

Drude and Sommerfeld (free electron) models

- The Drude model uses classical mechanics and treats the solid as a fixed array of nuclei in a 'sea' of unbound electrons. The electrons are assumed to move in straight lines, and not interact with each other. They are taken to scatter randomly by the nuclei and do not interact with each other.
- Understand how to derive and be able to discuss the Drude formula for DC conductivity.
- What kind of information can be obtained from measuring the Hall effect?
- Understand equation for thermal conductivity in the Drude model.
- What is the Wiedemann-Franz Law? Understand the Lorenz number and how it's obtained.
- Understand how the electron specific heat is a linear function of temperature for low temperature.
- What are typical values in metals for: (carrier) electron density, Drude relaxation times.

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Drude and Sommerfeld (free electron) models

- Understand the approximations made by Drude theory, what it describes well and what it does not.
- What is the main difference between the Drude and Sommerfeld models for metals?
- For a free electron gas, understand how the expressions for Fermi wavevector, Fermi energy, Fermi temperature are obtained in terms of the electron density.
- Know the Fermi distribution function and how it appears for $T = 0$ K and higher temperatures.
- What is the expression for the density of occupied states in the Sommerfeld model?

In the Sommerfeld (free electron) model:

- Have assumed only 1 electron per atom; but actually many
- Cannot explain optical spectra
- Specific heat, although better than Drude, is still off by up to factor of 10
- Can't explain magnetism
- Doesn't take into account electron-electron interactions

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The Sommerfeld (free electron) model

The Sommerfeld model is the simplest way to describe electronic properties of metals: the valence electrons of free atoms become conduction electrons in the crystal and move freely throughout the crystal. It gives a good insight into many properties of metals, such as the heat capacity, thermal conductivity and electrical conductivity. However, it also fails to explain a number of important properties and experimental facts, for example:

- The difference between metals, semiconductors and insulators.
- It does not explain the occurrence of positive values of the Hall coefficient.
- Does not take into account the atomic structure of the material.
- Need a more accurate theory, which would be able to describe these effects, namely band theory.

Some key equations:

Fermi energy $E_F = \frac{\hbar^2(3\pi^2n)^{2/3}}{2m}$

Fermi wavevector $k_F = (3\pi^2n)^{1/3}$

Fermi velocity $mv_F^2/2 \sim k_B T_F$

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

Density of states $g(\epsilon) = \frac{3n}{2E_F} \left(\frac{\epsilon}{E_F} \right)^{1/2}$

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The Sommerfeld (free electron) model

Some key equations:

Heat capacity of free electron gas at low temperature:

$$C = \tilde{\gamma} \left(\frac{3Nk_B}{2} \right) \left(\frac{T}{T_F} \right)$$

where $\tilde{\gamma} = \pi^2/3$.

Thermal conductivity: $\kappa = \frac{1}{3} n c_v \langle v \rangle \lambda$

and $\lambda = \langle v \rangle \tau$ is the scattering length.

Wiedemann-Franz law and the Lorenz number:

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

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Types of bonding

Type of Bonding	Description	Typical of which compounds	Typical Properties
Ionic	Electron is transferred from one atom to another, and the resulting ions attract each other	Binary compounds made of constituents with very different electronegativity: Ex, group I-VII compounds such as NaCl.	<ul style="list-style-type: none"> • Hard, Very Brittle • High Melting Temperature • Electrical Insulator • Water Soluble
Covalent	Electron is shared equally between two atoms forming a bond. Energy lowered by delocalization of wave-function	Compounds made of constituents with similar electronegativities (ex, III-V compounds such as GaAs), or solids made of one element only such as diamond (C)	<ul style="list-style-type: none"> • Very Hard (Brittle) • High Melting Temperature • Electrical Insulators or Semiconductors
Metallic Bonds	Electrons delocalized throughout the solid forming a glue between positive ions.	Metals. Left and Middle of Periodic Table.	<ul style="list-style-type: none"> • Ductile, Malleable (due to non-directional nature of bond. Can be hardened by preventing dislocation motion with impurities) • Lower Melting Temperature • Good electrical and thermal conductors.
Molecular (van der Waals or Fluctuating Dipole)	No transfer of electrons. Dipole moments on constituents align to cause attraction. Bonding strength increases with size of molecule or polarity of constituent.	Noble Gas Solids, Solids made of Non-Polar (or slightly polar) Molecules Binding to Each Other (Wax)	<ul style="list-style-type: none"> • Soft, Weak • Low Melting Temperature • Electrical Insulators
Hydrogen	Involves Hydrogen ion bound to one atom but still attracted to another. Special case because H is so small.	Important in organic and biological materials	<ul style="list-style-type: none"> • Weak Bond (stronger than VdW though) • Important for maintaining shape of DNA and proteins

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Crystal structure and symmetry

- Crystal: atoms are arranged so that their positions are periodic in all three dimensions.
- Crystal lattice – the periodic array of points.
- An atom or a group of atoms associated with every lattice point is called a *basis*.
- In addition to periodicity, each lattice can have other symmetry properties (inversion, mirror planes, rotation axes).
- There are 14 Bravais lattices.
- Notation for crystallographic directions and planes: Miller indices.

Diffraction of waves by crystal lattices

- Most methods for determining the atomic structure of crystals are based on scattering of particles/radiation (X-rays, electrons, neutrons). The wavelength of the radiation should be comparable to a typical interatomic distance (few Å=10⁻⁸ cm).
- The Bragg law: condition for a sharp peak in the intensity of the scattered radiation. Various statements of the Bragg condition:

$$2d\sin\theta = n\lambda \quad \text{and} \quad \mathbf{k}' - \mathbf{k} = \mathbf{G}$$

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Diffraction, reciprocal lattices and Brillouin zones

- The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice.
- Know the reciprocal lattices for common structures: fcc ↔ bcc, sc ↔ sc, hex ↔ hex.
- Constructing the reciprocal lattice vectors from the direct lattice:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$$

- A reciprocal lattice vector has the form $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$.
- It is normal to the (hkl) plane of the direct lattice. The smallest reciprocal lattice vector normal to the plane is: $\mathbf{G} = 2\pi/d$, so

for orthogonal lattice: $\frac{1}{|d_{(hkl)}|^2} = \frac{h^2}{a_1^2} + \frac{k^2}{a_2^2} + \frac{l^2}{a_3^2}$ cubic: $d_{(hkl)}^{cubic} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

- The set of reciprocal lattice vectors determines the possible scattering wavevectors for diffraction.
- The diffraction amplitude (or intensity) is determined by the product of several quantities including the atomic form factor, structure factor, multiplicity.
- The structure factor for orthogonal lattices with a basis of several atoms is:

$$S_{(hkl)} = \sum_{\text{atom } j \text{ in unit cell}} f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad \text{with } f_j \text{ form factor}$$

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Diffraction, reciprocal lattices and Brillouin zones

Systematic Absences of Scattering	
Simple Cubic	all h, k, l allowed
bcc	$h + k + l$ must be even
fcc	h, k, l must be all odd or all even

Things to consider

- Understand how to define a Bravais lattice, primitive vectors, coordination number, primitive unit cell, conventional unit cell, lattice constant, Wigner-Seitz cell, crystal structure, basis, Miller indices, Brillouin zone and its relation to the Wigner-Seitz cell.
- How to derive the reciprocal lattice vectors from a given lattice.
- How to construct the first Brillouin zone for a two-dimensional lattice (e.g. square, rectangular, hexagonal).
- Discuss the von Laue and Bragg formulations for X-ray diffraction. What is a Bragg plane, why are X-rays suitable for probing crystal structures?
- Which crystals have a high/low packing factors?
- The structure factor and how to work it out for a given crystal structure.
- How large are typical lattice spacings.
- How to work out crystal structure for measured diffraction peaks (intensity versus 2θ) and viceversa (calculate diffraction peaks from crystal structure).

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Band theory

- Bloch's theorem: the wave function for an electron in a periodic potential can be written in the form $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$ where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$ is a periodic function with the period of the lattice.
- The energy spectrum of electrons consists of a set of effectively continuous energy bands, separated by regions with no allowed states – forbidden gaps.
- The function $E(\mathbf{k})$ satisfies the symmetry properties of a crystal, e.g. translational invariance: $E(\mathbf{k})=E(\mathbf{k}+\mathbf{G})$.
- This allows considering the first Brillouin zone only.
- Also, inversion symmetry $E(\mathbf{k})=E(-\mathbf{k})$.
- Nearly free electron model: weak crystal potential. Electrons behave essentially as free particles, except the wave vectors close to the zone boundaries. In these regions, energy gaps appear.
- Tight-binding model: strong crystal potential, weak overlap. The band width increases and electrons become more mobile (smaller effective mass) as the overlap between atomic wave functions increases.

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Band theory

- Concept of effective mass: in a periodic potential electron moves as in free space, but with different mass:

$$m^* = \frac{\hbar^2}{\partial^2 E / \partial k^2}$$

- Group velocity: $\mathbf{v}_n(\mathbf{k}) = \frac{dE_n(\mathbf{k})}{\hbar d\mathbf{k}}$
- Physical origin of the effective mass: crystal field.
- Metals: partially filled bands. Insulators: at 0 K the valence band is full, conduction band is empty. Semiconductors: smaller band gaps than insulators and conduct electricity for elevated temperatures.
- Perfect periodic lattice: no scattering of electrons, velocity remains constant (vibrations [phonons], impurities and defects cause electrons to scatter in real crystals).

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Band theory

Things to consider

- Define Bloch's theorem and discuss consequences.
- Crystal (or quasi momentum) is a momentum-like vector associated with electrons in a crystal lattice.
- Sketch the energy bands in a 1D metal in the extended, reduced and repeated zone schemes according to (i) the free-electron approximation, and (ii) the nearly free-electron approximation.
- Sketch how the energy levels change as atoms condense to form a crystal.
- How can one distinguish between metals, semi-metals, semiconductors and insulators?
- What is a hole, and its properties?
- Explain why the Hall coefficient can change sign.
- Sketch the dispersion curve for an electron with a small and a large effective mass.
- What is a heavy hole and a light hole?
- Why don't filled bands conduct electricity (and heat)?

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Lattice vibrations and phonons

- Sound velocity: $v = \sqrt{\frac{B}{\rho}} = \sqrt{\frac{1}{\rho\beta}}$
- All crystal vibrational waves can be described by wavevectors within the first Brillouin zone in reciprocal space.
- Frequency of modes for a 1D chain: $\omega = 2\sqrt{\frac{\kappa}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$ (only one branch, the acoustic).
- For more than one atom in a unit cell, we get acoustic and optical branches.
- Frequency of modes for a diatomic chain with different spring constants and the same mass:
$$\omega_{\pm} = \sqrt{\frac{\kappa_1 + \kappa_2}{m}} \pm \frac{1}{m} \sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos(ka)}$$
- In general, 3D lattice with M atoms per unit cell, there are $3M$ vibrational branches: 3 acoustic, $3M-3$ optical.
- Phonon: the quantum of lattice vibration, energy $\hbar\omega$.

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Lattice vibrations and phonons

Things to consider

- Discuss normal modes, the dispersion curve, acoustic branch, optical branch, phonons.
- Sketch the dispersion relation (curve) for acoustic and optical phonons for a lattice with one and two atoms per unit cell.
- What does the phonon dispersion curve look like for a 1D chain with one atom in the unit cell. And with two different atoms in the unit cell?
- Given the crystal structure, including number of atoms in the unit cell, how many normal modes will there be? How many acoustic and how many optical? Why are these modes given those two names? What physical meaning to they have?

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Semiconductors

- Semiconductors are mostly covalent crystals with moderate energy band gap (~0.5 to 3–4 eV).
- Intrinsic carrier concentration:

$$n_{intrinsic} = p_{intrinsic} = \sqrt{np} = \frac{1}{\sqrt{2}} \left(\frac{k_B T}{\pi \hbar^2} \right)^{3/2} (m_e^* m_h^*)^{3/4} e^{-\beta E_{gap}/2}$$

- Fermi level position in intrinsic semiconductors:

$$\mu = \frac{1}{2}(\epsilon_c + \epsilon_v) + \frac{3}{4}(k_B T) \log(m_h^*/m_e^*)$$

- In a doped semiconductor, many impurities (dopants) form shallow hydrogen-like levels close to the conduction band (donors) or valence band (acceptors), which are completely ionized at room temperature.

- In the Bohr model, their binding energy is: $E_n = -\frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \frac{1}{n^2}$

and the effective radius of their wavefunction is:

$$a_0^{\text{eff}} = a_0 \left(\epsilon_r \frac{m}{m_e^*} \right)$$

- Charge carriers are both electrons and holes. One carrier type is dominant in doped semiconductors.

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Semiconductors

Things to consider

- Why does the conductivity (resistance) of a semiconductor increase (decrease) with increasing temperature?
- What is the difference between intrinsic and extrinsic semiconductors?
- Explain/show why the chemical potential lies half-way in the band-gap for intrinsic semiconductors at low temperatures.
- What is the main effect of doping?
- Where are the energy levels of donors and acceptors preferably located in the energy band gap?
- What are typical values for the carrier concentrations in a semiconductor compared to a metal (and compared to intrinsic carrier concentrations)?
- Understand how to derive the density of electrons (holes) in the conduction (valence) band for non-degenerate semiconductors when ϵ_k is quadratic in k .
- Discuss the difference between direct and indirect band gaps.
- The law of mass action is:
$$n(T)p(T) = \frac{1}{2} \left(\frac{k_B T}{\pi \hbar^2} \right)^3 (m_e^* m_h^*)^{3/2} e^{-\beta E_{gap}}$$

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Magnetism

- When a material is placed in a magnetic field, the material is magnetised. Magnetisation is proportional to the magnetic field: $\mathbf{M} = \chi \mathbf{H}$
 χ is the magnetic susceptibility of the material.
- Magnetic permeability $\mu = \mu_0(1 + \chi)$.
- Larmor diamagnetism: ions or atoms with all electronic shells filled have negative magnetic susceptibility

$$\chi = -\frac{\rho e^2 \mu_0 \langle r^2 \rangle}{6m}$$

- Langevin or Curie's paramagnetism: paramagnetic susceptibility (Curie's Law)

$$\chi = \frac{n \mu_0 (\tilde{g} \mu_B)^2}{3} \frac{J(J+1)}{k_B T}$$

- In metals, conduction electrons make a spin paramagnetic contribution, called Pauli paramagnetism (independent of T)

$$\chi_{Pauli} = \frac{dM}{dH} = \mu_0 \frac{dM}{dB} = \mu_0 \mu_B^2 g(E_F)$$

- There is some amount of diamagnetism in all materials. For conduction electrons in a metal we have Landau diamagnetism:

$$\chi_{Landau} = -\frac{1}{3} \chi_{Pauli}$$

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Magnetism

Things to consider

- Describe diamagnetism and paramagnetism and their origin.
- Pauli paramagnetism applies to conduction electrons. How is this different to paramagnetism in an atom?
- The exchange-interaction is the origin of ferromagnetic order in solids.
- What is the difference between ferromagnetism, antiferromagnetism and ferrimagnetism?
- What are Hund's three rules?
- What does the Heisenberg Hamiltonian describe?
- Describe the Ising model.
- What are domains and domain walls? How are they related to hysteresis?

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Density functional theory (Adv.)

- Hohenberg and Kohn proved in 1964 that in order to determine the ground-state properties of a many-electron system, it suffices to know the ground-state density.
- They further proved that there is a universal functional of the density that becomes a minimum at the true ground-state density of the many-electron system. This minimum value is then equal to the true ground-state energy of the system.
- Kohn and Sham showed in 1965 that for the ground state, the many-electron problem can be mapped onto a system of one-electron equations, known as the Kohn-Sham equations (below).

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}).$$

- The Hartree potential is: $V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'$.
- The exchange-correlation (xc) potential is: $V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})}$.
- The electron density is: $n_{KS}(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$.
- Explain in simple terms the basic idea of DFT and the exchange-correlation term.

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