3. Lattice Dynamics

3.1 1D Chain of Identical Atoms

We will study the 1D problem, and then generalize to 3D. Consider a classical chain of N atoms (later $N \rightarrow \infty$). Treat the interactions between the atoms as springs (spring constant k) between nearest neighbours, with motion parallel to the chain.



Apply Newton's second law to j^{th} atom.

 $m\ddot{u}_{j} = k\left(u_{j+1} - u_{j}\right) - k\left(u_{j} - u_{j-1}\right)$

Apply periodic boundary conditions. $u_j = u_{j+N}$.

Look for wave-like solution $u_j = u_0 e^{i(Qja-\omega t)}$, where *ja* is the position, and *Q* will correspond to some wavenumber.

The boundary condition implies $e^{i(QNa)} = 1$, so $Q = \frac{2\pi n}{Na}$ where *n* is an integer.

Put trial solution into the equation of motion, and divide through by the common factors.

$$m(-\omega^{2}) = k(e^{iQa} + e^{-iQa} - 2) = 2k(\cos(Qa) - 1)$$

Take positive solution with n from 1 to N.



 $\omega(Q) = 2\sqrt{\frac{k}{m}} \sin\left(\frac{Qa}{2}\right)$ Could take *n* from $-\frac{N}{2}$ to $\frac{N}{2}$. Equivalent to a translation of part of wave by $-\frac{2\pi}{a}$.



Plot sin(1.8pi * x/a) vs sin(-0.2pi * x/a) for 0, 2a, 3a, ... and x between 1 and -1.

At a, 2a, 3a, etc. the two functions have the same value. i.e. everywhere there's an atom, the functions are the same. Where they are not the same, it doesn't matter, as there's nothing there.

Brillouin Zone

The Brillouin Zone is the primitive unit cell in the reciprocal lattice chosen in such a way that all points in the zone are closer to one reciprocal lattice point than to any other.

We usually represent the lattice dynamics in one Brillouin zone. The wavevector (\underline{Q}) mapped with the Brillouin zone (reduced wavevector) represented by q.

Dispersion Relation

Group velocity is $\frac{d\omega}{dq}$. This is usually 0 at the zone boundaries.

The phase velocity is $\frac{\omega}{q}$.

If small q, relation is usually linear, so group velocity and the phase velocity are the same. In general, this is not true.

3.2 Diatomic Linear Crystal

This is a 1D crystal with two types of atoms. For simplicity, we will model springs with the same force constants between nearest neighbours.



Apply Newton's Second Law $m_1 \ddot{u}_{1j} = k \left(u_{2j} - u_{1j} \right) - k \left(u_{1j} - u_{2j-1} \right)$ $m_2 \ddot{u}_{2j} = k \left(u_{1j+1} - u_{2j} \right) - k \left(u_{2j} - u_{1j} \right)$ Apply periodic boundary conditions. $u_{1j} = u_{1j+N}$ $u_{2j} = u_{2j+N}$

Look for wavelike solutions.

$$u_{1j} = u_{10}e^{i(qja-\omega t)}$$
$$u_{2j} = u_{20}e^{i(qja-\omega t)}$$
$$q = \frac{2\pi n}{Na}$$

But now, there are 2N degrees of freedom.

Put the trial solutions into the equations of motion, and divide through by the common factors.

$$-m_1\omega^2 u_{10} = k(u_{20} - u_{10}) - k(u_{10} - u_{20}e^{-iqa}) - (1)$$

$$-m_2\omega^2 u_{20} = k(u_{10}e^{iqa} - u_{20}) - k(u_{20} - u_{10}) - (2)$$

This is a pair of simultaneous equations in ω^2 . Write them in matrix form.

$$\begin{pmatrix} m_1\omega^2 - 2k & k(1+e^{-iqa}) \\ k(e^{iqa}+1) & m_2\omega^2 - 2k \end{pmatrix} \begin{pmatrix} u_{10} \\ u_{20} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

this is true for non-zero solutions u_{10}, u_{20} when the determinant of the matrix is 0.

$$(m_1\omega^2 - 2k)(m_2\omega^2 - 2k) - k^2(e^{iqa} + 1)(1 + e^{-iqa}) = 0$$

This is now a quadratic equation in ω^2 .

$$m_1 m_2 (\omega^2)^2 - 2k(m_1 + m_2)\omega^2 - 2k^2 (\cos(qa) - 1) = 0$$

Write it in the standard form for a quadratic.

$$\left(\omega^{2}\right)^{2} - 2k\frac{m_{1} + m_{2}}{m_{1}m_{2}}\omega^{2} + \frac{4k^{2}}{m_{1}m_{2}}\sin^{2}\left(\frac{qa}{2}\right) = 0$$

use the quadratic formula.

$$\omega^{2} = \frac{k(m_{1} + m_{2})}{m_{1}m_{2}} \pm \frac{k}{m_{1}m_{2}}\sqrt{(m_{1} + m_{2})^{2} - 4m_{1}m_{2}\sin^{2}\left(\frac{qa}{2}\right)}$$

For each q value, we now have two positive values of ω . We have N values of q, but 2N degrees of freedom. There are thus two branches of vibrational excitation.

http://solidstate.physics.sunysb.edu/teach/intlearn/



For $m_1 = m_2$, the gap disappears.

For
$$q = 0$$
, $\omega = 0$ or $\omega^2 = 2k \frac{(m_1 + m_2)}{m_1 m_2}$
For $q = \frac{\pi}{a}$, $\omega^2 = \frac{2k}{m_2}$ or $\frac{2k}{m_1}$.

For
$$q = 0$$
, put it into (1) and (2).
 $-m_1 \omega^2 u_{10} = 2k(u_{20} - u_{10})$
 $-m_2 \omega^2 u_{20} = 2k(u_{10} - u_{20})$

For $\omega = 0$, then $u_{10} = u_{20}$. i.e. the two atoms are vibrating in phase, with the same amplitude.

Solution (1), q = 0, $\omega = 0$

$$\bigcap_{m=1}^{\infty} \bigcap_{m=2}^{\infty} \bigcap_{m=1}^{\infty} \bigcap_{m=2}^{\infty}$$

$$\prod_{u=2j}^{\infty} u_{u=2j}^{2j+1} \cdots \prod_{u=2j+1}^{\infty} u_{u=2j+1}^{2j+1}$$
Solution (2)., $q = 0$, $\omega^2 = \frac{2k(m_1 + m_2)}{m_1 m_2}$
In (1):

$$-m_1 \omega^2 u_{10} = 2k (u_{20} - u_{10})$$
$$-m_1 2k \frac{(m_1 + m_2)}{m_1 m_2} u_{10} = 2k (u_{20} - u_{10})$$
$$-(m_1 + m_2) u_{10} = m_2 (u_{20} - u_{10})$$
$$-m_1 u_{10} = m_2 u_{20}$$

Solution (2) is the atoms in antiphase, with zero movement of the centre of gravity for each pair.



For the zone boundary, where $q = \pi/a$, $e^{iqa} = -1$, so (1) and (2) become: $-m_1\omega^2 u_{10} = k(u_{20} - u_{10}) - k(u_{10} + u_{20})$ $-m_2\omega^2 u_{20} = k(-u_{10} - u_{20}) - k(u_{20} - u_{10})$ These simplify to $-m_1\omega^2 u_{10} = -2ku_{10}$ $-m_2\omega^2 u_{20} = -2ku_{20}$ If $\omega^2 = \frac{2k}{m_2}$, since $m_1 \neq m_2$, $u_{10} = 0$.

So the m_1 atoms are stationary, and the neighbouring m_2 atoms vibrate in antiphase.

$$\bigcirc_{m_1} \qquad \bigoplus_{m_2} \qquad \bigoplus_{m_1} \qquad \bigoplus_{m_2} \qquad \bigoplus_{m_1} \qquad \bigoplus_{m_2} \qquad \bigoplus_{m_1} \qquad \bigoplus_{m_2} \qquad \bigoplus_{m$$

3.3 Linear Crystal – one type of atom, but two different springs

Solutions also give two branches, as there are two atoms in the basis. In 1D, the number of branches is equal to the number of atoms in the basis. One, and only one, mode is acoustic. This means that the frequency goes to 0 as the wavevector goes to 0.

3.4 Vibrations in 3 Dimensions

In general, the atoms are bound in a potential which gives restoring forces in 3 dimensions, which are not necessarily the same. Each atom has 3 degrees of (vibrational) freedom, so the number of modes is equal to three times the number of atoms in the basis. Three of these modes are acoustic; one longitudinal, two transverse.

Speed of Sound

The velocities of the compression (longitudinal) and the shear (transverse) waves are not the same. Where the transverse waves are not constrained by symmetry to be the same, they are different. The symmetry constraint is a 4- or 3-fold rotation axis. Longitudinal speeds are usually about twice the transverse.

Speeds in solids are typically $10^3 ms^{-1}$, or 10THzA.

3.5 Quantum Effects in Lattice Dynamics

In the harmonic approximation, the Hamiltonian is the sum of the 3N independent oscillator Hamiltonians, all of which commute. The quantum mechanical frequencies turn out to be the same as those of the classical normal modes.

The energy in any given mode $\omega(q)$, where q is the reduced wavevector, is given by Bose-Einstein statistics with zero chemical potential.

$$\varepsilon(q) = \left(n + \frac{1}{2}\right)\hbar\omega(q),$$

where n is an integer. The expected value for n is

$$\langle n \rangle = \frac{1}{e^{\hbar \omega \beta} - 1}$$

where $\beta = \frac{1}{k_B T}$.

So we can treat the occupied vibrational states as Bose particles, just like photon states, which are occupied EM wave states in a box. By analogy, the quantized vibrational states in a solid are called phonons (quantized sound waves).

Examples of phonon dispersion relations Diagrams will be on the Teaching Web.

3.7 Neutron Inelastic Scattering Static (time averaged) lattice gives the Bragg scattering. Phonons can scatter neutrons (and X-rays), but the neutron energy changes on scattering. For neutrons the energy change is significant compared with the incident energy. For X-rays, the change is a very small fraction (10's of mV compared with 10's of kV).

Peaks in the scattering when the energy change on scattering and the momentum change (Q) lie on a phonon dispersion curve.



3.8 Specific Heat

 $C_v = \frac{1}{V} \frac{\partial \varepsilon}{\partial T}$

Classical specific heat, equipartition says that the energy for each quadratic term is $\frac{1}{2}k_BT$. For N atoms, there are 6N such terms. So

$$C_v = 3\left(\frac{N}{V}\right)k_B$$

This is Dulong & Petit's Law.

In the quantum case, the high T limit of the energy is the same. When $k_B T >> \hbar \omega_{\text{max}}$, we expect Dulong and Petit's law to hold.



Density of States:

Energy of a .phonon defines its' thermal effects. Therefore we need to see how many phonons have which energy.



 $\rho(\omega)$ proportional to ω^2

Features:

- Always a maximum energy
- Shape can be very complicated
- Depends on dispersion relation
- Always quadratic at small energies
- Can have sharp peaks, discontinuities, energy gaps.

3.8.1 Einstein Model

We represent the density of states by a single energy ω_{F} .

$$\varepsilon = 3N \left[\frac{1}{e^{\hbar\omega_E\beta} - 1} + \frac{1}{2} \right] \hbar\omega_E$$

This is an exact result. We can then differentiate it to get the heat capacity.

$$C_{v} = 3\frac{N}{V}k_{B}\frac{\left(\hbar\omega_{E}\beta\right)^{2}e^{\hbar\omega_{E}\beta}}{\left(e^{\hbar\omega_{E}\beta}-1\right)^{2}}$$

At the high T limit $(T \to \infty, \beta \to 0)$, we get $3\frac{N}{V}k_B$.

At the low T limit, we get $C_v \approx 3 \frac{N}{V} k_B (\hbar \omega_E \beta)^2 e^{-\hbar \omega_E \beta}$.

As $T \to 0$, we get an exponential decay. This is broadly correct, but in fact it falls too quickly to 0 as $T \to 0$.

This suggests that Quantum Mechanics provides an explanation of the deviations from the Dulong and Petit law, but we need a better model to get the correct form.

3.8.2 Debye Model

Consider 3 acoustic phonon modes, all with the same velocity, and all linear with no deviations.

q-space density of states:

Do sum in cubic box – in fact it is independent of the shape, but a cubic box is easiest. Cube of edge L, volume $V = L^3$.

What standing wave states are allowed?

 $\psi = 0$ on walls. Look at the x-direction.

$$\lambda_x = 2L$$

$$\lambda_x = L = \frac{2L}{2}$$

$$\lambda_x = \frac{2L}{3}$$

$$\lambda = \frac{2L}{n}$$

$$q_x = \frac{2\pi}{\lambda} = \frac{n\pi}{L} = \frac{n_x \pi}{L}$$

Consider the other directions. We will have:

$$q_x = n_x \frac{\pi}{L}$$
$$q_y = n_y \frac{\pi}{L}$$
$$q_z = n_z \frac{\pi}{L}$$

This only makes sense for positive integers n_x, n_y, n_z . This can then be plotted in q-space.

$$\underline{q} = \frac{\pi}{L} \left(n_x, n_y, n_z \right)$$

The volume of q-space per state $=\frac{\pi^3}{L^3}=\frac{\pi^3}{V}$.

The density of states $\rho(\underline{q})\underline{dq} = \frac{V}{\pi^3}\underline{dq}$.

We are only concerned with the magnitude $|\underline{q}| = q$. These are the states within a spherical shell of radius q and thickness dq.

The volume within the shell will be the surface area times the thickness. Remember that we are looking only at the positive octant, so 1/8 of a complete shell.

Volume =
$$\frac{1}{8} 4\pi q^2 dq$$

So the number of states within the shell $\frac{\frac{1}{2}\pi q^2 dq}{\frac{\pi^3}{V}}$.

Hence the density of states $\rho(q)dq = \frac{Vq^2}{2\pi^2}dq$.

To find the density of states as a function of energy, $g(\varepsilon)d\varepsilon$, we write $\rho(q)$ using $\varepsilon(q)$, and dq using $\frac{d\varepsilon}{dq}$.

For phonons, $\rho(q)dq = 3\frac{Vq^2}{2\pi^2}dq$ where the 3 has come from the 3 polarization states; two transverse, one longitudinal.

Assume that $\omega = vq$, where v is the (average) speed of sound.

$$q^{2} = \frac{\omega^{2}}{v^{2}}$$
$$dq = \frac{d\omega}{dv}$$
then

$$\rho(\omega)d\omega = \frac{3V}{2\pi^2} \frac{\omega^2 d\omega}{v^3}$$

With the Debye model, we treat the density of states as quadratic up to a maximum frequency, the Debye frequency ω_D .

To get this frequency, use

$$\int_0^{\omega_D} \rho(\omega) d\omega = 3N$$

which gives

$$\omega_D^3 = 6 \frac{N}{V} \pi^2 v^3 \,.$$

We now want to find the total energy in these phonons.

$$\varepsilon = \int_0^{\omega_D} \left(\frac{1}{e^{\hbar\omega\beta} - 1} + \frac{1}{2} \right) \hbar\omega\rho(\omega) d\omega$$
$$= \frac{3V}{2\pi^2} \frac{\hbar}{v^3} \int_0^{\omega_D} \left(\frac{1}{e^{\hbar\omega\beta} - 1} + \frac{1}{2} \right) \omega^3 d\omega$$

We can now substitute $k = \hbar \omega \beta$, and note that the zero-point energy does not depend on temperature, hence will not come into the specific heat, and can be neglected.

$$\varepsilon = \frac{3V}{2\pi^2} \frac{\hbar}{v} \left(\frac{1}{\hbar\beta}\right)^4 \int_0^{\hbar\omega_D\beta} \frac{1}{e^x - 1} x^3 dx + \varepsilon_{ZPE}$$

At the low temperature limit, we can make the approximation $\hbar \omega_D \beta \sim \infty$. The lower the temperature, the better this approximation.

Use
$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}.$$
$$\varepsilon = \frac{\pi^2}{10} V \frac{\hbar}{v^3} \left(\frac{k_B T}{\hbar}\right)^4 + \varepsilon_{ZPE}$$
$$C_V = \frac{2}{5} \frac{\pi^2 k_B^4}{\hbar^3 v^3} T^3$$

or in terms of ω_D :

$$\lim_{T \to 0} C_v = \frac{12}{5} \pi^4 \left(\frac{N}{V}\right) k_B \left(\frac{k_B T}{\hbar \omega_D}\right)^3$$

This gets the low-temperature form correct (T^3) .

For the full specific heat as a function of temperature curve, we need the full density of states, and do the integrals numerically.

Note in real crystals, there are three speeds of sound which are not in general equal. We can treat v in the calculation above as an effective average speed of sound.