Applications of statistical physics to selected solid-state physics phenomena for metals

“similar” models for thermal and electrical conductivity for metals, on basis of free electron gas, treated with Maxwell-Boltzmann statistics – i.e. as if it were an ideal gas

Lorenz numbers, a fortuitous result, don’t be fooled, the physics (Maxwell-Boltzmann statistics) behind it is not applicable as we estimated earlier

But Fermi-Dirac statistics gets us the right physics

Table 12.5 Thermal Conductivity, *K*, and Electrical Conductivity, σ, of Selected Substances at Room Temperature

Substance	K in $W \cdot m^{-1} K^{-1}$	σ in $(\Omega \cdot m)^{-1}$
Silver	427	62×10^6
Copper	390	59×10^6
Gold	314	41×10^6
Aluminum	210	35×10^6
Iron	63	10×10^6
Steel	50	1.4×10^6
Nichrome	14	0.9×10^6
Quartz	13	
NaCl	7.0	$<10^{-4}$

Metals have high conductivities for both electricity and heat. To explain both the high conductivities and the trend in this table we need to have a model for both thermal and electrical conductivity, that model should be able to explain empirical observations, i.e. Ohm’s law, thermal conductivity, Wiedemann-Franz law,

Table 12.7 Experimental Lorentz Numbers $K/\sigma T$ in Units of $10^{-8}\ W \cdot \Omega/K^2$*

Metal	273 K	300K	373 K
Ag	2.31	2.3	2.37
Au	2.35	2.55	2.40
Cd	2.42		2.43
Cu	2.23	2.2	2.33
Ir	2.49		2.49
Mo	2.61		2.79
Pb	2.47		2.56
Pt	2.51		2.60
Sn	2.52		2.49
W	3.04		3.20
Zn	2.31		2.33

Wiedemann and Franz Law, 1853, ratio K/sT = Lorenz number = constant $\approx 2.4\ 10^{-8}$ W O K $^{-2}$

independent of the metal considered !! So both phenomena should be based on similar physical idea !!!

Classical from Drude (early 1900s) theory of free electron gas

$$\frac{K}{sT} = \frac{3k_B^2}{2e^2} \approx 1.12 \cdot 10^{-8} W\Omega K^{-2}$$

Too small by factor 2, seems not too bad ???

To explain the high conductivities and the trend we need to have a model for both thermal and electrical conductivity, that model should be able to explain

Ohm's law, empirical for many metals and insulators, ohmic solids

Conductivity , resistivity is its reciprocal value

J = s E current density is proportional to applied electric field

R = $^{U}/_{I}$ for a wire R = $^{? l}/_{A}$

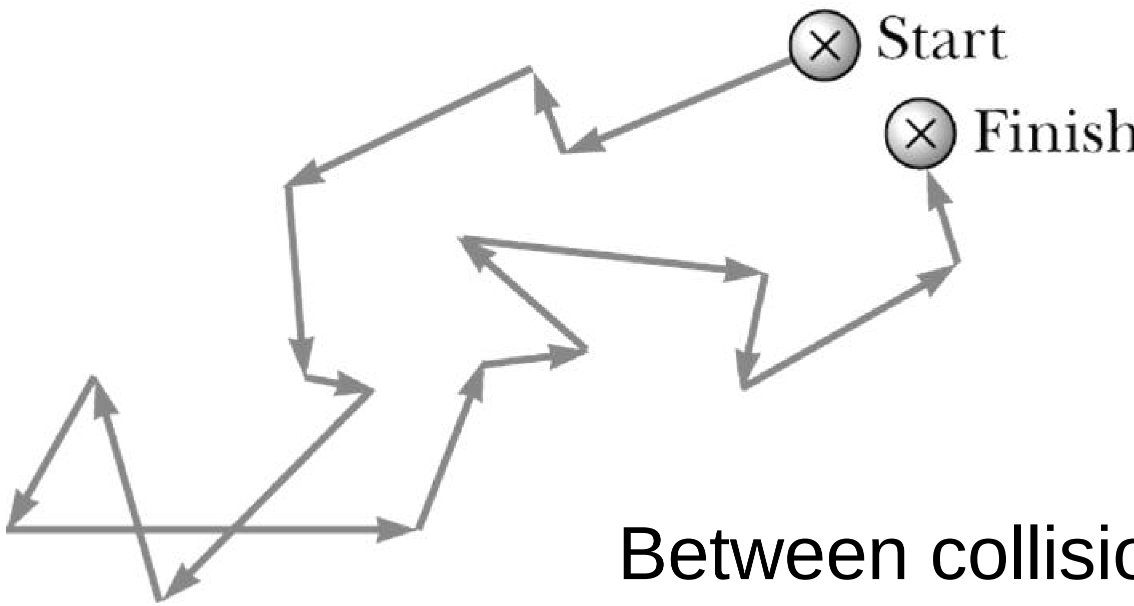
J: current density A/m^{2}

s: electrical conductivity O^{-1} m^{-1}, reciprocal value of electrical resistivity

E: electric field V/m

Also definition of s: a single constant that does depend on the material and temperature but not on applied electric field represents connection between I and U

Gas of classical charged particles, electrons, moves through immobile heavy ions arranged in a lattice, v_{rms} from equipartition theorem (which is of course derived from Boltzmann statistics)



(a)

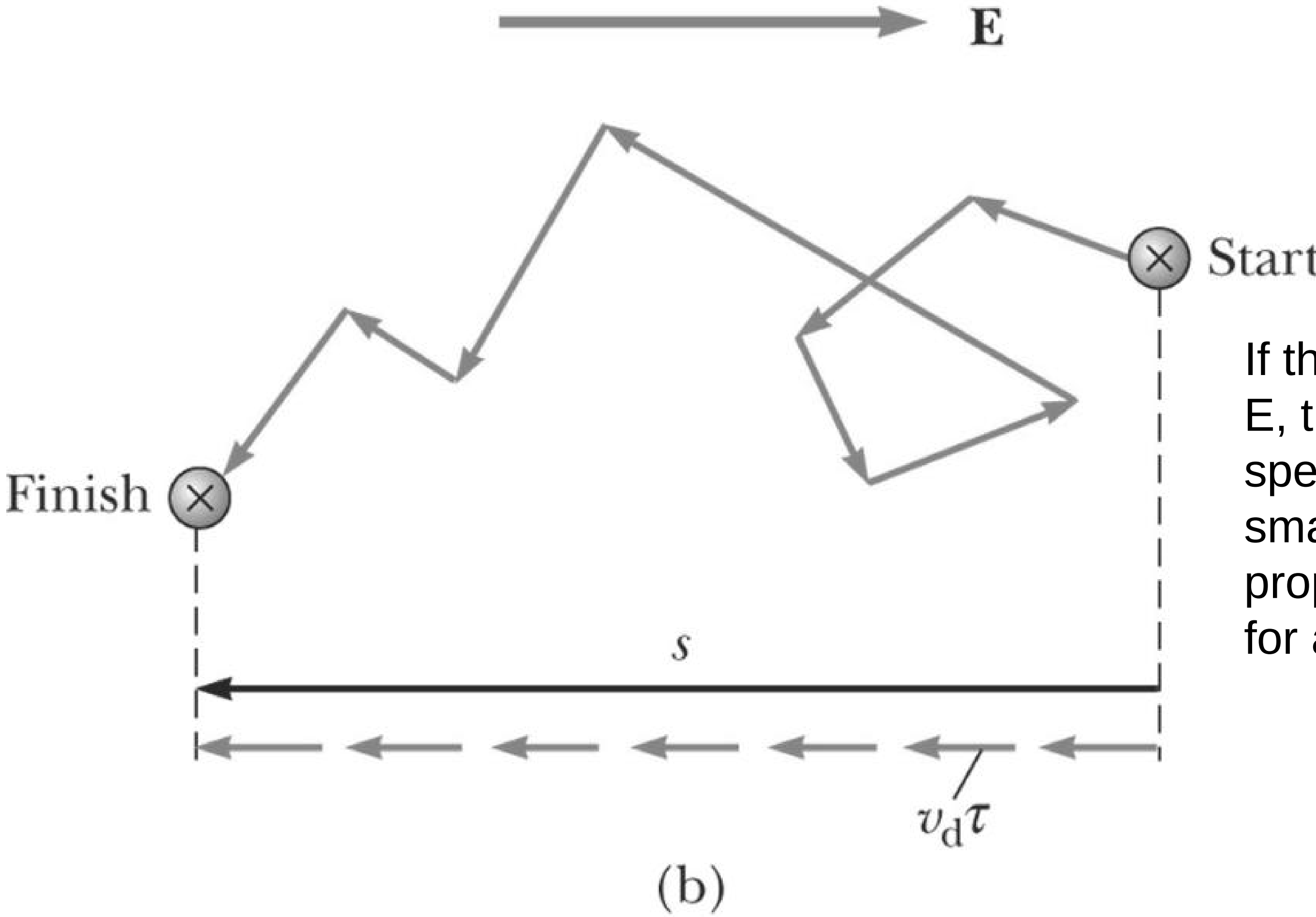
$$\frac{1}{2} m_e \bar{v}^2 = \frac{3}{2} k_B T$$

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3 k_B T}{m_e}}$$

Between collisions, there is a mean free path length: $L = v_{rms}\, t$

and a mean free time t (tau)

Figure 12.11 (a) Random successive displacements of an electron in a metal without an applied electric field.



If there is an electric field E, there is also a drift speed v_d (10^8 times smaller than v_{rms}) but proportional to E, equal for all electrons

$$v_d = \frac{eEt}{m_e}$$

Figure 12.11 (b) A combination of random displacements and displacements produced by an external electric field. The net effect of the electric field is to add together multiple displacements of length $v_d\,\tau$ opposite the field direction. For purposes of illustration, this figure greatly exaggerates the size of v_d compared with v_{rms}.

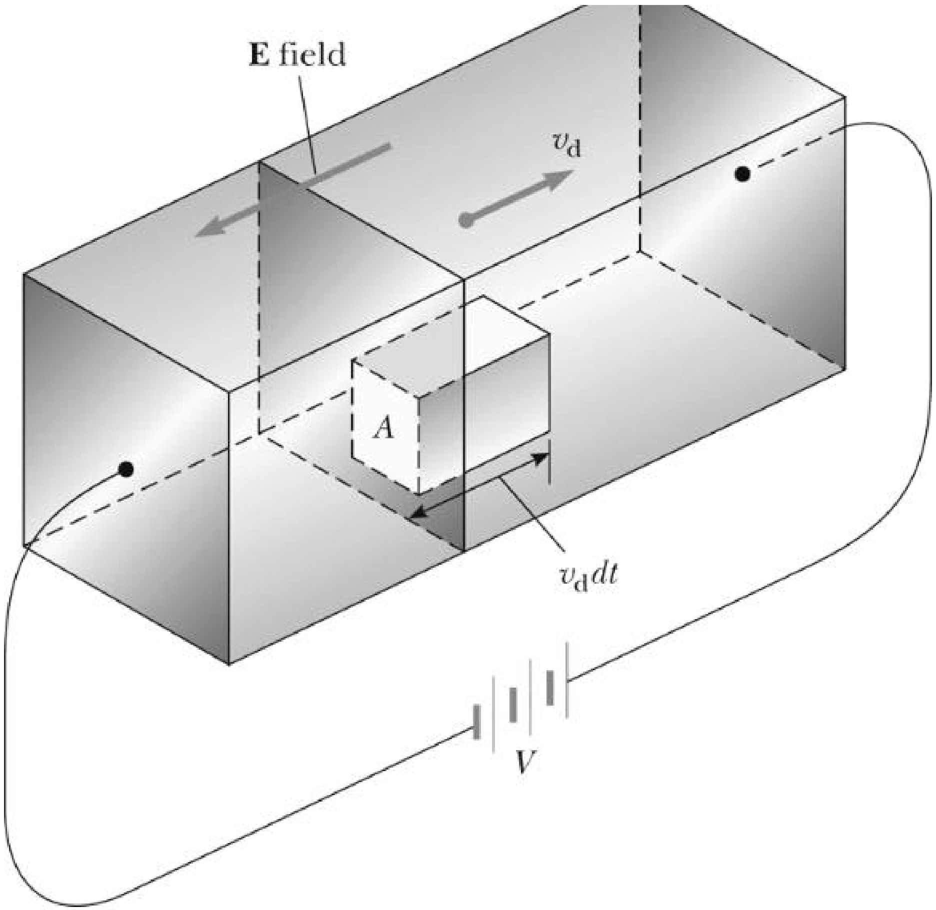


Figure 12.12 The connection between current density, *J*, and drift velocity, v_d. The charge that passes through *A* in time *dt* is the charge contained in the small parallelepiped, $neAv_d\,dt$.

$$J = \frac{neAv_d dt}{Adt} = nev_d$$

Substituting for v_d

$$J = \frac{ne^2 t}{m_e} E$$

So the correct form of Ohm's law is predicted by the Drude model !!

$$s = \frac{ne^2 t}{m_e}$$

With mean free time t = L/v_{rms}

$$s = \frac{ne^2 L}{m_e v_{rms}}$$

With v_{rms} according to Maxwell-Boltzmann statistics

$$s = \frac{ne^2 L}{\sqrt{3k_B T m_e}}$$

Proof of the pudding: L should be on the order of magnitude of the inter-atomic distances, e.g. for Cu 0.26 nm

$$s = \frac{8.49 \cdot 10^{22} cm^{-3} (6.02 \cdot 10^{-19} C)^2 \cdot 0.26 nm}{\sqrt{3 \cdot 1.381 \cdot 10^{-23} JK^{-1} \cdot 300K \cdot 9.109 \cdot 10^{-31} kg}}$$

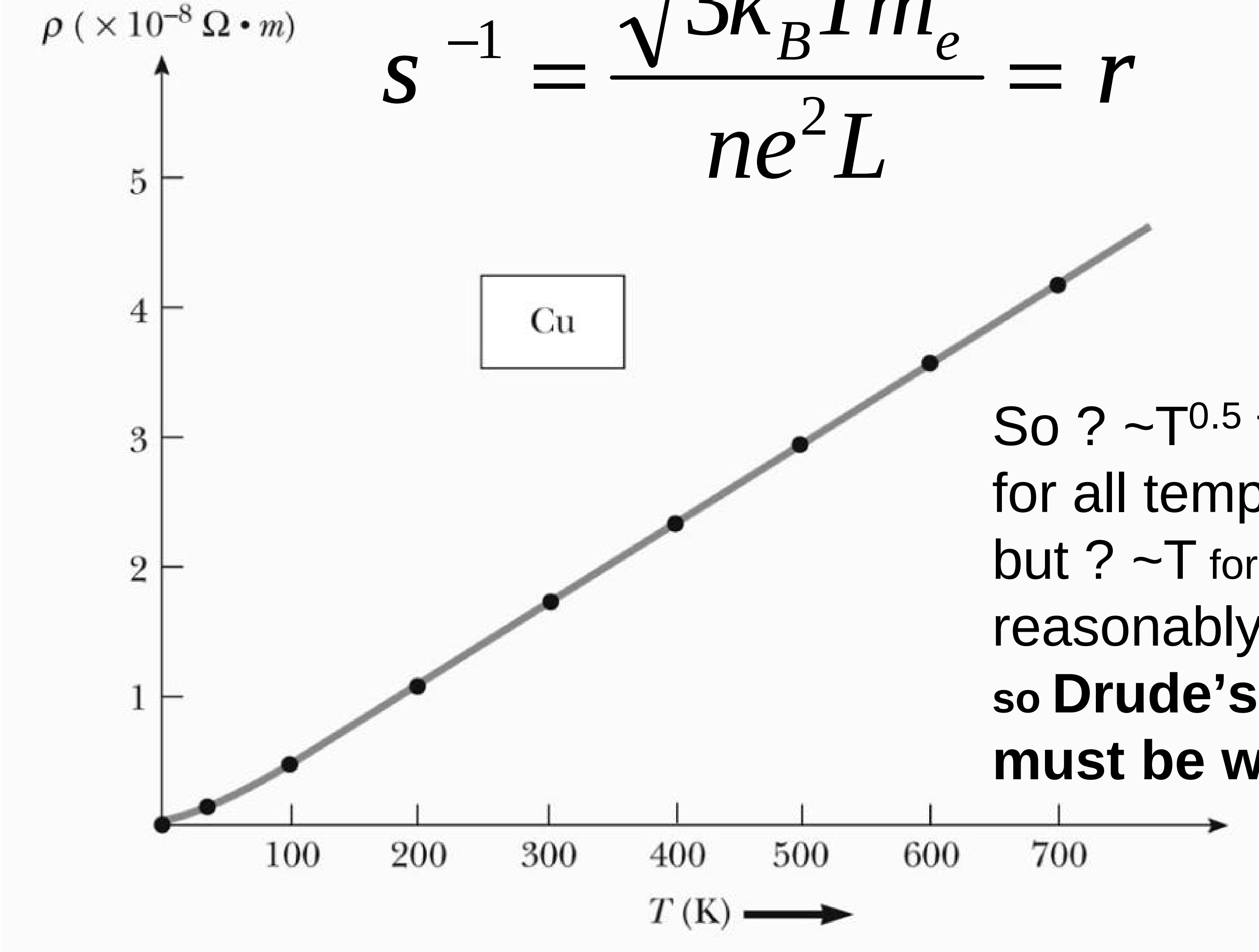
$s_{Cu,\ 300\ K}$ = 5.3 10^6 $(Om)^{-1}$ compare with experimental value 59 10^6 $(Om)^{-1}$, something must we wrong with the classical L and v_{rms}

Result of Drude theory one order of magnitude too small, so L must be much larger, this is because the electrons are not classical particles, but wavicals, don't scatter like particles, in addition, the v_{rms} from Boltzmann-Maxwell is one order of magnitude smaller than the v_{fermi} following from Fermi-Dirac statistics

Table 12.6 Electrical Conductivity of Metals at 300 K

Substance	Measured σ in $(\Omega \cdot m)^{-1}$
Copper	59×10^6
Aluminum	35×10^6
Sodium	22×10^6
Iron	10×10^6
Mercury	1.0×10^6

$$s^{-1} = \frac{\sqrt{3k_B T m_e}}{ne^2 L} = r$$



So ? ~$T^{0.5}$ theory for all temperatures, but ? ~T for reasonably high T , so **Drude's theory must be wrong !**

Figure 12.13 The resistivity of pure copper as a function of temperature.

Phenomenological similarity conduction of electricity and conduction of heat, so free electron gas should also be the key to understanding thermal conductivity

$$J = -s \frac{\Delta V}{\Delta x}$$

Ohm's law with Voltage gradient,

$$\frac{\Delta Q}{A \Delta t} = -K \frac{\Delta T}{\Delta x}$$

thermal energy conducted through area A in time interval ?t is proportional to temperature gradient

$$K = \frac{1}{3} C_V v_{rms} L$$

Using Maxwell-Boltzmann statistics, equipartion theorem, formulae of C_v for ideal gas = $^3/_2$ k_B n

$$K = \frac{k_B n v_{rms} L}{2}$$

Classical expression for K

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3k_BT}{m_e}}$$

For 300 K and Cu

$$v_{rms} = \sqrt{\frac{3\cdot 1.381\cdot 10^{-23}JK^{-1}300K}{9.109\cdot 10^{-31}kg}}$$

Lets continue

$$K = \frac{k_B n v_{rms} L}{2}$$

$$K = \frac{1.381\cdot 10^{-23}JK^{-1}\cdot 8.48\cdot 10^{22}cm^{-3}\cdot 1.1681\cdot 10^{5}ms^{-1}\cdot 0.26nm}{2}$$

$$K = \frac{1.381\cdot 10^{-23}JK^{-1}\cdot 8.48\cdot 10^{28}m^{-3}\cdot 1.1681\cdot 10^{5}ms^{-1}\cdot 0.26\cdot 10^{-9}m}{2}$$

$$K = 17.78\frac{Ws}{Kms}$$

Experimental value for Cu at (300 K) = 390 $Wm^{-1}K^{-1}$, again one order of magnitude too small, actually roughly 20 times too small

$$s = \frac{ne^2 L}{m_e v_{rms}}$$

This was also one order of magnitude too small,

$$K/s = \frac{k_B n v_{rms} L m_e v_{mrs}}{2ne^2 L} = \frac{k_B m_e v_{mrs}^2}{2e^2}$$

With Maxwell-Boltzmann

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3k_B T}{m_e}}$$

$$K/s = \frac{3k_B^2}{2e^2} T$$

Lorenz number classical K/s

$$\frac{K}{sT} = \frac{3k_B^2}{2e^2} \approx 1.12 \cdot 10^{-8} W\Omega K^{-2}$$

Wrong only by a factor of about 2, Such an agreement is called fortuitous

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replace $L_{for\_a\_particle}$ with $L_{for\_a\_wavial}$ and v_{rms} with v_{fermi},

$$s_{classical} = \frac{ne^2 L_{for\_a\_particle}}{m_e v_{rms}} \longrightarrow s_{quantum} = \frac{ne^2 L_{for\_a\_wavical}}{m_e v_{fermi}}$$

$$L_{for\_a\_wavical} = \frac{m_e v_{fermi} s_{quantum}}{ne^2}$$

$$v_{rms} = \sqrt{\bar{v}}^2 = \sqrt{\frac{3k_B T}{m_e}} \longrightarrow v_{fermi} == \sqrt{\frac{2E_F}{m_e}}$$

For Cu (at 300 K), E_F = 7.05 eV , Fermi energies have only small temperature dependency, frequently neglected

$$v_{fermi} == \sqrt{\frac{2E_F}{m_e}} \qquad v_{fermi,copper,300K} = \sqrt{\frac{2 \cdot 7.05 \cdot 1.602 \cdot 10^{-9} J}{9.109 \cdot 10^{-31} kg}} = 1.57 \cdot 10^6 ms^{-1}$$

one order of magnitude larger than classical v_{rms}

for ideal gas

$$L_{for\_a\_wavical} = \frac{m_e v_{fermi} s_{quantum}}{ne^2}$$

$$L_{for\_a\_wavical\_cooper} =$$

$$\frac{9.109 \cdot 10^{-31} kg \cdot 1.57 \cdot 10^6 ms^{-1} \cdot 5.9 \cdot 10^7 \Omega^{-1} m^{-1}}{8.49 \cdot 10^{28} m^{-3} (1.602 \cdot 10^{-19} C)^2}$$

$$L_{for\_a\_wavical\_cooper} = 39nm$$

two orders of magnitude larger than classical result for particle

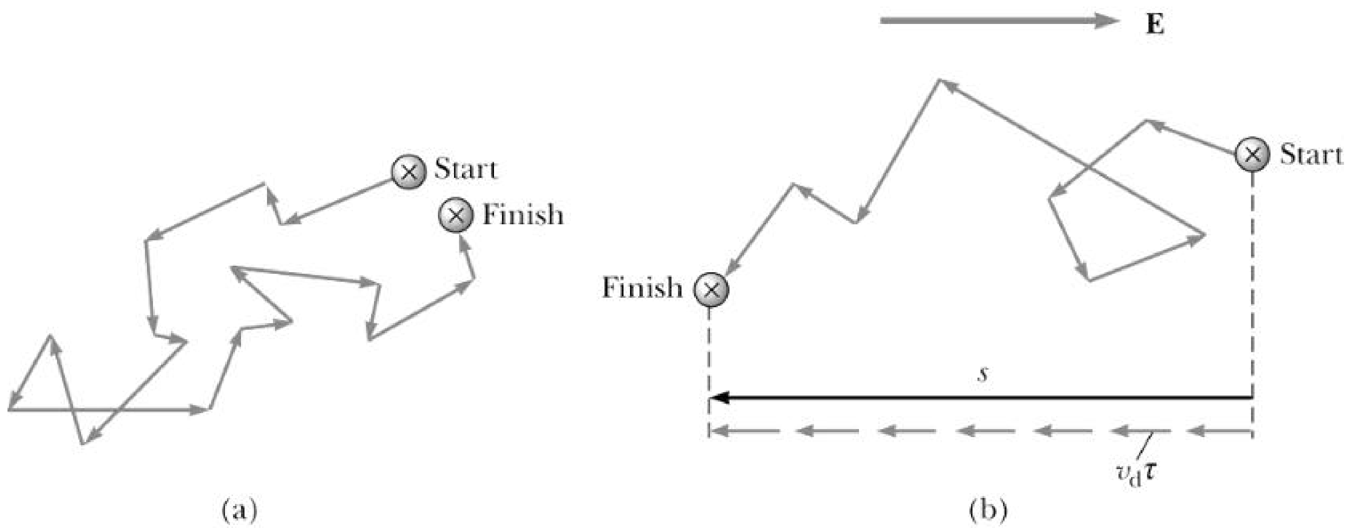
$$s_{classical} = \frac{ne^2 L_{for\_a\_particle}}{m_e v_{rms}}$$

So here something two orders of two magnitude too small (L) gets divided by something one order of magnitude too small (v_{rms}),

i.e. the result for electrical conductivity must be one order of magnitude too small, which is observed !!

But $L_{\text{for particle}}$ is quite reasonable, so replace V_{rms} with V_{fermi} and the conductivity gets one order of magnitude larger, which is close to the experimental observation, so that one keeps the Drude theory of electrical conductivity as a classical approximation for room temperature

- in effect, neither the high v_{rms} of 10^5 m/s of the electrons derived from the equipartion theorem or the 10 times higher Fermi speed do not contribute directly to conducting a current since each electrons goes in any directions with an equal likelihood and this speeds averages out to zero charge transport in the absence of E



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$$K_{classical} = \frac{k_B n v_{rms} L_{classical}}{2}$$

V_{rms} was too small by one order of magnitude, $L_{classical}$ was too small by two orders of magnitude, the classical calculations should give a result 3 orders of magnitude smaller than the observation (which is of course well described by a quantum statistical treatment)

so there must be something fundamentally wrong with our ideas on how to calculate K, **any idea ???**

Wait a minute, K has something to do with the heat capacity that we derived from the equipartion theorem

$$K_{classical} = \frac{1}{3} C_{V\_for\_ideal\_gas} v_{rms} L_{for\_particle}$$

We had the result earlier that the contribution of the electron gas is only about one hundredth of what one would expect from an ideal gas, $C_{v \text{ for ideal gas}}$ is actually two orders or magnitude larger than for a real electron gas, so that are two orders of magnitude in excess, with the product of vrms and $L_{\text{for particle}}$ three orders of magnitude too small, we should calculate classically thermal conductivities that are one order of magnitude too small, which is observed !!!

$$K/s = \frac{k_B n v_{rms} L m_e v_{mrs}}{2ne^2 L} = \frac{k_B m_e v_{mrs}^2}{2e^2}$$

$$\frac{K}{sT} = \frac{3k_B^2}{2e^2} \approx 1.12 \cdot 10^{-8} W\Omega K^{-2}$$

fortunately L cancelled, but v_{rms} gets squared, we are indeed very very very fortuitous to get the right order of magnitude for the Lorenz number from a classical treatment

(one order of magnitude too small squared is about two orders of magnitude too small, but this is “compensated” by assuming that the heat capacity of the free electron gas can be treated classically which in turn results in a value that is by itself two order of magnitude too large- two “missing” orders of magnitude times two “excessive orders of magnitudes levels about out

$$K_{fermi} = \frac{p^{2}}{3}\left(\frac{k_B^2 T}{m_e v_{fermi}}\right) n L_{for\_a\_wavical}$$

$$s_{quantum} = \frac{ne^2 L_{for\_a\_wavical}}{m_e v_{fermi}}$$

That gives for the Lorenz number in a quantum treatment

$$\frac{K}{sT} = \frac{p^{2} k_B^2}{3e^2} = 2.45 \cdot 10^{-8} W\Omega K^{-2}$$

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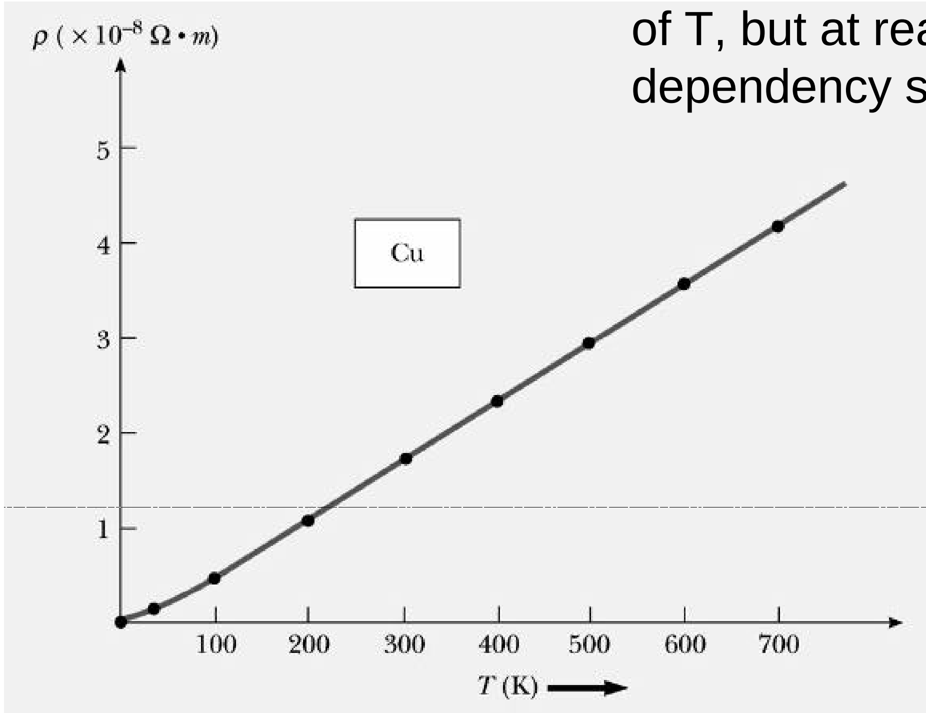
Back to the problem of the temperature dependency of resistivity

Drude's theory predicted a dependency on square root of T, but at reasonably high temperatures, the dependency seems to be linear



This is due to Debye's phonons (lattice vibrations), which are bosons and need to be treated by Bose-Einstein statistics, electrons scatter on phonons, so the more phonons, the more scattering

Number of phonons proportional to Bose-Einstein distribution function

$$n_{phonons} \propto \frac{1}{e^{\hbar w / k_B T} - 1}$$

Which becomes for reasonably large T

$$n_{phonons} \propto \frac{k_B T}{\hbar w}$$

At low temperatures, there are hardly any phonons, scattering of electrons is due to impurity atoms and lattice defects, if it were not for them, there would not be any resistance to the flow of electricity at zero temperature

Matthiessen’s rule, the resistivity of a metal can be written as

$$s = s_{\text{lattice defects}} + s_{\text{lattice vibrations}}$$