only at very low T.



$$\gamma = \frac{C_e}{T}$$

Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).)

Observed γ in mJ mol⁻¹ K⁻².
Calculated free electron γ in mJ mol⁻¹ K⁻².
m_{th}/m = (observed γ)/(free electron γ).

Li 1.63 0.749 2.18	Be 0.17 0.500 0.34											B	C	N
Na 1.38 1.094 1.26	Mg 1.3 0.992 1.3											Al 1.35 0.912 1.48	Si	P
K 2.08 1.668 1.25	Ca 2.9 1.511 1.9	Sc 10.7	Ti 3.35	V 9.26	Cr 1.40	Mn(γ) 9.20	Fe 4.98	Co 4.73	Ni 7.02	Cu 0.695 0.505 1.38	Zn 0.64 0.753 0.85	Ga 0.596 1.025 0.58	Ge	As 0.19
Rb 2.41 1.911 1.26	Sr 3.6 1.790 2.0	Y 10.2	Zr 2.80	Nb 7.79	Mo 2.0	Tc —	Ru 3.3	Rh 4.9	Pd 9.42	Ag 0.646 0.645 1.00	Cd 0.688 0.948 0.73	In 1.69 1.233 1.37	Sn (w) 1.78 1.410 1.26	Sb 0.11
Cs 3.20 2.238 1.43	Ba 2.7 1.937 1.4	La 10.	Hf 2.16	Ta 5.9	W 1.3	Re 2.3	Os 2.4	Ir 3.1	Pt 6.8	Au 0.729 0.642 1.14	Hg(α) 1.79 0.952 1.88	Tl 1.47 1.29 1.14	Pb 2.98 1.509 1.97	Bi 0.008

- counting of states
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Electrical transport (q=–e<0)

Classical view

$$m_e \frac{d\langle \vec{v} \rangle}{dt} = -e\vec{E} - m_e \frac{\langle \vec{v} \rangle}{\tau}$$

Relaxation (scattering) time 弛豫時間

$$\Rightarrow \langle \vec{v} \rangle = -\frac{e\tau}{m_e}\vec{E} \quad \text{at steady state}$$

Drift velocity 漂移速度

- Electric resistance comes from electron scattering with defects and phonons.
- If these two types of scatterings are not related, then scattering rates can be added up:

$$\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_{ph}(T)} \qquad (\text{Matthiessenns rule})$$

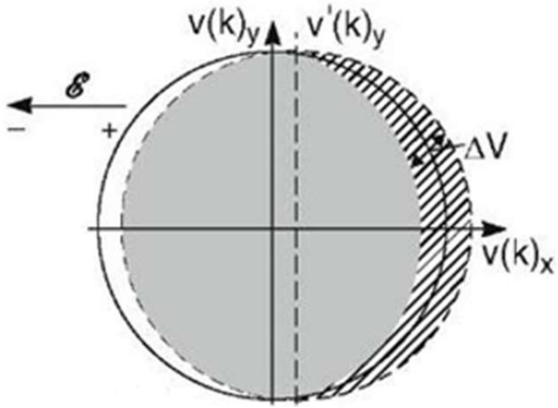
- Current density (n is electron density)

$$\vec{j} = (-e)n\langle \vec{v} \rangle = \frac{ne^2\tau}{m}\vec{E} = \sigma\vec{E} \qquad (\text{Ohmn's law})$$

導電率 Electric conductivity

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

Semi-classical view



$$\hbar \frac{d\vec{k}}{dt} = -e\vec{E}$$

$$\Rightarrow \Delta\vec{k} = \vec{k}(\tau) - \vec{k}(0) = -\frac{e}{\hbar}\vec{E}\tau$$

- Center of Fermi sphere is shifted by Δk

  Drift velocity $m\vec{v}_d = \hbar\Delta\vec{k}$

- One can show that when $\Delta k \ll k_F$, $V_{沒重疊}/V_{重疊} \sim 3/2(\Delta k/k_F)$.
- Therefore, the number of electrons away from equilibrium is about

  $(\Delta k/k_F)N_e$, or $(v_d/v_F)N_e$

$$j = (-e)\left(\frac{v_d}{v_F} n\right) v_F = -env_d \qquad \vec{v}_d = \hbar\Delta\vec{k}/m$$

$$= -(e\tau/m)\vec{E} \qquad \therefore \vec{j} = \frac{ne^2\tau}{m}\vec{E}$$

- Semiclassical view vs classical view:

  The results are the same, but the microscopic pictures are very different:

  - v_F vs v_d (differ by 10^9 !) Note: $v_d \simeq 10^{-4}\frac{m}{s}$
  - $(v_d/v_F)\, N_e$ vs N_e

Calculate the scattering time τ from measured resistivity ρ

• Cu at room temp $\rho = 1.7\times10^{-8}\,\Omega\, m$

Electron density $n = 8.5\times10^{28} m^{-3}$ $\rightarrow \tau = m/\rho n e^2 = 2.5\times10^{-14}$ s

• Fermi velocity of copper: $1.6\times10^{6}\, ms^{-1}$

∴ mean free path $\ell = v_F\tau$ = 40 nm.

• For very pure Cu crystal at 4K, the resistivity reduces by a factor of 10^5, which means that ℓ increases by the same amount (ℓ = 0.4 cm!).

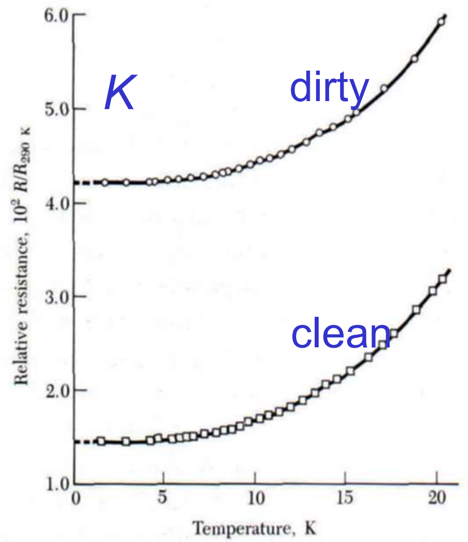
This cannot be explained using classical theory.

• For a crystal without any defect, the only resistance comes from phonon. Therefore, at very low T, the electron mean free path should approach infinity.

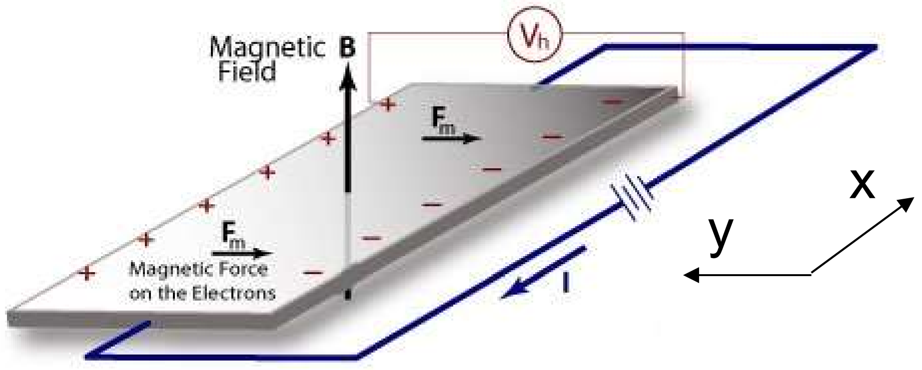
Why the ions do not block electrons?
See next chapter

$$\rho = \frac{m}{ne^2}\frac{1}{\tau_i} + \frac{m}{ne^2}\frac{1}{\tau_{ph}(T)}$$

Residual resistance at T=0 剩餘電阻



Hall effect (1879)



Classical view:

(in 2-dimension)

$$m_e \frac{d\vec{v}}{dt} = -e\vec{E} - e\vec{v}\times\vec{B} - m_e\frac{\vec{v}}{\tau}$$

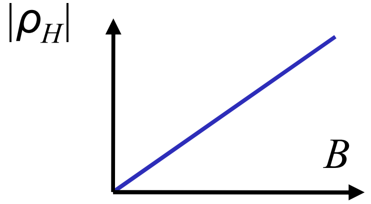
$$\vec{B} = B\hat{z};\quad d\vec{v}/dt = \vec{0} \text{ at steady state}$$

$$\begin{pmatrix} m/\tau & eB \\ -eB & m/\tau \end{pmatrix}\begin{pmatrix} v_x \\ v_y \end{pmatrix} = -e\begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

$$\vec{j} = -en\vec{v}$$

$$\begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} \frac{m}{ne^2\tau} & \frac{B}{ne} \\ -\frac{B}{ne} & \frac{m}{ne^2\tau} \end{pmatrix}\begin{pmatrix} j_x \\ j_y \end{pmatrix} = \underset{\sim}{\rho}\vec{j},$$

$$j_y = 0 \Rightarrow \begin{cases} E_x = \rho_L j_x,\ \rho_L = \frac{m}{ne^2\tau} & \text{縱向電阻率} \\ E_y = \rho_H j_x,\ \rho_H = -\frac{B}{ne} & \text{橫向電阻率} \end{cases}$$



Comparison of observed Hall coefficients with free electron theory

Metal	Method	Experimental R_H, in 10^{-24} CGS units	Assumed carriers per atom	Calculated $-1/nec$, in 10^{-24} CGS units
Li	conv.	−1.89	1 electron	−1.48
Na	helicon	−2.619	1 electron	−2.603
	conv.	−2.3		
K	helicon	−4.946	1 electron	−4.944
	conv.	−4.7		
Rb	conv.	−5.6	1 electron	−6.04
Cu	conv.	−0.6	1 electron	−0.82
Ag	conv.	−1.0	1 electron	−1.19
Au	conv.	−0.8	1 electron	−1.18
Be	conv.	+2.7	—	—
Mg	conv.	−0.92	—	—
Al	helicon	+1.136	1 hole	+1.135
In	helicon	+1.774	1 hole	+1.780

Hall coefficient

$$R_H \equiv \frac{E_y}{j_x B} = -\frac{1}{ne}$$

Positive Hall coefficient?

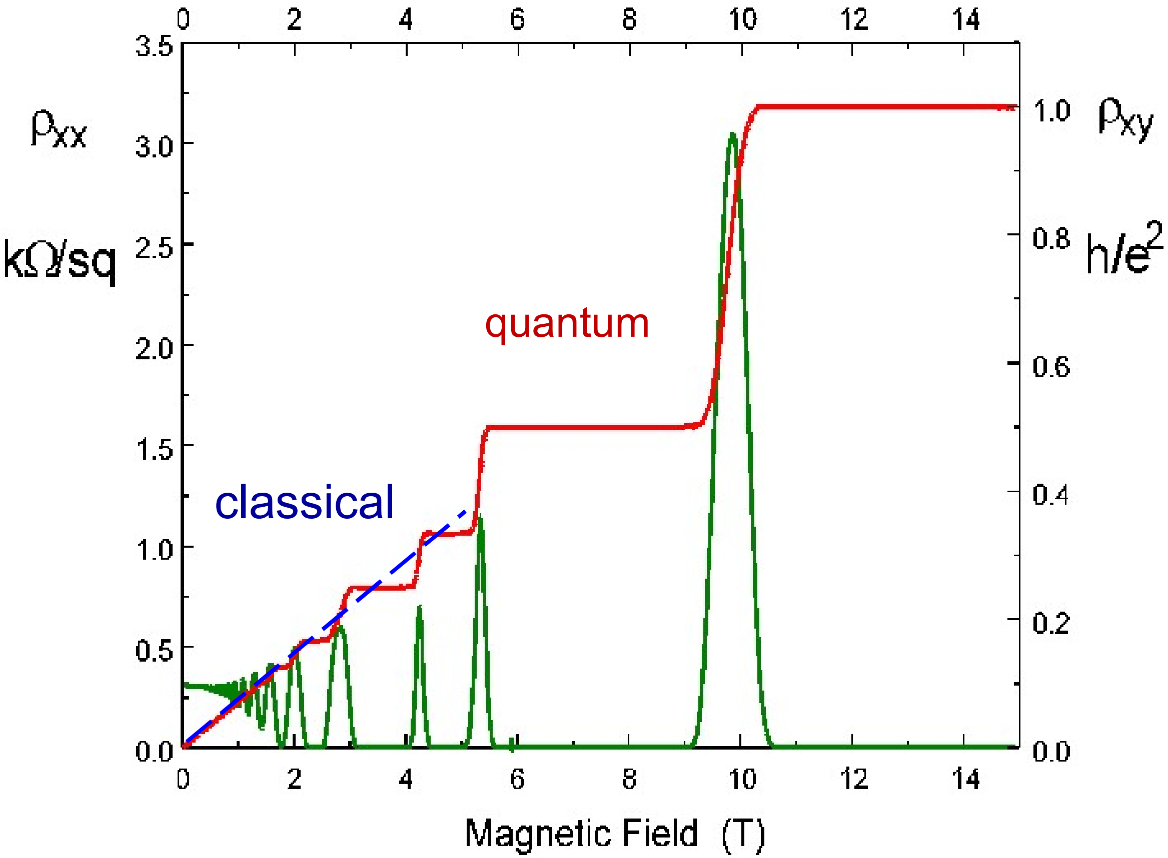
Can't be explained by free electron theory.

Band theory (next chap) is required.

One can determine electron density *n* by measuring the Hall coefficient.

optional

A surprising discovery: Quantum Hall effect (1980)



1985

- This result is independent of the shape/size of sample.
- *h/e^2*=25812.80745 Ω ← exact (1990)

optional

An accurate and stable resistance standard (1990)

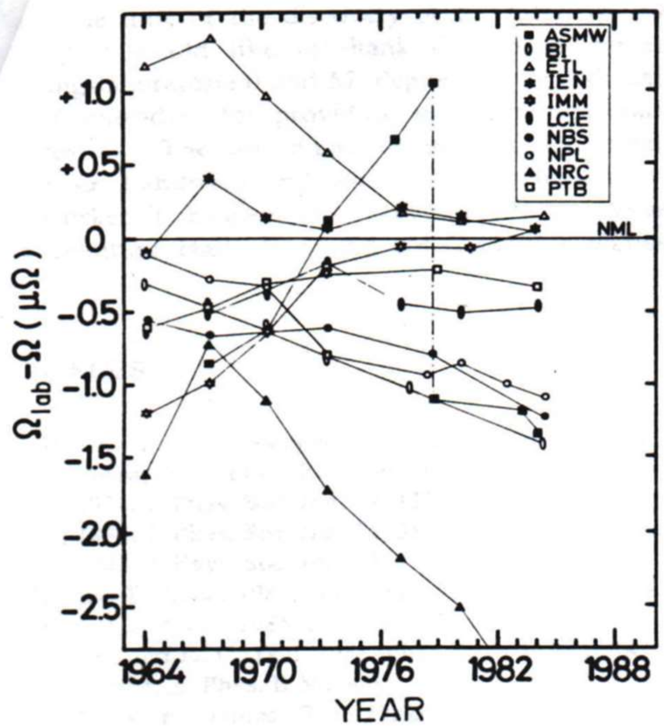


FIG. 26. Time dependence of the 1-Ω standard resistors maintained at the different national laboratories.

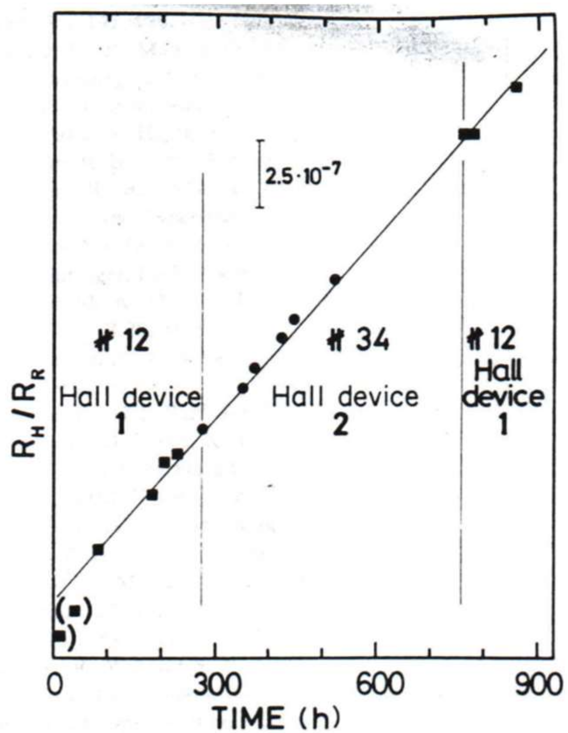


FIG. 27. Ratio R_H/R_R between the quantized Hall resistance R_H and a wire resistor R_R as a function of time. The result is time dependent but independent of the Hall device used in the experiment.

Offers one of the most accurate way to determine the Planck constant *h*.

Update (2019): the values of c,h,e are now defined (therefore exact).

Thermal conduction in metal

• Both electron and phonon can carry thermal energy (Electrons dominate in metal).

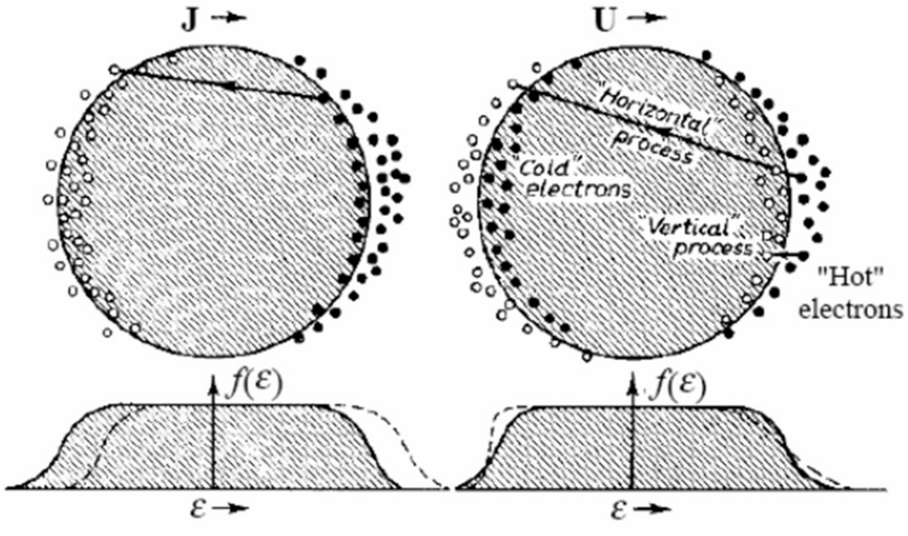
• Similar to electrical conduction, only the electrons near the Fermi energy can contribute to the thermal current.

$$c_V = \frac{\pi^2}{2} n k_B \frac{k_B T}{\varepsilon_F}$$

Heat capacity per unit volume

Thermal conductivity

$$K = \frac{1}{3} c_v v \ell = \frac{1}{3}\left(\frac{\pi^2 n k_B^2 T}{2\varepsilon_F}\right) v_F (v_F \tau) = \frac{\pi^2}{3}\frac{n k_B^2 T}{m}\tau$$



(a) electrical conduction (b) thermal conduction

- Wiedemann-Franz law (1853)

κ/σ has approximately the same value for different metals at the same temperature (a good electrical conductor is also a good thermal conductor.)

Lorenz number L

$$\frac{K}{\sigma}=\frac{\frac{\pi^2}{3}\frac{nk_B^2T}{m}\tau}{\frac{ne^2\tau}{m}}=\boxed{\frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2}T$$

$= 2.45\times10^{-8}$ W-ohm/K^2

The thermal conductivities of some materials at room temperature

Material	k, w/m°C
Diamond	2300
Silver	430
Copper	400
Gold	320
Aluminium	240
Iron	80
Glass	0.8
Brick	0.7
Water	0.61
Wood	0.17
Helium	0.15
Air	0.026

element	κ (W/m·K)	L (10^{-8} V^2/K^2)
Ag	436	2.34
Al	236	2.10
Au	318	2.39
Ca	186	2.13
Cs	37	2.5
Cu	404	2.27
Fe	80	2.57
K	98	2.24
Li	65	2.05
Mg	151	2.29
Na	142	2.23
Ni	93	2.19
Pb	36	2.50
Pd	72	2.57
Pt	72	2.59
Rb	56	2.30
Ru	131	2.52
Sn	62	2.5
Zn	127	2.60

273K

K/σ~T is discovered by L. Lorenz (1872)

$$\frac{K}{\sigma}=LT$$

Free-electron model can explain

- Electron heat capacity
- Electrical conductivity
- Thermal conductivity
- Magnetic susceptibility
- Hall effect

However, it fails to explain

- Why there is insulator
- Positive Hall coefficient
- …

Next step, take lattice into account.

Note: Is electron-electron interaction important?

Not really for many materials (see Chap 14). But when it's important, the physics behind is interesting .