

STEFANO  
CURTAROLO

## CONDUCTIVITY

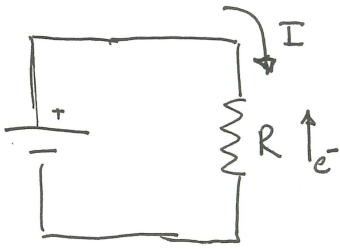
- DRUDE
- HALL
- AC ( $\omega$ )  $\Rightarrow \sigma(\omega)$

D0 - D10

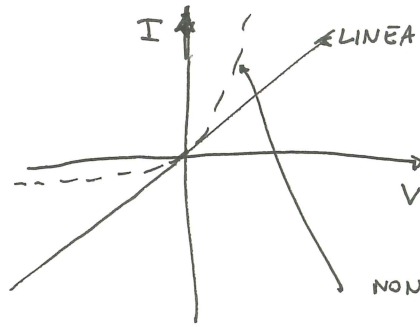
2004 original  
2005 ADDED  $\bar{v} = -kVT$   
& TABLES.

CONDUCTIVITY: Apply voltage and get current.

4



$I(V)$



LINEAR  $\Rightarrow \frac{I}{V} = \frac{\partial I}{\partial V} = \frac{1}{R}$

NON LINEAR

$\frac{I}{V}(V) \neq \frac{\partial I(V)}{\partial V}$

Questions.

1) which are the carriers

2) Linear: number (density) of carriers does not depend on  $V$   $\frac{\partial n_{\text{core}}(V)}{\partial V} = 0$   
 $\Rightarrow$  OHM'S LAW

Examples:

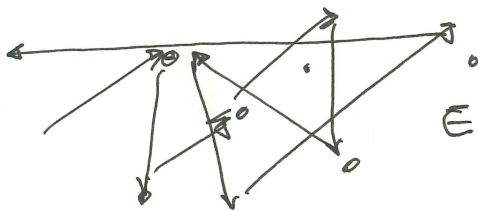
3) NON Linear: number of carriers does depend on  $V$   $\frac{\partial n_{\text{core}}(V)}{\partial V} \neq 0$   
 specify  $V(I)$ ,  $\frac{\partial I}{\partial V} \dots$  etc..

Examples:

DRUDE MODEL

- 1) sea of electrons
  - 2) sometimes they collide (SCATTERING)
- IDEA

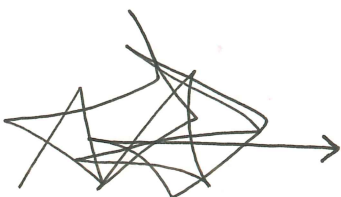
MODEL  $\Rightarrow$



$E = 0 \Rightarrow \langle v \rangle = 0$   
 $\langle v^2 \rangle = \text{thermo}$

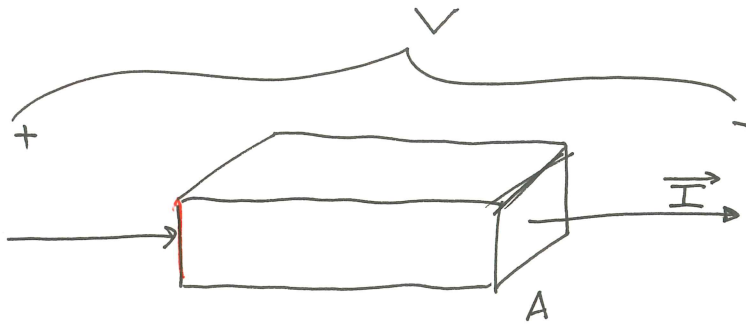
- 1) between collisions electrons are free (no e-e, e-c interactions)
- 2) probability of collision per unit time is  $1/\tau$  (relax time)  
 $\Rightarrow$  in time  $dt \Rightarrow \frac{dt}{\tau}$
- 3) collision: instantaneous events

- 4) thermal equilibrium = local thermal dynamical equilibrium, (only way to share energy)  
 After interaction, speed is random but appropriate to local temperature



$E \neq 0 \Rightarrow \langle v \rangle = \text{drift}$   
 $\langle v^2 \rangle = \text{thermo} + \text{little drift.}$

$\langle E_{\text{KIN}} \rangle = \frac{1}{2} m_e \langle v_e^2 \rangle = \frac{3}{2} kT$



FROM OBSERVATION

turn on E  
get extensive I

I is extensive

OHM'S law

$$I = \frac{V}{R}$$

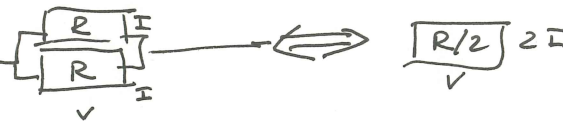
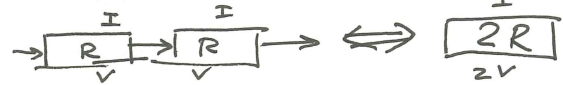
R in  $[\Omega]$

$$R \propto L$$

longer  $\Rightarrow$  more resistance

$$+$$

$$R \propto 1/A$$



current flux

$$J = \frac{I}{A} = \frac{V}{AR}$$

$$= \frac{V}{AL} = \sigma \left( \frac{V}{L} \right) = \sigma E$$

$\nwarrow$  potential  
 $\nwarrow$  E field

$$R = \rho \frac{L}{A} = \frac{L}{\sigma A}$$

$$\rho = \text{resistivity } \rho \left[ \frac{\Omega \cdot \text{m}^2}{\text{m}} \right] = \left[ \frac{\Omega \cdot \text{m}}{\text{m}^2} \right]$$

$\sigma = \text{conductivity}$

$$J \propto E \text{ field}$$

scalar  $\epsilon \Rightarrow J$   
 $\vec{J} = \sigma \vec{E}$  isotropic

2 tensor  $\epsilon \Rightarrow J$   
 $\vec{J} = \underline{\underline{\sigma}} \vec{E}$  anisotropic

MATRIX

$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

- $\rightarrow$  inversion symmetry
- $\rightarrow$  cubic
- $\rightarrow$  NYE BOOK

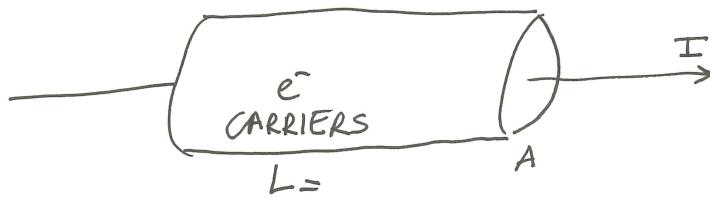
EINSTEIN

CONDUCTIVITY

$$J_i = \sigma_{ij} E_j$$

repeated indices  $= \sum_j$

FROM THINKING



electrons are:  $E = 0$   $\langle v \rangle = 0$   
 $\langle v^2 \rangle = \text{thermal}$

$E \neq 0$   $\langle v \rangle = v = \text{drift} \Rightarrow \text{container } L = v dt$   
 $\langle v^2 \rangle = \text{thermal} + \text{little drift}$

$I = \frac{dQ}{dt}$  all charge that goes through A per unit time  
 $\Rightarrow$  charge inside container  $AL = A v dt$   
 $\Rightarrow$  density of electron  $= n$   
 charge  $= -e$  (charge (e) is + COULOMBS)  
 volume  $= A v dt$

charge that goes ~~is~~ through A in time  $dt$  is

charge inside value  $dQ = \underset{\substack{\uparrow \\ \text{density}}}{n} \underset{\substack{\uparrow \\ \text{charge}}}{e} A v dt$

$I = -n e A v \Rightarrow \boxed{J = -n e v}$  THINKING STEADY STATE

BUT  $J = \sigma E \Rightarrow \sigma E = -n e v$

Force  $\propto E$  ( $F = -eE$ )  
 $\Rightarrow$  acceleration (NEWTON)  
 $m \ddot{x} = -eE +$

$\Rightarrow \boxed{v = -\frac{\sigma}{n e} E}$

$v \propto E$   
 $v = -\mu E$

increase ~~potential~~ Field  
 $\Rightarrow$  increase speed drift

$\boxed{\mu = \frac{+\sigma}{n e}}$  MOBILITY  
 $E \Rightarrow \mu$



# NEED COLLISIONS : MOBILITY IN HYDRODYNAMICAL MODEL

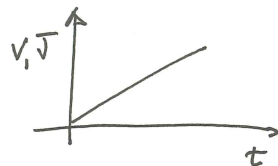
1) NO COLLISIONS

$p = mv$  momentum

$$\vec{E} \Rightarrow F = -eE = ma = m\dot{v} = \frac{\partial p}{\partial t}$$

$$\frac{\partial p}{\partial t} = -eE \quad \text{constant} \Rightarrow$$

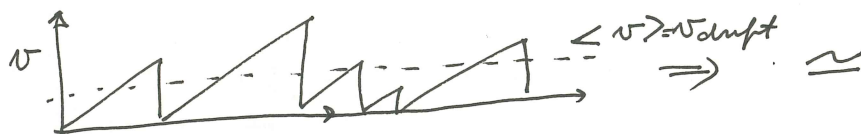
$$\Rightarrow p = p_0 - eEt \Rightarrow v = v_0 - \frac{eEt}{m}$$



$$\mu = \frac{et}{m} \rightarrow \infty$$

$$\sigma = \frac{me^2t}{m} \rightarrow \infty$$

2) COLLISIONS  $\simeq$  VISCOSITY IN A FLUID  $\equiv$  DRAG



$$\frac{\partial p}{\partial t} = F_{acc} + \text{drag per unit time} = -eE - \frac{p(t)}{\tau}$$

$$\dot{p} = -eE - \frac{p}{\tau} \Rightarrow p = a + be^{\beta t} \Rightarrow p = p_{\infty}(1 - e^{-t/\tau})$$

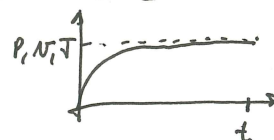
MECH. DUALITY  
 $\frac{1}{\tau} \Leftrightarrow \text{viscosity}$

relax  $\uparrow \Leftrightarrow$  viscosity  $\downarrow$

STATIONARY STATE  $= \langle \frac{\partial p}{\partial t} \rangle = 0 \Rightarrow \langle -eE - \frac{p(t)}{\tau} \rangle = 0 \Rightarrow p(t) = p_{\infty}(1 - e^{-t/\tau})$

$$p_{\infty} = -eE\tau$$

$$\left\langle \frac{p = mv}{\tau} \right\rangle = \langle eE \rangle = -eE$$



$$v_{drift} = \langle v \rangle = \frac{e\tau E}{m}$$

$v = \frac{e\tau E}{m}$

$$\sigma = ne\mu$$

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

$$\mu = \frac{e\tau}{m}$$

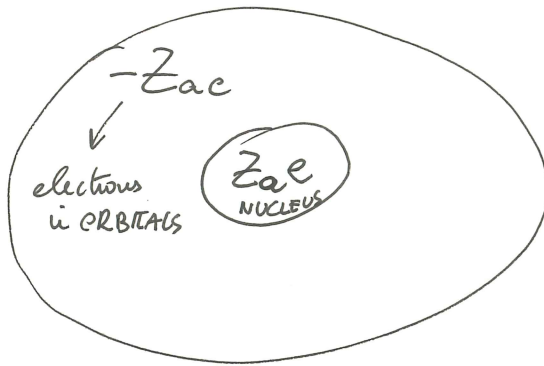
heavier mass  $\uparrow \mu \downarrow \sigma \downarrow$

$$\mu = \frac{e\tau}{m} = \frac{\sigma}{ne} \Rightarrow$$

$$\sigma = ne\mu$$

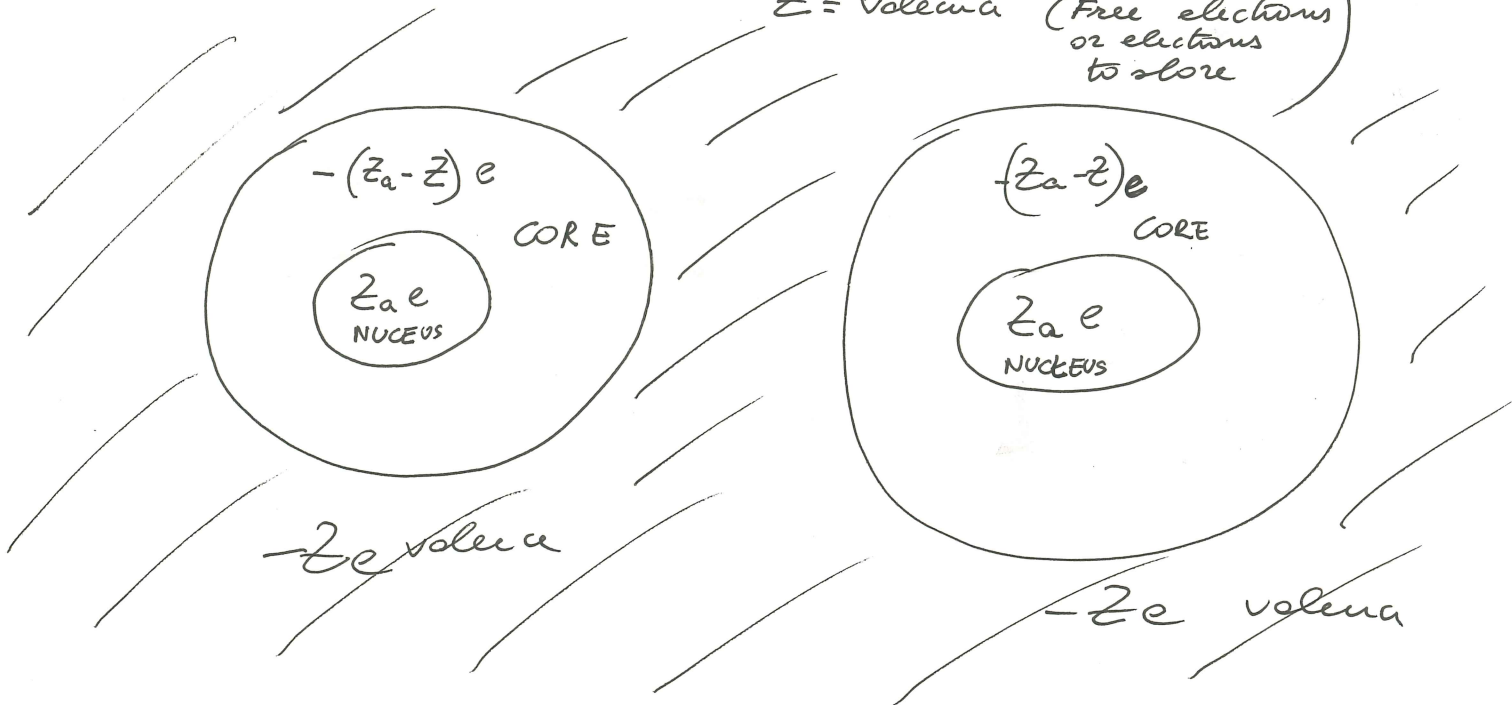
# HOW BIG IS $n$ ?

ISOLATED ATOM HAS  $Z_a$  ~~electrons~~ charge in NUCLEUS



MATERIAL HAS BONDS AND CORE ELECTRONS

$Z = \text{valence}$  (Free electrons or electrons to share)



$Z \text{ valence} \sim 1, 2, 3 \dots$  Few!!

How BIG is atom  $\sim$  Atomic  $\frac{4}{3} \pi r_s^3 = \frac{V}{N} \Rightarrow \text{density} = \frac{1}{n} = \frac{4}{3} \pi r_s^3$

OR 
$$n = Z \rho_m \frac{N_A}{M_A} \rightarrow \text{Mass of mole in kg}$$

Electrons + atoms per cubic meters (density  $\frac{\text{kg}}{\text{m}^3}$ )

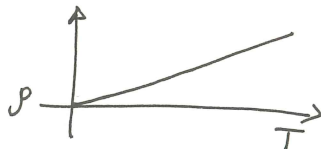
$N_A \leftarrow$  Avogadro's  $N$

See TABLE

AM 1.1

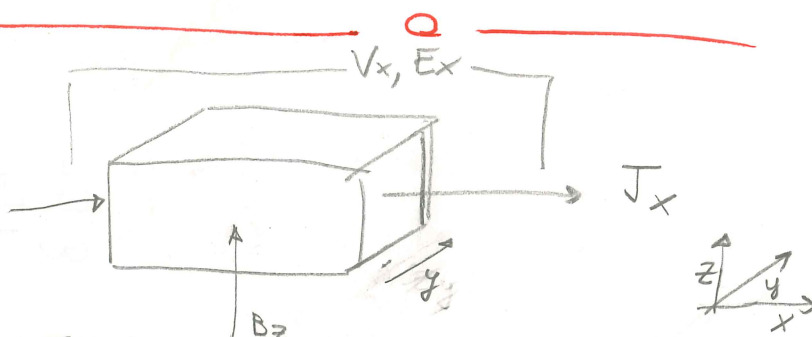
# SCATTERING

- 1) DEFECTS (DISLOCATIONS, IMPURITIES)
- 2) IONS (CORE) MOVING!  $\Rightarrow T \downarrow z \uparrow \Rightarrow$  perfect metals  $\sigma(T=0) = \infty$   
 $\rho=0$



## HALL EFFECT

apply  $B_z$  to conductor,  
what happen?



STATIONARY STATE eh  $B_z$  does not affect  $\bar{v}_x$

$$\vec{F} = q\vec{E} + q\vec{v} \times \vec{B} \quad \vec{v} = v_x \hat{x}$$

$$\vec{v} \times \vec{B} \Rightarrow$$

$$\epsilon_{ijk} v_j B_k = \epsilon_{yxz} v_x B_z = -v_x B_z$$

$$\vec{F} = q(\vec{E}_x - \hat{y} v_x B_z)$$

$\downarrow$   
in steady state

$$F_y = -v_x B_z q \Rightarrow$$

$$= v_x B_z e$$

$$E_{\text{HALL}} \triangleq v_x B_z$$

in steady state

$$\vec{J} = -ne\vec{v} \Rightarrow v_x = \frac{\vec{J}_x}{-ne} \Rightarrow$$

$$E_{\text{HALL}} = -\frac{J_x B_z}{ne} = R_H J_x B_z$$

$$R_H = \frac{1}{-ne} \quad \text{HALL COEFFICIENT}$$

very small

ASSUMPTIONS :

density of carriers  $\frac{dn(B)}{dB} \approx 0$   
magnetic population

works for ALKALI METALS OK valence 1  
 NOBLE METALS  $\sim 50 \& 50$  } valence 2,3  
 Aluminium : NO  
 $\Rightarrow$  need quantum

copy AM 1.4 T

# AC RESPONSE of free electrons (NO CURRENT)



Stationary  
Sinusoidal  
wave

$$\text{Real}[E_z = E_0 e^{-i\omega t}]$$

$$F = \frac{\partial p}{\partial t}$$

Electrons  
vibrate

NO CU.

NO H because  
Hall effect is small

$$\vec{F} = -e \vec{E}_0 e^{-i\omega t}$$

$$\frac{\partial \vec{p}}{\partial t} = -e \vec{E}_0 e^{-i\omega t} - \frac{\vec{p}}{\tau} \Rightarrow \frac{\partial p_z}{\partial t} = -e E_0 e^{-i\omega t} - \frac{p_z}{\tau}$$

stationary  
 $\Rightarrow p \sim \sin$

$$p_z = p_0 e^{-i\omega t} \Rightarrow -i\omega p_z = -e E_0 e^{-i\omega t} - \frac{p_z}{\tau}$$

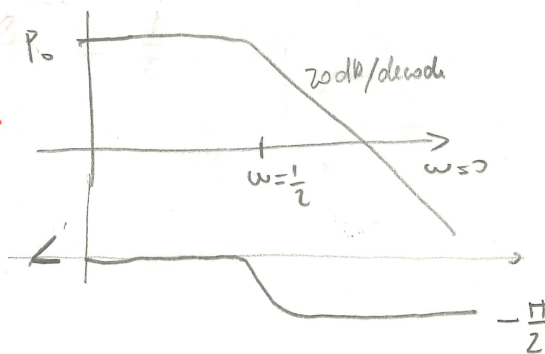
$$p_z (1 - i\omega\tau) = -e E_0 \tau e^{-i\omega t}$$

$$p_z = \frac{e E_0 \tau}{i\omega\tau - 1} e^{-i\omega t}$$

$$\omega\tau \ll 1 \quad \omega \ll \frac{1}{\tau} \Rightarrow p_0 \sim E_0 \tau \text{ IN PHASE}$$

$$\omega\tau \gg 1 \quad \omega \gg \frac{1}{\tau} \Rightarrow p_0 \sim -i \frac{e E_0 \tau}{\omega} \text{ OUT OF PHASE } -90^\circ \text{ OFF}$$

BODE



$$p = m v \Rightarrow J = -ne v = \sigma E \Rightarrow \sigma = \frac{-nev}{E} = -\frac{ne}{Em} p$$

$$\omega \ll \frac{1}{\tau} \quad \vec{J} \text{ in phase with } \vec{E}$$

$$\omega \gg \frac{1}{\tau} \quad \vec{J} \text{ out of phase with } \vec{E}$$

$$\tau = 10^{-14}$$

$$\Rightarrow \omega_0 \sim 10^{14} \text{ Hz} \sim 100 \text{ THz}$$

$$\sigma(\omega) = \left( \frac{ne^2\tau}{m} \right) \frac{1}{1 - i\omega\tau}$$

Conductivity  $\sigma_0$

$$\sigma(\omega) \sim \frac{ne^2}{i\omega} \text{ NO } \tau$$

in phase  
reflection

out of phase  
transmission

electron lives (moves) for  $\sim 2$  time

$\omega \ll \frac{1}{2} \Rightarrow$  Electron sees <sup>space</sup> constant FIELD

$\omega \gg \frac{1}{2} \Rightarrow$  Electrons see <sup>space</sup> variable FIELD  
Wave much shorter than "mean free path"

$$\Rightarrow E \sim E_0 e^{i(kx - \omega t)} \text{ variable}$$

## MAXWELL

$$\nabla \cdot \bar{D} = \nabla \cdot (\epsilon E) = \rho_c \quad \text{GAUSS}$$

$$\nabla \cdot \bar{B} = 0 \quad (\text{no monopoles})$$

$$\nabla \times \bar{E} = -\frac{\partial \bar{B}}{\partial t} \quad \text{Faraday}$$

$$\nabla \times \bar{H} = \bar{J} + \frac{\partial \bar{D}}{\partial t} \quad \text{Ampere}$$

$$\bar{D} = \epsilon_0 \bar{E} + \bar{P} = \epsilon \bar{E} \quad \epsilon = \epsilon_r \epsilon_0$$

$$\bar{B} = \mu_0 \bar{H} + \mu_0 \bar{M} = \mu \bar{H} \quad \mu = \mu_r \mu_0$$

etc

Solutions of

$\mu = \mu_0$  non magnetic M=0

P no Polarization (free electrons)  
(distortion of orbitals)

$$\nabla \times \nabla \times E = -\frac{\partial}{\partial t} \nabla \times \mu H = -\mu_0 \frac{\partial}{\partial t} \left[ \bar{J} + \epsilon_0 \frac{\partial \bar{E}}{\partial t} \right]$$

$$\nabla \times \nabla \times E = \nabla (\underbrace{\nabla \cdot E}_0) - \nabla^2 E$$

NO POLARIZATION

$$\Rightarrow + \nabla^2 E = \mu_0 \sigma(\omega) \frac{\partial E}{\partial t} + \mu_0 \epsilon_0 \frac{\partial^2 E}{\partial t^2}$$

$$E = E_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad \text{STYLE}$$

$$-k^2 E_0 = -i\omega \mu_0 \sigma(\omega) E_0 - \mu_0 \epsilon_0 \omega^2 E_0$$

$$k^2 = i\omega \mu_0 \sigma(\omega) + \mu_0 \epsilon_0 \omega^2 \Rightarrow k^2 = \frac{\omega^2}{c^2} \epsilon_r(\omega)$$

$$\epsilon_r = 1 + \frac{i\sigma(\omega)}{\epsilon_0 \omega}$$

$$\bar{J} = \sigma(\omega) \bar{E}$$

$$\mu_0 \epsilon_0 = \frac{1}{c^2}$$

WAVE

$$v = \frac{c}{\sqrt{\mu_r \epsilon_r}} \Rightarrow k^2 = \frac{\omega^2}{v^2}$$

$$k^2 = \frac{\omega^2}{c^2} \left( 1 + \frac{i\sigma(\omega)}{\epsilon_0 \omega} \right)$$

$$\epsilon_r(\omega) = 1 + \frac{i\sigma(\omega)}{\epsilon_0 \omega}$$

WAVE

$$k^2 = \frac{\omega^2}{v^2}$$

$$\Rightarrow v = \frac{\omega}{k}$$

$$v = \frac{c}{\sqrt{\epsilon_r}}$$



$$\epsilon_r = 1 + \frac{i\sigma(\omega)}{\epsilon_0 \omega}$$

IF  $\omega z \gg 1 \Rightarrow$

$$\sigma(\omega) = \sigma_0 \frac{1}{1 - i\omega z} = \left( \frac{e^2 n z}{m} \right) \frac{1}{1 - i\omega z}$$

$$= - \frac{e^2 n z}{i m \omega z} \quad \text{losses depend on } z$$

$$\Rightarrow \epsilon_r = 1 - \frac{e^2 n}{\epsilon_0 m \omega^2} = 1 - \frac{e^2 n}{\epsilon_0 m \omega^2}$$

$$\epsilon_r = 1 - \frac{\omega_p^2}{\omega^2}$$

$$\omega_p^2 = \frac{e^2 n}{m \epsilon_0} \quad \text{PLASMA HF}$$

$\omega < \omega_p$  Reflective  
 $\omega > \omega_p$  transparent  
 ULTRAVIOLETS

For  $\omega z \gg \gg \gg 1 \quad \epsilon_r \sim 1 \Rightarrow \epsilon \sim \epsilon_0$

$\omega z \ll 1$

$$\epsilon_r = 1 + \frac{i}{\epsilon_0 \omega} \left( \frac{e^2 n z}{m} \right) \frac{1}{1 - i\omega z} = 1 + \frac{i}{\omega} \frac{z}{1 - i\omega z} \omega_p^2 \approx 1 + i \frac{z \omega_p^2}{\omega} \approx i \frac{z \omega_p^2}{\omega}$$

Smell      Smell

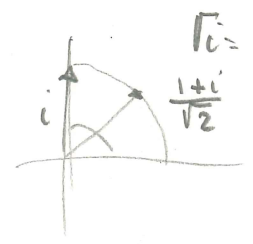
$$\epsilon_r = i \frac{z \omega_p^2}{\omega} \quad \text{LF}$$

OR

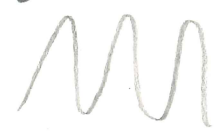
$$\epsilon_r = \frac{i \sigma_0}{\epsilon_0 \omega}$$

$$K^2 = \frac{\omega^2}{c^2} \epsilon_r \Rightarrow K = \frac{\omega}{c} \sqrt{\epsilon_r} = \frac{\omega}{c} \sqrt{\frac{i \sigma_0}{\epsilon_0 \omega}}$$

$$= \frac{\omega}{c} \frac{1+i}{\sqrt{2}} \sqrt{\frac{\sigma_0}{\epsilon_0 \omega}} = \sqrt{\frac{\sigma_0 \omega}{2 \epsilon_0 c^2}} (1+i) = K_R + i K_I$$



$$\Rightarrow E = E_0 e^{i(kz - \omega t)} = e^{i(k_R z - \omega t)} e^{-k_I z}$$

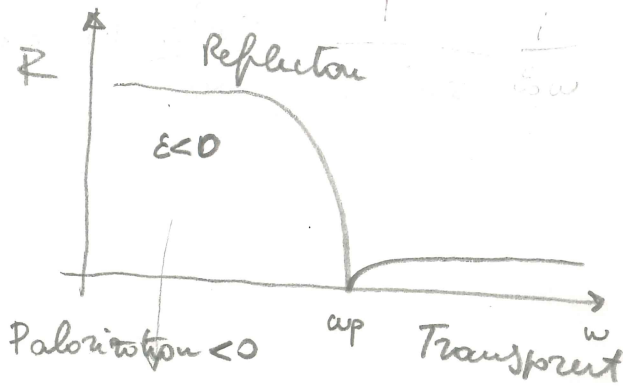


$$\delta = \frac{1}{K_I} = \sqrt{\frac{2 \epsilon_0 c^2}{\sigma_0 \omega}}$$

SKIN



$$\omega \gg \omega_p$$



$$\omega_p^2 = \frac{e^2 n}{m \epsilon_0}$$

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

REFLECTION

$E_r \sim -E_{incident} \Rightarrow$  Reflection

WIEDMANN-FRANZ

THERMAL CONDUCTIVITY in DRUDE

$\Rightarrow$  FLUX OF ENERGY PER UNIT TIME

(thermal conductivity given by electrons)

$$K = \frac{1}{3} C_V v_{THERM}^2 \quad \text{per unit volume}$$

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \left( \frac{3}{2} kT n \right) = \frac{3}{2} n k$$

$$v_{THERM}^2 = \frac{3kT}{m}$$

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

$$\frac{K}{\sigma} = \frac{\text{ther cond}}{\text{electr cond}} \approx T$$

$$= \frac{1}{3} \frac{3}{2} n k \frac{3kT}{m} \tau = \frac{3}{2} \left( \frac{k_B}{e} \right)^2 T \propto T \quad \text{SUCCESS}$$

Does not depend on material!

Big Luck

$$C_V \text{ real} \approx C_V \text{ class}$$

$$v_{\text{real}}^2 \approx v_{\text{class}}^2$$

NEEDS: PERIODICITY LATTICE  
• WAVE ELECTRONS  
• INTERACTION CRYSTAL  
give SEMI CONDUCTORS

NEED PERIODICITY  $\hat{x}$   
DIFFRACTION  $\hat{k}$

FAILURE

- INSULATORS, SEMICONDUCTORS
- HALL with volume  $> 1$
- THERMOELECTRIC EFFECT  $E = qVT$
- COLOR OF METALS

$$q = -\frac{C_V}{3me} = -\frac{nk_B}{2e}$$

too TOO LARGE

# MORE ABOUT WIEDMANN-FRANZ RULE

## THERMAL DIFFUSION

heat goes from hot to cold!

EMPIRIC

$$\bar{j}_q \propto -\nabla T \Leftrightarrow$$

↑ heat is prop to the difference of temperature

$$\bar{j}_q = -K \nabla T \quad \text{FOURIER}$$

↑ thermal conductivity.

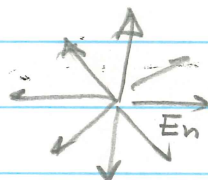
why?

classical approach to K: only electronic,  $e$  in eq with the position they are

ELECTRONS in 1D

$$\dot{j}_q = -K \frac{\partial T}{\partial x}$$

x



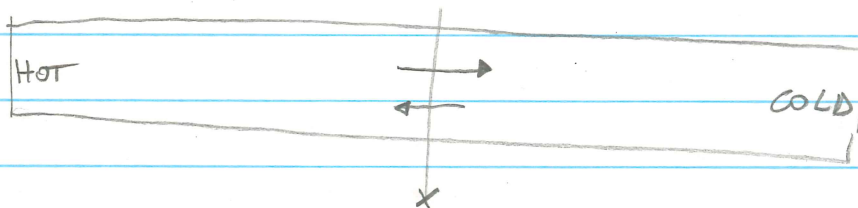
hot electron



cold electron

total  
hot + cold ⇒

1D BAR, CUT at point x



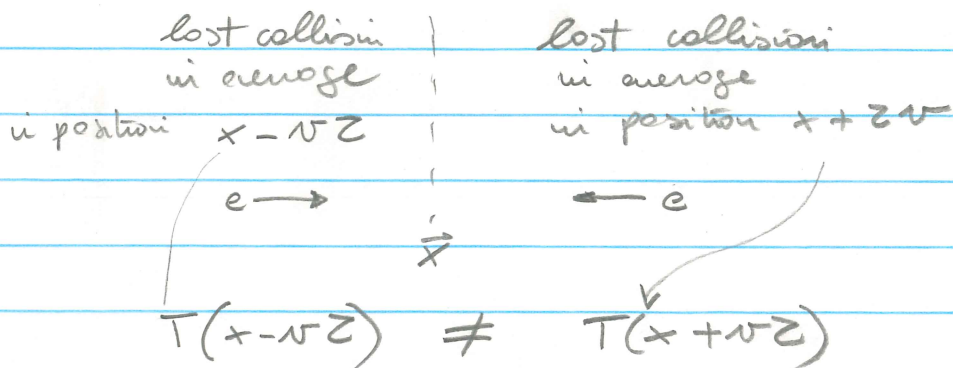
$$n(H \rightarrow C) = n(C \rightarrow H)$$

otherwise we would have accumulation of charge, then current, then ELECTRICAL energy, then mechanical work, then mechanical energy from heat without exchange with reservoir... violation thermodynamics

$\Rightarrow n(H \rightarrow C) = n(C \rightarrow H)$   
 but H brings more energy than C!!

$T \Rightarrow$  equilibrium, electron  $E(T)$  energy

electrons change energy & temp every collision,  $Z$  time in average



$\Rightarrow$

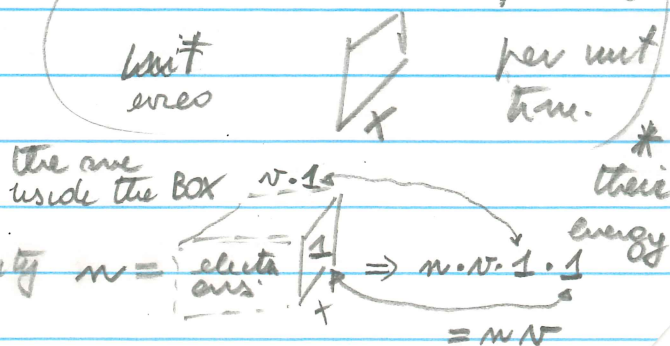
Energy of electron  $\rightarrow$

$$E[T(x - vZ)] \rightarrow + E[T(x + vZ)]$$

How many electrons?

but in 1D, once electrons collide, they  
 can go left or right  $\Rightarrow \frac{1}{2}$  probability.  
 and to balance  $J$ ?

$J = \text{FLUX of HEAT} = \frac{\# \text{ of electrons passing}}{\# \text{ area}} \text{ per unit time.}$



D10c



$$\Rightarrow J = \overrightarrow{J} + \overleftarrow{J}$$

$$\Rightarrow J = Nn \cdot \frac{1}{2} \overrightarrow{E(T(x-vz))} - Nn \frac{1}{2} \overleftarrow{E(T(x+vz))}$$

$\left| \begin{array}{c} 1 \\ \#e/V \end{array} \right| \quad \uparrow \text{left/right}$

$$= \frac{1}{2} n v \left[ E(T(x-vz)) - E(T(x+vz)) \right]$$

$\downarrow$   $Nz$  small

$$T(x-vz) = T(x) - \frac{\partial T}{\partial x} Nz$$

$$T(x+vz) = T(x) + \frac{\partial T}{\partial x} Nz$$

$$= \frac{1}{2} n v \left[ E \left[ T(x) - Nz \frac{\partial T}{\partial x} \right] - E \left[ T(x) + \frac{\partial T}{\partial x} Nz \right] \right]$$

$\underbrace{\quad}_{\text{small products}}$

$$= \left[ \cancel{E(T)} - Nz \frac{\partial T}{\partial x} \frac{\partial E}{\partial T} \right] - \left[ \cancel{E(T)} + Nz \frac{\partial T}{\partial x} \frac{\partial E}{\partial T} \right]$$

$$\Rightarrow J = -\frac{1}{2} n v^2 z \frac{\partial E}{\partial T} \frac{\partial T}{\partial x} \Rightarrow -\frac{1}{2} n v^2 z C_V \frac{\partial T}{\partial x}$$

$\frac{n \partial E}{\partial T} = \frac{N \partial E}{V \partial T} = \frac{1}{V} \frac{\partial E}{\partial T}$

$= C_V = \text{specific heat at constant volume per unit } V$

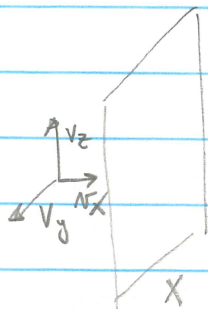
$J = \frac{1}{2} n v^2 z C_V \left( -\frac{\partial T}{\partial x} \right)$

Diod

$$J^{1D} = \frac{N^2}{2} C_V \left( -\frac{\partial T}{\partial x} \right)$$

in 3d

only  $v_x$  is important



$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$$

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

$$\frac{1}{2} m v^2 = \frac{3}{2} kT \quad \text{thermodynamic}$$

$$\Rightarrow J^{3D} = \underbrace{\frac{1}{3} N^2 C_V}_K \left( -\frac{\partial T}{\partial x} \right)$$

Pic

Table 1.1  
FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS<sup>a</sup>

ELEMENT	Z	$n$ ( $10^{22}/\text{cm}^3$ )	$r_s$ (Å)	$r_s/a_0$
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62
Cu	1	8.47	1.41	2.67
Ag	1	5.86	1.60	3.02
Au	1	5.90	1.59	3.01
Be	2	24.7	0.99	1.87
Mg	2	8.61	1.41	2.66
Ca	2	4.61	1.73	3.27
Sr	2	3.55	1.89	3.57
Ba	2	3.15	1.96	3.71
Nb	1	5.56	1.63	3.07
Fe	2	17.0	1.12	2.12
Mn ( $\alpha$ )	2	16.5	1.13	2.14
Zn	2	13.2	1.22	2.30
Cd	2	9.27	1.37	2.59
Hg (78 K)	2	8.65	1.40	2.65
Al	3	18.1	1.10	2.07
Ga	3	15.4	1.16	2.19
In	3	11.5	1.27	2.41
Tl	3	10.5	1.31	2.48
Sn	4	14.8	1.17	2.22
Pb	4	13.2	1.22	2.30
Bi	5	14.1	1.19	2.25
Sb	5	16.5	1.13	2.14

<sup>a</sup> At room temperature (about 300 K) and atmospheric pressure, unless otherwise noted. The radius  $r_s$  of the free electron sphere is defined in Eq. (1.2). We have arbitrarily selected one value of  $Z$  for those elements that display more than one chemical valence. The Drude model gives no theoretical basis for the choice. Values of  $n$  are based on data from R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Interscience, New York, 1963.

although the independent electron approximation is in many contexts surprisingly good, the free electron approximation must be abandoned if one is to arrive at even a qualitative understanding of much of metallic behavior.

2. Collisions in the Drude model, as in kinetic theory, are instantaneous events that abruptly alter the velocity of an electron. Drude attributed them to the electrons bouncing off the impenetrable ion cores (rather than to electron-electron collisions, the analogue of the predominant collision mechanism in an ordinary gas). We shall find later that electron-electron scattering is indeed one of the least important of the several scattering mechanisms in a metal, except under unusual conditions. However,



## 8 Chapter 1 The Drude Theory of Metals

This establishes the linear dependence of  $\mathbf{j}$  on  $\mathbf{E}$  and gives an estimate of the conductivity  $\sigma$  in terms of quantities that are all known except for the relaxation time  $\tau$ . We may therefore use (1.6) and the observed resistivities to estimate the size of the relaxation time:

$$\tau = \frac{m}{\rho n e^2}. \quad (1.7)$$

Table 1.2 gives the resistivities of several representative metals at several temperatures. Note the strong temperature dependence. At room temperature the resistivity is roughly linear in  $T$ , but it falls away much more steeply as low temperatures are

Table 1.2  
ELECTRICAL RESISTIVITIES OF SELECTED ELEMENTS<sup>a</sup>

ELEMENT	77 K	273 K	373 K	$\frac{(\rho/T)_{373 \text{ K}}}{(\rho/T)_{273 \text{ K}}}$
Li	1.04	8.55	12.4	1.06
Na	0.8	4.2	Melted	
K	1.38	6.1	Melted	
Rb	2.2	11.0	Melted	
Cs	4.5	18.8	Melted	
Cu	0.2	1.56	2.24	1.05
Ag	0.3	1.51	2.13	1.03
Au	0.5	2.04	2.84	1.02
Be		2.8	5.3	1.39
Mg	0.62	3.9	5.6	1.05
Ca		3.43	5.0	1.07
Sr	7	23		
Ba	17	60		
Nb	3.0	15.2	19.2	0.92
Fe	0.66	8.9	14.7	1.21
Zn	1.1	5.5	7.8	1.04
Cd	1.6	6.8		
Hg	5.8	Melted	Melted	
Al	0.3	2.45	3.55	1.06
Ga	2.75	13.6	Melted	
In	1.8	8.0	12.1	1.11
Tl	3.7	15	22.8	1.11
Sn	2.1	10.6	15.8	1.09
Pb	4.7	19.0	27.0	1.04
Bi	35	107	156	1.07
Sb	8	39	59	1.11

<sup>a</sup> Resistivities in microhm centimeters are given at 77 K (the boiling point of liquid nitrogen at atmospheric pressure), 273 K, and 373 K. The last column gives the ratio of  $\rho/T$  at 373 K and 273 K to display the approximate linear temperature dependence of the resistivity near room temperature.

Source: G. W. C. Kaye and T. H. Laby, *Table of Physical and Chemical Constants*, Longmans Green, London, 1966.

Table 1.3  
**DRUDE RELAXATION TIMES IN UNITS OF  $10^{-14}$  SECOND<sup>a</sup>**

ELEMENT	77 K	273 K	373 K
Li	7.3	0.88	0.61
Na	17	3.2	
K	18	4.1	
Rb	14	2.8	
Cs	8.6	2.1	
Cu	21	2.7	1.9
Ag	20	4.0	2.8
Au	12	3.0	2.1
Be		0.51	0.27
Mg	6.7	1.1	0.74
Ca		2.2	1.5
Sr	1.4	0.44	
Ba	0.66	0.19	
Nb	2.1	0.42	0.33
Fe	3.2	0.24	0.14
Zn	2.4	0.49	0.34
Cd	2.4	0.56	
Hg	0.71		
Al	6.5	0.80	0.55
Ga	0.84	0.17	
In	1.7	0.38	0.25
Tl	0.91	0.22	0.15
Sn	1.1	0.23	0.15
Pb	0.57	0.14	0.099
Bi	0.072	0.023	0.016
Sb	0.27	0.055	0.036

<sup>a</sup> Relaxation times are calculated from the data in Tables 1.1 and 1.2, and Eq. (1.8). The slight temperature dependence of  $n$  is ignored.

is spatially uniform but time-dependent. Both of these cases are most simply dealt with by the following observation:

At any time  $t$  the average electronic velocity  $\mathbf{v}$  is just  $\mathbf{p}(t)/m$ , where  $\mathbf{p}$  is the total momentum per electron. Hence the current density is

$$\mathbf{j} = - \frac{ne\mathbf{p}(t)}{m}. \quad (1.9)$$

Given that the momentum per electron is  $\mathbf{p}(t)$  at time  $t$ , let us calculate the momentum per electron  $\mathbf{p}(t + dt)$  an infinitesimal time  $dt$  later. An electron taken at random at time  $t$  will have a collision before time  $t + dt$ , with probability  $dt/\tau$ , and will therefore survive to time  $t + dt$  without suffering a collision with probability  $1 - dt/\tau$ . If it experiences no collision, however, it simply evolves under the influence of the force  $\mathbf{f}(t)$  (due to the spatially uniform electric and/or magnetic fields) and will therefore



Table 1.4  
HALL COEFFICIENTS OF SELECTED ELEMENTS  
IN MODERATE TO HIGH FIELDS<sup>a</sup>

METAL	VALENCE	$-1/R_H n e c$
Li	1	0.8
Na	1	1.2
K	1	1.1
Rb	1	1.0
Cs	1	0.9
Cu	1	1.5
Ag	1	1.3
Au	1	1.5
Be	2	-0.2
Mg	2	-0.4
In	3	-0.3
Al	3	-0.3

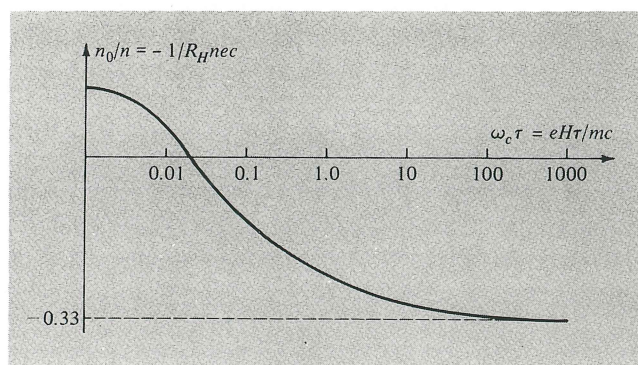
<sup>a</sup> These are roughly the limiting values assumed by  $R_H$  as the field becomes very large (of order  $10^4$  G), and the temperature very low, in carefully prepared specimens. The data are quoted in the form  $n_0/n$ , where  $n_0$  is the density for which the Drude form (1.21) agrees with the measured  $R_H$ :  $n_0 = -1/R_H e c$ . Evidently the alkali metals obey the Drude result reasonably well, the noble metals (Cu, Ag, Au) less well, and the remaining entries, not at all.

of a free electron in the magnetic field  $H$ . Thus  $\omega_c \tau$  will be small if electrons can complete only a small part of a revolution between collisions, and large if they can complete many revolutions. Alternatively, when  $\omega_c \tau$  is small the magnetic field deforms the electronic orbits only slightly, but when  $\omega_c \tau$  is comparable to unity or larger, the effect of the magnetic field on the electronic orbits is quite drastic. A useful numerical evaluation of the cyclotron frequency is

$$\nu_c (10^9 \text{ hertz}) = 2.80 \times H (\text{kilogauss}), \quad \omega_c = 2\pi\nu_c. \quad (1.22)$$

Figure 1.4

The quantity  $n_0/n = -1/R_H n e c$ , for aluminum, as a function of  $\omega_c \tau$ . The free electron density  $n$  is based on a nominal chemical valence of 3. The high field value suggests only one carrier per primitive cell, with a positive charge. (From R. Lück, *Phys. Stat. Sol.* **18**, 49 (1966).)



then, to a first approximation, Eqs. (1.35) and (1.29) give

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}, \quad (1.37)$$

where  $\omega_p$ , known as the plasma frequency, is given by

$$\omega_p^2 = \frac{4\pi ne^2}{m}. \quad (1.38)$$

When  $\epsilon$  is real and negative ( $\omega < \omega_p$ ) the solutions to (1.34) decay exponentially in space; i.e., no radiation can propagate. However, when  $\epsilon$  is positive ( $\omega > \omega_p$ ) the solutions to (1.34) become oscillatory, radiation can propagate, and the metal should become transparent. This conclusion is only valid, of course, if our high-frequency assumption (1.36) is satisfied in the neighborhood of  $\omega = \omega_p$ . If we express  $\tau$  in terms of the resistivity through Eq. (1.8), then we can use the definition (1.38) of the plasma frequency to compute that

$$\omega_p \tau = 1.6 \times 10^2 \left( \frac{r_s}{a_0} \right)^{3/2} \left( \frac{1}{\rho_\mu} \right). \quad (1.39)$$

Since the resistivity in microhm centimeters,  $\rho_\mu$ , is of the order of unity or less, and since  $r_s/a_0$  is in the range from 2 to 6, the high frequency condition (1.36) will be well satisfied at the plasma frequency.

The alkali metals have, in fact, been observed to become transparent in the ultraviolet. A numerical evaluation of (1.38) gives the frequency at which transparency should set in as

$$\nu_p = \frac{\omega_p}{2\pi} = 11.4 \times \left( \frac{r_s}{a_0} \right)^{-3/2} \times 10^{15} \text{ Hz} \quad (1.40)$$

or

$$\lambda_p = \frac{c}{\nu_p} = 0.26 \left( \frac{r_s}{a_0} \right)^{3/2} \times 10^3 \text{ Å}. \quad \Rightarrow r_s \approx \left( \frac{\lambda}{0.26} \right)^{2/3} \quad (1.41)$$

In Table 1.5 we list the threshold wavelengths calculated from (1.41), along with the

Table 1.5

**OBSERVED AND THEORETICAL WAVELENGTHS BELOW WHICH THE ALKALI METALS BECOME TRANSPARENT**

ELEMENT	THEORETICAL <sup>a</sup> $\lambda$ ( $10^3$ Å)	OBSERVED $\lambda$ ( $10^3$ Å)
Li	1.5	2.0
Na	2.0	2.1
K	2.8	3.1
Rb	3.1	3.6
Cs	3.5	4.4

<sup>a</sup> From Eq. (1.41).

Source: M. Born and E. Wolf, *Principles of Optics*, Pergamon, New York, 1964.

(m\*/m)  
See notes on p. 48

$\sqrt{m^*/m}$   
1.52  
1.14



Table 1.6

EXPERIMENTAL THERMAL CONDUCTIVITIES AND LORENZ NUMBERS  
OF SELECTED METALS

ELEMENT	273 K		373 K	
	$\kappa$ (watt-cm/K)	$\kappa/\sigma T$ (watt-ohm/K <sup>2</sup> )	$\kappa$ (watt-cm/K)	$\kappa/\sigma T$ (watt-ohm/K <sup>2</sup> )
Li	0.71	$2.22 \times 10^{-8}$	0.73	$2.43 \times 10^{-8}$
Na	1.38	2.12		
K	1.0	2.23		
Rb	0.6	2.42		
Cu	3.85	2.20	3.82	2.29
Ag	4.18	2.31	4.17	2.38
Au	3.1	2.32	3.1	2.36
Be	2.3	2.36	1.7	2.42
Mg	1.5	2.14	1.5	2.25
Nb	0.52	2.90	0.54	2.78
Fe	0.80	2.61	0.73	2.88
Zn	1.13	2.28	1.1	2.30
Cd	1.0	2.49	1.0	
Al	2.38	2.14	2.30	2.19
In	0.88	2.58	0.80	2.60
Tl	0.5	2.75	0.45	2.75
Sn	0.64	2.48	0.60	2.54
Pb	0.38	2.64	0.35	2.53
Bi	0.09	3.53	0.08	3.35
Sb	0.18	2.57	0.17	2.69

Source: G. W. C. Kaye and T. H. Laby, *Table of Physical and Chemical Constants*, Longmans Green, London, 1966.

As a concrete example let us examine a case where the temperature drop is uniform in the positive  $x$ -direction. In the steady state the thermal current will also flow in the  $x$ -direction and have a magnitude  $j^q = -\kappa dT/dx$ . To calculate the thermal current we note (assumption 4, page 6) that after each collision an electron emerges with a speed appropriate to the local temperature; the hotter the place of the collision, the more energetic the emerging electron. Consequently, even though the mean electronic velocity at a point may vanish (in contrast to the case when an electric current flows) electrons arriving at the point from the high-temperature side will have higher energies than those arriving from the low-temperature side leading to a net flow of thermal energy toward the low-temperature side (Figure 1.6).

To extract a quantitative estimate of the thermal conductivity from this picture, consider first an oversimplified "one-dimensional" model, in which the electrons can only move along the  $x$ -axis, so that at a point  $x$  half the electrons come from the high-temperature side of  $x$ , and half from the low. If  $\varepsilon(T)$  is the thermal energy per electron in a metal in equilibrium at temperature  $T$ , then an electron whose last collision was at  $x'$  will, on the average, have a thermal energy  $\varepsilon(T[x'])$ . The electrons arriving at  $x$  from the high-temperature side will, on the average, have had their last collision at