PY3P03: Thermal and Electronic Properties of Solids

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February 15, 2011

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Equilibrium separation of atoms is given by:

$$R_{\rm eq} = 2^{1/6} \sigma \approx 1.12 \sigma.$$

Repulsive exponent must be greater than 6 to produce potential well, and is taken as 12 mainly for simplicity.

The attractive term describes induced dipole-dipole interaction.

Dipole electric field: $E \approx -\frac{dV}{dr} \approx \frac{1}{r^3}$. Induced dipole $p \propto \alpha E$, where α is polarisability. Induced dipole-dipole potential $V_p \approx pE \approx E^2 \approx \frac{1}{6}$. \longrightarrow *slide* 6 Slide $6 \longrightarrow$

Lattice sum involves only one atom per unit cell:

$$U_B = \frac{1}{2} \sum_{j \neq 1} V_{\rm LJ}(R_{ij})$$

 $(V_{LJ}$ is the Lennard-Jones potential)

In counting, nearest neighbours (nns) dominate because potentials have a very short range (powers of -6 and -12); next nns and others make only small contributions.

For fcc structure there are 12 nns:

$$U_B = -2\epsilon \left[14.45 \left(\frac{\sigma}{R_0} \right)^6 - 12.13 \left(\frac{\sigma}{R_0} \right)^{12} \right],$$

where R_0 is found from minimum energy requirement:

$$\frac{dU}{dR} = 0 \Rightarrow R_0 = 1.09\sigma.$$

The **cohesive energy** is the ground-state internal energy of the solid, and knowing its functional form allows other properties of the solid to be determined.

The LJ potential is an empirical potential: *ab initio* quantum mechanical energy calculations can determine the potential from first principles.

Cohesion in ionic crystals

Electron transfer between atoms creates ionic crystals when:

- 1 atom has small ionisation potential, e.g. groups I, II, giving a CATION.
- 1 atom has large electron affinity, e.g. groups VI, VII, giving an ANION.

The ion formed has highly spherical charge distribution, so we can treat the Coulomb potential as a point charge at the centre of mass of the ion.

All Coulomb interactions between point charges have to be summed, with ion core repulsion taken into account. This is *complicated*, since the Coulomb potential is long-range.

The Coulomb interaction potential is:

$$V_C(r_{12}) = \frac{e^2}{4\pi\epsilon_0} \frac{q_1 q_2}{r_{12}}$$
, where q_i are integer charges.

For ionic solids, there is also a Pauli repulsion potential:

$$V_R(r_{12}) = \lambda \exp\left(\frac{-r_{12}}{\rho}\right)$$

where λ and ρ are constants determined by experiment.

The bulk modulus *B* is given by:

$$B = -V \frac{dP}{dV} = V \left(\frac{d^2 U}{dV^2}\right)_{T, V=V_0} \quad \text{where } U = V_C + V_R.$$

The total potential of one ion *i* in the lattice is:

$$U_i = \sum_j' V(r_{ij})$$
, where $V(r_{ij}) = V_C(r_{ij}) + V_R(r_{ij})$ and $\sum_j' \equiv \sum_{j \neq i}$

which can be simplified by scaling to nearest-neighbour distance, $r_{ij} = R_{nn}a_{ij}$:

$$U_i(R_{\rm nn}) = z \exp\left(\frac{-R_{\rm nn}}{\rho}\right) + \frac{e^2}{4\pi\epsilon_0} \sum_j' \frac{q_i q_j}{R_{\rm nn} a_{ij}}$$

where *z* is the number of nearest neighbours.

For a stable structure, an ion of one sign generally has nearest neighbours of the opposite sign:

$$\frac{e^2}{4\pi\epsilon} \sum_{j}' \frac{q_i q_j}{R_{\rm nn} a_{ij}} = -\frac{e^2 |q_i| |q_j|}{4\pi\epsilon_0 R_{\rm nn}} \sum_{j}' \frac{\pm 1}{a_{ij}} = -\frac{e^2 |q_+| |q_-|}{4\pi\epsilon_0 R_{\rm nn}} A$$

where the \pm refers to ions of same/opposite charge, and *A* is called the *Madelung constant*, which is positive and depends only on the structure.

These summations are difficult.

Properties

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Phase must repeat in space every 2π :

$$k \cdot r' = k \cdot r + 2\pi \Longrightarrow |k| \left[|r'_{\perp}| - |r_{\perp}| \right] = 2\pi.$$

Neighbouring planes of equal phase are separated by wavelength:

$$|r'_{\perp}| - |r_{\perp}| = \lambda \Rightarrow |k|\lambda = 2\pi \Rightarrow k = \frac{2\pi}{\lambda}.$$

For plane waves in crystalline solids, the physical properties must have the same periodicity as the lattice. A plane wave whose period matches that of the lattice must have the same amplitude at r and r + R:

$$\exp [ik \cdot (r+R)] = \exp [ik \cdot r]$$
$$\implies \exp [ik \cdot R] = 1.$$

But exp $[iG \cdot R] = 1$, and $G \cdot R = 2\pi n$. So k = G, the wavevector is a reciprocal lattice vector.

Brillouin zones

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In real space, the Wigner–Seitz cell is the atom-centred unit cell of minimum volume. In reciprocal space, the WS cell is called the *first Brillouin zone*.

BZs are formed from perpendicular bisectors (planes) of the *G* vectors: the first BZ is formed from the nearest reciprocal lattice points, the second from the next-to-nearest (subtracting first BZ), etc.

All BZs have the same volume.

Points and lines of high symmetry in a BZ are labelled, because experiments and theory usually exploit symmetry in order to simplify measurement and interpretation of results.

The centre of the zone – the point of highest symmetry – is the *gamma point*: $\Gamma(0, 0, 0)$.

Atom dynamics in crystals

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At length scales much larger than atomic dimensions, solids behave as *continuous media*. Their properties may be *anisotropic* due to the underlying crystal symmetry, but this is treated phenomenologically – the properties are measured in different macroscopic directions of the crystal.

Sound propagation is a good example, because $v = f\lambda$; $v \sim 5000 \text{ ms}^{-1}$, $f \sim 10,000 \text{ Hz} \Longrightarrow \lambda \sim 0.5 \text{ m}$.

A sound (acoustic) wave is just an elastic wave propagating through a medium where a timedependent stress, σ , produces a strain *e* via the elastic stiffness, *c*:

$$\sigma_i = \sum_{j=1}^{6} c_{ij} e_j$$
 $i = 1, \dots, 6$ and $c_{ij} = c_{ji}$.

With no crystal symmetry, we have 21 independent components, but any symmetry reduces this number dramatically, e.g. cubic crystals only have 3 independent components:

$$c_{11}(=c_{22}=c_{33}), \quad c_{12}(=c_{13}=c_{14}), \quad c_{44}(=c_{55}=c_{66}).$$

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Solids are more complicated because they support shear stresses and have more than one nonzero value of *c*: displacements can occur which are not aligned with the stress.

For an isotropic solid, there are two independent values of *c*: *B* and μ (the **shear modulus**), allowing both a longitudinal and two transverse waves (polarisation unit vectors \hat{e} (7) orthogonal to one another) to propagate.

$$v_{\text{long}} = \sqrt{\frac{B + \frac{4}{3}\mu}{\rho}}, \quad v_{\text{trans}} = \sqrt{\frac{\mu}{\rho}}.$$
 (12)

 $\Rightarrow v_{\text{long}} > v_{\text{trans}}.$

For anisotropic solids, the simple division into longitudinal and transverse waves may not be possible, e.g. k may not be parallel to \hat{e} where a longitudinal wave is expected.

Thus, in general, we have plane waves propagating through the solid as a consequence of the solid possessing restoring forces (quantified by the moduli) that respond to the displacement.

Debye heat capacity: We can progress further with the continuum model by recognising that the solid is finite and has boundaries, so the wave equation has boundary conditions that restrict the allowed values of k.

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We now know that for an isotropic solid, we have one longitudinal and two transverse waves:

$$D(\omega) d\omega = \frac{V}{(2\pi\nu)^3} 4\pi\omega^2 d\omega = \frac{V}{(2\pi)^3} \left(\frac{1}{\nu_{\text{long}}^3} + \frac{2}{\nu_{\text{trans}}^3} \right) 4\pi\omega^2 d\omega.$$

$$\Rightarrow D(\omega) d\omega = \frac{3V}{(2\pi\nu_0)^3} 4\pi\omega^2 d\omega, \qquad (13)$$

the **Debye density** of vibrational states (~ ω^2), where v_0 is the weighted, non-dispersing average.

We introduce **atoms** at this stage, because we know that this oscillating system has 3N-6 degrees of vibrational freedom, and thus can only have this number of modes ($\approx 3N$ for real systems): this means that there is a maximum frequency ω_D :

$$3N = \int_{0}^{\omega_{D}} D(\omega) \, d\omega = \frac{3V}{(2\pi\nu_{0})^{3}} \int_{0}^{\omega_{D}} 4\pi\omega^{2} \, d\omega$$
$$3N = \frac{4\pi\omega_{0}^{3}V}{(2\pi\nu_{0})^{3}} \Rightarrow \omega_{D} = \nu_{0} \left(\frac{6\pi^{2}N}{V}\right)^{\frac{1}{3}}.$$
(14)

 ω_D is called the **Debye frequency.**

Debye heat capacity

Einstein assumed that each atom in the solid oscillates at a single frequency ω_E , characteristic of the solid:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = 3Nk \left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2},$$

where $\theta_E = \frac{\hbar \omega_E}{k}$ is called the **Einstein characteristic temperature. Debye model:** the thermal average value of *X* is:

$$\langle X \rangle = \int D(\epsilon) f(\epsilon, T, \mu) X d\epsilon$$

with:

$$f^{\text{phonon}}(\epsilon) = [\exp(\epsilon/kT) - 1]^{-1}$$

(a **phonon** is a quantised vibration.)

$$U = \langle E \rangle = \frac{3V}{(2\pi\nu_0)^3} \int_0^{\omega_D} \frac{\hbar\omega 4\pi\omega^2}{\exp(\hbar\omega/kT) - 1} d\omega$$

Using $x = \hbar \omega / kT$, we have:

$$U = \frac{3V(kT)^4}{2\hbar^3 \pi^2 v_0^3} \int_0^{x_D} \frac{x^3}{\exp(x) - 1} dx$$

But:

$$\omega_0 = \nu_0 \left(\frac{6\pi^2 N}{V}\right)^{1/3} \Rightarrow \nu_0^3 = \omega_0^3 \frac{V}{6\pi^2 N} = \frac{(x_D k T)^3}{\hbar^3} \frac{V}{6\pi^2 N}$$

so

$$U = \frac{9NkT}{x_0^3} \int_0^{x_0} \frac{x^3}{\exp(x) - 1} dx$$
(15)

(neglecting zero-point energy).

In general, this integral must be evaluated numerically (because of upper limit), but some particular cases can be treated analytically.

1. Low temperature behaviour:

 $kt \ll \hbar \omega$, so $x \gg 1 \Rightarrow x_D \to \infty$ at upper limit; standard integral $= \frac{\pi^4}{15}$.

We define a **Debye temperature:** $k\theta_D = \hbar\omega_D$, and $x_D = \frac{\omega_D}{T}$.

$$U(t) = \frac{3\pi^4 N k T^4}{5\omega_D^3} \quad \text{and} \quad C_V(T) = \frac{\partial U}{\partial T} = \frac{12\pi^4 N k}{5} \left(\frac{T}{\theta_D}\right)^3 \tag{16}$$

So $C_V \sim T^3$ for non-metallic solids at low temperatures, in agreement with experiment.

Note:

As $x_D = \frac{\omega_D}{T}$, a high Debye temperature means a wide temperature range over which (16) is applicable.

High θ_D comes from strong bonds and light atoms:

$$\theta_D = \frac{\hbar\omega_{\max}}{k}, \quad \omega \sim \sqrt{\frac{k'}{m}}.$$

For elements, highest is diamond at 2230 K, lowest is caesium at 38 K.

2. High temperature behaviour:

 $kt \gg \hbar\omega \Rightarrow x \ll 1.$ $\int_{0}^{x_{D}} \frac{x^{3} dx}{\exp(x) - 1} = \int_{0}^{x_{D}} \frac{x^{3} dx}{x + \frac{x^{2}}{2!} + \dots} = \int_{0}^{x_{D}} \frac{x^{2} dx}{1 + \frac{x}{2!} + \dots} = \frac{1}{3}x_{0}^{3}.$

From (15),

$$U = \frac{9NkT}{x_D^3} \frac{x_D^3}{3} = 3NkT.$$

$$\Rightarrow C_V = \frac{\partial U}{\partial T} = 3Nk = 3R,$$

the Dulong-Petit law.

3. Between these limits,

numerical methods are used.

Note that plotting the **reduced variable** $\frac{T}{\theta_D}$ results in a **universal curve** to within about 15%.

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The 1D atomic chain

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Periodic boundary conditions – 'Born–Von Karman conditions' – for a periodic array of *N* atoms, separated by *a*, of total length L = Na:

$$u(r) = u(r+L) \tag{17}$$

(imagine the first and last atom 'linked' in some way.)

The solutions become **running waves** with an integer number of wavelengths fitting into *L*:

$$k_i^r = 0, \pm n_i \frac{2\pi}{L}, \dots, \frac{N\pi}{L}$$
 $(i = x, y, z)$ (18)

The separation of the k values is twice that of the standing waves, but there are twice as many allowed values, so the density of states is the same.

Running wave solutions are useful because net transfer of energy occurs.

The 1D chain

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Springs have return forces analogous to interactomic potential (bottom of well is parabolic for small displacements) – look at longitudinal motion.

The masses are analogous to ion cores – apply $F = m \frac{d^2x}{dt^2}$ to each mass. The model reveals essential physics of atom dynamics of 3D solids.

For n^{th} atom:

at equilibrium,
$$x_n^0 = na$$

when displaced, $x_n = na + u_n \quad \left(\Rightarrow \frac{\partial}{\partial x} = \frac{\partial}{\partial u}\right)$

If the interactomic potential is $\phi(a)$, and only nearest-neighbour interactions matter, total potential energy $U = N\phi(a)$.

Use Taylor expansion, summing over all atoms:

$$U(x) = N\phi(a) + \sum_{m \ge 1} \frac{1}{m!} \frac{\partial^m \phi}{\partial u^m} \sum_{n=1}^N (u_n - u_{n+1})^m$$
(22)

a is equilibrium separation $\rightarrow 0$ net force on atom:

$$\left(\frac{\partial\phi}{\partial u}\right)_{u=0}=0.$$

Dominant term is quadratic, and if we neglect higher terms we have the **harmonic approximation**, a simple spring; but also small atomic displacements. From (22),

$$U_{\text{harm}} = \frac{1}{2} K \sum_{n=1}^{N} (u_n - u_{n+1})^2, \quad \text{with } K = \left(\frac{\partial^2 \phi}{\partial u^2}\right)_{u=0}.$$

Net force on the n^{th} atom is $F_n = K(u_{n+1} - u_n) - K(u_n - u_{n-1}) = K(u_{n+1} - 2u_n + u_{n-1})$. Equation of motion for n^{th} atom is:

$$m\frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1} - 2u_n + u_{n-1}) \quad \left(= -\frac{\partial u_{\text{harm}}}{\partial u_n} \right)$$
(23)

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We know the most general solution for this periodic system is a Bloch wave (20):

$$u_n(x_n^0, t) = A \exp\left[i(kx_n^0 - \omega_k t)\right],$$

where $A = u_k^0(r) = u_k^0(r + a)$, the unit cell function.

For discrete values of *k* corresponding to running waves with periodic boundary conditions, using $x_n^0 = na$, we have $u_n = A \exp[i(kna - \omega_k t)]$ and $\tilde{u}_n = -\omega_k^2 A \exp[i(kna - \omega_k t)]$.

Substituting into equation of motion and cancelling:

$$-m\omega_k^2 = K \left[\exp(ika) - 2 + \exp(-ika) \right] = 2K \left[\cos(ka) - 1 \right]$$

$$\Rightarrow \omega_k = 2\sqrt{\frac{K}{m}} \left| \sin\left(\frac{1}{2}ka\right) \right|$$
(24)

There is a maximum cutoff value $\omega_k^{\max} = 2\sqrt{\frac{K}{m}}$ for $k = \frac{n\pi}{a}$, $n = \pm 1, \pm 3, ...$

The frequency is *not* proportional to *k*, as in elastic medium, but has a periodic sinusoidal behaviour. The periodicity is that of the reciprocal lattice: $\frac{2\pi}{a}$.

Phase velocity and group velocity

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The velocity of points of constant phase in a wave is called the **phase velocity**, v_{ϕ} .

$$\phi(x,t) = kx - \omega t$$
, and $\frac{d\phi}{dt} = \frac{\partial \phi}{\partial x} \frac{dx}{dt} + \frac{\partial \phi}{\partial t} = k \frac{dx}{dt} - \omega$

Constant phase: $\frac{d\phi}{dt} = 0 \Rightarrow k \frac{dx}{dt} - \omega = 0$, and:

$$\frac{dx}{dt} = v_{\phi} = \frac{\omega}{k}.$$
(25)

Since $v_{\phi} = f(k)$, waves of different frequency have different phase velocities:

- A pulse or wave packet can be represented as a Fourier sum of sinusoidal components
- The wave packet will travel at the **group velocity**, but will broaden due to the dispersion of phase velocities of sinusoidal components, e.g.

 $u_{1} = \cos(kx - \omega t) \text{ and } u_{2} = \cos([k + 2\Delta k]x - [\omega - 2\Delta \omega]t)$ $u_{1} + u_{2} = 2\cos([k + \Delta k]x - [\omega + \Delta \omega]t) \cdot \underbrace{\cos([\Delta k]x - [\Delta \omega]t)}_{\text{"beat amplitude"}}$

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The phase and group velocities of the vibrational waves are then:

$$v_{\phi} = \frac{\omega}{k} = \frac{2}{k} \sqrt{\frac{K}{m}} \sin\left(\frac{1}{2}ka\right)$$
 $v_{g} = \frac{d\omega}{dk} = a \sqrt{\frac{K}{m}} \cos\left(\frac{1}{2}ka\right)$

It is clear that the group velocity is zero at the BZ boundaries, $\pm \frac{\pi}{a}$, since gradient is zero; so we have **standing waves** there – the interference between waves travelling in opposite directions after **Bragg reflection** from the periodic array of atoms:

$$n\lambda = 2d\sin\theta \Rightarrow n\left(\frac{2\pi}{k}\right) = 2a \Rightarrow k = n\left(\frac{\pi}{a}\right) \text{ with } 2\theta = 180^{\circ}$$

Note: this is a generic result for waves in a solid – applied to electrons in Section VI.

In the long wavelength limit (zone centre), $ka \ll 1$, and we expect to regain the continuum model:

$$v_{\phi} = \frac{\omega}{k} = \frac{2}{k} \sqrt{\frac{K}{m} (\frac{1}{2}ka)} = a \sqrt{\frac{K}{m}} = v_g$$
 (no dispersion.)

Three-dimensional crystals

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The main additional contributions come from transverse (shear) modes.

Transverse acoustic (TA) modes will generally have different frequencies to LA modes, because of their different velocities (section V1).

Modulus and branches for N unit cells each containing p atoms.

- 3*pN* degrees of vibrational freedom (ignore 6).
- Each branch has *N* modes, $\rightarrow 3p$ branches.
- There can only be one LA and two TA branches $\rightarrow 3(p-1)$ optic branches.
- There are *p*−1 LO and 2(*p*−*q*) TO branches (only one LO, but two orthogonal TO displacements.)

Calculation of the vibrational behaviour of 3D crystals starts by calculating the interatomic potential using the Born–Oppenheimer approximation and varying the interatomic separation – matrix methods are needed and symmetry relations are used to simplify the problem.

Theory is compared with experimental results from, most commonly, inelastic neutron scattering studies along high-symmetry directions of the BZ.

Phonons and crystal momentum

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We have used quantum theory to derive the Bloch theorem, but otherwise classical mechanics has been used.

The energy (\propto amplitude²) of a *classical* normal mode can take any value.

The quantum oscillator has certain allowed energy eigenvalues, characterised by an integer n(k, p), where p is the branch index:

$$\epsilon(k,p) = \left[n(k,p) + \frac{1}{2}\right]\hbar\omega_k(p) \tag{31}$$

The quantised oscillation is called a **phonon**, and *n* is the number of phonons excited in the system.

The solid has energy even with no phonons excited: the **zero-point energy**:

$$\sum_{p} \frac{1}{2} \hbar \omega_k(p).$$

The total vibrational energy of the solid is:

$$E = \sum_{k,p} \epsilon(k,p).$$

Phonons are spin-zero, and are not conserved; so they act like photons and have the same distribution function.

The free electron gas

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From our basic iron core and valence electron model, the simplest assumption is that the valence electrons form a gas that is free to move throughout the volume of the solid, experiencing a constant potential everywhere except at the surface of the solid, where a potential barrier prevents escape.

The **Drude model** treats these electrons as point particles using classical statistics and, although some useful results are obtained (see later), **Fermi–Dirac statistics** are needed.

We return to the 3D square well particle-in-a-box problem.

The electron wavefunction is:

$$\psi(r) = A \exp(ik \cdot r)$$

Note: a plane wave. The nodes at surfaces implies standing waves:

$$\psi(r) = \sqrt{\frac{8}{L^3}} \sin\left(n_1 \frac{\pi x}{L}\right) \sin\left(n_2 \frac{\pi y}{L}\right) \sin\left(n_3 \frac{\pi z}{L}\right)$$

where n_i are nonzero positive quantum numbers.

Note: vibrations in elastic solid – similar result from antinodes at surface.

In *k*-space, we have:

$$k_i = n_i \frac{\pi}{L}$$
, and $\epsilon(k) = \frac{\hbar^2 k^2}{2m_e}$.

From the Pauli exclusion principle, each allowed *k*-state can contain two electrons of opposite spin (no magnetic field), and we can work out the DOS, Fermi energy, etc., at 0 K.

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$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e} \left(\frac{3\pi^2 N}{V}\right)^{3/2}.$$

For metals, $\epsilon_F > 2.5$ eV and $kT \sim 20.025$ eV at room temperature. This implies that $\mu_{\text{RT}} \approx \epsilon_F$ and the Fermi surface is quite sharp.

The Fermi wavevector is:

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

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Solutions of the Schrödinger equation in the weak perodic potential of lattice are Bloch functions:

$$\psi_k(r) = \exp(ik \cdot r)u_k(r) \quad \text{and} \quad u_k(r+R) = u_k(r).$$
 (20)

We make progress by using the symmetry of the system to expand the Schrödinger equation as a Fourier series in *k*-space (plane wave expansion of potential and wavefunction)

Recall complex Fourier series:

$$f(x) = \sum_{n=-\infty}^{\infty} C_n \exp(i2\pi nx/a),$$

where a is the period of f.

$$V(r) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} V_{hkl} \exp(iG_{hkl} \cdot r) = \sum_{G} V_{G} \exp(iG \cdot r)$$

(period is *R*) and:

$$V_G = \frac{1}{\Omega} \int_{\text{unit cell}} dr V(r) \exp(-iG \cdot r).$$

All physically distinct values lie within a unit cell.

Schrödinger equation:

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(r) + V\psi(r) = \epsilon\psi(r), \text{ and } V(r+R) = V(r).$$

Now we expand:

$$V(r) = \sum_{G} V_{G} \exp(iG \cdot r)$$
 and $\psi_{k}(r) = \sum_{k} C_{k} \exp(ik \cdot r)$

giving:

$$\sum_{k} \frac{\hbar^2 k^2}{2m_e} C_k \exp(ik \cdot r) + \sum_{k',G} C_k V_G \exp\left(i(k'+g) \cdot r\right) = \epsilon \sum_{k} C_k \exp(ik \cdot r)$$

Choosing k = k' - G,

$$\sum_{k} \exp(ik \cdot r) \left[\left(\frac{\hbar^2 k^2}{2m_e} - \epsilon \right) C_k + \sum_{G} V_G C_{k-G} \right] = 0.$$

Thus, for all *k*,

$$\left(\frac{\hbar^2 k^2}{2m_e} - \epsilon\right) C_k + \sum_G V_G C_{k-G} = 0.$$
(37)

Note that expansion coefficients in (37) differ only by G, as a result of periodicity.

Using the expansions we can easily show that:

$$u_k(r) = \sum_G C_{k-G} \exp(-iG \cdot r), \quad \psi_{k+G}(r) = \psi_k(r), \quad \epsilon(k+G) = \epsilon(k)$$
(38)

We can now carry over the results on BZs from section V4, as the structure and arguments are the same, with ω becoming ϵ . The ϵ vs. k plots are called the **band structure**.

The simplest energy band structure is that of the empty lattice, where the ion core potential tends to zero, and thus the Fourier coefficients of the potential tend to zero. In the limit, this should be the free electron gas parabola in k-space.

From (37),

$$\left[\frac{\hbar^2 k^2}{2m_e} - \epsilon\right] C_k = 0, \text{ and } u_k(r) = 1.$$

$$\epsilon = \frac{\hbar^2 k^2}{2m_e} \text{ and } \psi_k(r) = \exp(ik \cdot r)$$

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We now introduce a weak pseudopotential and take first term in potential: this is the NFE model. We expect differences at the 1st BZ boundaries; where $k = \pm G/2$. (37) becomes:

$$\left[\frac{\hbar^{2}(G/2)^{2}}{2m_{e}} - \epsilon\right]C_{G/2} + V_{G}C_{-G/2} = 0$$

$$\left[\frac{\hbar^{2}(G/2)^{2}}{2m_{e}} - \epsilon\right]C_{-G/2} + V_{-G}C_{G/2} = 0.$$

$$\Rightarrow \left|\frac{\hbar^{2}(G/2)^{2}}{2m_{e}} - \epsilon\right|C_{-G/2} - \epsilon = 0.$$

$$\varepsilon^{\pm} = \frac{\hbar^{2}(G/2)^{2}}{2m_{e}} + |V_{G}|, \quad \epsilon^{\text{gap}} = 2|V_{G}|, \quad \frac{C_{-G/2}}{C_{G/2}} = \pm 1$$
(39)

Note: V(r) is real, so $V_G \exp[-iG \cdot r] + V_{-G} \exp[iG \cdot r]$ is real,

$$\Rightarrow (V_G \exp[-iG \cdot r])^* = V_{-G} \exp[iG \cdot r]$$
$$\Rightarrow V_G^* = V_{-G}$$

Beyond NFE model

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The NFE model is appropriate for the following types of solids:

- insulators with wide band gaps, since wide band gap \Rightarrow strong lattice potential.
- transition metals, lanthamides and actinides where *d* and *f*-electrons which are more tightly bound to the ion core are important.
- covalent solids with directional bonds formed from the combination (and hybridisation) of directed atomic orbitals.

Theory may start from atomic orbitals and examine the interaction of neighbouring atoms – the **tight-bonding** or **linear combination of atomic orbitals** (LCAO) approach; this closely resembles the simple picture of interactions leading to band formation (Fig. 2) and is widely used for molecules.

The independent-electron picture is also limited in that e-e interactions *are* important. The approximation works reasonably well because of screening, and because the electron and its exchange-correlation hole, taken together, behave roughly as independent **quasi-particles.**

The simplest approach to screening is the **Thomas–Fermi model**, which produces a screened Coulomb potential that falls exponentially with distance from nucleus.

Electron-phonon scattering and umklapp processes

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Only longitudinal phonons couple with electrons (via $V_{e-ph} \propto n \cdot q$ where q = phonon vector).

LA phonons are the most important because they have lower energies.

The temperature dependence of e-ph relaxation time τ_{ph} , has different regimes:

• $T \gg \theta_D$, no. of phonons per mole:

$$\langle n(\omega_q, T) \rangle = f^{\text{ph}}(\omega_q, T) \approx \frac{kT}{h\omega_q}$$

So e-ph collision rate $\propto T$, and

$$\tau_{\rm e-ph} \propto T^{-1} \quad (\text{when } T \gg \theta_D)$$
 (51)

• At low *T*, the energy requirement that $h\omega q \le kT$ means that electrons scatter to and from states very close to the Fermi surface, and also $\omega_q = vq$ so the allowed surface area in *k*-space $\propto q^2 \propto T^2$. In addition, scattering rate $\propto V_{e-ph} \propto q$.

$$\Rightarrow$$
 e-ph collision rate $\propto T^3$, and $\tau_{e-ph} \propto T^{-3}$ (when $T \ll \theta_D$) (52)

Lattice contribution to thermal conductivity of insulators

Slide 82 \longrightarrow

We know that insulators conduct heat much less well than metals, so we expect that the lattice contribution to the thermal conductivity of metallic solids to be small.

From (54), if we follow Debye and use the velocity of sound (5010 ms⁻¹ for Cu, as compared to ~ 10^5 ms⁻¹ for electrons as classical particles), we get a value of κ which is ~ $500 \times$ smaller, assuming the relaxation time is comparable. This is a *bad* estimate of κ .

To go further, we adapt (54) for phonons, where we introduce the group velocity and sum over phonon branch *p* and wavevector *k*:

$$\kappa = \frac{1}{3V} \sum_{k,p} C_V(k,p) v_g^2(k,p) \tau_{k,p}$$
(55)

where c_V is the mode heat capacity of phonon *k* in branch *p*.

Recalling section V4, near the BZ centre (i.e. small k, long wavelength), the group velocity can be replaced by the phase velocity, i.e. the velocity of sound.

The temperature dependence of the thermal conductivity is then determined by the behaviour of the heat capacity and the relaxation time.

Electron contribution to thermal conductivity in metallic systems

Slide $84 \rightarrow$

Modify the Drude expression to account for Fermi-Dirac statistics and Fermi surface, from (54):

$$\kappa = \frac{C_V}{3V}\overline{\nu}^2 \Rightarrow \kappa = \frac{C_V}{3V}\nu_F^2\tau \tag{56}$$

because only electrons very close to the Fermi energy contribute to transport (assuming Fermi surface is spherical).

Applying this approach to Wiedemann–Franz expression:

$$C_V = \frac{\pi^2 N k^2 T}{2\epsilon_F} \quad (36); \quad \sigma = \frac{n_c e^2 \tau}{m_e} \quad (45); \quad v_F^2 = \frac{2\epsilon_F}{m_e},$$
$$\Rightarrow \frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k}{e}\right)^2 = 2.433 \times 10^{-8} \text{ W}\Omega \text{K}^{-2},$$

better agreement than Drude model, which has $\frac{3}{2}$ from (55).

The Drude $C_V = \frac{3}{2}Nk$ is too large by $0.3(\epsilon_F/kT)$ but this is compensated by a squared classical velocity which is too small by $0.67 \times$ same factor; hence the very good agreement which Drude obtained.