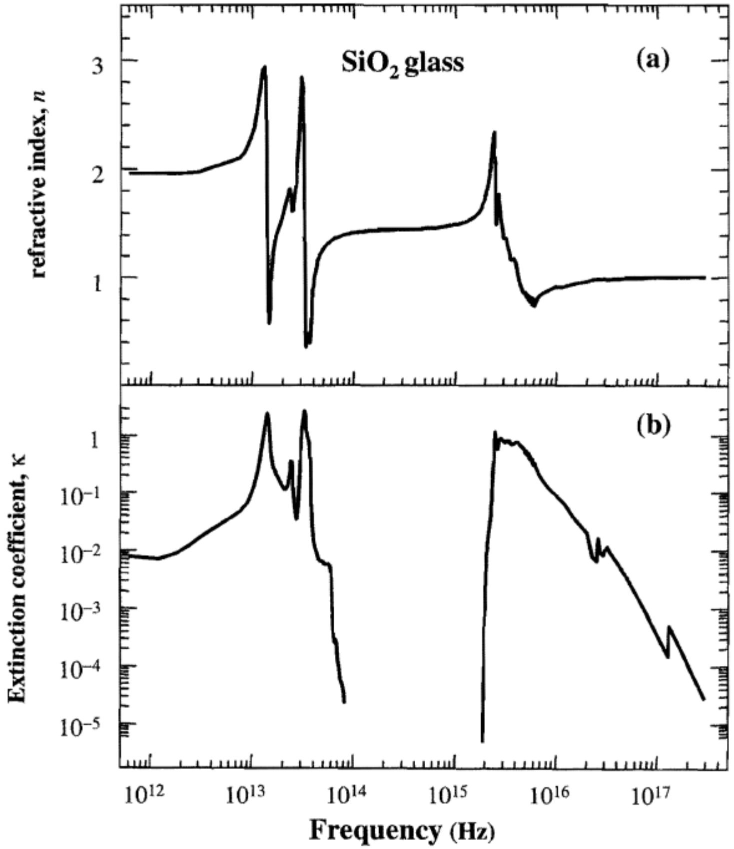
Quantum Condensed Matter Physics

Lecture 1



David Ritchie

http://www.sp.phy.cam.ac.uk/drp2/home

Quantum Condensed Matter Physics: synopsis (1)

1. Classical and Semi-classical models for electrons in solids (3L)

Lorentz dipole oscillator, optical properties of insulators. Drude model and optical properties of metals, plasma oscillations. Semi-classical approach to electron transport in electric and magnetic fields, the Hall effect. Sommerfeld model, density of states, specific heat of; electrons in metals, liquid ^{3}He/^{4}He mixtures. Screening and the Thomas-Fermi approximation.

2. Electrons and phonons in periodic solids (6L)

Types of bonding; Van der Waals, ionic, covalent. Crystal structures. Reciprocal space, x-ray diffraction and Brillouin zones. Lattice dynamics and phonons; 1D monoatomic and diatomic chains, 3D crystals. Heat capacity due to lattice vibrations; Einstein and Debye models. Thermal conductivity of insulators. Electrons in a periodic potential; Bloch's theorem. Nearly free electron approximation; plane waves and bandgaps. Tight binding approximation; linear combination of atomic orbitals, linear chain and three dimensions, two bands. Pseudopotentials. Band structure of real materials; properties of metals (aluminium and copper) and semiconductors.

Semi-classical model of electron dynamics in bands; Bloch oscillations, effective mass, density of states, electrons and holes in semiconductors

Quantum Condensed Matter Physics: synopsis (2)

3. Experimental probes of band structure (4L)

Photon absorption; transition rates, experimental arrangement for absorption spectroscopy, direct and indirect semiconductors, excitons. Quantum oscillations; de Haas-Van Alphen effect in copper and strontium ruthenate. Photoemission; angle resolved photoemission spectroscopy (ARPES) in GaAs and strontium ruthenate. Tunnelling; scanning tunnelling microscopy. Cyclotron resonance.

Scattering in metals; Wiedemann-Franz law, theory of electrical and thermal transport, Matthiessen's rule, emission and absorption of phonons. Experiments demonstrating electron-phonon and electron–electron scattering at low temperatures.

Quantum Condensed Matter Physics: synopsis (3)

4. Semiconductors and semiconductor devices (5L)

Intrinsic semiconductors, law of mass action, doping in semiconductors, impurity ionisation, variation of carrier concentration and mobility with temperature - impurity and phonon scattering, Hall effect with two carrier types.

Metal to semiconductor contact. P-n junction; charge redistribution, band bending and equilibrium, balance of currents, voltage bias. Light emitting diodes; GaN, organic.

Photovoltaic solar cell; Shockley-Queisser limit, efficiencies, commercialisation. Field effect transistor; JFET, MOSFET. Microelectronics and the integrated circuit.

Band structure engineering; electron beam lithography, molecular beam epitaxy. Two-dimensional electron gas, Shubnikov-de Haas oscillations, quantum Hall effect, conductance quantisation in 1D. Single electron pumping and current quantisation, single and entangled-photon emission, quantum cascade laser.

Quantum Condensed Matter Physics: synopsis (4)

5. Electronic instabilities (2L)

The Peierls transition, charge density waves, magnetism, local magnetic moments, Curie Law. Types of magnetic interactions; direct exchange, Heisenberg hamiltonian, superexchange and insulating ferromagnets, band magnetism in metals, local moment magnetism in metals, indirect exchange, magnetic order and the Weiss exchange field.

6. Fermi Liquids (2L)

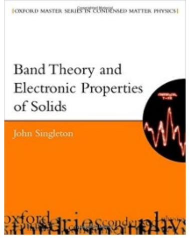
Fermi liquid theory; the problem with the Fermi gas. Liquid Helium; specific heat and viscosity. Collective excitations, adiabatic continuity, total energy expansion for Landau Fermi liquid, energy dependence of quasiparticle scattering rate.

Quasiparticles and holes near the Fermi surface, quasiparticle spectral function, tuning of the quasiparticle interaction, heavy fermions, renormalised band picture for heavy fermions, quasiparticles detected by dHvA, tuning the quasiparticle interaction. $CePd_2Si_2$; heavy-fermion magnet to unconventional superconductor phase transitions.

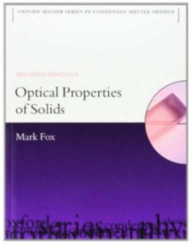
- Course material will be useful for several part III courses.
- Printed overheads & problem sheets provided.
- All available in pdf on web: http://www.sp.phy.cam.ac.uk/drp2/home

Books

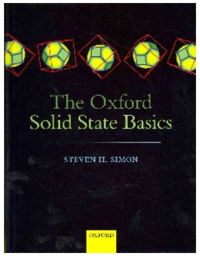
1. Band Theory and Electronic Properties of Solids, Singleton J (OUP 2008)



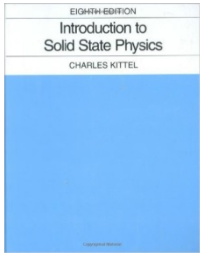
2. Optical properties of Solids, Fox M (2nd edn OUP 2010)

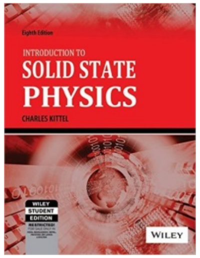


3. The Oxford Solid State Basics, Simon S H (OUP 2013)

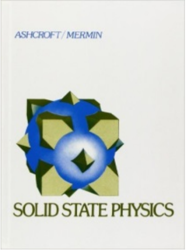


4. Introduction to Solid State Physics, Kittel C (8th edn Wiley 1996)





5. Solid State Physics, Ashcroft N W and Mermin N D, (Holt, Rinehart and Winston 1976)



Quantum Condensed Matter Physics

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2. Electrons and phonons in periodic solids (6L)
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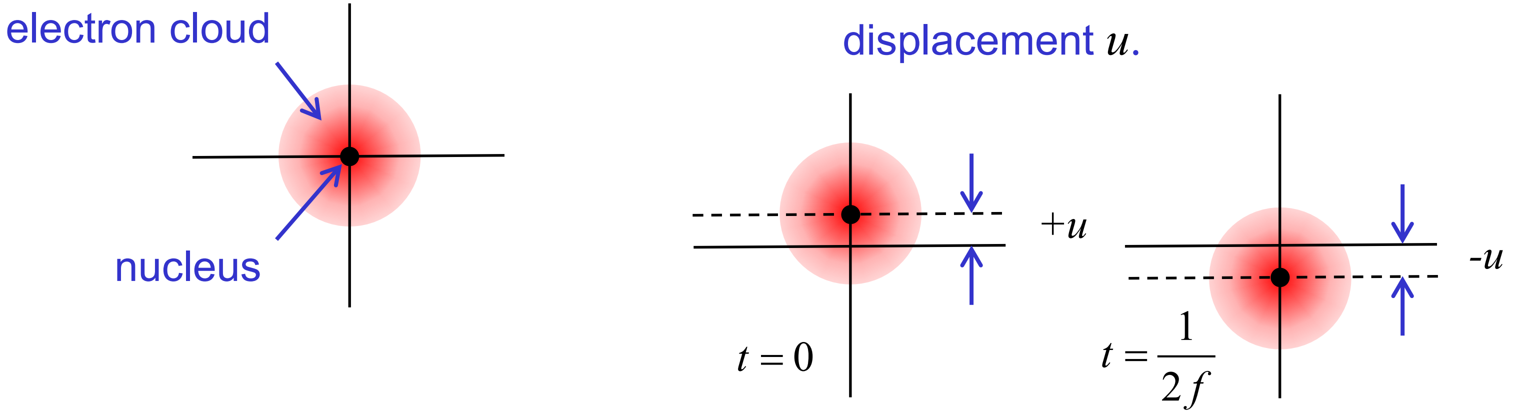
5. Electronic instabilities (2L)
6. Fermi Liquids (2L)

Optical properties of insulators

- Response to high frequency electric field in electromagnetic waves.
- Wavelength long compared to interatomic spacing.
- Classical picture – Lorentz dipole oscillator model



No EM wave

EM wave – electron cloud oscillates about nucleus displacement u.

- Model atoms as nucleus + electron cloud.
- Applied electric field causes displacement of electron cloud,
- Assume restoring force is proportional to displacement.

Optical properties of insulators

- Electron cloud behaves as damped harmonic oscillator

$$m\ddot{u} + m\gamma\dot{u} + m\omega_T^2 u = qE$$

- ω_T natural frequency, determined by force constant and mass; γ damping rate (no model for this yet…)
- Consider oscillating electric field $E(t) = E_\omega e^{-i\omega t}$, which induces oscillating displacement $u(t) = u_\omega e^{-i\omega t}$
- Resulting dipole moment per atom at angular frequency ω_T : $p_\omega = qu_\omega$
- Polarisation = dipole moment per unit volume

$$P_\omega = p_\omega N / V = np_\omega$$

- From $P_\omega = \epsilon_0 \chi_\omega E_\omega$ and the equation of motion we obtain for the polarisability:

$$\chi_\omega = \frac{N}{V}\frac{q^2}{m\epsilon_0(\omega_T^2 - \omega^2 - i\omega\gamma)} = n\frac{q^2}{m\epsilon_0(\omega_T^2 - \omega^2 - i\omega\gamma)}$$

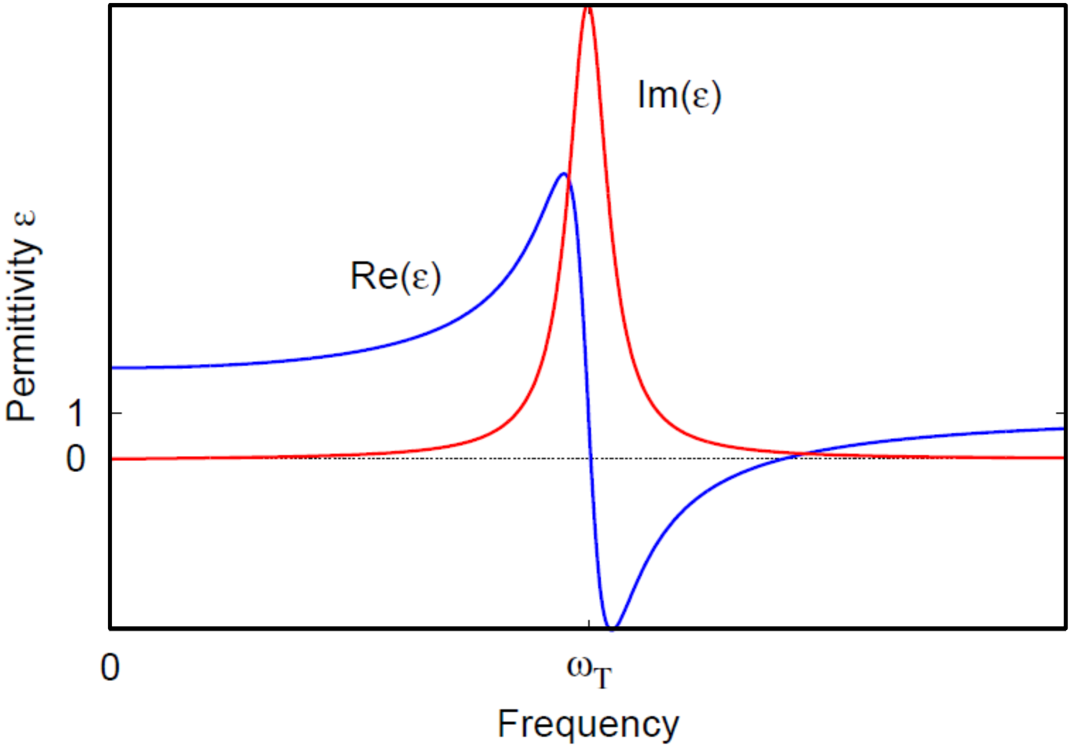
- Frequency dependence of χ_ω typical of harmonic oscillator

Optical properties of insulators

- Permittivity from model:

$$\epsilon_\omega = 1 + \chi_\omega = 1 + n \frac{q^2}{m\epsilon_0(\omega_T^2 - \omega^2 - i\omega\gamma)}$$

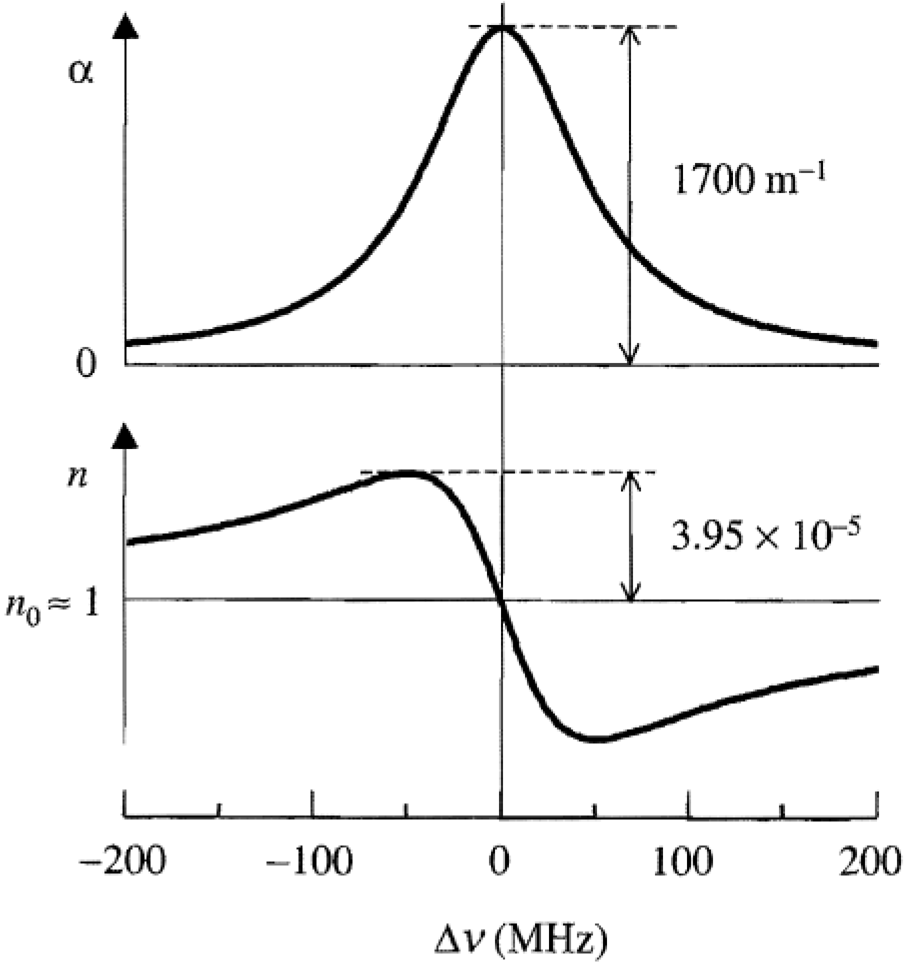
- Figure shows typical frequency dependence



- Analogy with damped SHO tells us that power absorbed by electron cloud is determined by $\mathrm{Im}(\epsilon_\omega)$:
  $P = \frac{1}{2}\omega\epsilon_0 |E_\omega|^2 \,\mathrm{Im}(\epsilon_\omega)$
- Simple way to think of absorption lines in optical spectra
- At low frequencies:
  $\epsilon(\omega \to 0) = 1 + nq^2 / m\epsilon_0\omega_T^2$
- Explains why different materials have very different static permittivities
- Reflectivity between media of different permittivities: $r = \frac{\sqrt{\epsilon_1} - \sqrt{\epsilon_2}}{\sqrt{\epsilon_1} + \sqrt{\epsilon_2}}$,
- Power reflection coefficient given by: $R = |r|^2$
- In a solid polarization fields of other atoms can alter resonant frequency

Example – atomic absorption line

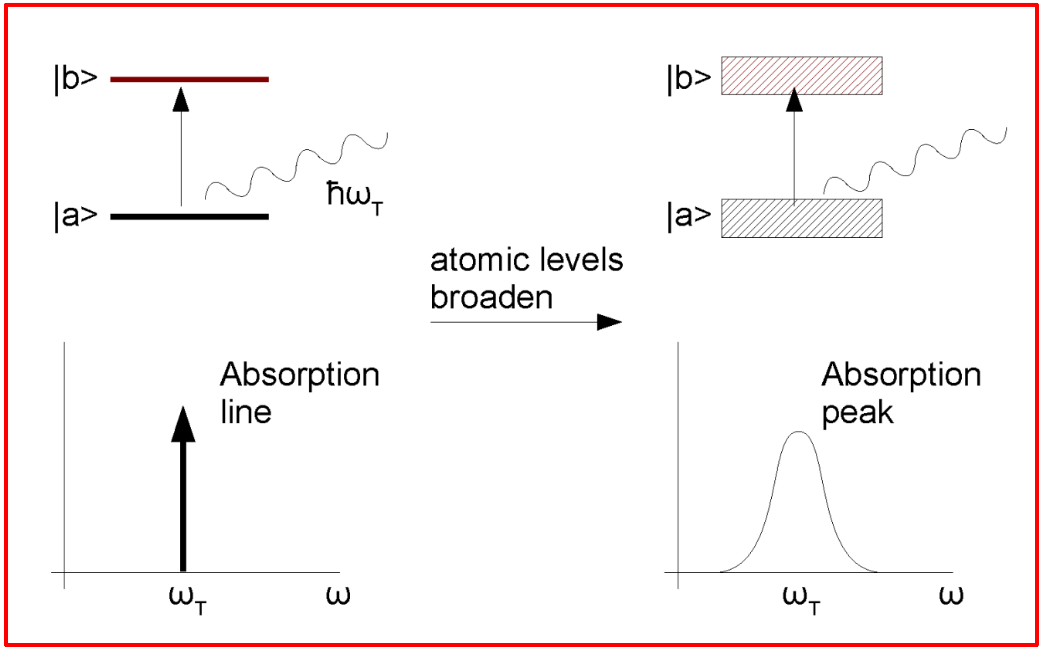
- Absorption coefficient α and refractive index n of sodium gas
- Atom density is $1\times10^{7}\,\mathrm{m}^{-3}$
- n_0 is the off resonance refractive index
- Absorption due strongest hyperfine component of the D2 line at $\lambda = 589\mathrm{nm}$ so $\nu = 5.1\times10^{14}\,\mathrm{Hz}$
- Linewidth $\Delta\nu \approx 100\mathrm{MHz}$ hence $\Delta\nu/\nu = 2\times10^{-7}$
- Very narrow…..



Taken from *Optical properties of solids* by M Fox

Lorentz oscillator model: connection to quantum mechanics

- This classical oscillator model cannot be the whole story – works as a phenomenological description of optical response function



- For two sharp levels, from time-dependent perturbation theory

$$\chi_\omega \propto (E_b - E_a - \hbar\omega)^{-1} + i\delta(E_b - E_a - \hbar\omega)$$

- Where the imaginary part is the transition rate
- This can also be written

$$\chi_\omega \propto \frac{1}{E_b - E_a - \hbar\omega - i\hbar\gamma/2}$$

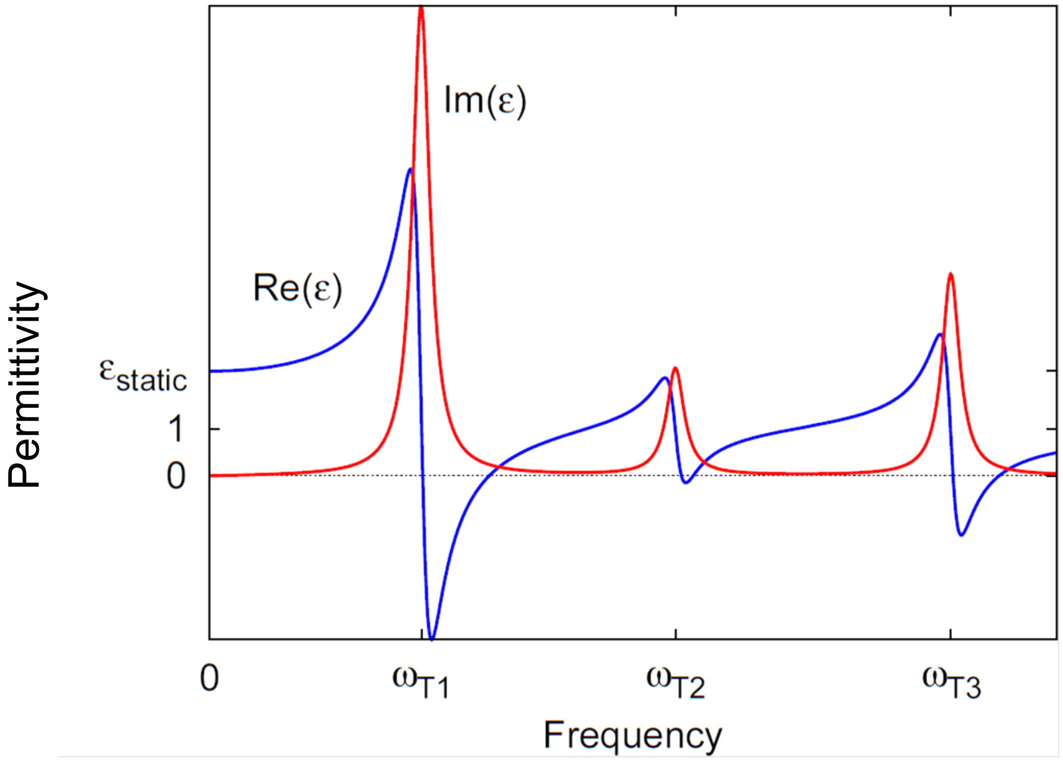
where γ is very small

- As energy levels broaden into bands and γ increases, this expression becomes similar to Lorentz model close to resonance where $\hbar\omega_T = E_b - E_a$
- We multiply by $\omega_T + \omega$ on top and bottom and approximate: $\omega_T + \omega \approx 2\omega_T$ hence:

$$\chi_\omega \propto \frac{\omega_T + \omega}{\omega_T^2 - \omega^2 - i(\omega_T + \omega)\gamma/2} \simeq \frac{2\omega_T}{\omega_T^2 - \omega^2 - i\omega\gamma}$$

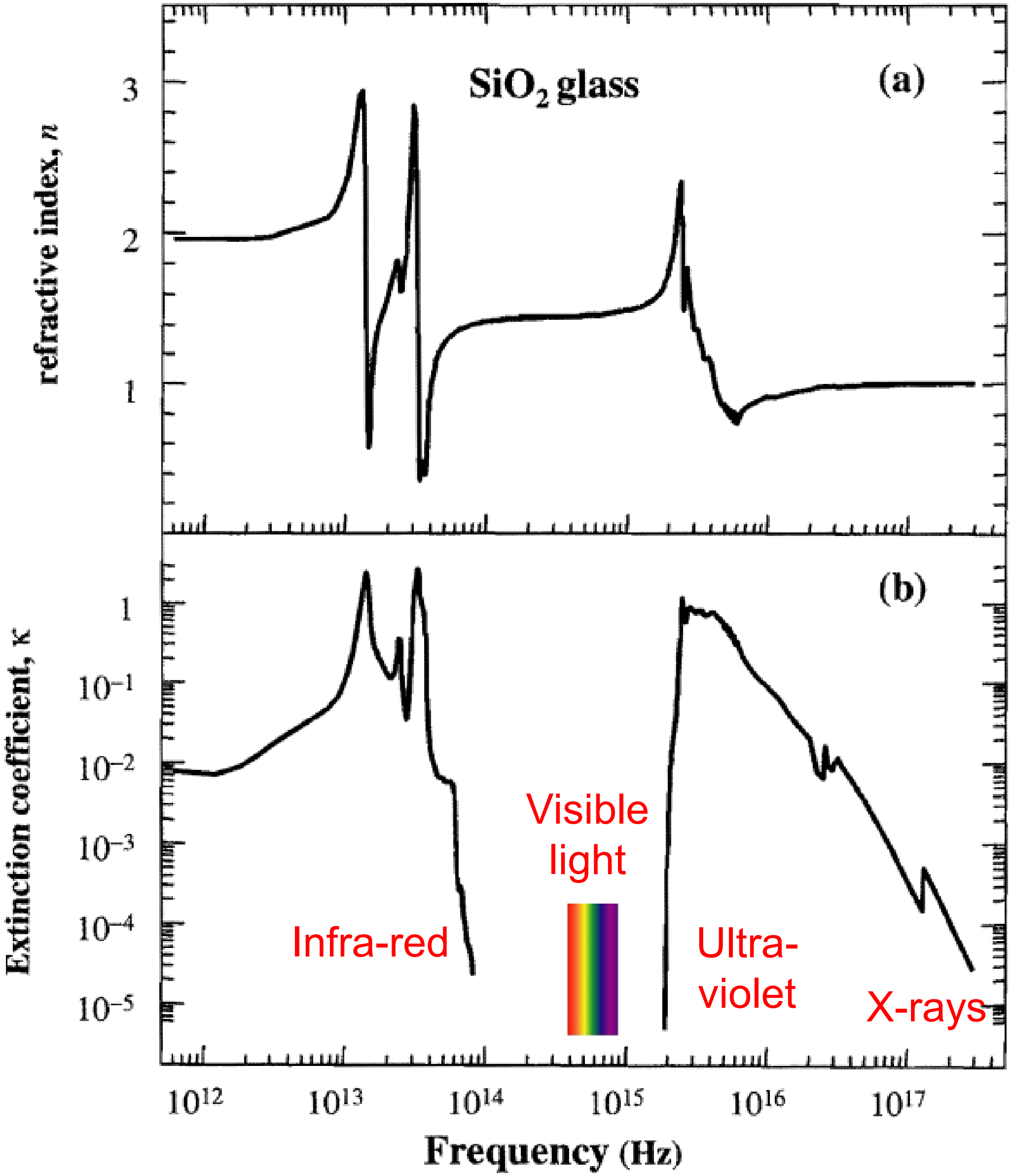
Optical properties of insulators

- Lorentz oscillator model, superposition of spectra
- May have a number of allowed transitions at energies $\hbar\omega_{T_1}......\hbar\omega_{T_2}$
- Usually high frequency – terahertz to ultraviolet
- Resulting frequency-dependent permittivity from adding responses associated with each transition: $\epsilon(\omega) = 1 + \sum \chi_i(\omega)$



Optical properties of insulators – comparison with experiments

- Fused silica glass SiO_2
- Expected general characteristics observed
- Transparent in visible light
- Strong absorption peaks in infrared and ultraviolet
- IR peaks due to vibrations of SiO_2 molecules
- UV absorption background across 10eV bandgap
- UV absorption peaks caused by inner core electron transitions in Si and O



For weakly absorbing medium with $n \gg \kappa$

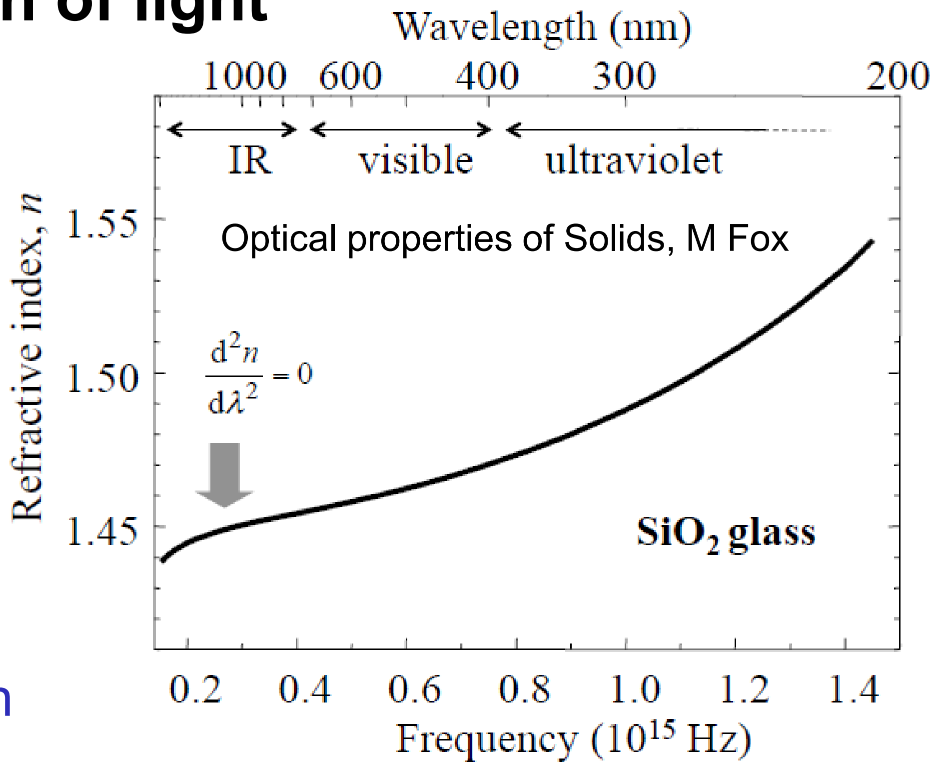
$$n \approx \sqrt{\mathrm{Re}(\epsilon)}$$

$$\kappa \approx \frac{\mathrm{Im}(\epsilon)}{2n}$$

Optical properties of Solids, M Fox

Dispersion of light

- SiO_2 refractive index in more detail
- n increases with frequency – 'normal dispersion' caused by tails of absorption peaks in IR and UV
- Can be used to separate colours of light using a prism
- Short light pulses of duration t_p have spread of frequencies $\delta f \approx 1/t_p$
- Different velocities of frequency components causes problems in high speed optical fibre communications

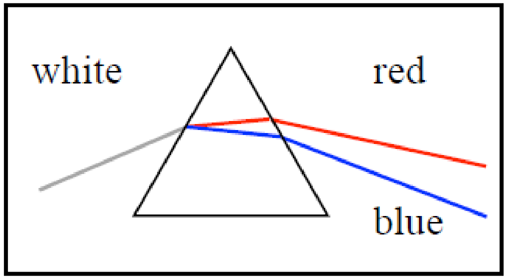


Optical properties of Solids, M Fox

- Temporal broadening of pulse of spectral width $\Delta\lambda$ in a dispersive medium length L

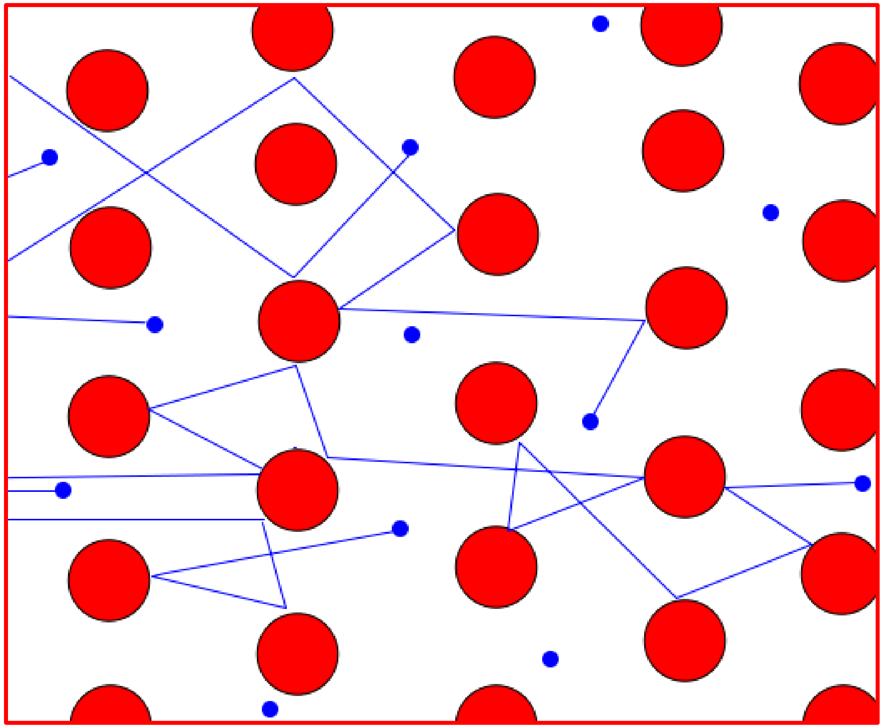
$$\Delta\tau = L\left|\frac{\lambda}{c}\frac{d^2 n}{d\lambda^2}\right|\Delta\lambda$$

- Lorentz model gives $\mathrm{d}^2 n/\mathrm{d}\lambda^2 < 0$ above one absorption line and $\mathrm{d}^2 n/\mathrm{d}\lambda^2 > 0$ below next absorption line
- Choosing $\mathrm{d}^2 n/\mathrm{d}\lambda^2 = 0$ we minimise dispersion
- For SiO_2 this is at $\lambda \simeq 1.3\mu m$ – a preferred optical fibre wavelength



Drude Model

- Assume we have a gas of electrons free to move between positive ion cores
- These electrons are only scattered by the ion cores
- Between collisions with the ion cores the electrons do not interact with each other.
- Collisions are instantaneous resulting in a change of electron velocity.
- The probability an electron has a collision in unit time is τ^{-1}, the scattering rate.
- Electrons achieve thermal equilibrium with their surroundings only through collisions.



taken from wikipedia

Drude Model - relaxation time approximation

- The current density $\mathbf{J}$ due to electrons of number density n, mass m, of average velocity $\mathbf{v}$ and momentum $\mathbf{p}$ is given by:

$$\mathbf{J} = -ne\mathbf{v} = -\frac{ne}{m}\mathbf{p}$$

- Consider the evolution of $\mathbf{p}$ in time δt under the action of an external force $\mathbf{f}\left(t\right)$
- Probability of a collision during δt is $\delta t/\tau$ where τ is the average time between collisions.
- Probability of no collision during δt is $1-\delta t/\tau$
- For electrons that *have not collided* momentum increases:

$$\delta\mathbf{p} = \mathbf{f}(t)\delta t + \mathrm{O}(\delta t)^2$$

- So the contribution to the average momentum during δt for electrons that *have not* collided is:

$$\mathbf{p}(t+\delta t) = (1-\delta t/\tau)(\mathbf{p}(t) + \mathbf{f}(t)\delta t + O(\delta t)^2)$$

Drude Model - relaxation time approximation

- Electrons which *have* collided are a fraction $\delta t / \tau$ of the total.
- The momentum they will have acquired since colliding (where their momentum was randomised) is $\sim \mathbf{f}(t)\delta t$
- So contribution to average momentum for electrons which have collided is of order $(\delta t)^2$ - small
- For momentum as before:

$$\mathbf{p}(t+\delta t) = (1-\delta t/\tau)(\mathbf{p}(t)+\mathbf{f}(t)\delta t + O(\delta t)^2)$$

- If $\delta t \to 0$ we can rearrange this to give

$$\frac{\mathrm{d}\mathbf{p}(t)}{\mathrm{d}t} = -\frac{\mathbf{p}(t)}{\tau} + \mathbf{f}(t)$$

- Hence the collisions produce frictional damping.
- Apply to electrical conductivity σ defined by $\mathbf{J} = \sigma \mathbf{E}$, assume steady state so: $\frac{\mathrm{d}\mathbf{p}(t)}{\mathrm{d}t} = 0$ and the force on an electron is $\mathbf{f}(t) = -e\mathbf{E}$
- From above $\mathbf{J} = -\frac{ne}{m}\mathbf{p}$
- Hence

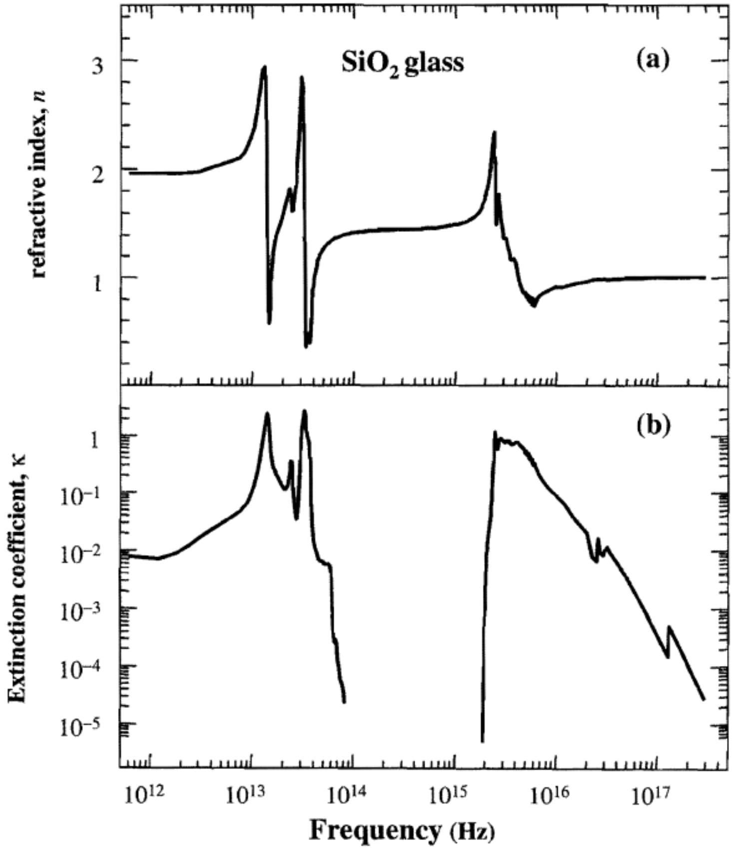
$$\mathbf{f}(t) = \frac{\mathbf{p}(t)}{\tau} = -\frac{m}{ne\tau}\mathbf{J} = -e\mathbf{E} \Rightarrow \sigma = \frac{ne^2\tau}{m}$$

Summary of Lecture 1

- Introduction to course and recommended text books
- Lorentz oscillator model for optical absorption in solids
- Comparison with atomic absorption
- Comparison of Lorentz model with experimental results
- The Drude model of electron motion in solids
- The relaxation time approximation, scattering and electrical conductivity

Quantum Condensed Matter Physics

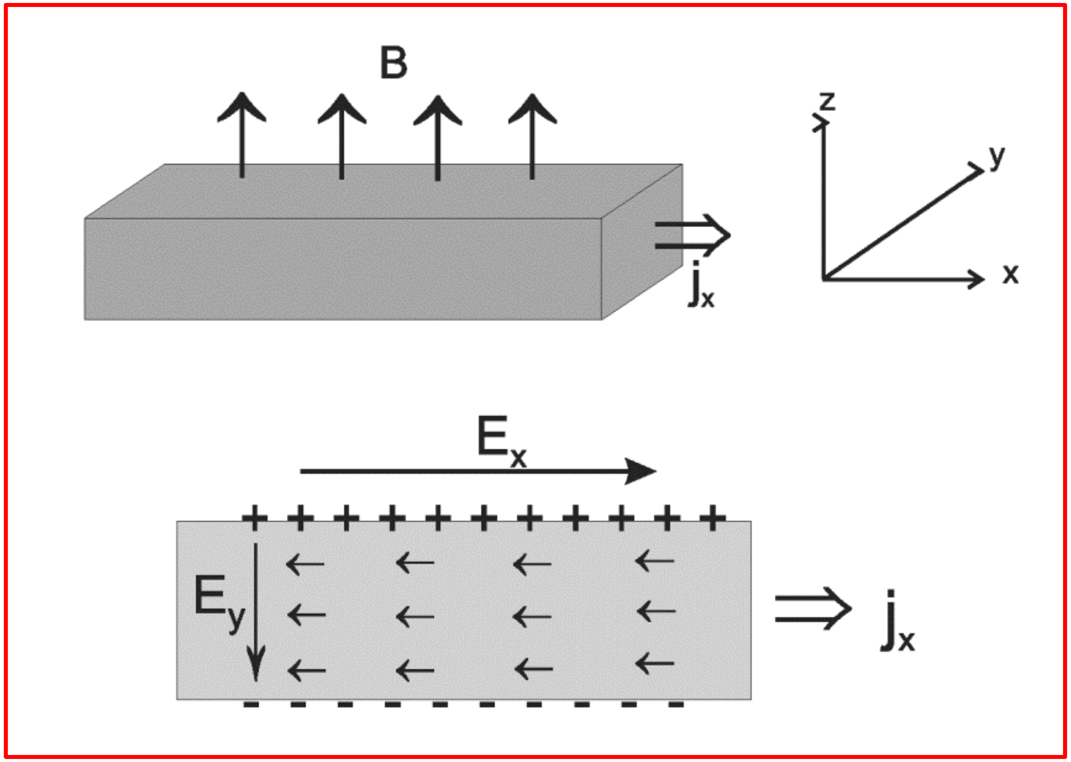
Lecture 1



The End

Quantum Condensed Matter Physics

Lecture 2



David Ritchie

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Drude model

- From above: $\dfrac{\mathrm{d}\mathbf{p}(t)}{\mathrm{d}t} = -\dfrac{\mathbf{p}(t)}{\tau} + \mathbf{f}(t)$
- In magnetic and electric fields: $\mathbf{f} = q\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$ and $\mathbf{j} = nq\mathbf{v}$
- Hence the same equation in different forms:

$$\frac{\mathrm{d}\mathbf{p}(t)}{\mathrm{d}t} = -\frac{\mathbf{p}(t)}{\tau} + q\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$$

$$\frac{\mathrm{d}\mathbf{v}(t)}{\mathrm{d}t} = -\frac{\mathbf{v}(t)}{\tau} + \frac{q}{m}\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$$

$$\frac{\mathrm{d}\mathbf{j}(t)}{\mathrm{d}t} = -\frac{\mathbf{j}(t)}{\tau} + \frac{nq^2}{m}\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$$

$$\frac{\mathrm{d}\mathbf{j}(t)}{\mathrm{d}t} = -\frac{\mathbf{j}(t)}{\tau} + \frac{nq^2\mathbf{E}}{m} + \frac{q}{m}\left(\mathbf{j} \times \mathbf{B}\right)$$

Drude model: Frequency dependant conductivity

- From above $\dfrac{\mathrm{d}\mathbf{j}(t)}{\mathrm{d}t} = -\dfrac{\mathbf{j}(t)}{\tau} + \dfrac{nq^2\mathbf{E}}{m} + \dfrac{q}{m}(\mathbf{j}\times\mathbf{B})$
- If B=0: $\dfrac{\mathrm{d}\mathbf{j}(t)}{\mathrm{d}t} + \dfrac{\mathbf{j}(t)}{\tau} = \dfrac{nq^2}{m}\mathbf{E}$ and if $\mathbf{j} = \mathbf{j}_\omega \exp(-i\omega t), \mathbf{E} = \mathbf{E}_\omega \exp(-i\omega t)$
- Then $\left(\tau^{-1} - i\omega\right)\mathbf{j}_\omega = \frac{nq^2}{m}\mathbf{E}_\omega \Rightarrow \mathbf{j}_\omega = \dfrac{nq^2\mathbf{E}_\omega}{m\left(\tau^{-1} - i\omega\right)} = \dfrac{nq^2\tau\mathbf{E}_\omega}{m(1 - i\omega\tau)}$
- And given $\mathbf{j} = \sigma\mathbf{E}$ we have $\sigma_\omega = \dfrac{nq^2\tau}{m(1 - i\omega\tau)} = \dfrac{\varepsilon_0\omega_p^2\tau}{(1 - i\omega\tau)}$
- Where $\omega_p^2 = \dfrac{nq^2}{m\epsilon_0}$ defines the Plasma frequency.
- At low frequencies $\omega\tau \ll 1$ we get $\sigma_0 = \dfrac{nq^2\tau}{m}, \mu = \dfrac{q\tau}{m} \Rightarrow \sigma_0 = nq\mu$
- Where μ is defined as the carrier mobility

Optical properties of metals: connection to ac conductivity

- Current density $\mathbf{j} = \dot{\mathbf{u}}nq$ (velocity x density x charge)
- Polarisation $\mathbf{P} = n\mathbf{u}q$ Hence, $\dot{\mathbf{P}}_c = \mathbf{j}$ for the conduction electrons
- Adding in the polarisation of the core electrons as χ_∞ - the background polarisability we get: $\dot{\mathbf{P}} = \mathbf{j} + \epsilon_0 \chi_\infty \dot{\mathbf{E}}$
- At angular frequency ω, substituting:

$$\mathbf{E} = \mathbf{E}_\omega \exp(-i\omega t), \mathbf{j} = \mathbf{j}_\omega \exp(-i\omega t), \mathbf{P} = \mathbf{P}_\omega \exp(-i\omega t), \mathbf{P}_\omega = \epsilon_0 \chi_\omega \mathbf{E}_\omega$$

- We get $\mathbf{j}_\omega = -i\omega(\epsilon_0 \chi_\omega \mathbf{E}_\omega - \epsilon_0 \chi_\infty \mathbf{E}_\omega) = -i\omega\epsilon_0 \mathbf{E}_\omega (\chi_\omega - \chi_\infty) = \sigma_\omega \mathbf{E}_\omega$
- Hence

$$\sigma_\omega = -i\omega\epsilon_0 (\chi_\omega - \chi_\infty), \;\; \sigma_\omega = -i\omega\epsilon_0 (\epsilon_\omega - \epsilon_\infty) \Rightarrow \epsilon_\omega = \frac{i\sigma_\omega}{\epsilon_0 \omega} + \epsilon_\infty$$

- This relates the imaginary part of the permittivity to the real part of the frequency dependant conductivity.
- Combining this with our expression $\sigma_\omega = \varepsilon_0 \omega_p^2 \tau (1 - i\omega\tau)^{-1}$ from above we obtain:

$$\epsilon_\omega = \epsilon_\infty + \frac{i\omega_p^2 \tau}{\omega(1 - i\omega\tau)} = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau}$$

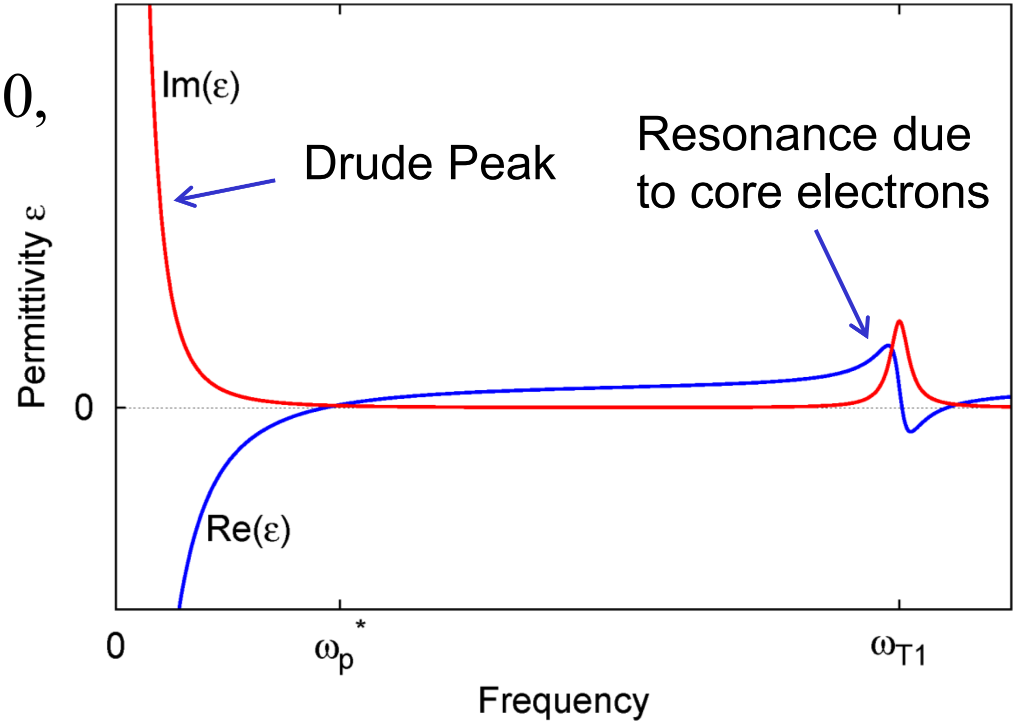
Optical properties of metals

- Use Lorentz oscillator model for bound electrons giving background ϵ_∞
- Use Drude model for conduction electrons, zero restoring force $\Rightarrow \omega_T = 0$

$$\chi_\omega = \frac{nq^2}{m\epsilon_0(\omega_T^2 - \omega^2 - i\omega\gamma)}, \ \omega_T = 0,$$

$$\Rightarrow \epsilon_\omega = \epsilon_\infty - \frac{nq^2}{m\epsilon_0(\omega^2 + i\omega\gamma)}$$

$$= \epsilon_\infty - \frac{\omega_p^2}{(\omega^2 + i\omega\gamma)}, \ \omega_p^2 = \frac{nq^2}{m\epsilon_0}$$

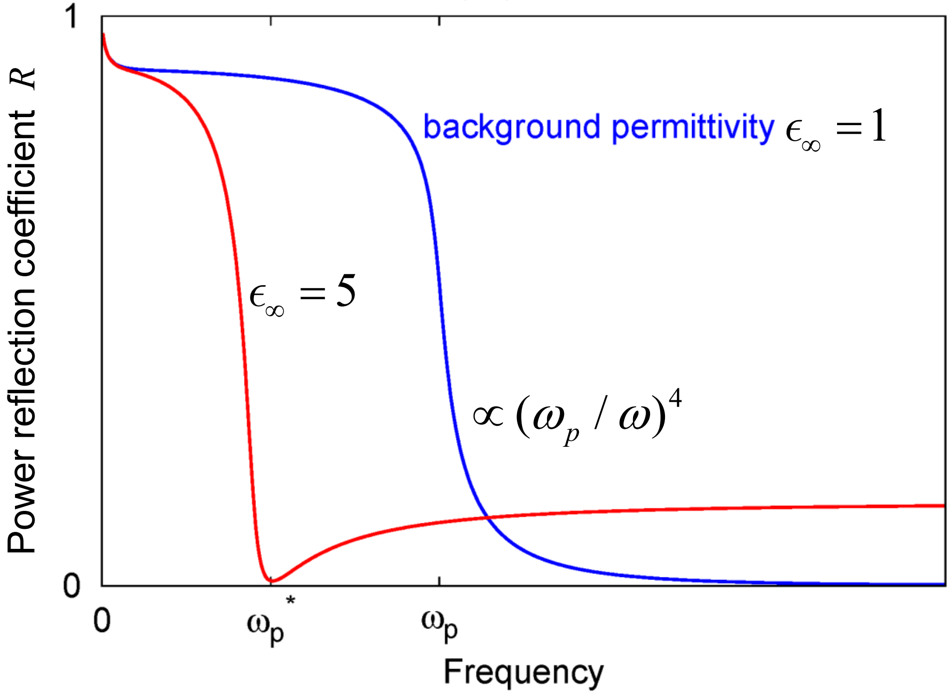


- $|\epsilon(\omega)|$ diverges as $\omega \rightarrow 0$ so metals are highly reflecting at low frequency
- Peak in $\mathrm{Im}(\epsilon_\omega)$ at low ω, due to enhanced absorption, ‘Drude peak’:
- $\epsilon(\omega)$ crosses zero at ω_P^* and approaches 1 at a high frequency so metals become transparent in the ultraviolet.

Optical properties of metals

- Reflectivity at the interface between two media using the Drude model
- If permeability is unchanged at interface:
- Power reflection coefficient $R = |r|^2$

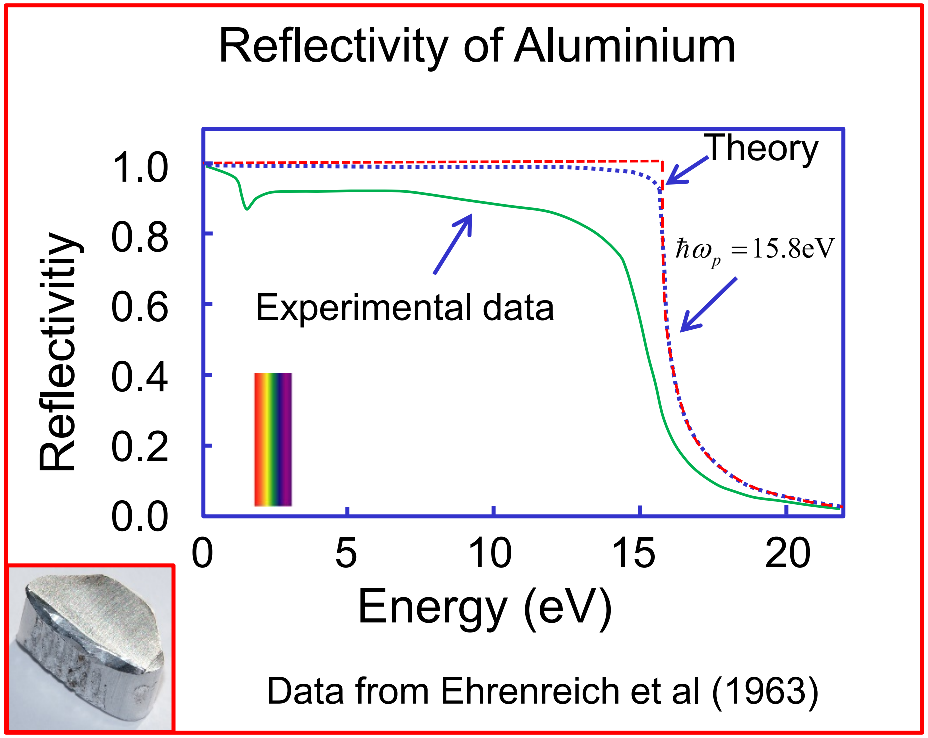
$$r = \frac{\sqrt{\epsilon_1} - \sqrt{\epsilon_2}}{\sqrt{\epsilon_1} + \sqrt{\epsilon_2}}$$



- Plateau in R at low frequency, related to conductivity of material
- $R \propto \omega^{-4}$ at high frequency – blue line on figure
- If background permittivity ϵ_∞ - due to polarisability of core electrons is significant, R can go to zero at finite frequency – red line

Experimental reflectivity of Aluminium

- Experimental Reflectivity of Aluminium as a function of photon energy - green curve, (solid)
- Reflectivity above 80% for visible region of spectrum - aluminium coating is used for commercial mirrors
- Plasma frequency in ultra-violet
- Both theory curves assume we have $\hbar\omega_p = 15.8\text{eV}$
- Red (dashed) no damping



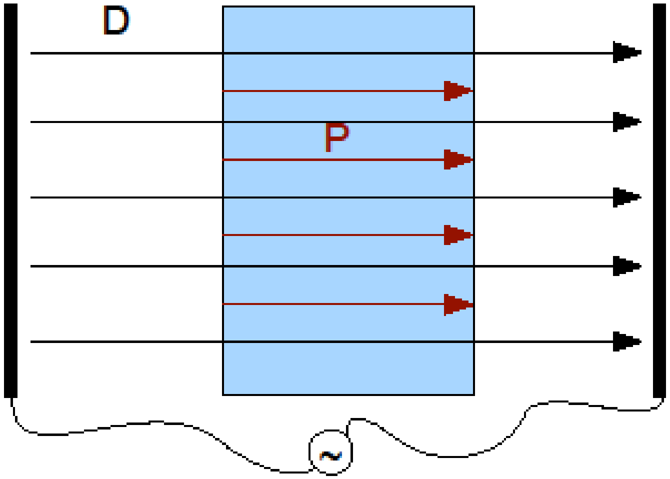
Data from Ehrenreich et al (1963)

- Blue (Dotted) with $\tau = 8.0\times10^{-15}s$ value deduced from DC conductivity values - slightly better fit
- Two unexplained features in experimental results: (1) reflectivity is smaller than predicted (2) small dip in reflectivity around 1.5eV
- Both explained by considering interband absorption rates

Optical properties of Solids, M Fox

Optical properties of metals: plasma oscillations

- Part IB electromagnetism – “Plasma Oscillations”
- electrons moving in a positively charged environment - model for metal.
- Consider probing a slab of material by applying an oscillating field $\mathbf{D}$:



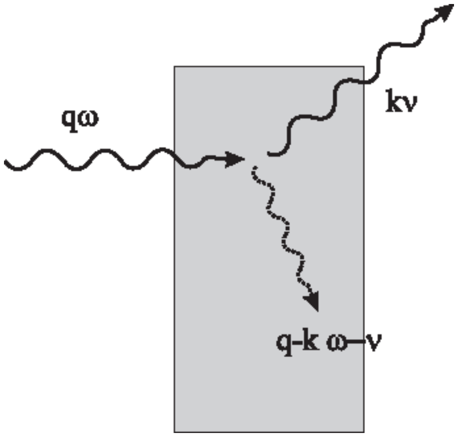
$$\mathbf{D} = \epsilon_0 \epsilon_\omega \mathbf{E} = \epsilon_0 \mathbf{E} + \mathbf{P} \Rightarrow \mathbf{P} = \mathbf{D}\left(1 - \epsilon_\omega^{-1}\right)$$

$$\epsilon_\omega = \epsilon_\infty - \frac{\omega_p^2}{(\omega^2 + i\omega\gamma)}$$

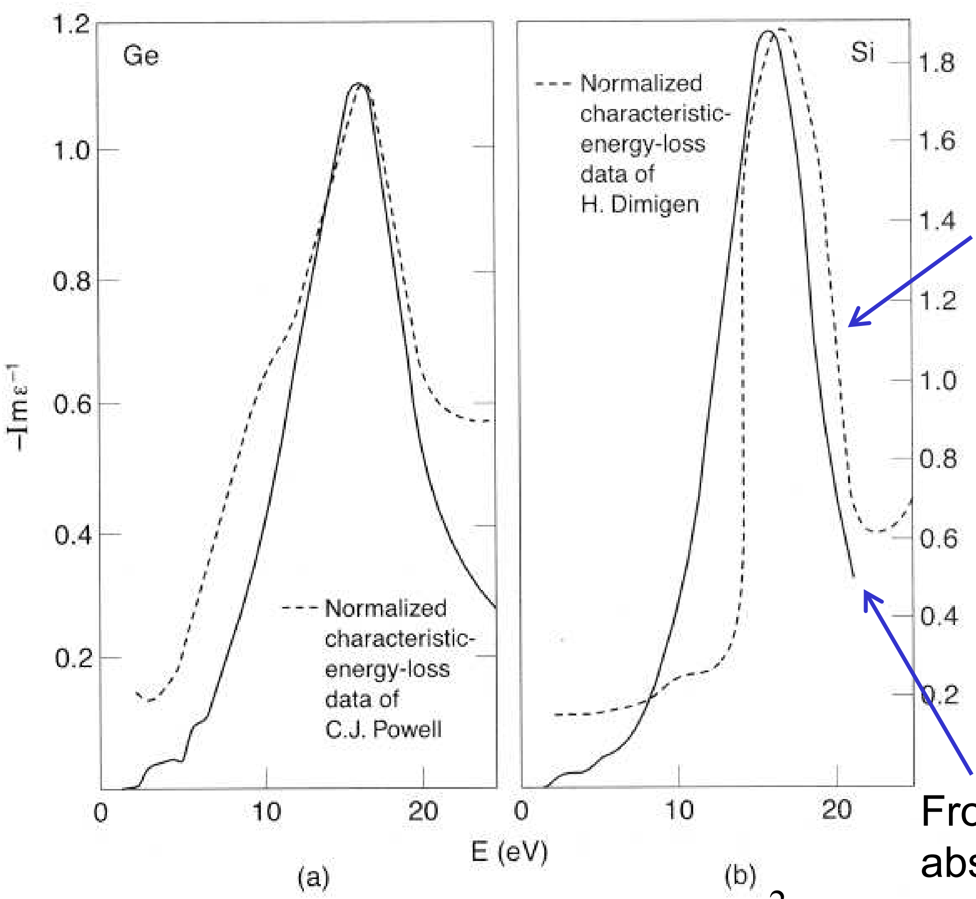
$$\epsilon_\infty \approx 1 \Rightarrow \epsilon_\omega^{-1} = \frac{\omega^2 + i\omega\gamma}{\omega^2 - \omega_p^2 + i\omega\gamma}$$

- In metals $\omega_p \gg \gamma = \tau^{-1}$ and usually $\epsilon_\infty = 1$ so ϵ_ω^{-1} peaks and $\epsilon_{\omega_p} \approx 0$
- More generally as $\epsilon_\omega \to 0$ at $\omega = \omega_p \epsilon_\infty^{-1/2}$ we get *Plasma Oscillations* at a frequency defined by $\omega_p^2 = ne^2 / m\epsilon_0$
- Polarisation causes build-up of surface charge, which generates the restoring force driving the oscillations. The electrons slosh back and forth.

Optical properties of metals: plasma oscillations and electron energy loss spectroscopy in Ge and Si



- Incoming electron at wavevector q, energy $\hbar\omega$. Outgoing electron at wavevector k, energy $\hbar\nu$. Plasmon generated with energy $\hbar(\omega-\nu)$

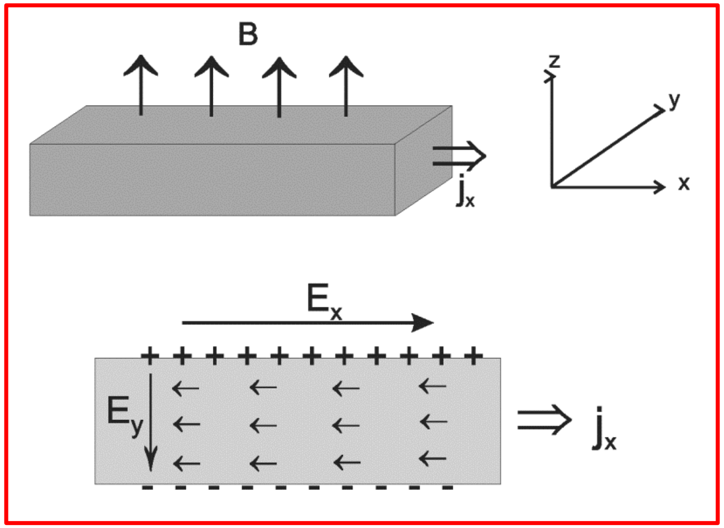


EELs

From optical absorption

- Response to oscillating applied $\mathbf{D}$ field given by $\epsilon_\omega^{-1} = \dfrac{\omega^2 + i\omega\gamma}{\omega^2 - \omega_p^2 + i\omega\gamma}$
- Resonance at plasma frequency $\omega_p^2 = \dfrac{ne^2}{m\epsilon_0}$ width τ^{-1}.

Transport in electric and magnetic fields



- Previously $\dfrac{\mathrm{d}\mathbf{j}(t)}{\mathrm{d}t} = -\dfrac{\mathbf{j}(t)}{\tau} + \dfrac{nq^2\mathbf{E}}{m} + \dfrac{q}{m}(\mathbf{j}\times\mathbf{B})$
- If B is parallel to z-axis, taking components

$$\left(\tfrac{\mathrm{d}}{\mathrm{d}t} + \tau^{-1}\right) j_y = \tfrac{q}{m}\left(nqE_y - Bj_x\right)$$

$$\left(\tfrac{\mathrm{d}}{\mathrm{d}t} + \tau^{-1}\right) j_x = \tfrac{q}{m}\left(nqE_x + Bj_y\right)$$

- Steady state $\tfrac{\mathrm{d}\mathbf{j}}{\mathrm{d}t} = 0$

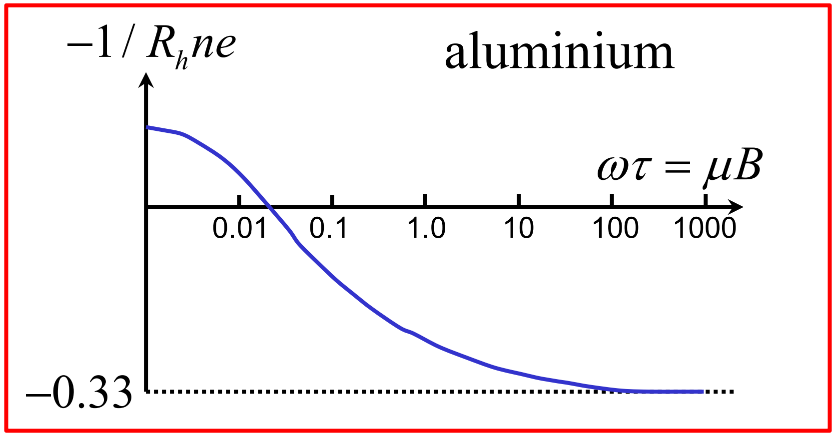
$$j_y = \tfrac{q\tau}{m}\left(nqE_y - Bj_x\right),\; j_x = \tfrac{q\tau}{m}\left(nqE_x + Bj_y\right)$$

- *Hall effect:* current confined to x-axis $(j_y = 0)$ by transverse field (E_y) due to charge build up.
- Hall coefficient $R_H = \dfrac{E_y}{j_x B} = \dfrac{1}{nq}$ gives carrier density and sign of charge
- If $B = 0$ then $j_x = \tfrac{q\tau}{m} nqE_x \Rightarrow \tfrac{j_x}{nqE_x} = \tfrac{v_x}{E_x} = \tfrac{q\tau}{m} = \mu$ carrier 'mobility'
- Mobility defined as velocity of charge carrier per unit electric field.
- since $\mathbf{j} = \sigma\mathbf{E} \Rightarrow \sigma = \tfrac{nq^2\tau}{m} = nq\mu$
- Cyclotron frequency defined as $\omega_c = \tfrac{eB}{m} \Rightarrow \omega_c\tau = \mu B$

Hall effect in metals

- First measured 1879 E H Hall
- From the last slide $R_H = 1/nq$
- Drude theory predicts R_H is independent of B and τ
- In metals however it is found that R_H does vary with magnetic field as well as temperature and sample purity
- Measuring pure samples at low temperatures and high magnetic fields (1T) limiting values are obtained.
- Comparison made between observed and predicted number of free electrons per atom for a range of metals
- Theory seems to work quite well for alkali metals & noble metals but not for the others - new theories needed!

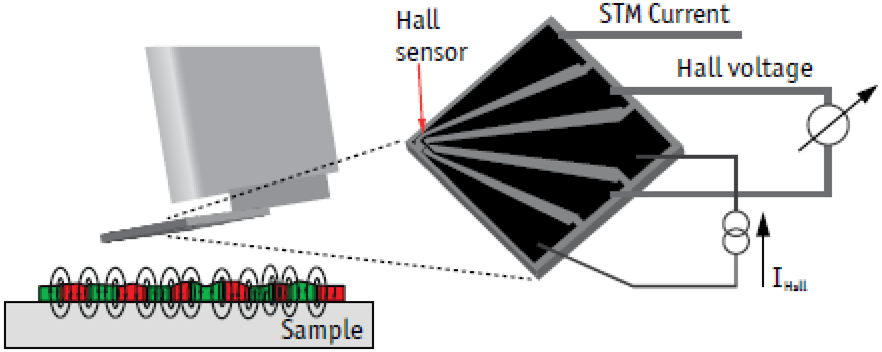
R Lück, Phys Stat. Sol. **18**, 49(1966)

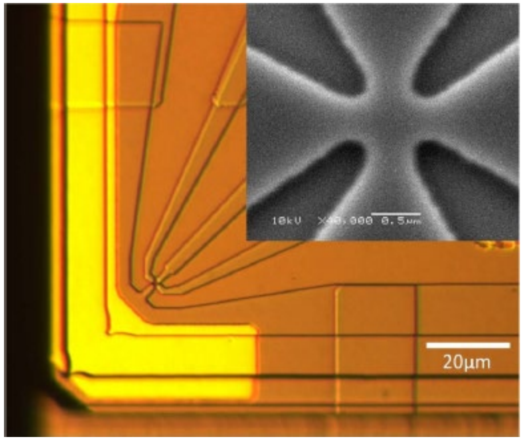


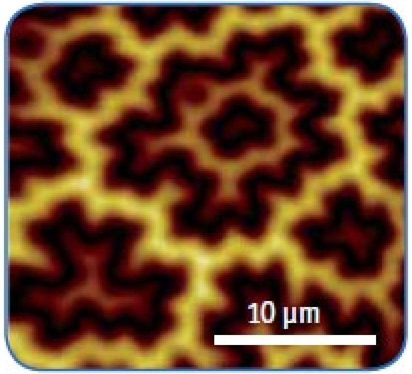
Metal	Valence	$-1/R_h ne$
Li	1	0.8
Na	1	1.2
K	1	1.1
Cu	1	1.5
Ag	1	1.3
Au	1	1.5
Be	2	-0.2
Mg	2	-0.4
In	3	-0.3
Al	3	-0.3

Scanning Hall Probe Microscopy

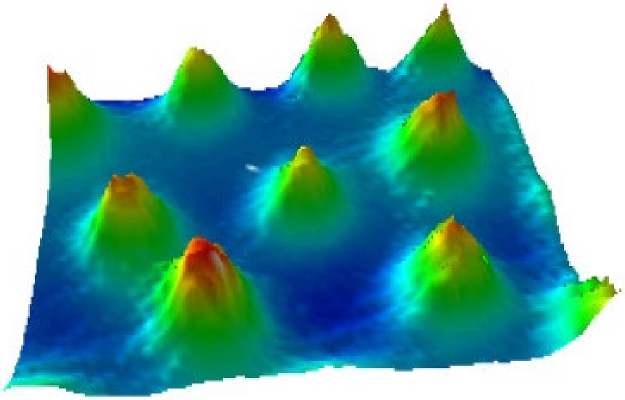
- First report Chang et al Appl Phys Lett **61**, 1974 (1992)
- Hall sensor mounted on scanning system to measure local magnetic field
- Magnetic field sensitivity $10^{-5}\,\mathrm{T}$ spatial resolution $0.35\,\mu\mathrm{m}$
- Now commercial product from Attocube, Nanomagnetics, Magcam……







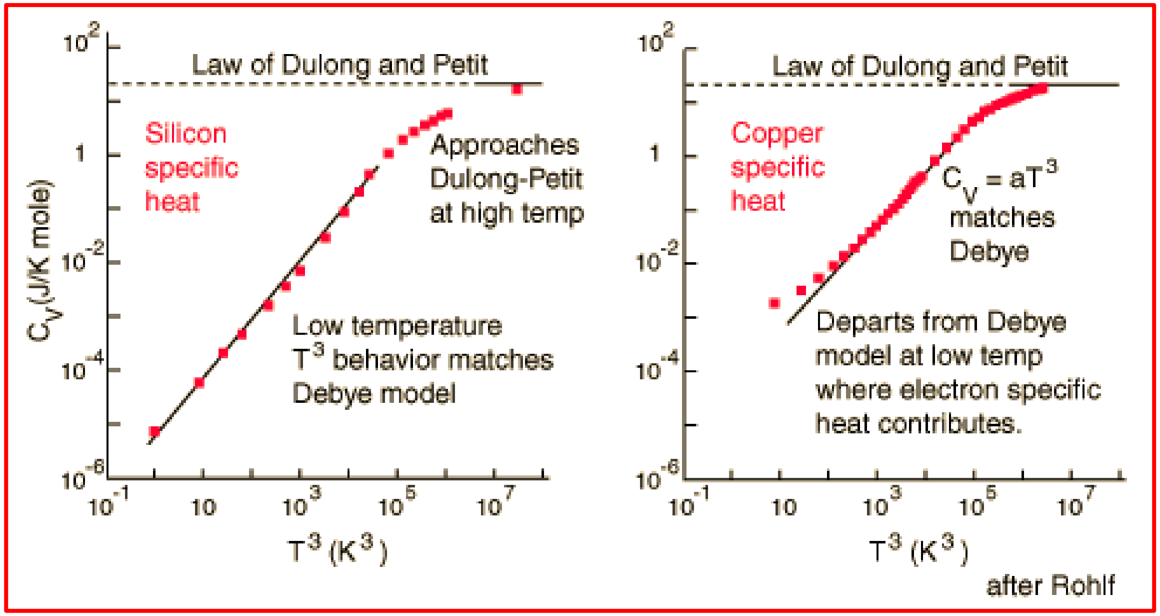
SHPM image of BaFeO, recorded at 4.2 K in constant height mode. The color scale spans 106 mT (black to white), while the S/N ratio of this measurement yields 2x10⁵.



SHPM image of superconducting vortices in a thin Pb film at 4 Kelvin

Problems with Drude Theory

- Drude model predicts the electronic head capacity to be from equipartition of energy $C_{el} = \frac{3}{2} n k_B$ independent of T.
- Measured heat capacity falls far below that expected from equipartition theorem and is temperature dependent.

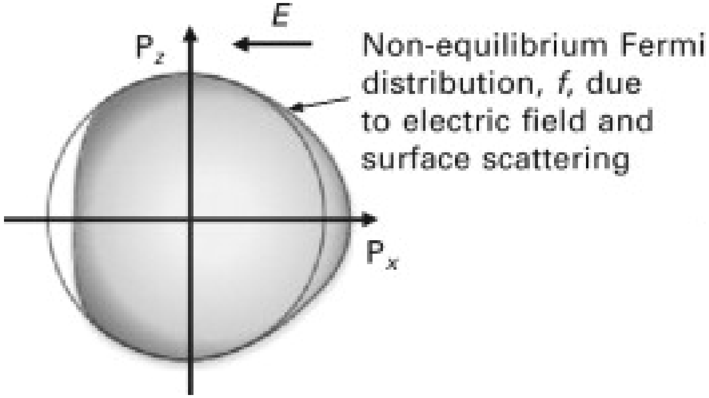


after Rohlf

- Correct description: degenerate Fermi gas (cf. Stat. Phys. course).
- Interpret velocity u in Drude model as *drift velocity*, averaged over many particles. Individual electrons actually travel at up to 1% of speed of light!

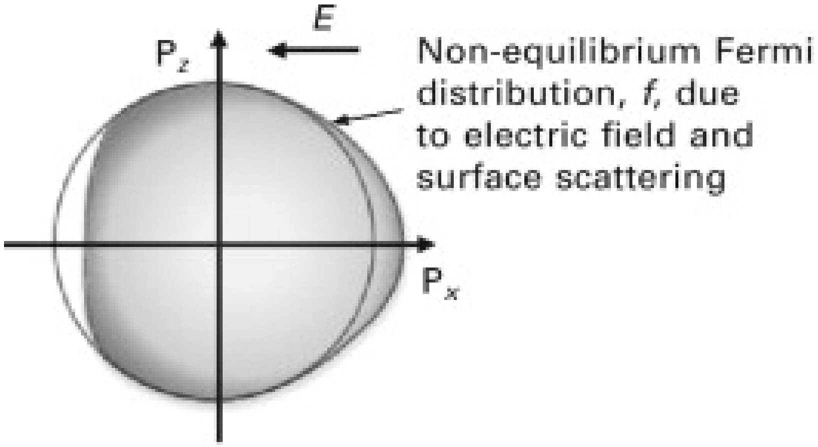
Drude Model – is it valid?

- The Drude model is very crude (devised only 3 years after discovery of electron by J J Thomson in 1897!)
  - assumes electrons have random (or 0) momentum after a collision
  - assumes scatterers are all the positive ions (but mean free path can be much longer than atomic spacing)
  - no concept of QM, Pauli exclusion principle, fermions, …
- We should instead consider a Fermi sphere of electrons occupying all the states in *k*-space up to the Fermi energy E_F
  - only two electrons in each state (two spins)
  - only electrons near Fermi surface can gain energy or scatter
  - Fermi-Dirac function f gives probability of finding electron in a state
  - distribution function f is modified by electric field, which provides momentum, so there are more electrons moving in one direction than in the opposite one



Drude model – its replacement

- Describe using Boltzmann transport formalism (Part III major option AQCMP)
  - scattering causes total momentum to decay, same results
- Various types of scattering in metals (and semiconductors):
  - phonons (dominate at room temperature T)
  - impurities and lattice defects (important at low T)
  - other electrons (surprisingly unimportant; total momentum conserved so no effect on current)
  - we will see that the ions themselves have no effect provided that they are in a periodic lattice (band structure)



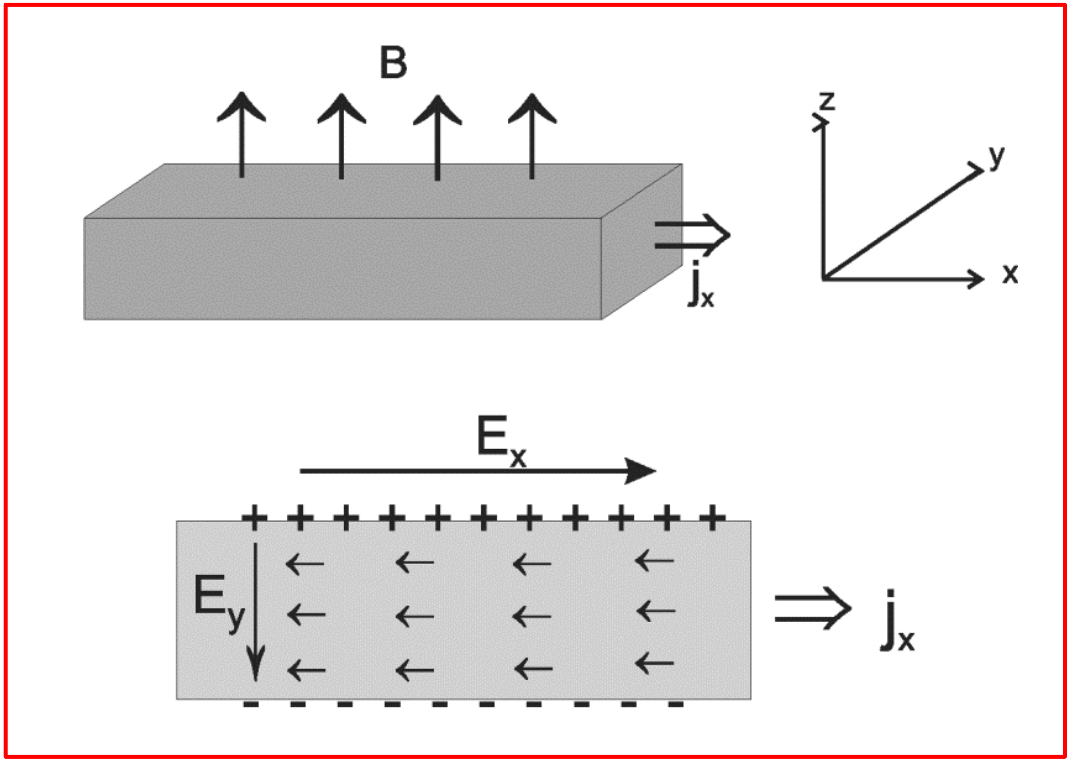
(a)

Summary of Lecture 2

- The Drude model – frequency dependant conductivity
- Optical properties of metals
- Experimental reflectivity of aluminium
- Plasma oscillations, electron energy loss spectroscopy
- Hall effect from Drude model
- Hall effect in metals
- Applications of Hall effect – scanning Hall probe microscopy
- Problems with Drude theory

Quantum Condensed Matter Physics

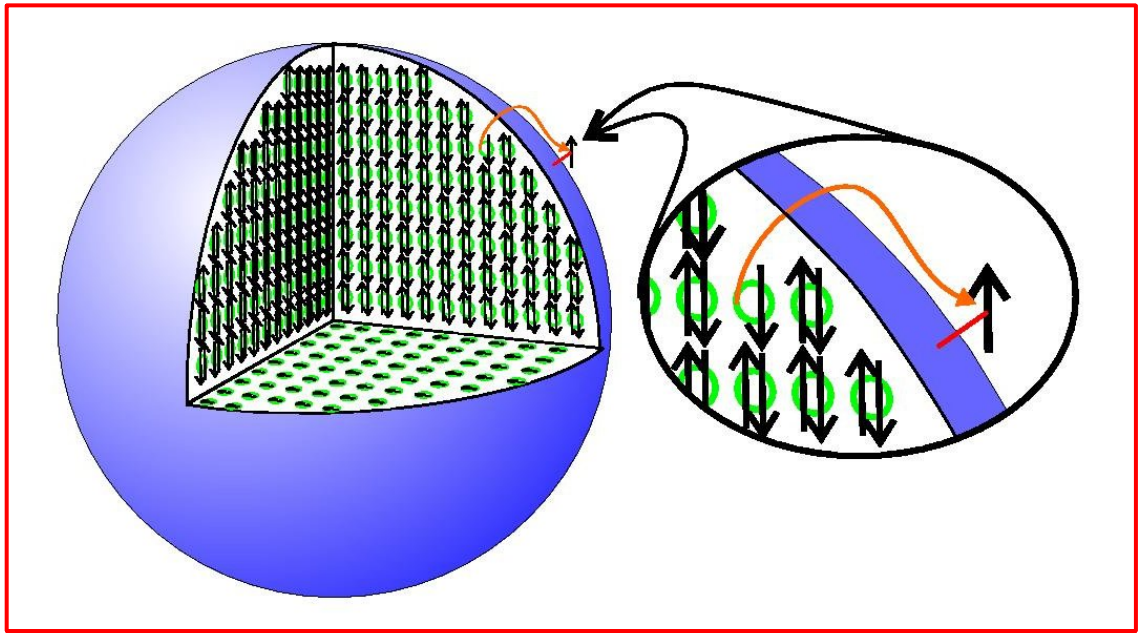
Lecture 2



The End

Quantum Condensed Matter Physics

Lecture 3



David Ritchie

http://www.sp.phy.cam.ac.uk/drp2/home

Quantum Condensed Matter Physics

1. Classical and Semi-classical models for electrons in solids (3L)

Lorentz dipole oscillator, optical properties of insulators. Drude model and optical properties of metals, plasma oscillations. Semi-classical approach to electron transport in electric and magnetic fields, the Hall effect. *Sommerfeld model, density of states, specific heat of; electrons in metals, liquid ^{3}He/^{4}He mixtures. Screening and the Thomas-Fermi approximation.*

2. Electrons and phonons in periodic solids (6L)
3. Experimental probes of band structure (4L)
4. Semiconductors and semiconductor devices (5L)
5. Electronic instabilities (2L)
6. Fermi Liquids (2L)

Sommerfeld Model – density of states

- Free electron gas - Schrodinger equation: $-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r})$
- Introduce eigenstates

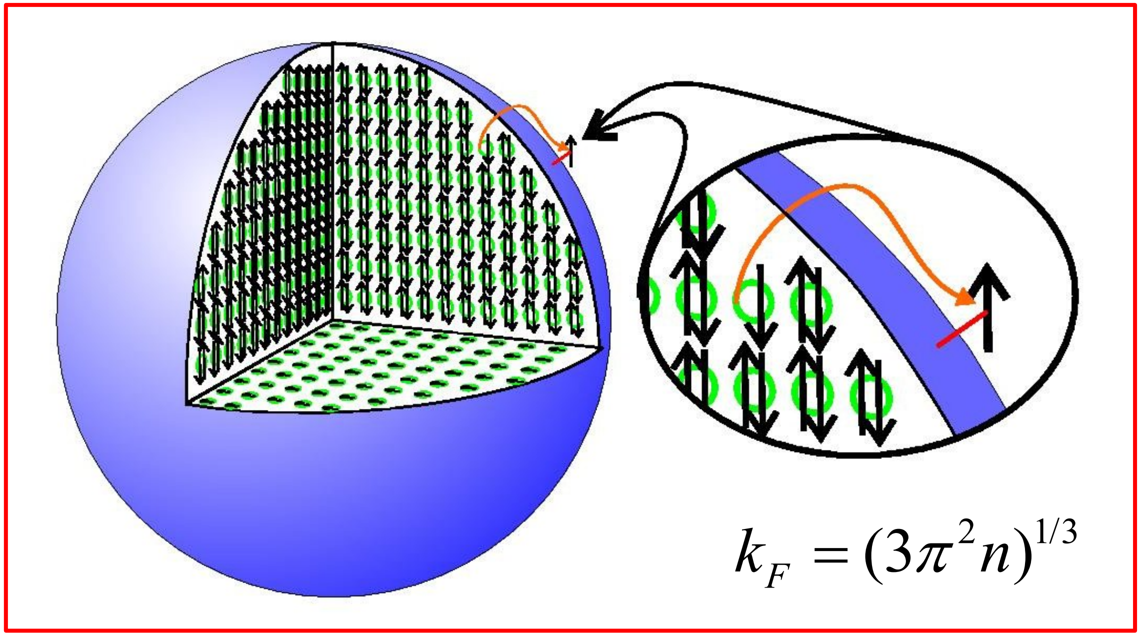
$$\psi_{\mathbf{k}}(\mathbf{r}) = A\exp(i\mathbf{k}\cdot\mathbf{r}),\ E_{\mathbf{k}} = \hbar^2|\mathbf{k}|^2/2m$$

satisfying periodic boundary conditions $\psi(x+L,y,z) = \psi(x,y,z)$ etc.

- Allowed values of momentum are discrete: $\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ where n_x, n_y, n_z are positive or negative integers

- At zero temperature fill up Fermi sphere to the Fermi energy E_F

- Each triplet of quantum numbers corresponds to 2 states – electron spin degeneracy
- volume in k-space $(2\pi/L)^3$


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

Sommerfeld Model – density of states

- Number of occupied states in Fermi sphere: $N = 2 \cdot \dfrac{4/3\pi k_F^3}{(2\pi/L)^3}$
- Hence if $n = N/V = N/L^3$ then $k_F = (3\pi^2 n)^{1/3}$
- Also

$$E_F = \hbar^2 k_F^2 / 2m = \hbar^2 (3\pi^2 n)^{2/3} / 2m \Rightarrow \ln(E_F) = \tfrac{2}{3}\ln(n) + \text{const}$$

$$\Rightarrow \frac{\mathrm{d}E_F}{E_F} = \frac{2}{3}\frac{\mathrm{d}n}{n} \Rightarrow \frac{\mathrm{d}n}{\mathrm{d}E_F} = g(E_F) = \frac{3}{2}\frac{n}{E_F}$$

- Density of states

$$g(E)dE = 2 \cdot \frac{\text{Volume of shell in k} - \text{space}}{\text{Volume of k} - \text{space per state}} = 2 \cdot \frac{4\pi k^2 dk}{(2\pi)^3 / V}$$

- Hence

$$g(E) = 2\frac{V}{(2\pi)^3} 4\pi k^2 \frac{dk}{dE} = \frac{V}{\pi^2}\frac{m}{\hbar^2}\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$$

- Factor of 2 for spin degeneracy
- Often $g(E)$ is given per unit volume so V disappears.

Sommerfeld Model – electronic specific heat

- Occupancy of states in thermal equilibrium – Fermi distribution:

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

- Chemical potential $T = 0 \Rightarrow \mu = E_F$
- Number density of particles $n = N/V = \frac{1}{V}\sum_i f(E_i) = \int g(E) f(E)\,\mathrm{d}E$
- Energy density $u = \int E g(E) f(E)\,\mathrm{d}E$
- At room temperature $k_B T \approx 0.025 eV$ For metals E_F $\approx$ a few eV hence $k_B T \ll E_F$
- From above $c_v = \partial u / \partial T |_v = \int E g(E) \frac{\partial f(E)}{\partial T} \mathrm{d}E$
- Since the Fermi function is a step function $\frac{\partial f(E)}{\partial T}$ is sharply peaked at the chemical potential
- Contributions to the specific heat only come from states within $k_B T$ of the chemical potential, with each state having specific heat k_B and we can guess that

$$c_v \approx n \frac{k_B T}{E_F} k_B$$

Sommerfeld Model – electronic specific heat

- To calculate this more accurately…. We take the density of states as a constant so
$$c_v = \int Eg(E)\frac{\partial f(E)}{\partial T}\mathrm{d}E \approx g(E)\int E\frac{\partial f(E)}{\partial T}\mathrm{d}E$$
- changing variables $x = (E-\mu)/k_BT \Rightarrow \frac{\partial f}{\partial T} = \frac{e^x}{(e^x+1)^2}\times\left[\frac{x}{T}+\frac{1}{k_BT}\frac{\partial \mu}{\partial T}\right]$
- The number of particles is conserved so
$$\frac{dn}{dT} = 0 = g(E_F)\int\frac{\partial f(E)}{\partial T}\mathrm{d}E = g(E_F)k_BT\int_{-\infty}^{\infty}\frac{e^x}{(e^x+1)^2}\times\left[\frac{x}{T}+\frac{1}{k_BT}\frac{\partial \mu}{\partial T}\right]\mathrm{d}x$$
- The first term in the square brackets is odd, $\frac{e^x}{(e^x+1)^2}$ is even so $\frac{\partial \mu}{\partial T} \simeq 0$
- To the same level of accuracy:

$$c_v = g(E_F)\int E\frac{\partial f(E)}{\partial T}\mathrm{d}E = g(E_F)k_BT\int_{-\infty}^{\infty}(\mu + k_BT\,x)\frac{e^x}{(e^x+1)^2}\frac{x}{T}\mathrm{d}x$$

$$= g(E_F)k_B^2T\int_{-\infty}^{\infty}\frac{x^2e^x}{(e^x+1)^2}\mathrm{d}x = \frac{\pi^2}{3}k_B^2Tg(E_F)$$

Sommerfeld Model – electronic specific heat

- Since $g(E_F)=\frac{3}{2}\frac{n}{E_F}$ we can write

$$c_v=\frac{\pi^2}{3}k_B^2Tg(E_F)=\frac{\pi^2}{3}k_B^2T\frac{3}{2}\frac{n}{E_F}=\frac{\pi^2}{2}\frac{k_BT}{E_F}nk_B=\frac{\pi^2}{2}\frac{T}{T_F}nk_B$$

- This result is of the same form as the equation above obtained from a simple argument but with a different prefactor - $\pi^2/2$ as opposed to 1.
- This calculation is the leading order term in an expansion in powers of $(k_BT/E_F)^2$.
- To next order the chemical potential is temperature dependent (see below) but because for metals $k_BT \ll E_F$ we can usually ignore it.

$$\mu=E_F\left[1-\frac{1}{3}\left(\frac{\pi k_BT}{2E_F}\right)^2+O(k_BT/E_F)^4\right]$$

- Examples:
- Electron gas in solids – often much smaller than lattice specific heat
- Liquid helium mixtures of ^{3}He in ^{4}He – near ideal Fermi gas

Specific Heat of mixtures of ^{3}He and ^{4}He

- Experimental procedure:
- Cool helium mixtures to mK temperatures,
- Isolate from surroundings
- Input heat for given time
- Measure temperature rise
- Calculate specific heat at particular temperatures and pressures

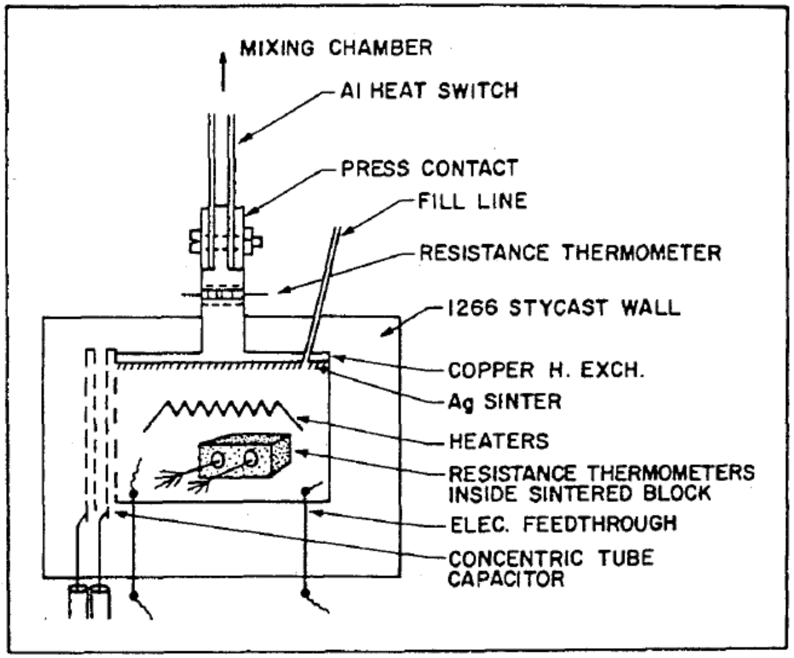
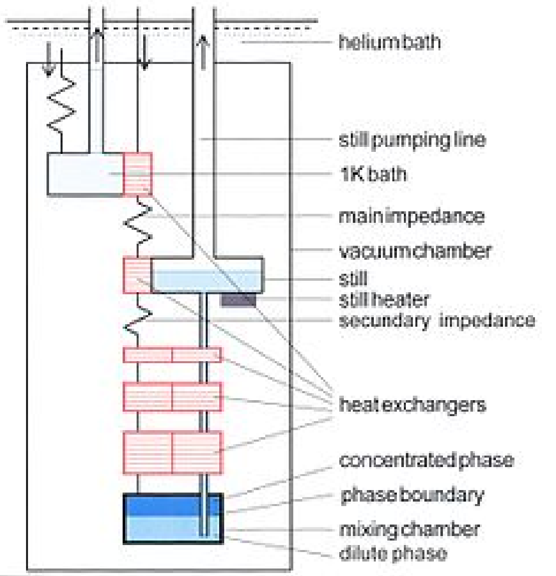
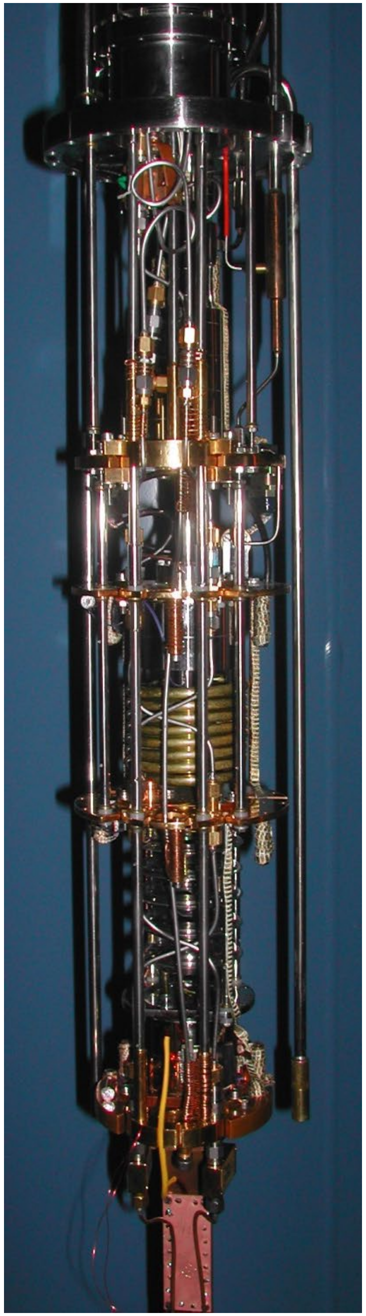


Fig. 1. A schematic view of the calorimeter. The internal parts are spaced from the walls and from each other by layers of nylon lace (not shown).

Helium dilution refrigerator



From wikipedia



Polturak and Rosenbaum JLTP, **43,** 477 (1981)

Specific heat of mixtures of liquid ^{3}He and ^{4}He

- From above $c_v = \dfrac{\pi^2}{2}\dfrac{T}{T_F} n k_B, \;\; T_F = \dfrac{E_F}{k_B} = \dfrac{\hbar^2}{2mk_B}\left(3\pi^2 n\right)^{2/3}$
- Linear behaviour in Fermi gas regime $T \ll T_F$

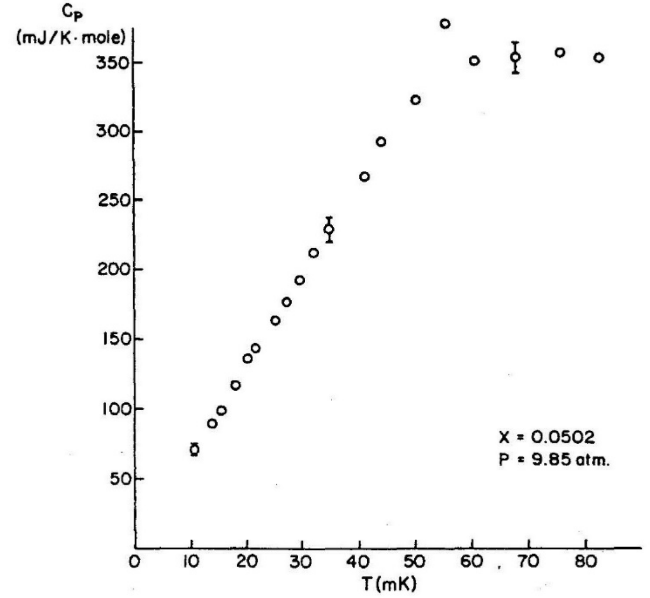


Fig. 2. Specific heat per mole of solution for $X = 0.0502$ at 10 atm. Error bars represent the experimental uncertainties.

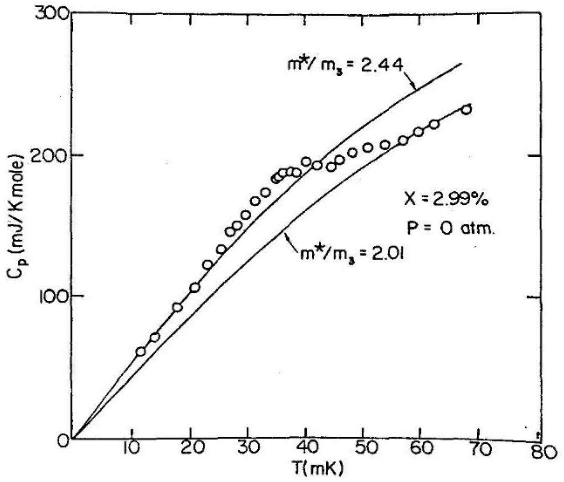


Fig. 3. Specific heat per mole of solution for $X = 0.0299$ at zero pressure. Error bars represent experimental uncertainties. The upper line is the specific heat of a free Fermi gas of the same number density having an effective mass determined by the low-temperature slope of the data ($T_F^* = 235$ mK, $m^*/m_3 = 2.44$). The lower curve was fitted to the higher temperature data above 50 mK by adjusting $m^* = 2.01 m_3$.

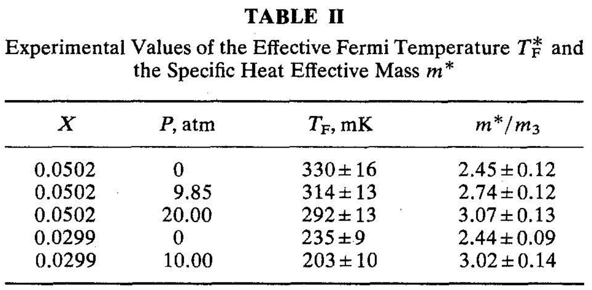


TABLE II

Experimental Values of the Effective Fermi Temperature T_F^* and the Specific Heat Effective Mass m^*

X	P, atm	T_F, mK	m^*/m_3
0.0502	0	330 ± 16	2.45 ± 0.12
0.0502	9.85	314 ± 13	2.74 ± 0.12
0.0502	20.00	292 ± 13	3.07 ± 0.13
0.0299	0	235 ± 9	2.44 ± 0.09
0.0299	10.00	203 ± 10	3.02 ± 0.14

- So knowing c_v, T, n we can calculate T_F the Fermi temperature and m the effective mass
- Effective mass 2.44 to 3.07 time bare ^{3}He mass – due to interactions

Polturak and Rosenbaum JLTP, **43,** 477 (1981)

Screening and Thomas-Fermi approximation

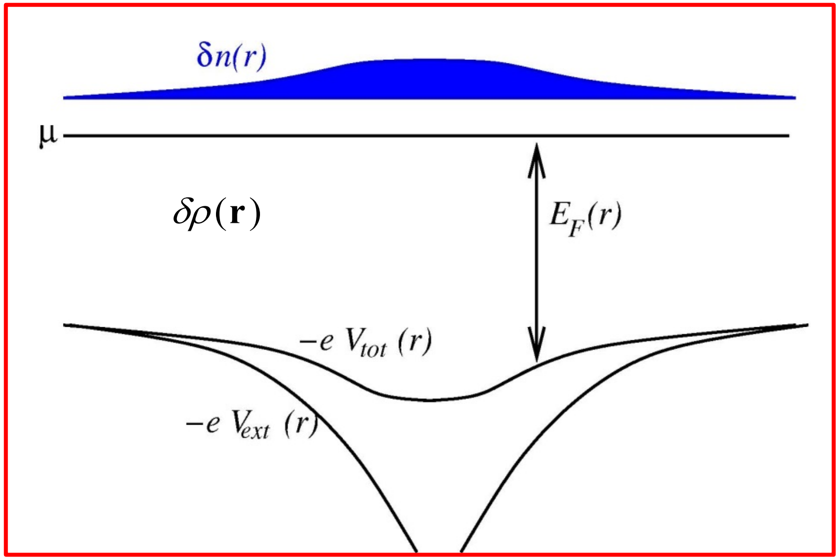
- Placing a positive charge in a metal will result in electrons moving around to screen its potential resulting in zero electric field.
- This is quite different from a dielectric where electrons are not able to move freely and the potential is reduced by dielectric constant
- In a classical picture electrons can move anywhere, but quantum mechanics dictates this is not possible - an electron cannot sit right on top of a nucleus.
- In metals a balance is reached between minimising potential and kinetic energy, screening over a short but finite distance.
- We estimate the response of a free electron gas to a perturbing potential. $V_0(\mathbf{r})$ is the electrostatic potential, $\rho_0(\mathbf{r})$ the charge distribution.

$$\nabla^2 V_0(\mathbf{r}) = -\frac{\rho_0(\mathbf{r})}{\epsilon_0}$$

- Consider the positive background charge to be homogeneous with the electron gas moving around - plasma or “Jellium” model and in this case $\rho_0(\mathbf{r}) = 0$ everywhere (this does not include the charges used to set up the perturbing potential).

Screening and Thomas-Fermi approximation

- In the presence of a perturbing potential $V_{ext}(\mathbf{r})$ the electron charge density redistributes $\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})$ which changes the potential $V(\mathbf{r}) = V_0(\mathbf{r}) + \delta V(\mathbf{r})$. The changes are related by: $\nabla^2 \delta V(\mathbf{r}) = -\frac{\delta\rho(\mathbf{r})}{\epsilon_0}$
- We link the charge redistribution to the applied potential by assuming the perturbing potential shifts free electron energy levels – the same as assuming a spatially varying Fermi energy. This is the “Thomas-Fermi” approximation.



- The potential is the total produced by the added external charge and the induced “screening” charge $V_{tot} = V_{ext} + \delta V$ hence:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + (-e)(\delta V(\mathbf{r}) + V_{ext}(\mathbf{r}))\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Screening and the Thomas-Fermi approximation

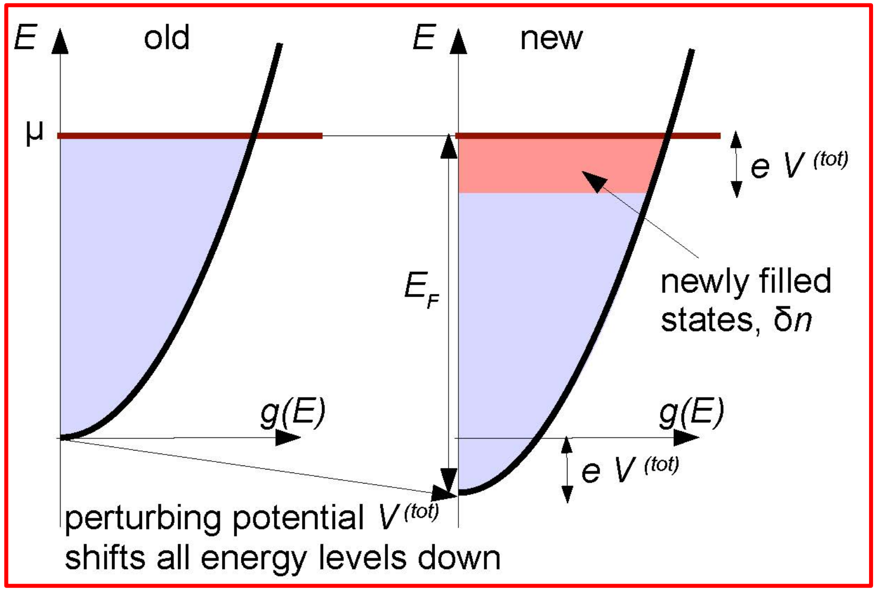
- Assume the induced potential is slowly varying on the scale of the Fermi wavelength $2\pi / k_F$ so the energy eigenvalues are just shifted by potential as a function of position:

$$E(\mathbf{k},\mathbf{r}) = E_0(\mathbf{k}) - eV_{tot}(\mathbf{r})$$

where $E_0(\mathbf{k})$ has a free electron parabolic dispersion $\frac{\hbar^2 k^2}{2m}$

- Keeping the electron states filled up to a constant energy μ means we adjust the local Fermi energy $E_F(\mathbf{r})$ as measured from the bottom of the band so:

$$\mu = E_F(\mathbf{r}) - eV_{tot}(\mathbf{r})$$



- A small shift in the local Fermi Energy leads to a change in the local electron number density, n.

$$\delta n = g_V(E_F)\delta E_F = eg_V(E_F)V_{tot}$$

- And from above $V_{tot} = V_{ext} + \delta V$ so we have:

$$\delta n = eg_V(E_F)\left(V_{ext} + \delta V\right)$$

Screening and the Thomas-Fermi approximation

- Since the added potential and induced electron number density are small we can use Poisson's equation to write:

$$\nabla^2 \delta V(\mathbf{r}) = \frac{e}{\epsilon_0}\delta n = \frac{e^2 g_V(E_\mathbf{F})}{\epsilon_0}(\delta V(\mathbf{r}) + V_{ext}(\mathbf{r}))$$

- We can calculate the induced potential and density response using Fourier transformation. Assume an oscillatory perturbing potential : $V_{ext} = V_{ext}(\mathbf{q})\mathbf{e}^{\mathbf{iq.r}}$ and a resulting oscillatory induced potential: $\delta V = \delta V(\mathbf{q})\mathbf{e}^{\mathbf{iq.r}}$ substituting into the equation above:

$$\nabla^2\left(\delta V(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}\right) = -q^2\delta V(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}} = \frac{e^2 g_V(E_F)}{\epsilon_0}(\delta V(\mathbf{q}) + V_{ext}(\mathbf{q}))e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$\Rightarrow \delta V(\mathbf{q})\left[q^2 + e^2 g_V(E_F)/\epsilon_0\right] = -V_{ext}(\mathbf{q})e^2 g_V(E_F)/\epsilon_0$$

$$\Rightarrow \delta V(\mathbf{q}) = -V_{ext}(\mathbf{q})\frac{e^2 g_V(E_F)/\epsilon_0}{q^2 + e^2 g_V(E_F)/\epsilon_0} = -\frac{q_{TF}^2}{q^2 + q_{TF}^2}V_{ext}(\mathbf{q})$$

- Where we define the Thomas–Fermi wavevector:

$$q_{TF} = \left(e^2 g_V(E_F)/\epsilon_0\right)^{\frac{1}{2}}$$

Screening and the Thomas-Fermi approximation

- The Thomas-Fermi wavevector $q_{TF} = \left(e^2 g_V(E_F)/\epsilon_0\right)^{\frac{1}{2}}$, and given that for the free electron gas:

$$g_V(E) = \tfrac{1}{2\pi^2}\left(\tfrac{2m}{\hbar^2}\right)^{3/2} E^{1/2}, \qquad E_F = \tfrac{\hbar^2 k_F^2}{2m} \quad \Rightarrow g_V(E_F) = \tfrac{m}{\pi^2\hbar^2} k_F$$

- We obtain: $q_{TF}^2 = \dfrac{1}{\pi^2}\dfrac{me^2}{\epsilon_0\hbar^2}k_F = \dfrac{4}{\pi}\dfrac{k_F}{a_B} = \left(\dfrac{2.95}{r_s^{1/2}}\text{Å}^{-1}\right)^2$
- where the Bohr radius is $a_B = \frac{4\pi\hbar^2\epsilon_0}{me^2} \simeq 0.53\text{Å}$

  and the Wigner-Seitz radius, r_s is defined by $(4\pi/3)r_S^3 = n^{-1}$
- To find the induced electron number density – from above we have

$$\delta n = eg_V(E_F)\left(V_{ext} + \delta V\right),\ \delta V(\mathbf{q}) = -\frac{q_{TF}^2}{q^2 + q_{TF}^2}V_{ext}(\mathbf{q}),\ \ q_{TF}^2 = e^2 g_V(E_F)/\epsilon_0$$

$$\Rightarrow \delta n(\mathbf{q}) = n_{ind}(\mathbf{q}) = \frac{q_{TF}^2\epsilon_0}{e}V_{ext}(\mathbf{q})\left(1 - \frac{q_{TF}^2}{q^2 + q_{TF}^2}\right) = \frac{\epsilon_0}{e}V_{ext}(\mathbf{q})\left(\frac{q^2}{q^2/q_{TF}^2 + 1}\right)$$

The Thomas-Fermi dielectric function

- The wavevector dependent dielectric function $\epsilon(\mathbf{q})$ relates the electric displacement $\mathbf{D}$ to the electric field $\mathbf{E}$ by $\epsilon_0\epsilon(\mathbf{q})\mathbf{E}(\mathbf{q})=\mathbf{D}(\mathbf{q})$
- given:

$$\nabla V_{ext}=-\mathbf{D}(\mathbf{q})/\epsilon_0,\ \nabla V_{tot}=-\mathbf{E}(\mathbf{q})\Rightarrow\nabla V_{ext}=\epsilon(\mathbf{q})\nabla V_{tot}$$

- Since from above

$$V_{tot}=V_{ext}+\delta V\Rightarrow V_{ext}(\mathbf{q})=\epsilon(\mathbf{q})\underbrace{\left(\delta V(\mathbf{q})+V_{ext}(\mathbf{q})\right)}_{V_{tot}}$$

- Using

$$\delta V(\mathbf{q})=-\frac{q_{TF}^2}{q^2+q_{TF}^2}V_{ext}(\mathbf{q})\Rightarrow V_{tot}(\mathbf{q})=V_{ext}(\mathbf{q})\frac{q^2}{q^2+q_{TF}^2}$$

- And hence the “Thomas Fermi dielectric function” is given by:

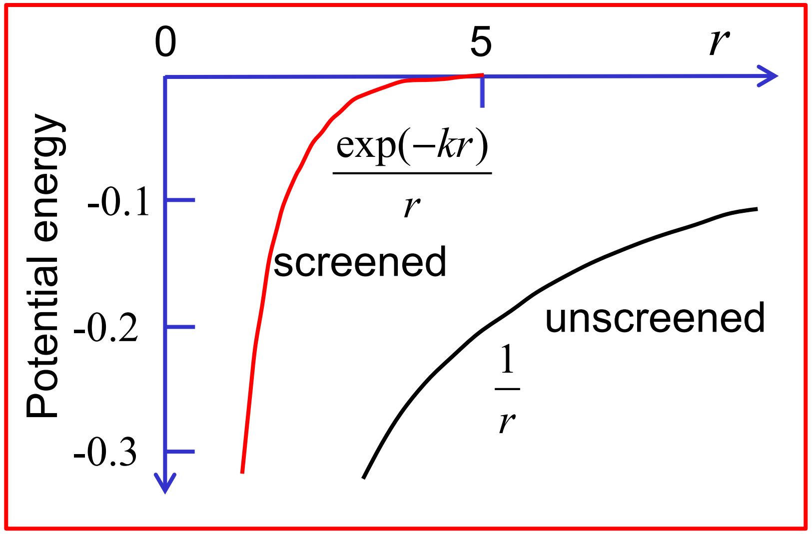
$$\epsilon^{TF}(\mathbf{q})=1+\frac{q_{TF}^2}{q^2}$$

- q_{TF}^{-1} is the Thomas-Fermi screening length, for copper where the electron density $n=8.5\times10^{22}\,\mathrm{cm}^{-3}$ we have $1/q_{TF}=0.055\mathrm{nm}$.

Thomas-Fermi screening

- From last slide $\epsilon^{TF}(\mathbf{q}) = 1 + q_{TF}^2 / q^2$
- For small q (long distances) $\epsilon^{TF} \propto q^{-2}$
- Long range part of Coulomb potential also $\propto q^{-2}$ so it is exactly cancelled
- In real space if $V_{ext} = Q / r$ (Coulombic and long range) then $V(r) = (Q/r)e^{-q_{TF}r}$ is the short range screened potential.

(problem sheet 1 question 6)



In this graph screening length $1/k=1$

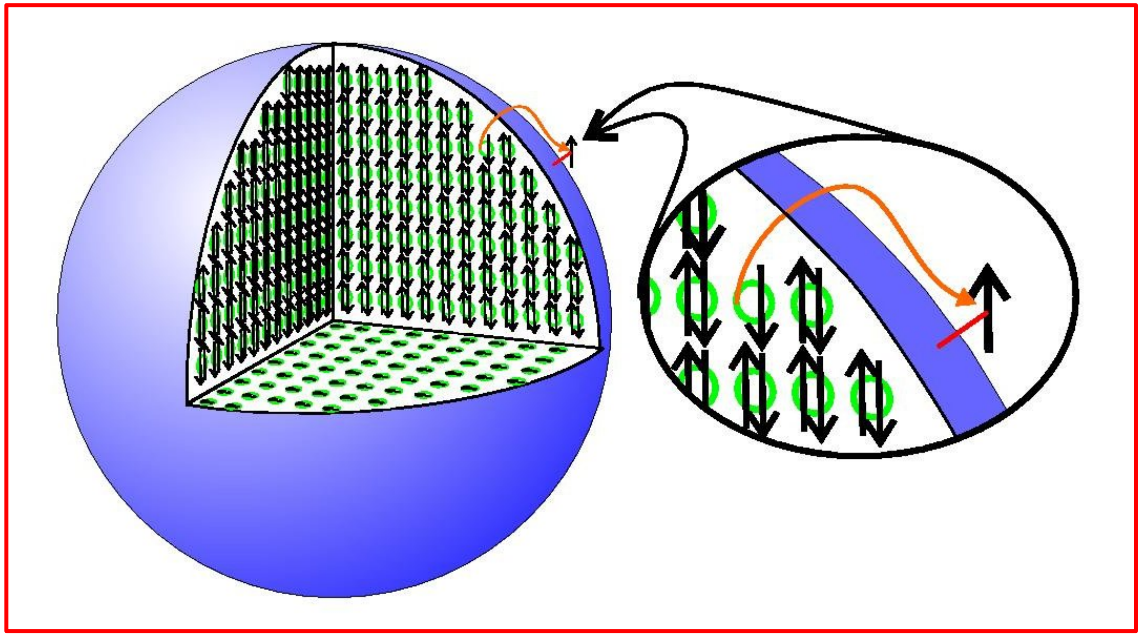
- The screened potential is known as the “Yukawa potential” in particle physics
- Exponential factor reduces range of Coulomb potential – screened over distances comparable to inter-particle spacing
- Mobile electron gas highly effective at screening external charges.
- Application to resistivity of alloys – atoms of Zn (valency 2) added substitutionally to metallic copper, (valency 1) has an excess charge.
- Foreign atom scatters conduction electrons with interaction given by screened Coulomb potential – scattering contributes to increase in in resistivity, theory and experiment in agreement.

Summary of Lecture 3

- The Sommerfeld model – electrons in a degenerate Fermi gas
- Free electron gas in three dimensions
- Fermi surface and density of states
- Thermal properties of the Fermi gas – specific heat
- Experimental measurements of specific heat in liquid helium.
- Screening and the Thomas-Fermi approximation,
- Thomas-Fermi wavevector and dielectric function
- Effect of screening on a Coulomb potential

Quantum Condensed Matter Physics

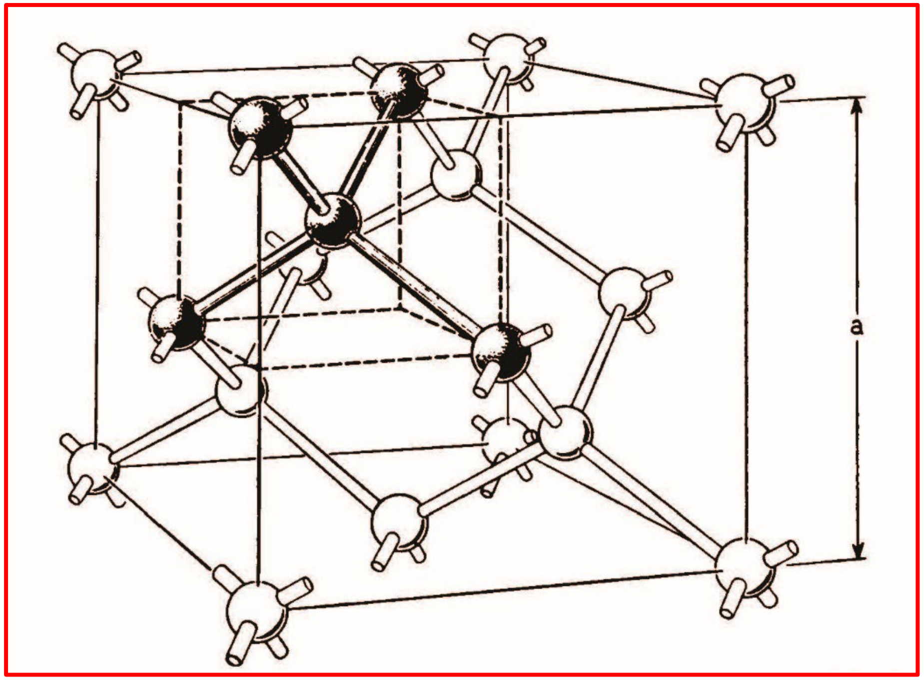
Lecture 3



The End

Quantum Condensed Matter Physics

Lecture 4



David Ritchie

Quantum Condensed Matter Physics

1. Classical and Semi-classical models for electrons in solids (3L)
2. Electrons and phonons in periodic solids (6L)

Types of bonding; Van der Waals, ionic, covalent. Crystal structures. Reciprocal space, x-ray diffraction and Brillouin zones. Lattice dynamics and phonons; 1D monoatomic and diatomic chains, 3D crystals. Heat capacity due to lattice vibrations; Einstein and Debye models. Thermal conductivity of insulators. Electrons in a periodic potential; Bloch's theorem. Nearly free electron approximation; plane waves and bandgaps. Tight binding approximation; linear combination of atomic orbitals, linear chain and three dimensions, two bands. Pseudopotentials.. ……….

3. Experimental probes of band structure (4L)
4. Semiconductors and semiconductor devices (5L)
5. Electronic instabilities (2L)
6. Fermi Liquids (2L)

From atoms to solids – the binding of crystals

- Cohesion due to interaction between electrons and nuclei giving rise to effective interaction potential between atoms
- Several different types of bonds – firstly Van der Waals
- Example: Inert gases – filled electron shells, large ionization energies
- Electron configuration in solid similar to that in separated atoms
- Atoms neutral – interaction weak, due to Van der Waals interaction
- Consider atom as oscillator – electrons fluctuate around nucleus
- Zero point fluctuations cause dipole moment p_1, a second atom at distance R experiences induced electric field $E \propto p_1 / R^3$
- This field induces a dipole at the second atom $p_2 \propto \alpha p_1 / R^3$ where α is the atomic polarizability
- The second atom induces an electric field at the first

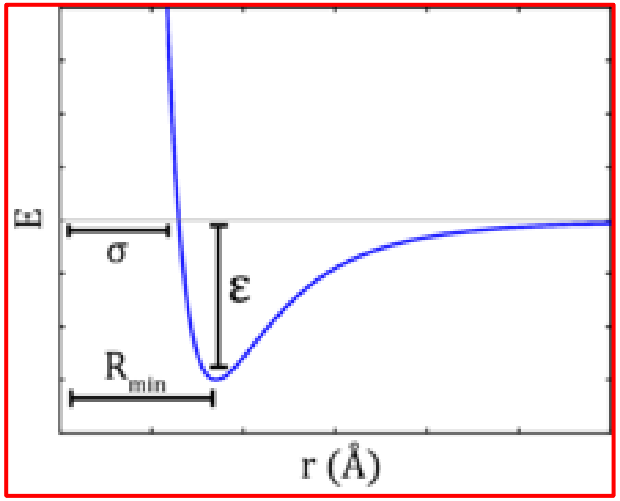
$$E_1 \propto p_2 / R^3 \propto \alpha p_1 / R^6 .$$

- The energy of the system changes by: $\Delta U = \left\langle -p_1 \cdot E_1 \right\rangle \propto -\alpha \left\langle p_1^2 \right\rangle / R^6 .$
- Induced interaction $\propto < p_1^2 >$ and is always attractive
- Note - Energy depends on $< p_1^2 >$ and not $< p_1 >^2$ which is zero

From atoms to solids – Van der Waals bonding

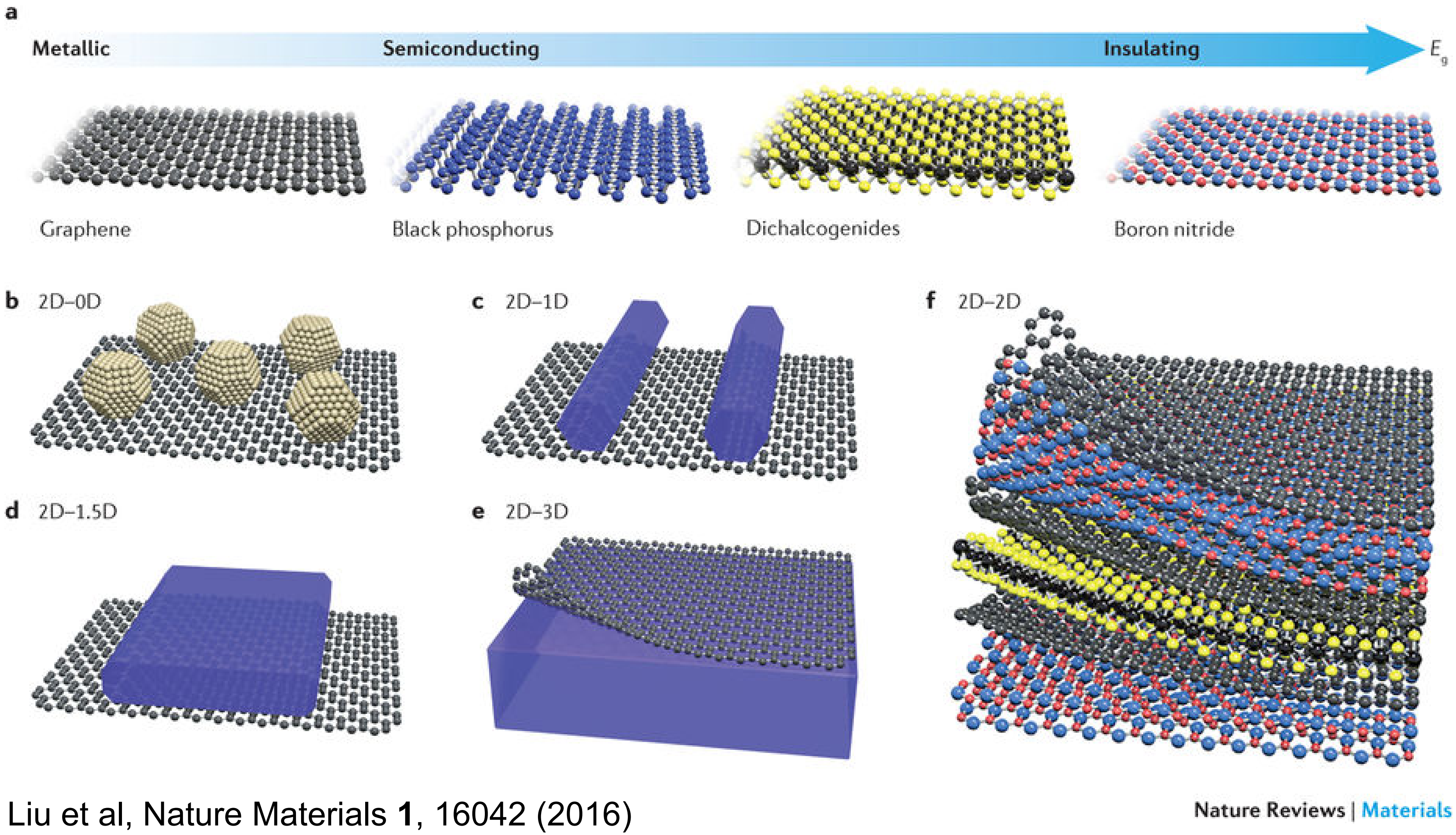
- If atoms move together so the electron charge distributions overlap they repel each other
- Repulsion due to electrostatic forces and the Pauli exclusion principle which prevents electrons having the same quantum numbers
- For example if we try to force 2 spin parallel electrons into the same 1s state in H, one will go into the 2s state at a large energy cost
- Calculations of repulsive interactions is complex there is a short range (hard core) potential
- Common empirical “Lennard-Jones” potential

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] = \varepsilon\left[\left(\frac{R_{\min}}{r}\right)^{12} - 2\left(\frac{R_{\min}}{r}\right)^{6}\right]$$



- ε, σ are constants depending on atoms involved
- Except He, Inert gases form close-packed face-centered cubic solids with high coordination nos. (10-12), low cohesive energies and melting points
- He is special – due to zero point motion does not solidify even at absolute zero, unless pressurised to 30 Bar!

Van de Waals bonding for low-dimensional structures



Liu et al, Nature Materials **1**, 16042 (2016)

From atoms to solids – Ionic bonding

- Atoms with electronic configuration close to a filled shell will tend to gain or lose electrons to fill the shell
- Energy for reaction $M \rightarrow M^+ + e^-$ in gas phase is ionization energy I
- Energy for reaction $X + e^- \rightarrow X^-$ in gas phase is electron affinity A
- To form ionic molecules it costs an energy $I + A$ but the electrostatic potential energy between charges is reduced by a greater amount.
- Electrostatic interaction for a diatomic crystal: $$U_{electrostatic} = \frac{1}{2}\sum_i \sum_j U_{ij}$$
- Where $U_{ij} = \pm q^2 / 4\pi\varepsilon_0 R_{ij}$ is sum of all Coulomb energies between ions.
- If the system is on a regular lattice with constant R then we can write:
  $$U_{electrostatic} = -\alpha_M q^2 / 4\pi\varepsilon_0 R$$
  where the Madelung constant depends on structure NaCl $(\alpha_M = 1.7476)$ CsCl $(\alpha_M = 1.7627)$ cubic ZnS or Zincblende $(\alpha_M = 1.6381)$
- We must add repulsive short range force, since ions are different sizes we get different energies - explains why NaCl has rocksalt structure and not CsCl structure
- Intermediate coordination numbers (6-8)

Crystal structures

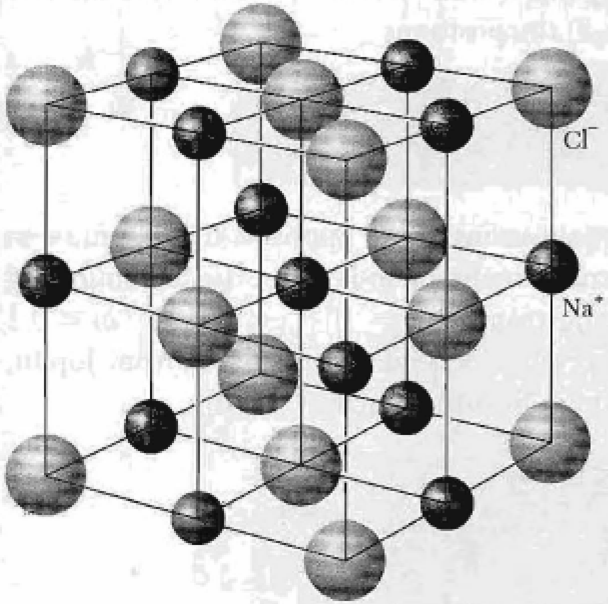


Figure 15 We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.

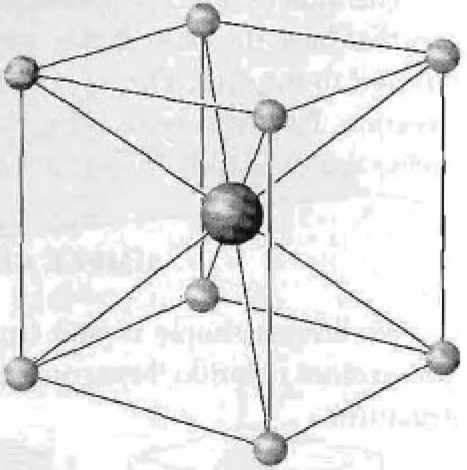


Figure 18 The cesium chloride crystal structure. The space lattice is simple cubic, and the basis has one Cs^+ ion at 000 and one Cl^- ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

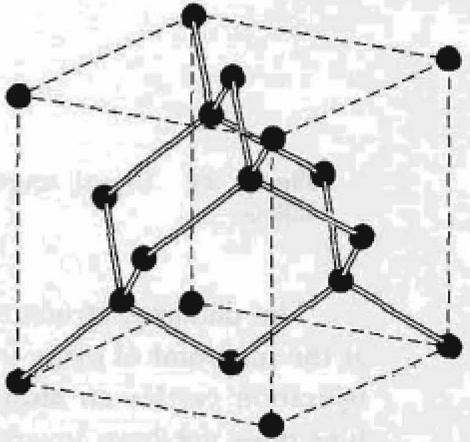


Figure 23 Crystal structure of diamond, showing the tetrahedral bond arrangement.

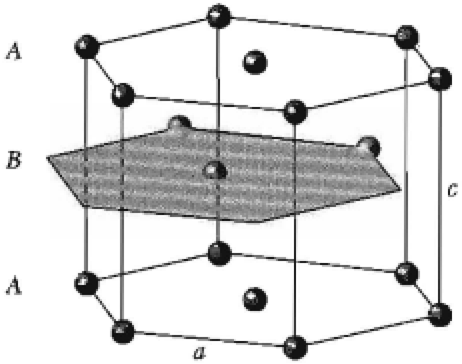


Figure 20 The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point. The lattice parameters a and c are indicated, where a is in the basal plane and c is the magnitude of the axis $\mathbf{a}_3$ of Fig. 12.

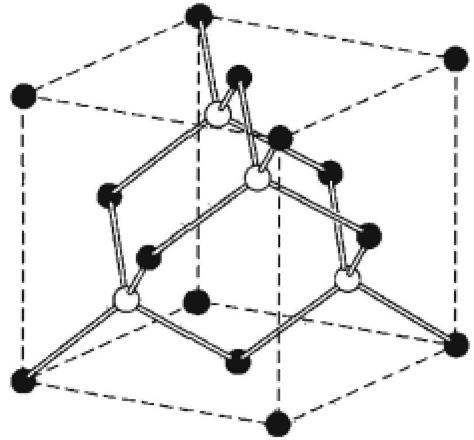


Figure 24 Crystal structure of cubic zinc sulfide.

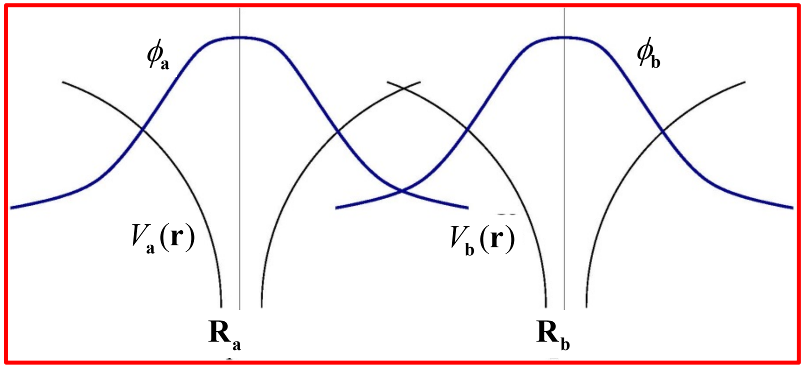
From Kittel

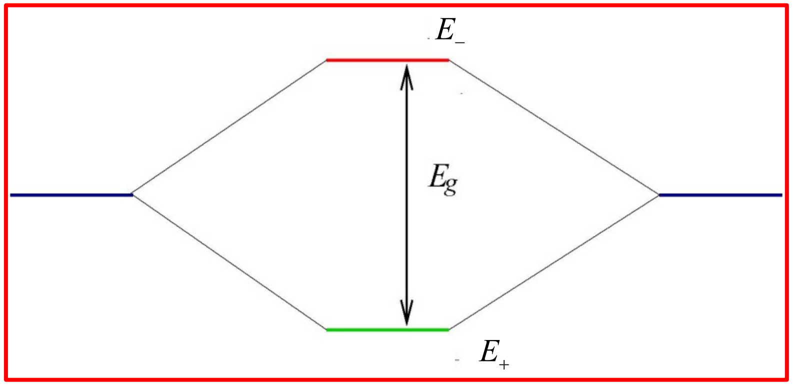
From atoms to solids – Covalent bonding

- Consider covalent bonding in hydrogen molecule – due to electron pair
- Overlapping orbitals on neighbouring atoms hybridise
- Hamiltonian symmetric about point between nuclei, hence eigenstates have odd or even parity about this point
- With a basis of atomic states $\phi(\mathbf{r}-\mathbf{R})$ where the nucleus is at $\mathbf{R}$ we get two states, of odd and even parity

$$\psi_{\pm}(r)=\phi(\mathbf{r}-\mathbf{R}_{\mathbf{a}})\pm\phi(\mathbf{r}-\mathbf{R}_{\mathbf{b}})$$

- ψ_{+} is non zero and ψ_{-} has a node between the nuclei
- For an attractive potential we will have $E_{+}<E_{-}$ and the two electrons of opposite spin will fill the lower 'bonding' state ψ_{+}.
- The 'anti-bonding' state will be separated from the bonding state by an energy gap $E_g=E_{-}-E_{+}$ and will be unfilled





From atoms to solids – Covalent bonding

- An example of degenerate perturbation theory
- We calculate single-electron energy levels, ignore electron-electron repulsion and use Dirac notation, so:

$$\left|a\right\rangle = \phi(\mathbf{r}-\mathbf{R_a}) \qquad \left|b\right\rangle = \phi(\mathbf{r}-\mathbf{R_b})$$

- Look for energy eigenfunction within subspace spanned by orthonormal basis functions: $\left|\psi\right\rangle = \alpha\left|a\right\rangle + \beta\left|b\right\rangle$
- Apply Hamiltonian, and since $\left|a\right\rangle$ and $\left|b\right\rangle$ have the same eigenenergy:

$$\mathbf{H}\left|\psi\right\rangle = E\left|\psi\right\rangle \Rightarrow \alpha\mathbf{H}\left|a\right\rangle + \beta\mathbf{H}\left|b\right\rangle = \alpha E\left|a\right\rangle + \beta E\left|b\right\rangle$$

- Left multiply by $\left|a\right\rangle$ and $\left|b\right\rangle$ we obtain two equations:

$$\alpha\left\langle a\right|\mathbf{H}\left|a\right\rangle + \beta\left\langle a\right|\mathbf{H}\left|b\right\rangle = \alpha E$$

$$\alpha\left\langle b\right|\mathbf{H}\left|a\right\rangle + \beta\left\langle b\right|\mathbf{H}\left|b\right\rangle = \beta E$$

- From this, given $H_{ba} = H_{ab}^*$ we can obtain an eigenvector equation for the coefficients α, β which only has a non trivial solution if the determinant is zero:

$$\begin{vmatrix} H_{aa} - E & H_{ab} \\ H_{ab}^* & H_{bb} - E \end{vmatrix} = 0$$

From atoms to solids – Covalent bonding

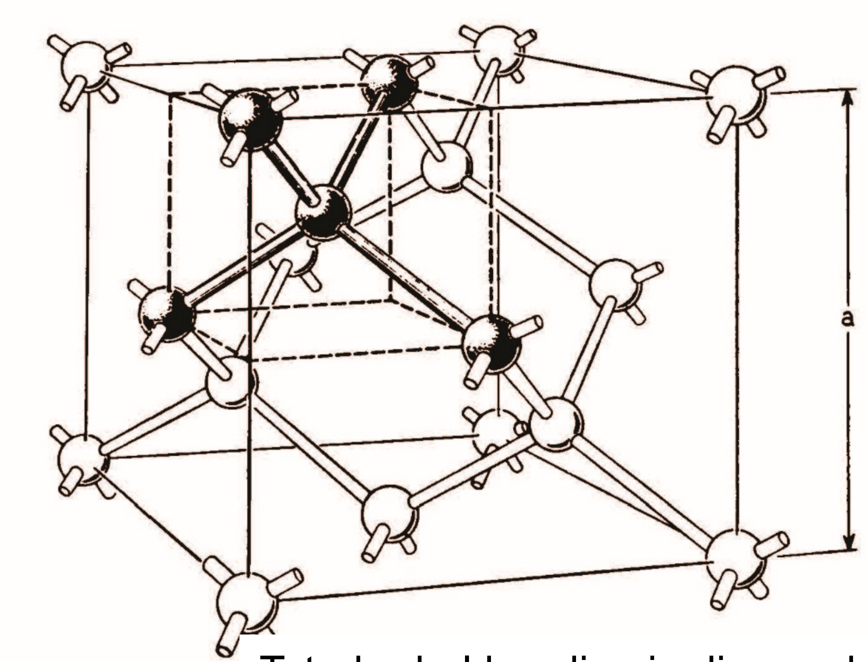
- From previous slide: $$\begin{vmatrix} H_{aa}-E & H_{ab} \\ H_{ab}^{*} & H_{bb}-E \end{vmatrix} = 0$$
- From this we can find the energy eigenvalues which are distributed around the average of H_{aa} and H_{bb}

$$E = \frac{H_{aa}+H_{bb}}{2} \pm \frac{\Delta E}{2} \quad , \quad \frac{\Delta E}{2} = \left(\left(\frac{H_{aa}-H_{bb}}{2} \right)^{2} + \left| H_{ab} \right|^{2} \right)^{1/2}$$

- For $H_{aa} \simeq H_{bb},\ \Delta E/2 = |H_{ab}|$ we get covalent bonding
- If $H_{aa} << H_{bb}$ or $H_{aa} >> H_{bb}$ then $E = H_{aa}$ or $E = H_{bb}$ and H_{ab} is irrelevant - we have ionic bonding
- See Problem Sheet 1 question 7

Covalent and ionic semiconductors

- With s electrons molecules are formed which form a weakly bound molecular solid.
- With p and d orbitals, bonds become directional such as sp^3 in C, Si and Ge
- These hybrids point in tetrahedral directions $(111),(\bar{1}\bar{1}1),(\bar{1}1\bar{1}),(1\bar{1}\bar{1})$ and each atom donates 1 electron
- This forms an open tetrahedral network – “diamond structure”

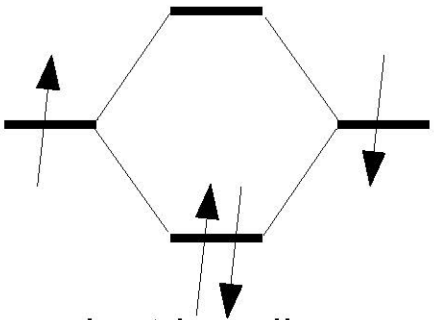


Tetrahedral bonding in diamond

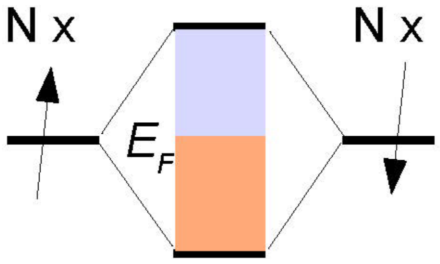
- In GaAs and cubic ZnS the total number of electrons satisfies “octet rule”
- Same tetrahedral structure as diamond with alternating atoms - “zincblende”
- Zincblende structure cohesion is partly covalent and partly ionic
- Hexagonal crystal structure based on local tetrahedral network - “wurtzite”
- Wurtzite structure favoured in more ionic systems.
- With increasing ionicity we get : Group IV Ge (diamond), III-V GaAs (zincblende), II-VI ZnS (zincblende or wurtzite), II-VI CdS (wurtzite), I-VII NaCl (rocksalt)

Metals

- *Band* forms from atomic states. Partially filled which implies energy gain generalisation of covalent bond to ‘giant molecule’
- Electrons in band states *delocalised*, high conductivity. Bonding is isotropic, like van der Waals.
- *Close packing*. to maximise density while keeping atomic cores far apart: fcc or hcp. High coordination numbers $\approx 10-12$
- Screening by *conduction electrons*. Screening length of order atomic spacing $\simeq 1\text{Å}$
- *Within a row* in periodic table: ion core potential grows, density increases, crossover to covalent semiconductors, then insulating molecular structures.
- *Transition metals*. d-electrons more localised, inside s- and p- orbitals. Are often spin-polarised hence magnetism in 3d elements. 4d and 5d orbitals overlap giving high binding energy (e.g. W melts at 3700K).



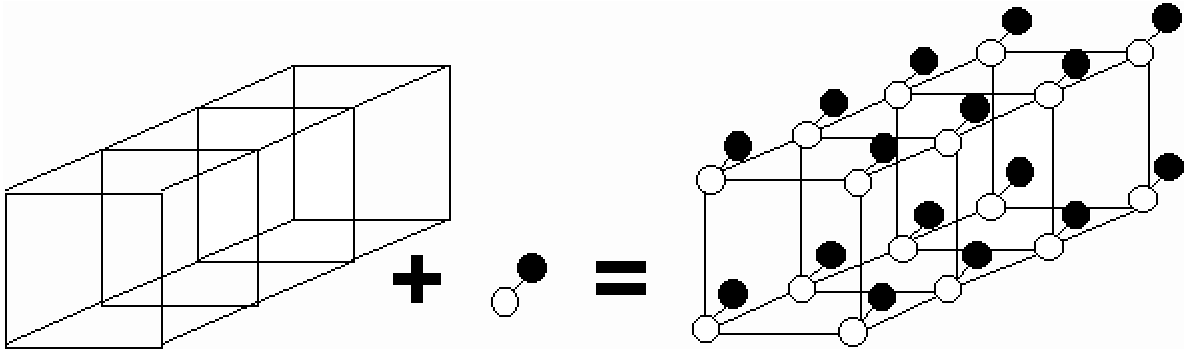
covalent bonding: molecular orbitals out of states from two atoms



metallic bonding: band out of states from many atoms

Crystal Lattices

- An ideal crystal is an infinite repetition of structural unit in space
- Repeating structure called the *lattice*
- Group of atoms which is repeated is called the *basis*
- The basis may be a single atom or very complex – such as a polymer



Lattice Basis Crystal

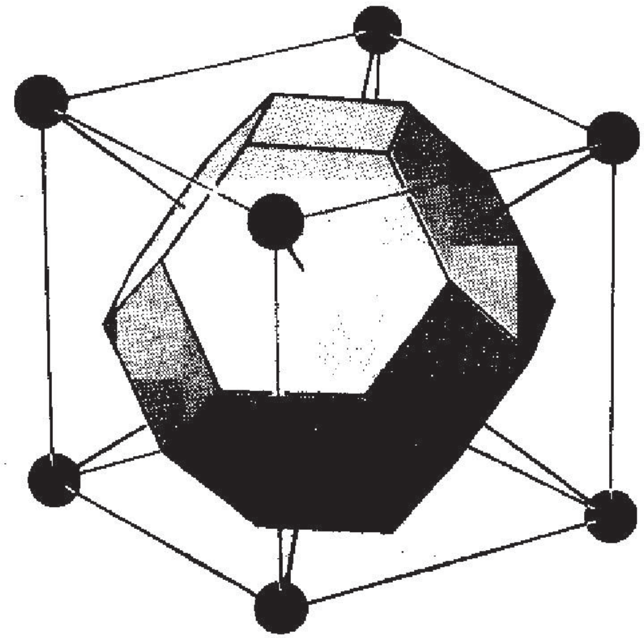
- Lattice is defined by primitive translation vectors: $\mathbf{a}_i, \quad i = 1,2,3$
- An arbitrary lattice translation is: $\mathbf{T} = \sum_i n_i \mathbf{a}_i$
- The atomic arrangement looks the same from equivalent points in the unit cell:

$$\mathbf{r}' = \mathbf{r} + \sum_{\mathbf{i}} n_i \mathbf{a_i} \quad \forall \ \text{integer} \ \ n_i$$

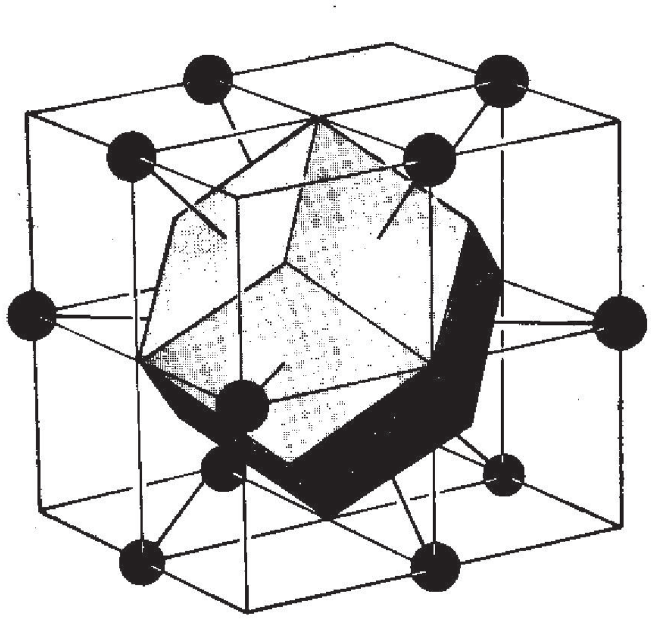
- The lattice formed is called a *Bravais* lattice

Wigner-Seitz cell

- The region in space around a particular lattice point closer to it than any other lattice point
- To construct – draw lines from a given lattice point to all of its neighbours.
- Draw planes perpendicular with each line intersecting at the line midpoint.
- The smallest volume enclosed is the *Wigner-Seitz* primitive unit cell



Bcc lattice, Wigner-Seitz cell



fcc lattice, Wigner-Seitz cell

Space and point groups

- Symmetry operations which map lattice onto itself *Space group*
- Map lattice onto itself, but keep one point fixed *Point group*.
- Point group operations: reflections, inversions, rotations
- Seven point groups for Bravais lattices = *Seven crystal systems*
- cubic, tetragonal, orthorhombic, monoclinic, triclinic, trigonal, hexagonal.
- Fourteen space groups for Bravais lattices
- *General crystal structures* (Bravais lattice + basis): 32 point groups, 230 space groups.

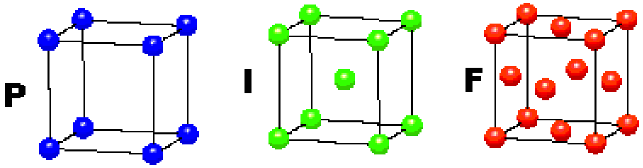
The Bravais lattice types

See also p.170 Singleton

CUBIC

$a = b = c$

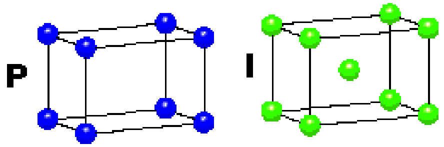
$\alpha = \beta = \gamma = 90°$



TETRAGONAL

$a = b \neq c$

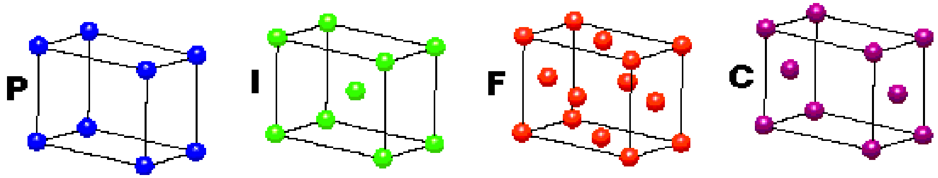
$\alpha = \beta = \gamma = 90°$



ORTHORHOMBIC

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

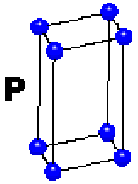


HEXAGONAL

$a = b \neq c$

$\alpha = \beta = 90°$

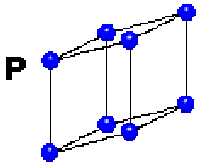
$\gamma = 120°$



TRIGONAL

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

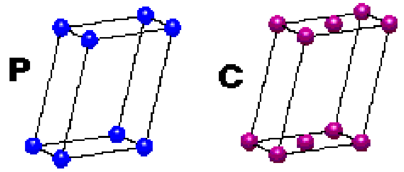


MONOCLINIC

$a \neq b \neq c$

$\alpha = \gamma = 90°$

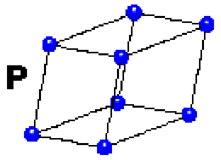
$\beta \neq 120°$



TRICLINIC

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
\+
7 Crystal Classes
→ 14 Bravais Lattices

Index system for crystal planes

- Coordinates of three lattice points enough to define crystal plane
- Label plane by coordinates where it *cuts* axes.

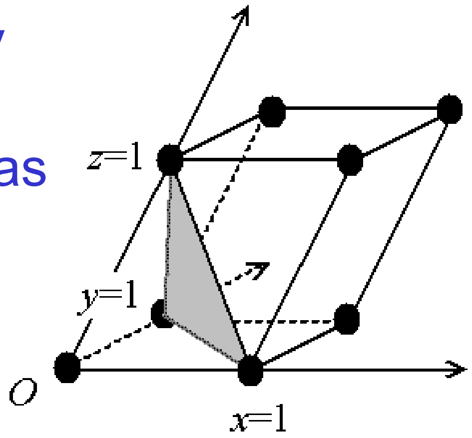
$$\{\mathbf{r}_\mathbf{i}\} = \{x\mathbf{a}_1, y\mathbf{a}_2, z\mathbf{a}_3\}$$

- (hkl) denotes plane which cuts axes at $\mathbf{a}_1 / h, \quad \mathbf{a}_2 / k, \quad \mathbf{a}_3 / l$
  or multiple thereof, so that $xh = yk = zl = \text{integer}$

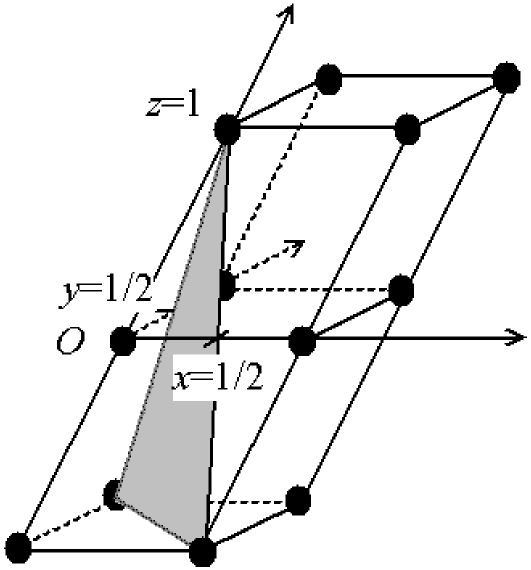
- (hkl) is the index of the plane
- For set of planes equivalent by symmetry use $\{\ \}$
- e.g. $\{100\}$ For a cubic crystal has equivalent symmetry planes:

$$(100),(010),(010),$$
$$(\bar{1}00),(0\bar{1}0),(00\bar{1})$$

plan (111)



plan (221)



- Note that overbar $\bar{1}$ denotes negation

Crystal plane indices

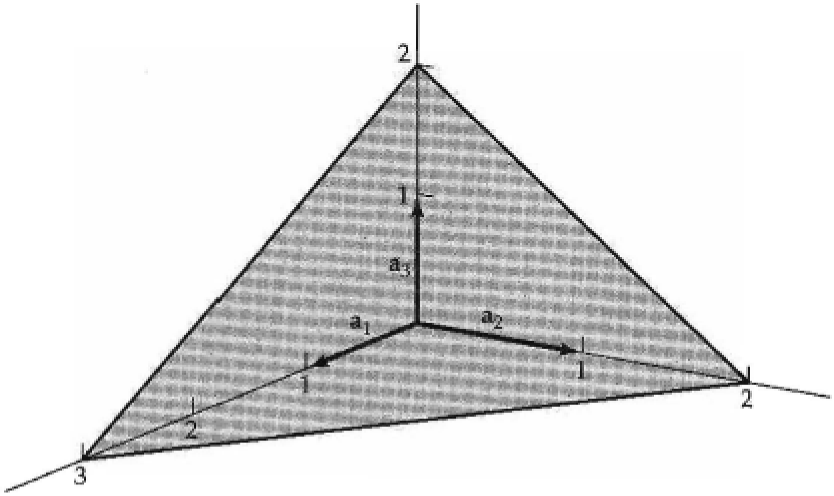
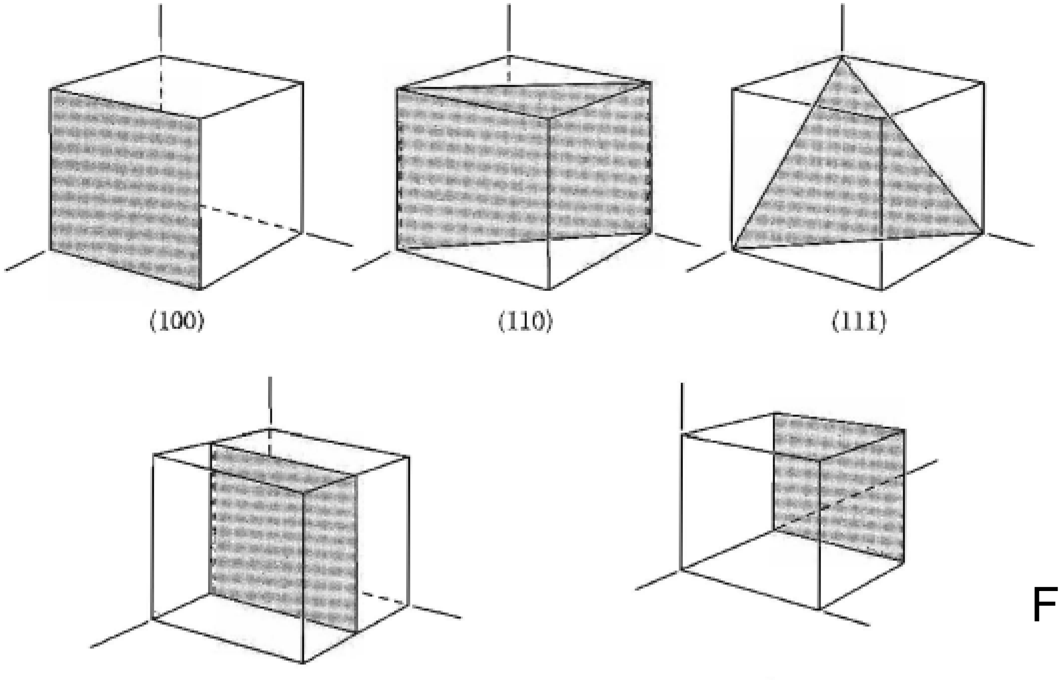


Figure 13 This plane intercepts the $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ axes at $3\mathbf{a}_1$, $2\mathbf{a}_2$, $2\mathbf{a}_3$. The reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).



(100) (110) (111)

(200) $(\bar{1}00)$

Figure 14 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100).

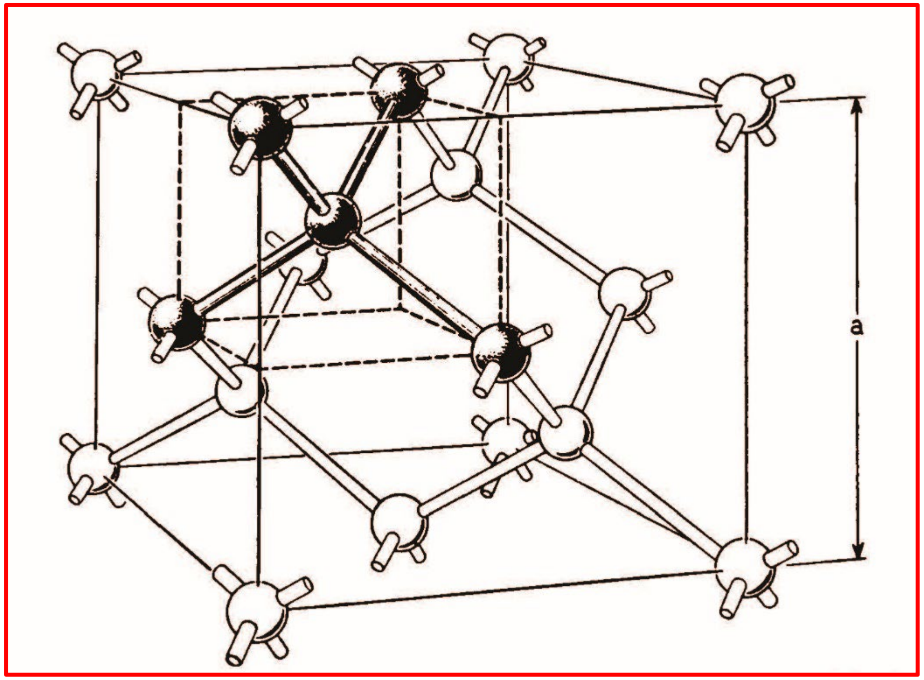
From Kittel

Summary of Lecture 4

- The binding of crystals
- Van der Waals
- Ionic
- Covalent
- Metals
- Crystal lattices
- Wigner –Seitz cell
- Space and Point groups
- Index system for crystal planes

Quantum Condensed Matter Physics

Lecture 4



The End