

NORMAL MODES

Failures of static Lattice model

Recap- Start with Drude and Sommerfeld models

DRUDE MODEL - Classical theory (Maxwell-Boltzmann distribution)

Can explain Wiedemann-Franz law (in high T and low T regimes)

Fails everywhere else.

- $C_v = 3/2k_B T$
- Electrical resistance = 0
- Thermal expansion – no clue.

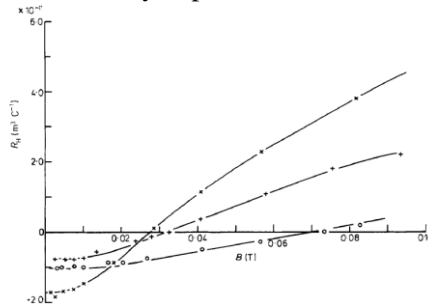
SOMMERFELD MODEL – Used Fermi Dirac distribution

Triumphs –

- $C_v \sim T$ (valid at low temperatures for alkali metals) – got even the magnitude right

Failures –

- Hall coefficient $R_H = -1/ne$ (in reality depends on B, T, scattering time) – sign for Al is wrong



- At intermediate T, Wiedemann Franz law is T dependent
- T^3 term in specific heat

Ad-hoc points in the theory:

- How to determine the number of free electrons in the system?
- No free electrons in insulator – so no degree of freedom to have any physical effect!
- T^3 term in specific heat for both metals and insulators – something common between them!
- What is # electrons for transition metals (Fe, Mn, V) that show multiple valence?
- C as diamond is insulator but good conductor as graphite - # free electrons same?????
- B insulator while Al good conductor (same column of periodic table)!!!!

Why did Drude and Sommerfeld models fail? – go back and review basic assumptions.

1. Independent electron model – Good enough in most cases due to FD statistics – only case where relaxing it helps is calculating compressibilities of metals. Relaxing this condition gives Hartree- Fock equation; screening of electrons (very important); Fermi liquid theory.

2. Relaxation time approximation – (Outcome of collision does not depend on local electron concentration) – Wiedemann-Franz law at intermediate temperatures can be explained if we invoke this. Relax this condition – you have to consider different sources of scattering, two main ones are – intrinsic defects and lattice vibrations- leads to Boltzmann transport equation (will cover it if we have time)
3. Free electron approximation - Main culprit – only scattering from static rigid ions, no electric/magnetic effect of ions on electron dynamics.
 - Ions have no effect on electronic motion in between collisions (ions positive electron negative!!) (NON COLLISIONAL EFFECT)... main culprit
 - What do we mean by collision?? (COLLISIONAL EFFECT)
 - Ions are dynamical entities – can contribute independently to specific heat, thermal conductivity etc.

Relax the free electron approx in two stages:

- Electrons move in a static periodic lattice – very important (distinguishes crystalline materials from liquid and even amorphous solids) – static lattice model
- Electrons move in a dynamic non-static lattice

STATIC LATTICE MODEL:

Electrons move in a constant rigid periodic background potential – not scattered by it except for specific k values at Brillouin zone boundaries – form standing waves – gaps at electronic spectrum – used to explain x-ray spectrum, equilibrium and transport properties of metals and insulators that are dominated by electrons.

Why is static lattice model unrealistic?

1. Ions are not infinitely massive – not held by infinite forces – must move about at finite T because of kinetic energy
2. Quantum zero point mean square momentum even at zero T – uncertainty principle.... so large in He that it is called Quantum Fluid.

Where does static lattice model fail?

1. **Equilibrium properties** – Specific heat of metals (T^3 term above 10K and constant above Debye temperatures). Specific heat of insulators (# excited electrons $\sim \exp(-E_g/2kT)$ so $C \sim du/dt$ also exponential in T ; experimentally $C \sim T^3$). Thermal expansion; Melting of solids.
2. **Transport properties** – Static periodic crystal has infinite conductivity – main resistance comes from scattering from lattice vibrations ($R \sim T^5$ at low T and $R \sim T$ at high T); Superconductivity (lattice vibration mediated attractive interaction between two electrons); Thermal conduction in insulators (not so good as metals but substantial); Transmission of sound in insulators.
3. **Interaction with radiation** – Reflectivity of ionic crystals (show a maximum at frequency far below the gap – because E field exerts force on +ve and –ve ions, displace them); Inelastic scattering of light (Raman scattering and Brillouin scattering); X-ray scattering(Amplitude of Bragg peaks diminished by lattice vibration).

PHONONS – NORMAL MODES I

Relax the constraint of static lattice gradually – replace by two weaker constraints:

1. Idea of Bravais lattice still holds - it is now the mean position rather than instantaneous position – ions move about the Bravais lattice site but never diffuse away from it – assumption valid except near melting point of the solid.
2. The displacement of atoms about the equilibrium position is small as compared to the inter-atomic distance. Made for analytical convenience – so that harmonic assumption holds – can ignore higher order terms in displacement- again not valid at high temperatures. The assumption fails completely in light element like solid Helium – need a Quantum theory from scratch.

Consider elastic vibrations of crystal with single-atom basis.

AIM: Find dispersion relation (relation between frequency and wavevector of the wave – dependence on the elastic constants of the medium).

Start with a one-dimensional case. Valid for high-symmetry planes like [100], [110], [111] of a cubic lattice – for wave propagating along this direction entire planes of atoms move in phase either longitudinally or transversely – can describe each plane by a single co-ordinate – problem reduces to a 1-D case.

Assume – linear force-displacement relation (Hooke's law type) – terms linear in relative displacement vanish at equilibrium – next term is quadratic in relative displacements of any two points in lattice – assume only nearest neighbour interactions.

Force on n^{th} plane caused by the relative displacement of the $(n+p)^{\text{th}}$ plane is

$$F \propto (u_{n+p} - u_n) = K(u_{n+p} - u_n)$$

K is the force constant

- Relates from now on to a single atom
- It is direction dependent

1-D chain of ions with one basis

Assume only nearest neighbour interactions: $p=1$



Force on the n^{th} ion is:

$$\begin{aligned} F_n &= K[(u_{n+1} - u_n) + (u_{n-1} - u_n)] \\ &= K(u_{n+1} + u_{n-1} - 2u_n) \end{aligned}$$

Equation of motion is: $m\ddot{u}_n = K(u_{n+1} + u_{n-1} - 2u_n)$

Want solutions like (travelling wave solutions): $u_n \propto e^{i(kna - \omega t)}$

$$\begin{aligned} m\ddot{u}_n &= K(u_{n+1} + u_{n-1} - 2u_n) \\ -m\omega^2 e^{i(kna - \omega t)} &= K(e^{i(ka)} + e^{-ika} - 2)e^{i(kna - \omega t)} \end{aligned}$$

$$m\omega^2 = K(2 - e^{i(ka)} - e^{-ika}) = 2K(1 - \cos ka) = 4K \sin^2\left(\frac{ka}{2}\right)$$

$$\omega(k) = 2 \sqrt{\frac{K}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

This is the dispersion relation relating the frequency of oscillation to the wavelength of oscillation.

What are the allowed values of k?

Ratio of the displacements of two neighbouring planes is:

$$\frac{u_{n+1}}{u_n} = \frac{e^{ik(n+1)a}}{e^{ikna}} = e^{ika}$$

The two planes oscillate with only a phase difference. Phase difference is meaningfully defined to only within $\pm\pi$. So allowed values of ka lie between $\pm\pi$ or $-\frac{\pi}{a} < k < \frac{\pi}{a}$ - this is just the first Brillouin zone.

Thus the allowed values of the wave-vectors are those that lie within the first Brillouin zone. Any value of k outside this range can be described by subtracting an appropriate reciprocal lattice vector.

How many modes?

Total N normal modes - N degrees of freedom – complete solution to problem!

Notes:

- Actual motion will be a linear combination of all the possible 3N modes (similar to Eigenvalue problems in quantum mechanics)
e.g.: consider two balls connected by a spring. The normal modes (2 in number) are $u_1 = u_2$ and $u_1 = -u_2$ – but the real motion is a complex combination of these two modes – the real motion need not be a plane wave propagating through the crystal – it will be a complex wave having contributions from all the 3N normal modes which are its Fourier components.
- Solution describes plane wave propagating through the lattice – phase velocity (velocity at which a particular crest/trough moves) ω/k and group velocity $\partial\omega/\partial k$ (velocity at which the envelope moves)

Features of the simple dispersion relation:

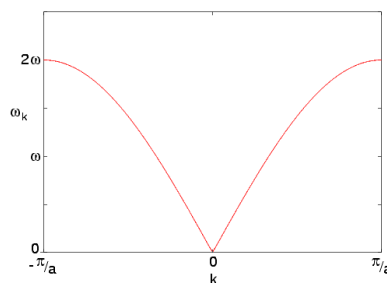


Figure 1: Dispersion relation for 1-D chain with single ion

Case I – small values of ka: Long wavelength response $\lambda \gg a$.

$$\omega(k) = 2 \sqrt{\frac{K}{m}} \left| \sin\left(\frac{ka}{2}\right) \right| = a \sqrt{\frac{K}{m}} |k|$$

$$v_g = \frac{\partial \omega}{\partial k} = a \sqrt{\frac{K}{m}} \left| \cos\left(\frac{ka}{2}\right) \right| = a \sqrt{\frac{K}{m}}$$

Linear dispersion $\omega \propto k$; like for light or sound waves – phase velocity and group velocity are identical and independent of frequency. This is also the result in continuum where $a=0 \Rightarrow ka=0$ identically.

Case II – $k = \pm\pi/a$: At the boundaries of the Brillouin zone

$$\omega(k) = 2 \sqrt{\frac{K}{m}} \left| \sin\left(\frac{ka}{2}\right) \right| = 2 \sqrt{\frac{K}{m}} = \text{constant}$$

$$v_g = \frac{\partial \omega}{\partial k} = a \sqrt{\frac{K}{m}} \left| \cos\left(\frac{ka}{2}\right) \right| = 0$$

The group velocity $\partial\omega/\partial k=0$, standing waves. At $k=\pm\pi$, the ratio of displacement of two neighbouring planes of ions is:

$$\frac{u_{n+1}}{u_n} = \frac{e^{ik(n+1)a}}{e^{ikna}} = e^{ika} = e^{\pm i\pi} = \pm 1$$

The alternate planes oscillate with same amplitude but out of phase by 180° – the wave moves neither to the left nor to the right – standing wave.

Have seen similar situation before – Bragg reflection of electrons at the Brillouin zone boundary. Is this the case here?

For Bragg reflection $2d\sin(\theta) = n\lambda$. Here the waves are propagating perpendicular to the planes; so $\theta=\pi/2$; $d=a$ (lattice spacing in the particular direction); $n=1$.

So, $2d\sin(\theta) = n\lambda$ implies $\lambda=2a$ or $k=2\pi/\lambda = \pi/a$

So the values of k at the Brillouin zone boundary satisfy the condition for Bragg reflection of lattice vibrations leading to the formation of standing waves.

1-D chain of ions with two ions per primitive cell

Consider NaCl – FCC structure with 2-ion basis – what will be the dispersion relation?

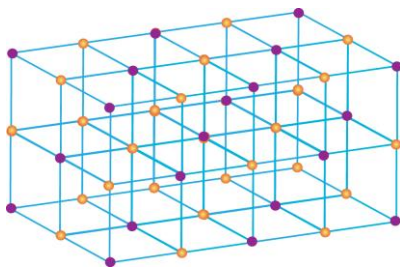


Figure 2: NaCl structure

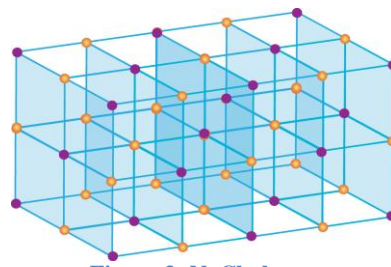


Figure 3: NaCl planes

Equilibrium positions of the ions for the n^{th} unit cell are na and $(na+d)$.

Displacements of the ions from their mean positions are :

$$\begin{aligned}
 &u_n \text{ for the ion at } na \\
 &v_n \text{ for the ion at } na+d \\
 m\ddot{u}_n &= K(v_n - u_n) + G(v_{n-1} - u_n) \text{ --- (1)} \\
 m\ddot{v}_n &= K(u_n - v_n) + G(u_{n+1} - v_n) \text{ --- (2)}
 \end{aligned}$$

Look for solutions of the form:

$$u_n = \varepsilon_1 e^{i(kna - \omega t)} \text{ --- (3)}$$

$$v_n = \varepsilon_2 e^{i(kna - \omega t)} \text{ --- (4)}$$

Substituting (3) and (4) in (1):

$$\begin{aligned}
 -m\omega^2 \varepsilon_1 e^{i(kna - \omega t)} &= K(\varepsilon_2 - \varepsilon_1) e^{i(kna - \omega t)} + G(\varepsilon_2 e^{-ika} - \varepsilon_1) e^{i(kna - \omega t)} \\
 -m\omega^2 \varepsilon_1 &= K(\varepsilon_2 - \varepsilon_1) + G(\varepsilon_2 e^{-ika} - \varepsilon_1)
 \end{aligned}$$

$$(m\omega^2 - K - G)\varepsilon_1 + (K + Ge^{-ika})\varepsilon_2 = 0 \text{ --- (5)}$$

Similarly using (3) and (4) in (2):

$$(K + Ge^{ika})\varepsilon_1 + (m\omega^2 - K - G)\varepsilon_2 = 0 \text{ --- (6)}$$

Set of homogeneous equations of type $ax+by=0$ and $cx+dy=0$ has a solution if and only if the determinants of the coefficients vanish $\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc = 0$

So,

$$(m\omega^2 - K - G)^2 = (K + Ge^{-ika})(K + Ge^{ika})$$

$$\omega^2 = \frac{K + G}{m} \pm \frac{1}{m} \sqrt{K^2 + G^2 + 2KG \cos(ka)}$$

This is the dispersion relation with the ratio of the displacements of the two ions in a cell given by

$$\frac{\varepsilon_1}{\varepsilon_2} = \mp \frac{K + Ge^{ika}}{|K + Ge^{ika}|}$$

How many modes?

Total allowed values of k (again lying in the first Brillouin zone) – for each value of k there are two possible values of ω – total $2N$ normal modes – $2N$ degrees of freedom for a 1D lattice with two ions in each cell – complete solution to problem!

Features of the dispersion relation:

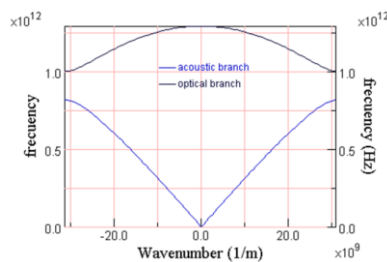


Figure 4: Dispersion relation for two-ion basis

Two values of ω for a given value of k – two *branches* of the dispersion curve

- Lower branch is acoustic branch - so called because the dispersion at long wavelength (small ka) is $\omega=vk$; like ordinary sound waves.
- Upper branch is optical branch - at long wavelength (small k) optical modes in ionic crystals interact with EM waves and are responsible for many of the optical properties like reflectivity, polarizability etc.

Case I – small values of ka : Long wavelength response $\lambda \gg a$.

$$\cos(ka) \sim 1 - (ka)^2/2$$

Solutions 1: $\omega = \sqrt{\frac{KG}{2m(K+G)}} (ka)$; $\epsilon_2 = \epsilon_1$; Acoustic mode; two ions in the cell move in phase; linear sound-wave like dispersion.

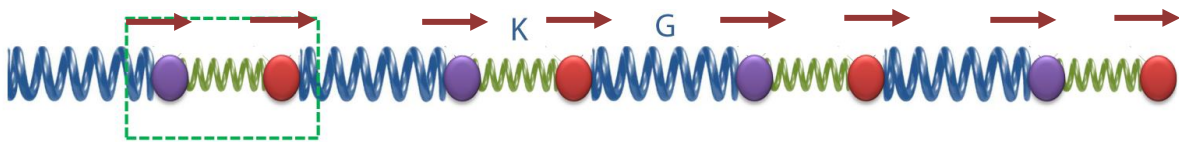


Figure 5: Acoustic mode

Solutions 2: $\omega = \sqrt{\frac{2(K+G)}{m}}$; $\epsilon_2 = -\epsilon_1$; Optical mode; two ions move out of phase.

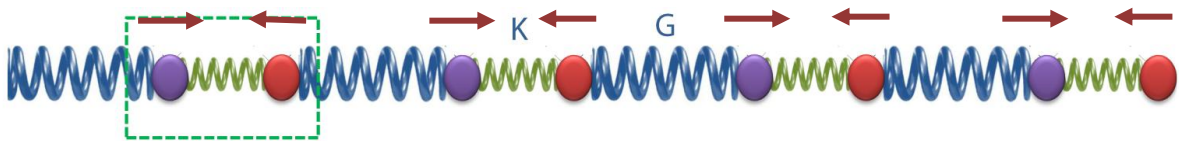


Figure 6: Optical mode

Case II – $k = \pm\pi/a$: At the boundaries of the Brillouin zone

Solutions 1: $\omega = \sqrt{\frac{2G}{m}}$; $\epsilon_2 = \epsilon_1$; Acoustic mode; two ions in the cell move in phase; only G spring is stretched/compressed; standing wave.

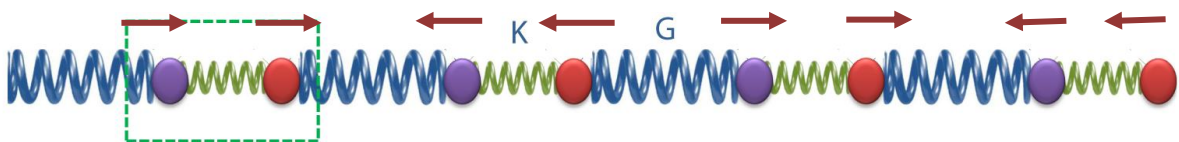


Figure 7: Acoustic mode

Solutions II: $\omega = \sqrt{\frac{2K}{m}}$; $\epsilon_2 = -\epsilon_1$; Optical mode; two ions in the cell move out of phase; only harder K spring is stretched/compressed; standing wave – cells oscillate independent of each other!

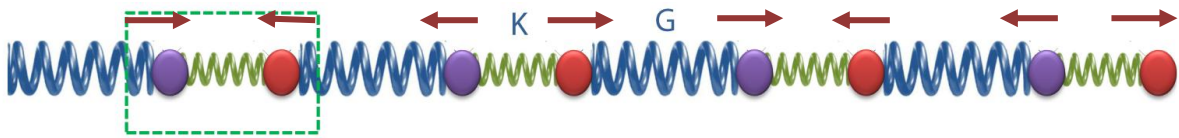


Figure 8: Optical mode

If $K=G$, the two modes are indistinguishable at zone boundaries, the two branches meet.

Case III – $K \gg G$: The two ions are connected by a very rigid spring

Solutions I: $\omega = \sqrt{\frac{2G}{m}} \left| \sin\left(\frac{ka}{2}\right) \right| \left[1 + O\left(\frac{G}{K}\right) \right]$; $\varepsilon_2 \approx \varepsilon_1$; Acoustic mode; behaves like a linear chain of ions of mass $2m$ connected by spring G – each cell behaves like a single unit – low energy oscillations so stiff K spring is unperturbed.

Solutions II: $\omega = \sqrt{\frac{2K}{m}} \left[1 + O\left(\frac{G}{K}\right) \right]$; $\varepsilon_2 \approx -\varepsilon_1$; Optical mode; ω approximately independent of k .

Behaves like a diatomic molecule of masses m connected by a spring of constant K . The two masses move approx out of phase.

G/K is still finite, so ω still has a dependence on k , although it is very weak. So as k changes the allowed value of ω also changes slightly. Thus the number of allowed energy values is not strictly one; it forms a narrow band of allowed energy values.

WHY? G/K is not zero, so there is a finite interaction between the cells. Like in the tight binding model, as the strength of interactions between the atoms increase, the single atomic levels spread out into bands.

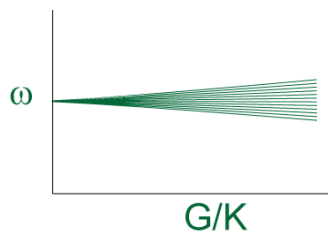


Figure 9: Spreading of energy values into band with increasing inter-cell interaction

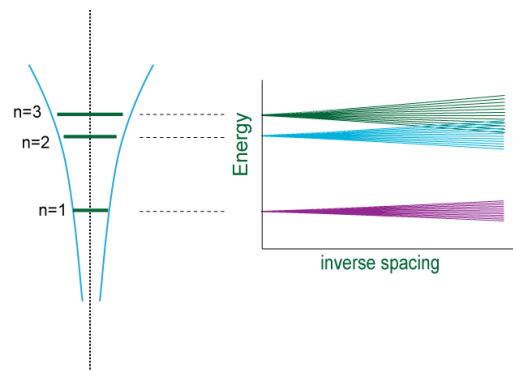


Figure 10: energy band formation in tight binding approx

Naive rule of thumb: Acoustic mode dynamics determined by inter-cellular interaction, units in the cell move in phase. In optical mode, the ions in each cell execute molecular vibrations; interactions between the different cells broaden out the allowed levels into a band.