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

Outline

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

Metals in the periodic table
Electron density

- We need to know how many electrons \( n \) we have per volume (\( n = \text{el/cm}^3 \)) in a metal
  - we have \( Z \) electrons per atom (valence electrons el/atom)
  - we have \( N \) atoms per mol (Avogadro number 6.023\times10^{23} \text{ atoms/mol})
  - we have \( A \) grams per mol (atomic weight g/mol)
  - we have \( \rho_\text{el} \) grams per unit volume (mass density g/cm^3)

\[
\begin{align*}
Z \cdot N & = \left( \frac{\text{el at at mol}}{\text{mol}} \right) \left( \frac{1}{\text{mol}} \right) \\
\rho_\text{el} & = \left( \frac{\text{g at mol}}{\text{mol}} \right) \left( \frac{1}{\text{g}} \right) \\
\frac{n}{N} & = \left( \frac{\text{el}}{\text{cm}^3} \right) \left( \frac{1}{\text{el}} \right)
\end{align*}
\]

- We define the effective volume per electron

\[
V = \frac{1}{n}
\]

- and an effective radius \( r_e \)

\[
\frac{4\pi r_e^3}{3} = \frac{1}{n} \quad \Rightarrow \quad r_e = \left( \frac{3}{4\pi n} \right)^{1/3}
\]

Bohr radius \( a_0 = h^2/e^2 = 0.529 \times 10^{-10} \text{ cm} \)

Electron motion in the Drude model

- In the Drude model the electron scatter form 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 \( \tau \)
  - \( \tau \) is the average time between scattering events
  - \( \tau \) depends on temperature, defects, impurities, etc.
  - we will use \( \tau \) as a parameter
  - typical order of magnitude for \( \tau \) 10^{-14} \text{ sec}
**DC electrical conductivity of a metal**

- We start with Ohm’s law: \( V = R \cdot I \)
- \( R = \frac{\rho \cdot L}{A} \)
- \( E = \rho \cdot J \)
- \( I = J \cdot A \)

  \[ E = \rho \cdot J \]

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

- **Definition of electric conductivity**

  \[ \sigma = \frac{1}{\rho} \cdot \frac{ne^2\tau}{m} \quad (1/\text{cm} \cdot \text{sec} \text{ cm}) \]

- **Electron relaxation length**

  \[ l = \nu_0\tau \]

  - \( \nu_0 \) average electronic speed
  - but what do we use for \( \nu_0 \)?

  - **Classical statistical mechanics, equipartition of energy:**
  - at thermal equilibrium in temperature \( T \), each degree of freedom carries energy of \( \frac{1}{2}k_BT \)
  - a free electron has 3 degrees of freedom (motion in the 3D space)
  - so total thermal energy \( \frac{1}{2}m\nu_0^2 = \frac{3}{2}k_BT \)
  - the Boltzmann constant \( k_B = 1.38 \times 10^{-23} \text{ J/K} \)
  - for \( T = 300 \text{ K} \) and \( m=9.11\times10^{-31} \text{ kg} \), we find \( \nu_0 = \sqrt{3k_BT/2m} \approx 10^7 \text{ cm/s} \)
  - and relaxation length
  \[ l = \nu_0\tau \approx 10^{17} \text{ cm} \times 10^{-14} \text{ s} = 1 \text{ Å} \]

- **AC electrical conductivity of a metal**

  \[ \sigma = \frac{1}{\rho} \cdot \frac{ne^2\tau}{m} \]

  - the electric field, and thus the driving force, oscillate with time
  - the average electron momentum at time \( t \): \( \mathbf{p}(t) = m\mathbf{v}(t) \)
  - scattering events occur on the average every \( \tau \) seconds
  - after a scattering event, the electron emerges with random velocity
  - to first order, at time \( t \) the momentum will change by
  \[ \frac{d\mathbf{p}(t)}{dt} = -e\mathbf{E}(t) \]
  - due to electron scattering
  - due to the electric force
  - so the evolution equation
  \[ \frac{d\mathbf{p}(t)}{dt} = \frac{\mathbf{p}(t)}{\tau} - e\mathbf{E}(t) \]

  - **Time dependent solution**

    - for harmonic fields \( \mathbf{E}(t) = \Re(\mathbf{E}(\omega)e^{-i\omega t}) \)
    - \( \mathbf{p}(t) = \Re(\mathbf{p}(\omega)e^{-i\omega t}) \)
    - evolution equation becomes
    \[ -i\omega\mathbf{p}(\omega) = -\mathbf{p}(\omega)/\tau - e\mathbf{E}(\omega) \]
    - \( \mathbf{p}(\omega) = \frac{-e\mathbf{E}(\omega)\tau}{1-i\omega\tau} \)
    - \( \mathbf{J}(\omega) = -ne\mathbf{p}(\omega)/m \)
    - \( \mathbf{J}(\omega) = \frac{(ne^2\tau/m)}{1-i\omega\tau} \mathbf{E}(\omega) \sigma(\omega) = \sigma(0) \frac{1}{1-i\omega\tau} \)
Thermal conductivity of a metal

- Electron motion and scattering cause conduction of heat
  - After any scattering event, an electron emerges with kinetic energy $e(T_{end})$
  - $n/2$ electrons move from left to right with kinetic energy $e(T_{end})$
  - $n/2$ electrons move from right to left with kinetic energy $e(T_{start})$
  - The rate of electrons arriving at $x$ is $nU/2$
  - So the total heat flux $j^T = \frac{1}{2} nU (e(T_{end}) - e(T_{start}))$
  - For $\epsilon$ small compared to the temperature variation scale $e(T_{end}) - e(T_{start}) \approx -\frac{\partial e}{\partial T} \frac{dT}{dx} 2\nu \tau$
  - And so $j^T = -nU \nu \frac{\partial e}{\partial T} \frac{dT}{dx}$

Wiedemann-Franz law

- The ratio between thermal and electrical conductivities in metals is linear to temperature
  - Thermal conductivity $\kappa = \frac{3 nk^2 T}{2m}$
  - Electrical conductivity $\sigma = \frac{n \epsilon^2 T}{m}$
  - Lorentz number (independent of $T$)
    $\frac{\kappa}{\sigma T} = \frac{1}{2} \frac{k_B}{e^2} = 1.11 \times 10^{-8} \text{ Wcm/K}^2$
  - 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)
- Once again, we should not use classical statistics!!

Classical electron statistics

- Classical: Maxwell-Boltzmann distribution
  - The probability to find an electron with velocity $\nu$ when the temperature is $T$
    \[
    f_{MB}(\nu) = C_{MB} e^{-\frac{1}{2} \frac{m\nu^2}{k_B T}}
    \]
  - In our simple metal, electrons have only kinetic energy
  - Thermal energy at room temperature
  - The distribution satisfies the charge conservation
    \[
    \int_{-\infty}^{\infty} f_{MB}(\nu) d\nu = n
    \]
  - How do we treat $d\nu$?
    - It is a differential over speed and solid angle. In isotropic case (all angles are the same):
      \[
      d\nu = 4\pi \nu^2 d\nu
      \]
      - So the number of electrons
      \[
      4\pi \int_{-\infty}^{\infty} f_{MB}(\nu) \nu^2 d\nu = n
      \]
Quantum electron statistics (Sommerfeld theory of metals)

- Quantum: Fermi-Dirac distribution
  - the probability to find an electron with velocity \( v \) when the temperature is \( T \)
  \[
  f_{FD}(v) = C_{FD} \frac{1}{e^{\frac{\mu}{k_B T}} + 1}
  \]
  \[\mu = \frac{1}{2} m v^2\]
  in our simple metal, electrons have only kinetic energy
  \[C_{FD} = \frac{(m/\hbar)^3}{4\pi^2}\]
  normalization constant

- the total number of electrons is found
  \[
  4\pi \int f_{FD}(v) v^2 dV = n
  \]
  when \( n \) is known, we use this to find the chemical potential \( \mu \)

- 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

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:
  \[
  -\frac{\hbar^2}{2m} \nabla^2 \psi(r) = \epsilon \psi(r)
  \]
  Laplacian
  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)
  \[
  \psi(x + L, y, z) = \psi(x, y, z)
  \]
  \[
  \psi(x, y + L, z) = \psi(x, y, z)
  \]
  \[
  \psi(x, y, z + L) = \psi(x, y, z)
  \]

  solution
  \[
  \psi_k(r) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}
  \]
  normalization condition
  \[
  \int |\psi(r)|^2 dV = 1
  \]

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

Comparison of electron statistics

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

\[
\begin{align*}
T = 0 \text{ K} \quad & f_{FD}(v) = C_{FD} e^{\frac{\mu}{k_B T}} \\
T = 300 \text{ K} \quad & f_{FD}(v) = C_{FD} e^{\frac{\mu}{k_B T}} \\
T = 1000 \text{ K} \quad & f_{FD}(v) = C_{FD} e^{\frac{\mu}{k_B T}}
\end{align*}
\]

Ground state of the free electron gas

- The proper \( k \) values are found from the boundary conditions
  \[
  \psi(x + L, y, z) = \psi(x, y, z)
  \]
  \[
  \psi(x, y + L, z) = \psi(x, y, z)
  \]
  \[
  \psi(x, y, z + L) = \psi(x, y, z)
  \]
  - 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
  \[
  e^{i(k_x x + k_y y + k_z z)} = e^{i(k_x x') e^{i(k_y y') e^{i(k_z z')}}}
  \]
  \[
  e^{i(k_x x + k_y y + k_z z)} = e^{i(k_x x') e^{i(k_y y') e^{i(k_z z')}}}
  \]
  \[
  e^{i(k_x x + k_y y + k_z z)} = e^{i(k_x x') e^{i(k_y y') e^{i(k_z z')}}}
  \]

  with solution
  \[
  e^{i\mathbf{k} \cdot \mathbf{r}} = 1 \Rightarrow k_x L = n_x 2\pi \Rightarrow k_x = n_x (2\pi / L)
  \]
  \[
  e^{i\mathbf{k} \cdot \mathbf{r}} = 1 \Rightarrow k_y L = n_y 2\pi \Rightarrow k_y = n_y (2\pi / L)
  \]
  \[
  e^{i\mathbf{k} \cdot \mathbf{r}} = 1 \Rightarrow k_z L = n_z 2\pi \Rightarrow k_z = n_z (2\pi / L)
  \]

- 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
    
    \[ (n_x, n_y, n_z) = (0,0,0) \]
    \[ (n_x, n_y, n_z) = (1,0,0) \]
    \[ (n_x, n_y, n_z) = (-1,0,0) \]
    \[ (n_x, n_y, n_z) = (0,1,0) \]
    \[ (n_x, n_y, n_z) = (0,-1,0) \]
    \[ (n_x, n_y, n_z) = (1,1,0) \]
    \[ \cdots \]

- the periodicity of the k-point lattice is \( 2\pi/L \)
- number of k-points is equal to number of electrons \( -10^{22} \text{e/cm}^3 \)

- The number of electrons determines the highest energy
  - highest k-point: Fermi wavevector \( k_F \)
  - highest energy: Fermi energy \( E_F = \frac{\hbar^2 k_F^2}{2m} \)
  - highest velocity: Fermi velocity \( v_F = \frac{\hbar k_F}{m} \)

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 \( \left( \frac{2\pi}{L} \right)^3 \)
  - number of points (each k-point \( \times 2 \) due to spin)
  \[ N = 2 \frac{4\pi k_F^3}{3} \frac{L^3}{8\pi^2} \Rightarrow \frac{N}{V} = n = \frac{k_F^3}{3\pi^2} \]

- But \( n \) is known for each metal
  \[ n = \frac{\rho_s \cdot Z \cdot N_A}{A} \] and \[ \frac{4\pi n^2}{3} = \frac{1}{n} \Rightarrow r_s = \left( \frac{3}{4\pi} \right)^{1/3} \]

  so we define

  \[ k_F = \frac{3.63}{r_s/a_0}, \quad \varepsilon_F = \frac{50.1}{(r_s/a_0)^2} \text{eV}, \quad \nu_F = 4.20 \frac{r_s}{a_0} \times 10^6 \text{cm/s} \]

Fermi energies etc for various metals

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<th>ELEMENT</th>
<th>( r_s/\text{a}_0 )</th>
<th>( E_F )</th>
<th>( \nu_F )</th>
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</table>

Summing over the electron states

- The number of states
  \[ N = \sum_k \frac{f(k)}{\varepsilon^3} = \frac{V}{8\pi^2} \sum_k \frac{f(k) \Delta k}{\varepsilon^3} \approx \frac{V}{4\pi^2} \int \frac{f(k) \Delta k}{\varepsilon^3} \]

- number density of states \( n = \frac{N}{V} = \frac{1}{V} \int \frac{\Delta k}{4\pi^2} f(k) \)

- for isotropic system, i.e. all directions are equivalent (as the free electron case) \( \Delta k = 4\pi^2 \Delta k \)

- We can evaluate any quantity

  - total energy \( \mu = \frac{E}{V} = \frac{1}{V} \int \frac{d\varepsilon}{4\pi^2} f(k) \varepsilon \)

  - at zero temperature \( E = \frac{\hbar^2 k_F^2}{2m} \int_0^{\frac{4\pi^2}{3\pi^2}} \frac{d\varepsilon}{4\pi^2} = \frac{1}{10\pi^2} \frac{\hbar^2 k_F^2}{2m} \)

  \[ E = \frac{1}{5\pi^2} \mu \]

- Average energy per electron

  - use \( N \frac{k_F^3}{3\pi^2} \) to get

  \[ \frac{E}{N} = \frac{3}{5} \mu \]
Compressibility of electron gas

- Pressure exerted on electron gas: \( P = \left( \frac{\partial E}{\partial V} \right)_N \)
  - Energy of the electron gas \( E = \frac{3}{5} T \mu \) where \( \mu = \frac{3}{2} \hbar^2 k_F^2 / 2m \)
  - Fermi wavevector \( k_F = \frac{\sqrt{\frac{2m}{\hbar^2} E}}{\frac{2\pi}{\sqrt{2}} N^{3/2}} \Rightarrow k_F^2 = \left( \frac{3\pi^2 N}{2} \right)^{2/3} V^{-2/3} \)
  - And so \( E = \left( \frac{3}{5} \hbar^2 N^{3/2} V^{-2/3} \right)^{2/3} \)
  - So pressure \( P = \left( \frac{\partial E}{\partial V} \right)_N = \frac{2}{3} \frac{E}{V} \)
- Bulk modulus: \( B = -\frac{V}{E} \left( \frac{\partial P}{\partial V} \right)_N \)
  - But \( P = \text{const.} V^{-1} \Rightarrow \frac{\partial P}{\partial V} = (5/3) \frac{P}{V} \)
  - So bulk modulus \( B = \frac{10}{9} \frac{E}{V} = \left( \frac{6.13}{N^3 \hbar^2} \right)^3 \times 10^4 \text{ dynes/cm}^2 \)

Synopsis of the free electron Fermi-Dirac distribution

- The FD distribution for free electrons depends only on energy
  - The energy is isotropic with \( \epsilon(k) = \hbar^2 k^2 / 2m \)
  - Fermi function \( f(k) = f(\epsilon(k)) = f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1} \)
- The distribution is the probability for a energy level to be occupied
  - for \( T \to 0 \) \( f(\epsilon) = 1 \) for \( \epsilon < \epsilon_F \)
  - \( f(\epsilon) = 0 \) for \( \epsilon > \epsilon_F \)
  - for \( T \to 0 \) the chemical potential is the Fermi energy: \( \mu = \epsilon_F \) (but even at room temperature \( \mu \approx \epsilon_F \))

Application of the Fermi-Dirac distribution

- The number of electrons is determined by summing up the distribution
  \[ n = \int \frac{dk}{4\pi^2} f(\epsilon) \]
  - but for isotropic distribution (free electrons) \( \int \frac{dk}{4\pi^2} f(\epsilon) = \int \frac{4\pi k^2}{4\pi^2} f(\epsilon) dk = \frac{1}{2\pi^2} \int k^2 f(\epsilon) dk \)
  - Use the free electron energy
  \[ \epsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k^2 = \frac{2me\epsilon}{\hbar^2} \Rightarrow 2dkd\epsilon = \frac{2m}{\hbar^2} d\epsilon \Rightarrow dk = \frac{m}{k \hbar^2} d\epsilon \Rightarrow \]
  \[ n = \frac{1}{2\pi^2} \int \frac{2me\epsilon}{\hbar^2} \frac{\hbar^2}{2me} f(\epsilon) d\epsilon \]
- Define the free electron density of states \( g(\epsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2me}{\hbar}} \)
  - Number of electrons \( n = \int g(\epsilon) f(\epsilon) d\epsilon \)
  - Total energy density of electrons \( E_F = \int \epsilon g(\epsilon) f(\epsilon) d\epsilon \)

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 \( g(\epsilon_F) k_F T \)
  - And their energy change is approximately \( \sim k_F T \)
  - So for an order of magnitude estimate \( \Delta u \sim g(\epsilon_F) (k_F T)^2 \)
- Our estimate for the thermal capacitance \( c_v = \left( \frac{\Delta u}{\Delta T} \right)_n \)
  - The correct value is \( c_v = \frac{\pi^2}{2} n k_F T / \epsilon_F \)
Thermal capacitance of free electron gas

- Classical thermal capacitance
  \[ c_v = \frac{3}{2} nk_S \]

- Quantum thermal capacitance
  \[ c_v = \frac{\pi^2}{2} nk_S k_b T / \varepsilon_F \]

  - a linear dependence on temperature
  - in reality there is also the ionic contribution, so
  \[ c_v = \gamma_d T + \gamma_{ion} T^3 \]

  \[ \gamma_d = 0.169 Z \frac{r_s^2}{a_0} \times 10^{-4} \text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \]

Other quantities in the Sommerfeld theory

- Mean free path \( l = v_F \tau \) or \( l = \left( \frac{r_s}{a_0} \right)^2 \times 92 \times 10^{-6} \text{Å} \)
  - with typical values of \(-100 \text{Å}\)
  - electrons do not scatter on the ions!

- Thermal conductivity
  \[ \kappa = \frac{1}{3} n v_F^2 c_v \]
  - using \( \frac{1}{2} m v_F^2 = \varepsilon_F \)
  \[ c_v = \frac{\pi^2}{2} nk_S k_b T / \varepsilon_F \]
  - we find \( \kappa = \frac{\pi^2}{3} nk_b \frac{k_F^2}{m} T \)

- Lorentz number
  \[ \frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \frac{nk_b^2}{m} T \]
  \[ \frac{\kappa}{\sigma T} = \frac{1}{3} \left( \frac{k_b}{e} \right)^2 = 2.44 \times 10^{-4} \text{Woka/K}^2 \]

Summary

- Classical (Drude) theory of metals
  - electrons scatter with relaxation time \( \tau \)
  - 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