

DPMS: Chemistry and Technology of Materials

Lecture: Theory of free electrons in metals

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Outline

- Classical (Drude) theory of metals
 - successes and limitations of the classical model
- Sommerfeld theory of metals
 - quantum statistics and semi-classical model

Properties of metals

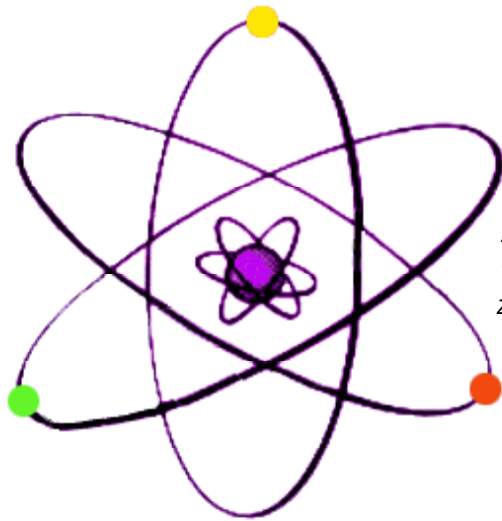
- All metals share common properties
 - excellent electrical conductors
 - excellent thermal conductors
 - shiny when polished
- All due to the free electrons of the metallic bond



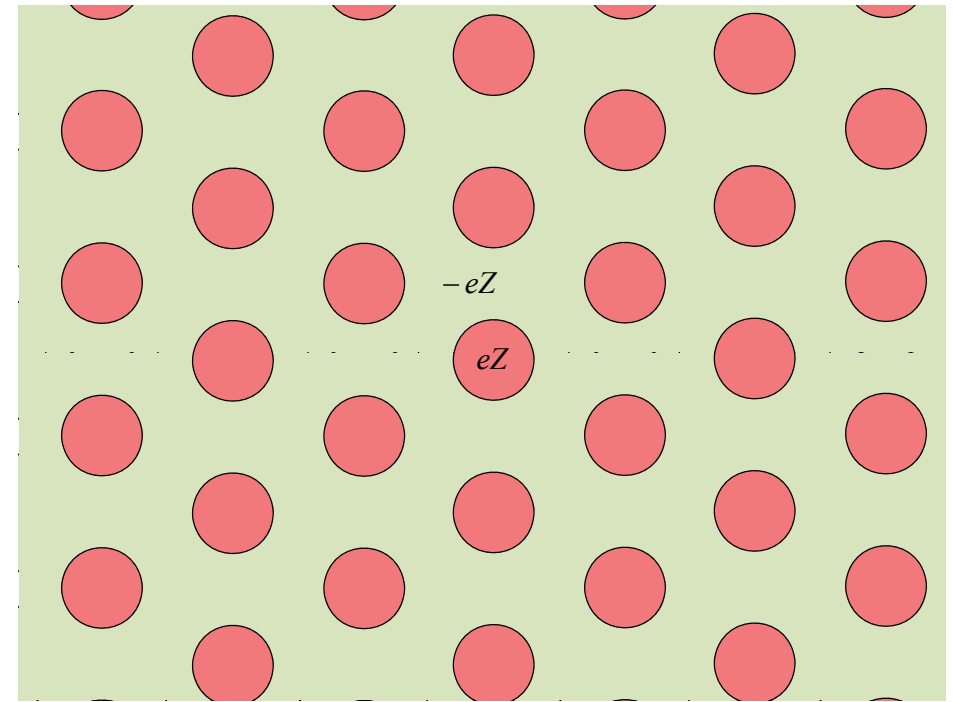
Metals in the periodic table

Periodic Table of the Elements

1	IA																2	O																		
1	H																2	He																		
2	IIA																VIIA		Ne																	
3	Na		Mg		IIIB - VIIIB										VII		IB		IIB		Al		Si		P		S		Cl		Ar					
4	K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr	
5	Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe	
6	Cs		Ba		*La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn	
7	Fr		Ra		+Ac		Rf		Ha		Sg		Ns		Hs		Mt		110		111		112		113											
* Lanthanide Series		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu								
+ Actinide Series		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr								



Z_o = atomic number
 e = electron charge
 Z = valence electrons



Electron density

- We need to know how many electrons n we have per volume ($n=e/cm^3$) in a metal
 - we have Z electrons per atom (valence electrons e /atom)
 - we have N_A atoms per mol (Avogadro number 6.023×10^{23} atoms/mol)
 - we have A grams per mol (atomic weight g/mol)
 - we have ρ_m grams per unit volume (mass density g/cm^3)

$$Z \cdot N_A \left(\frac{el \text{ at}}{at \text{ mol}} = \frac{el}{mol} \right)$$

$$\frac{\rho_m}{A} \left(\frac{g}{cm^3} \cdot \frac{mol}{g} = \frac{mol}{cm^3} \right)$$

$$n = \frac{\rho_m \cdot Z \cdot N_A}{A} \left(\frac{el}{cm^3} \right)$$

- We define the effective volume per electron

$$\frac{V}{N} = \frac{1}{n}$$

- and an effective radius r_s

$$\frac{4\pi r_s^3}{3} = \frac{1}{n} \Rightarrow r_s = \left(\frac{3}{4\pi n} \right)^{1/3}$$

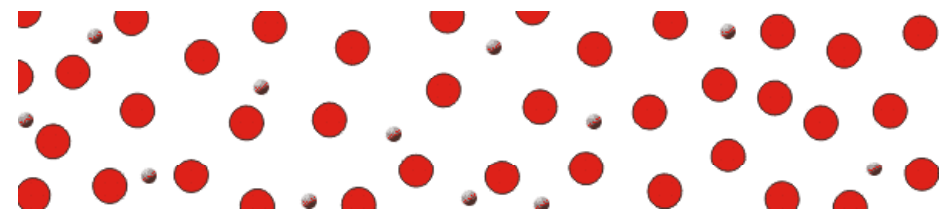
FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS*

ELEMENT	Z	n ($10^{22}/cm^3$)	$r_s(\text{\AA})$	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 (α)	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

Bohr radius $a_0 = \hbar^2 / me^2 = 0.529 \times 10^{-8}$ cm

Electron motion in the Drude model

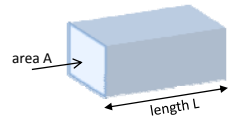
- In the Drude model the electron scatter from the ionic cores
 - however, from what we know now, is this picture correct?



- Not really, we now know that:
 - electrons do not scatter from the ionic cores
 - they only scatter on impurities, defects, phonons, etc
- In a more general picture, we define the relaxation time τ
 - τ is the average time between scattering events
 - τ depends on temperature, defects, impurities, etc.
 - we will use τ as a parameter
 - typical order of magnitude for τ 10^{-14} sec

DC electrical conductivity of a metal

- We start with Ohm's law $V = R \cdot I$



$$\left. \begin{aligned} V &= E \cdot L \\ R &= \rho \frac{L}{A} \\ I &= J \cdot A \end{aligned} \right\} E = \rho \cdot J$$

generally
 $E = \rho \cdot J$

E electric field (V/cm)
 J current density (A/cm²)
 ρ electric resistivity (Ωcm)

- the current density depends on the electron flow $J = -nev$ (v the average velocity)
- the acceleration from the field $a = -eE/m$
- the average velocity is acceleration times average time between collisions $v = -eE\tau/m$
- and so the current density $J = \left(\frac{ne^2\tau}{m}\right)E$

- Definition of electric conductivity

$$J = \sigma E \quad \sigma = \frac{1}{\rho} = \frac{ne^2\tau}{m} \quad (1/\Omega\text{cm or Siemens/cm})$$

Electron relaxation times

- We can now estimate τ from DC resistivity measurements

$$\tau = \frac{m}{ne^2\rho} \quad \tau = \left(\frac{0.22}{\rho[\mu\Omega\text{cm}]}\right)\left(\frac{r_s}{a_0}\right)^3 \times 10^{-14} \text{ sec}$$

ELECTRICAL RESISTIVITIES OF SELECTED ELEMENTS* $\mu\Omega\text{cm}$

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

DRUDE RELAXATION TIMES IN UNITS OF 10^{-14} SECOND*

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

Electron relaxation length

- What is the average distance l traveled by electrons?

$$l = v_0\tau \quad v_0 \text{ average electronic speed}$$

- but what do we use for v_0 ?

- Classical statistical mechanics, equipartition of energy:

- at thermal equilibrium in temperature T , each degree of freedom carries energy of $\frac{1}{2}k_B T$
- a free electron has 3 degrees of freedom (motion in the 3D space)

$$\frac{1}{2}mv_0^2 = \frac{3}{2}k_B T \quad \text{the Boltzmann constant } k_B = 1.38 \times 10^{-23} \text{ m}^2\text{kg s}^{-2}\text{K}^{-1}$$

$$\text{for } T = 300 \text{ K, and } m = 9.11 \times 10^{-31} \text{ kg, we find } v_0 = \sqrt{3k_B T / m} \approx 10^7 \text{ cm/s}$$

- and relaxation length

$$l = v_0\tau \approx 10^7 \left(\frac{\text{cm}}{\text{s}}\right) \times 10^{-14} \text{ s} = 10^{-7} \text{ cm} = 1 \text{ \AA}$$

l is smaller than the interatomic distances!!

- However, this is wrong! We know:

- relaxation lengths are much larger
- average velocities do not depend on temperature

- Conclusion: we should not use classical statistics!

AC electrical conductivity of a metal

- The electric field, and thus the driving force, oscillate with time

$$\text{the average electron momentum at time } t \quad \mathbf{p}(t) = m\mathbf{v}(t)$$

- scattering events occur on the average every τ seconds
- after a scattering event, the electron emerges with random velocity

- to first order, at time $t+dt$ the momentum will change by

$$\begin{aligned} -\left(\frac{dt}{\tau}\right)\mathbf{p}(t) & \quad \text{due to electron scattering} \\ -e\mathbf{E}(t)dt & \quad \text{due to the electric force} \end{aligned}$$

$$\text{so the evolution equation } \frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{\tau} - e\mathbf{E}(t)$$

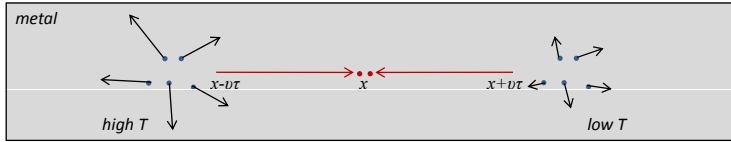
- Time dependent solution

$$\text{for harmonic fields } \mathbf{E}(t) = \Re(\mathbf{E}(\omega)e^{-i\omega t}) \quad \mathbf{p}(t) = \Re(\mathbf{p}(\omega)e^{-i\omega t})$$

$$\text{evolution equation becomes } -i\omega\mathbf{p}(\omega) = -\mathbf{p}(\omega)/\tau - e\mathbf{E}(\omega) \quad \mathbf{p}(\omega) = \frac{-e\mathbf{E}(\omega)\tau}{1-i\omega\tau}$$

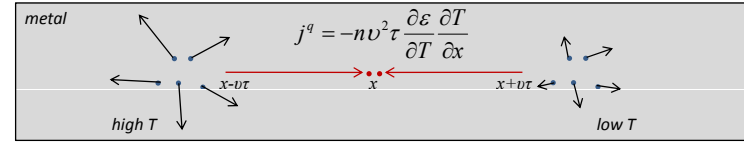
$$\mathbf{J}(\omega) = -ne\mathbf{p}(\omega)/m \quad \mathbf{J}(\omega) = \frac{(ne^2\tau/m)}{1-i\omega\tau}\mathbf{E}(\omega) \quad \sigma(\omega) = \frac{\sigma(0)}{1-i\omega\tau}$$

Thermal conductivity of a metal



- Electron motion and scattering cause conduction of heat
 - after any scattering event, an electron emerges with kinetic energy $\varepsilon(T_x)$
 - $n/2$ electrons move from left to right with kinetic energy $\varepsilon(T_{x-v\tau})$ in classical statistics
 - $n/2$ electrons move from right to left with kinetic energy $\varepsilon(T_{x+v\tau})$ $\varepsilon(T) = \frac{3}{2}k_B T$
 - the rate of electrons arriving at x is $n\nu/2$
 - so the total heat flux $j^q = \frac{1}{2}n\nu[\varepsilon(T_{x-v\tau}) - \varepsilon(T_{x+v\tau})]$
 - for $v\tau$ small compared to the temperature variation scale $[\varepsilon(T_{x-v\tau}) - \varepsilon(T_{x+v\tau})] \cong -\frac{\partial\varepsilon}{\partial T} \frac{\partial T}{\partial x} 2v\tau$
 - and so $j^q = -n\nu^2\tau \frac{\partial\varepsilon}{\partial T} \frac{\partial T}{\partial x}$

Thermal conductivity of a metal



- but the change in energy with temperature is the thermal capacitance $n \frac{\partial\varepsilon}{\partial T} = c_v$
- also, in 3D the average velocity along direction x is $v_x^2 + v_y^2 + v_z^2 = v^2 \Rightarrow v_x^2 = \frac{1}{3}v^2$
- so $j^q = -\frac{1}{3}v^2 c_v \nabla T$ or $j^q = -\kappa \nabla T$
- where we defined the thermal conductivity $\kappa = \frac{1}{3}v^2 c_v$ (W/cm-K)
- but what do we use for thermal capacitance?
- Again from classical statistical mechanics $\varepsilon(T) = \frac{3}{2}k_B T$
 - $c_v = n \frac{\partial\varepsilon}{\partial T} = \frac{3}{2}nk_B$ $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$
 - and so $\kappa = \frac{3}{2} \frac{nk_B^2 \tau}{m} T$

Wiedemann-Franz law

- The ratio between thermal and electrical conductivities in metals is linear to temperature

- thermal conductivity $\kappa = \frac{3}{2} \frac{nk_B^2 \tau}{m} T$

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

- Lorentz number (independent of τ)

$$\frac{\kappa}{\sigma T} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 = 1.11 \times 10^{-8} \text{ W}\Omega/\text{K}^2$$

EXPERIMENTAL THERMAL CONDUCTIVITIES AND LORENTZ NUMBERS OF SELECTED METALS

ELEMENT	273 K		373 K	
	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K ²)	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K ²)
Li	0.71	2.22×10^{-8}	0.73	2.43×10^{-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	2.19
Al	2.38	2.14	2.30	2.60
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

- Excellent agreement with experiment!

- but are we finished??

- What we know from experiment:

- average velocities are actually much larger (by ~10)
- average heat capacity is actually much smaller (by ~100)

$\kappa = \frac{1}{3} v^2 c_v$ in our classical treatment, these two cancel each other!

- Once again, we should not use classical statistics!!

Classical electron statistics

- Classical: Maxwell-Boltzmann distribution

- the probability to find an electron with velocity \mathbf{u} when the temperature is T

$$f_{MB}(\mathbf{u}) = C_{MB} n e^{-\varepsilon/k_B T}$$

$$\varepsilon = \frac{1}{2} m v^2$$

$$k_B 300K = 0.025 \text{ eV} = 4 \times 10^{-21} \text{ J}$$

$$C_{MB} = \left(\frac{m}{2\pi k_B T} \right)^{3/2}$$

normalization constant

in our simple metal, electrons have only kinetic energy

thermal energy at room temperature

- The distribution satisfies the charge conservation

$$\int_0^\infty f_{MB}(\mathbf{u}) d\mathbf{u} = n$$

- how do we treat $d\mathbf{u}$?

- it is a differential over speed and solid angle. In isotropic case (all angles are the same):

$$d\mathbf{u} = 4\pi v^2 dv$$

- so the number of electrons

$$4\pi \int_0^\infty f_{MB}(v) v^2 dv = n$$

Quantum electron statistics

(Sommerfeld theory of metals)

- Quantum: Fermi-Dirac distribution
 - the probability to find an electron with velocity \mathbf{v} when the temperature is T

$$f_{FD}(\mathbf{v}) = C_{FD} \frac{1}{e^{\frac{\epsilon - \mu}{k_B T}} + 1}$$

$$\epsilon = \frac{1}{2} m v^2$$

in our simple metal, electrons have only kinetic energy

μ

chemical potential

$$C_{FD} = \frac{(m/\hbar)^3}{4\pi^3}$$

normalization constant

- the total number of electrons is found

$$4\pi \int_0^\infty f_{FD}(v) v^2 dv = n$$

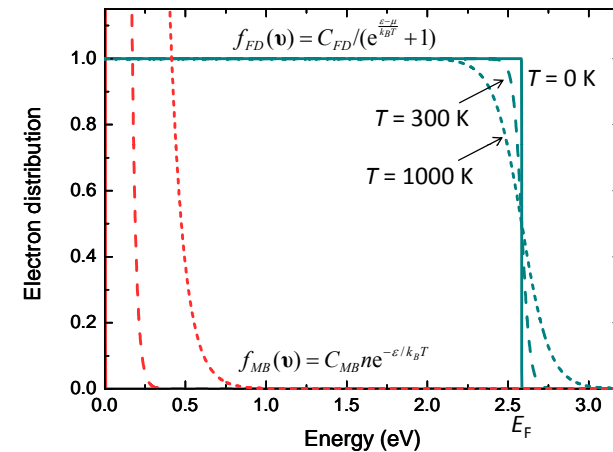
when n is known, we use this to find the chemical potential μ

- The Fermi-Dirac distribution comes from the Pauli exclusion principle:

- two electrons of opposite spin can occupy one level
- no two electrons can have identical states

Comparison of electron statistics

- The quantum distribution is very different from the classical due to Pauli exclusion



Ground state of the free electron gas

- But what are the states to be filled by the electron gas?
 - is there an equation satisfied by the electrons?

- Schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$$

Laplacian

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- as any wave solution, we need a boundary condition
- assume a hypothetical cube of side L , and volume $V=L^3$
- the electron wavefunctions are periodic at the cube edges (the cube periodically repeats itself)

$$\begin{aligned} \psi(x+L, y, z) &= \psi(x, y, z) \\ \psi(x, y+L, z) &= \psi(x, y, z) \\ \psi(x, y, z+L) &= \psi(x, y, z) \end{aligned}$$

solution

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\mathbf{r}}$$

$$\epsilon(\mathbf{k}) = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

normalization condition

$$\int |\psi(\mathbf{r})|^2 d\mathbf{r} = 1$$

- The electron gas properties should be independent of the choice of L
- Sure, but what is \mathbf{k} ?

Ground state of the free electron gas

- The proper \mathbf{k} values are found from the boundary conditions

$$\begin{aligned} \psi(x+L, y, z) &= \psi(x, y, z) \\ \psi(x, y+L, z) &= \psi(x, y, z) \\ \psi(x, y, z+L) &= \psi(x, y, z) \end{aligned} \quad \psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\mathbf{r}}$$

- the exponent is a vector product

$$\mathbf{k} \cdot \mathbf{r} = k_x x + k_y y + k_z z$$

- and so the boundary condition becomes

$$\begin{aligned} e^{i(k_x(x+L)+k_y y+k_z z)} &= e^{i k_x(x+L)} e^{i k_y y} e^{i k_z z} = e^{i k_x x} e^{i k_y y} e^{i k_z z} \\ e^{i k_x x} e^{i k_y(y+L)} e^{i k_z z} &= e^{i k_x x} e^{i k_y y} e^{i k_z z} \\ e^{i k_x x} e^{i k_y y} e^{i k_z(z+L)} &= e^{i k_x x} e^{i k_y y} e^{i k_z z} \end{aligned}$$

- with solution

$$\left. \begin{aligned} e^{i k_x L} &= 1 \\ e^{i k_y L} &= 1 \\ e^{i k_z L} &= 1 \end{aligned} \right\} \Rightarrow \left. \begin{aligned} k_x L &= n_x 2\pi \\ k_y L &= n_y 2\pi \\ k_z L &= n_z 2\pi \end{aligned} \right\} \Rightarrow \left. \begin{aligned} k_x &= n_x (2\pi / L) \\ k_y &= n_y (2\pi / L) \\ k_z &= n_z (2\pi / L) \end{aligned} \right\}$$

- The different wavefunctions correspond to different combinations of n_x, n_y, n_z

Ground state of the free electron gas

We populate the ground state

- two electrons (spin up and down) per energy level

$$(n_x, n_y, n_z) = (0, 0, 0)$$

$$(n_x, n_y, n_z) = (1, 0, 0)$$

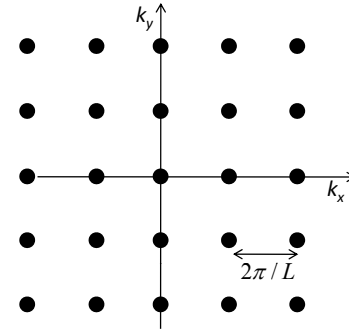
$$(n_x, n_y, n_z) = (-1, 0, 0)$$

$$(n_x, n_y, n_z) = (0, 1, 0)$$

$$(n_x, n_y, n_z) = (0, -1, 0)$$

$$(n_x, n_y, n_z) = (1, 1, 0)$$

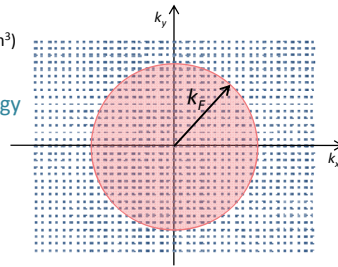
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- the periodicity of the k-point lattice is $2\pi/L$
- number of k-points is equal to number of electrons ($\sim 10^{22}$ el/cm³)

The number of electrons determines the highest energy

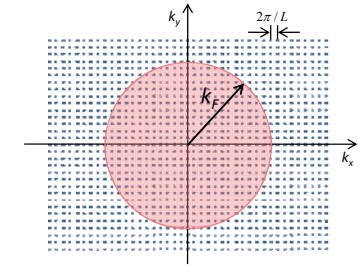
- highest k-point: *Fermi wavevector* k_F
- highest energy: *Fermi energy* $\varepsilon_F = \hbar^2 k_F^2 / 2m$
- highest velocity: *Fermi velocity* $v_F = \hbar k_F / m$



Number of states for the free electron gas

Number of k-points that fit within the Fermi sphere (in k-space)

- volume within Fermi surface $\frac{4\pi k_F^3}{3}$
 - volume occupied by each k-point $(2\pi/L)^3$
 - number of points (each k-point $\times 2$ due to spin)
- $$N = 2 \frac{4\pi k_F^3}{3} \frac{L^3}{8\pi^3} \Rightarrow \frac{N}{V} = n = \frac{k_F^3}{3\pi^2}$$



But n is known for each metal

$$n = \frac{\rho_m \cdot Z \cdot N_A}{A} \quad \text{and} \quad \frac{4\pi n^{3/3}}{3} = \frac{1}{n} \Rightarrow r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$$

- so we define

Fermi wavevector

$$k_F = \frac{3.63}{r_s / a_0} \text{ \AA}^{-1}$$

Fermi energy

$$\varepsilon_F = \frac{50.1}{(r_s / a_0)^2} \text{ eV}$$

Fermi velocity

$$v_F = \frac{4.20}{r_s / a_0} \times 10^8 \text{ cm/s}$$

Fermi energies etc for various metals

ELEMENT	r_s/a_0	ε_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	$1.12 \times 10^8 \text{ cm}^{-1}$	$1.29 \times 10^8 \text{ cm/sec}$
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
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

Summing over the electron states

The number of states

$$N = 2 \sum_{\mathbf{k}} f(\mathbf{k}) = 2 \frac{V}{8\pi^3} \sum_{\mathbf{k}} f(\mathbf{k}) \Delta \mathbf{k} \xrightarrow{V \rightarrow \infty} \frac{V}{4\pi^3} \int f(\mathbf{k}) d\mathbf{k}$$

- number density of states $n = \frac{N}{V} = \int \frac{d\mathbf{k}}{4\pi^3} f(\mathbf{k})$

- for isotropic system, i.e. all directions are equivalent (as the free electron case) $d\mathbf{k} = 4\pi k^2 dk$

We can evaluate any quantity

- total energy $u = \frac{E}{V} = \int \frac{d\mathbf{k}}{4\pi^3} \varepsilon(\mathbf{k}) f(\mathbf{k})$

- at zero temperature $\frac{E}{V} = \int_0^{k_F} \frac{4\pi k^2}{4\pi^3} \frac{\hbar^2 k^2}{2m} dk = \frac{1}{10\pi^2} \frac{\hbar^2 k_F^5}{m} = \frac{1}{5\pi^2} \varepsilon_F k_F^3$

Average energy per electron

- use $\frac{N}{V} = \frac{k_F^3}{3\pi^2}$ to get $\frac{E}{N} = \frac{3}{5} \varepsilon_F$

Compressibility of electron gas

- Pressure exerted on electron gas: $P = -\left(\frac{\partial E}{\partial V}\right)_N$

– energy of the electron gas $\frac{E}{N} = \frac{3}{5}\varepsilon_F = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m}$

– Fermi wavevector $n = \frac{N}{V} = \frac{k_F^3}{3\pi^2} \Rightarrow k_F^2 = (3\pi^2 N)^{2/3} V^{-2/3}$

– and so $E = N \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2 N)^{2/3} V^{-2/3} = \text{const} \cdot V^{-2/3}$

– so pressure is $P = -\left(\frac{\partial E}{\partial V}\right)_N = \frac{2}{3} \frac{E}{V}$

- Bulk modulus: $B = -V \frac{\partial P}{\partial V}$

– but $P = \text{const} \cdot V^{-5/3} \Rightarrow -V(\partial P / \partial V) = (5/3)P$

– so bulk modulus is $B = \frac{10}{9} \frac{E}{V} = \left(\frac{6.13}{r_s/a_0}\right)^5 \times 10^{10} \text{ dynes/cm}^2$

BULK MODULI IN 10^{10} DYNES/CM² FOR SOME TYPICAL METALS*

METAL	FREE ELECTRON B	MEASURED B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76.0

Synopsis of the free electron Fermi-Dirac distribution

- The FD distribution for free electrons depends only on energy

– the energy is isotropic with \mathbf{k} $\varepsilon(\mathbf{k}) = \hbar^2 k^2 / 2m$

– Fermi function $f(\mathbf{k}) = f(\varepsilon(\mathbf{k})) = f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}$

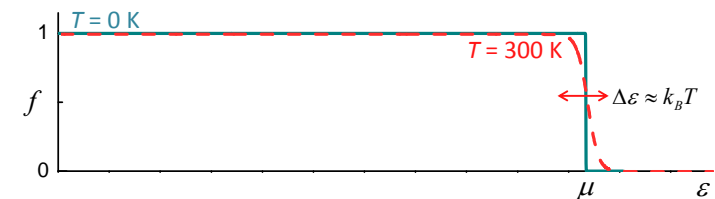
- The distribution is the probability for a energy level to be occupied

– for $T=0$

$$f(\varepsilon) = 1 \text{ for } \varepsilon < \varepsilon_F$$

$$f(\varepsilon) = 0 \text{ for } \varepsilon > \varepsilon_F$$

– for $T=0$ the chemical potential is the Fermi energy: $\mu = \varepsilon_F$ (but even at room temperature $\mu \approx \varepsilon_F$)



Application of the Fermi-Dirac distribution

- The number of electrons is determined by summing up the distribution

$$n = \int \frac{d\mathbf{k}}{4\pi^3} f(\varepsilon)$$

– but for isotropic distribution (free electrons) $d\mathbf{k} = 4\pi k^2 dk$

$$\int \frac{4\pi k^2 dk}{4\pi^3} f(\varepsilon) = \frac{1}{\pi^2} \int k^2 f(\varepsilon) dk$$

– use the free electron energy

$$\varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k^2 = \frac{2m\varepsilon}{\hbar^2} \Rightarrow 2kdk = \frac{2m}{\hbar^2} d\varepsilon \Rightarrow dk = \frac{1}{k} \frac{m}{\hbar^2} d\varepsilon \Rightarrow dk = \sqrt{\frac{\hbar^2}{2m\varepsilon}} \frac{m}{\hbar^2} d\varepsilon$$

$$n = \frac{1}{\pi^2} \int \frac{2m\varepsilon}{\hbar^2} \frac{m}{\hbar^2} \sqrt{\frac{\hbar^2}{2m\varepsilon}} f(\varepsilon) d\varepsilon$$

- Define the free electron density of states $g(\varepsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}}$

– number of electrons $n = \int g(\varepsilon) f(\varepsilon) d\varepsilon$

– total energy density of electrons $u = \int \varepsilon \cdot g(\varepsilon) f(\varepsilon) d\varepsilon$

important relationships at the Fermi level

$$g(\varepsilon_F) = \frac{mk_F}{\hbar^2 \pi^2} = \frac{3}{2} \frac{n}{\varepsilon_F}$$

Thermal capacitance of free electron gas

- Energy change per change in temperature $c_v = \left(\frac{\partial u}{\partial T}\right)_n$

– we approximate

$$c_v = \frac{\Delta u}{\Delta T}$$



– the number of electrons that change their energy is approximately $\sim g(\varepsilon_F) k_B T$

– and their energy change is approximately $\sim k_B T$

– so for an order of magnitude estimate $\Delta u \sim g(\varepsilon_F) (k_B T)^2$

- Our estimate for the thermal capacitance $c_v = \frac{\Delta u}{\Delta T} \sim 2g(\varepsilon_F) k_B^2 T = 3 \frac{n}{\varepsilon_F} k_B^2 T = 3nk_B \frac{k_B T}{\varepsilon_F}$

– The correct value is $c_v = \frac{\pi^2}{2} nk_B \frac{k_B T}{\varepsilon_F}$

Thermal capacitance of free electron gas

- Classical thermal capacitance

$$c_v = \frac{3}{2}nk_B$$

- Quantum thermal capacitance

$$c_v = \frac{\pi^2}{2}nk_B \frac{k_B T}{\epsilon_F}$$

- a linear dependence on temperature
- in reality there is also the ionic contribution, so

$$c_v = \gamma_{el}T + \gamma_{ion}T^3$$

$$\gamma_{el} = 0.169Z \left(\frac{r_s}{a_0} \right)^2 \times 10^{-4} \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$$

ELEMENT	FREE ELECTRON γ (in $10^{-4} \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-2}$)	MEASURED γ
Li	1.8	4.2
Na	2.6	3.5
K	4.0	4.7
Rb	4.6	5.8
Cs	5.3	7.7
Cu	1.2	1.6
Ag	1.5	1.6
Au	1.5	1.6
Be	1.2	0.5
Mg	2.4	3.2
Ca	3.6	6.5
Sr	4.3	8.7
Ba	4.7	6.5
Nb	1.6	20
Fe	1.5	12
Mn	1.5	40
Zn	1.8	1.4
Cd	2.3	1.7
Hg	2.4	5.0
Al	2.2	3.0
Ga	2.4	1.5
In	2.9	4.3
Tl	3.1	3.5
Sn	3.3	4.4
Pb	3.6	7.0
Bi	4.3	0.2
Sb	3.9	1.5

Other quantities in the Sommerfeld theory

- Mean free path $l = v_F \tau$ or $l = \frac{(r_s/a_0)^2}{\rho[\mu\Omega\text{cm}]} \times 92 \text{ \AA}$

- with typical values of $\sim 100 \text{ \AA}$
- electrons do not scatter on the ions!

- Thermal conductivity $\kappa = \frac{1}{3} \tau v_F^2 c_v$

$$\text{using } \frac{1}{2} m v_F^2 = \epsilon_F \quad c_v = \frac{\pi^2}{2} n k_B \frac{k_B T}{\epsilon_F}$$

$$\text{we find } \kappa = \frac{\pi^2 \tau n k_B^2}{3 m} T$$

- Lorentz number

$$\frac{\kappa}{\sigma T} = \frac{\frac{\pi^2 \tau n k_B^2}{3 m} T}{\frac{ne^2 \tau}{m} T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$$

EXPERIMENTAL THERMAL CONDUCTIVITIES AND LORENTZ NUMBERS OF SELECTED METALS

ELEMENT	273 K		373 K	
	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K ²)	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K ²)
Li	0.71	2.22×10^{-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

Summary

- Classical (Drude) theory of metals

- electrons scatter with relaxation time τ
- Classical statistical distribution of velocities
- Quantities that include the velocity or c_v are not accurate:
 - velocities are underestimated by an order of magnitude
 - thermal capacity is overestimated by 2 orders of magnitude

- Sommerfeld theory of metals

- Pauli exclusion principle, velocities follow a Fermi-Dirac distribution
- Definition of Fermi quantities: energy, velocity etc of the last occupied state
- Quantities with velocity and c_v are now accurate
 - velocity to be used is the Fermi velocity
 - only the electrons close to the Fermi energy can be thermally excited