Intro to Solid State Physics: Li Yang

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Chapter 1: Crystal Structure

Ideal crystal is constructed by the infinite repetition of identical structural groups of atoms.
A group is called the basis. Detecting crystal structure started with x-rays due to the wavelength of the
x-ray (≈ 1 angstrom) being comparable to the interatomic spacing in a crystal.

What is a *lattice*? 2D Bravais Lattices Wikipedia The gamous graphene has a hexagonal (honeycomb
structure) like lattice, but it does not have the center atom from the true hexagonal lattice. The primitive
of this lattice is made of up two atoms than can be translated to form the lattice. Thus graphene is like
a diatomic crystal.

3D Bravais Lattices There are 14 Bravais lattices in 3D. In both 2D and 3D, the primitive cells that
make up the lattice must fill the least amount of space and have no 'holes' or 'extras' left over. The 2
most common lattices now are the Primitive Hexagonal for its symmetry and the Body Centered Cubic
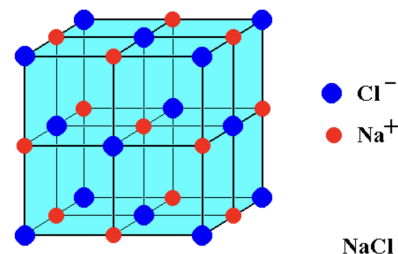(BCC) which is the lattice of Silicon, the most important material today.

Figure 1.1: Sodium Chloride Structure (FCC)

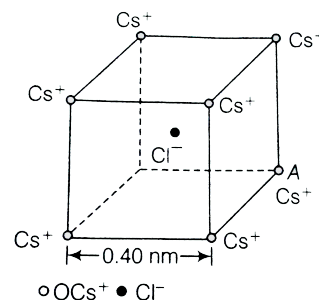**Example Structures** The lattice of Sodium Chloride is FCC as shown in Figure 1.1

Figure 1.2: Cesium Chloride Structure (SC)

Figure 1.2 shows the lattice of Cesium Chloride which is SC.

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Chapter 2: Wave Diffraction and the Reciprocal Lattice
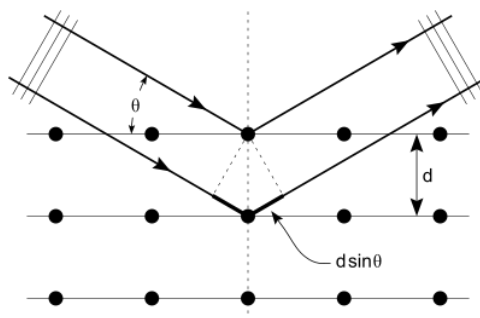

Figure 2.1: Bragg's Law

Scattering and Bragg's Law   When two beams of same phase meet, they constructively interfere. When they are out of phase, they destructively interfere. The location of constructive interference, or path difference, is shown by the bold lines in Figure 2.1. The path difference is

$$2d \sin \theta = n\lambda$$

known as Bragg's Law which is only valid for $\lambda \leq 2d$. In reality each lattice plane will reflect about $10^{-3} \sim 10^{-5}$ of the incident beam. Thus only about $10^3 \sim 10^5$ planes contribute to the diffraction. The periodicity of the lattice leads to a periodic observable. . .

aside: The electron wavefunction is not observable—ψ is a complex number, but the electron density, $\psi^*\psi$, is observable. Read about the quantized Hall effect (Queen):) and Superconductivity (King).

$$\psi(x + T) = \psi(x)e^{i\theta} n(x + T) = n(x)$$

Fourier Transform   The discrete Fourier transfrom is useful for periodic functions.

$$n(x) = \sum_{P \geq 0} \left[C_p \cos\left(\frac{2\pi}{a}x\right) + S_p \sin\left(\frac{2\pi}{a}x\right) \right]$$
$$= \sum_p n_p e^{i\frac{2\pi}{a}px}$$

or in vector notation

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_G e^{i\mathbf{G}\cdot\mathbf{r}}$$

Since $n(x)$ is real, there is a symmetry of the complex conjugate

$$n_p = n^*_{-p}$$

Inverse Fourier Transform

$$n_p = \frac{1}{a} \int_0^a n(x) e^{-i\frac{2\pi}{a}px} \, \mathrm{d}x$$

and in vector notation

$$n_G = \frac{1}{V} \int_{cell} n(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} \, \mathrm{d}V$$

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Reciprocal Space Vectors   The basis vectors of the reciprocal lattice are

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

where the denominator is the volume of the unit cell (parallelpiped) $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = V_c$. Taking the dot product of a primitive vector with a reciprocal lattice vector gives

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$$

where the Kronecker delta tells us that the dot product is either 2π or 0. With this we can write the $\mathbf{G}$ vector as a linear combination of the reciprocal lattice vectors

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

we can also show that

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$$

which means that this is invariant under tranlsations.

Scattering amplitude

$$F = \int d\mathbf{r} \, n(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{k}'\cdot\mathbf{r}}$$

where $|\mathbf{k}| = |\mathbf{k}'|$. In vector notation

$$F = \int d\mathbf{r} \sum_{\mathbf{G}} n_G e^{i(\mathbf{G}-\mathbf{r}')} e^{-i\Delta\mathbf{k}\cdot\mathbf{r}}$$
$$= \sum_{\mathbf{G}} n_G \int d\mathbf{r} \, e^{i(\mathbf{G}-\Delta\mathbf{k}')\cdot\mathbf{r}}$$

where $\Delta\mathbf{k} = -(\mathbf{k} - \mathbf{k}')$. When $\mathbf{G} = \Delta\mathbf{k}$ we can rewrite to

$$\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$$

in absolute value

$$|\mathbf{k} + \Delta\mathbf{k}| = |\mathbf{k}'| \rightarrow |\mathbf{k} + \Delta\mathbf{k}| = |\mathbf{k}| \rightarrow |\mathbf{k} + \mathbf{G}| = |\mathbf{k}|$$

and

$$(\mathbf{k} + \mathbf{G}) \cdot (\mathbf{k} + \mathbf{G}) = \mathbf{k} \cdot \mathbf{k} \rightarrow 2\mathbf{k} \cdot \mathbf{G} + \mathbf{G}^2 = 0$$

For the 1D crystal $G = 2\pi/a$. Since $\mathbf{k} \cdot \mathbf{G} = 2\pi/\lambda \mathbf{G} \sin\theta$ and $2\mathbf{k} \cdot \mathbf{G} = \mathbf{G}^2$ We get

$$2 \cdot \frac{2\pi}{\lambda} G \sin\theta = \mathbf{G}^2$$
$$\rightarrow \frac{4\pi}{\lambda} \sin\theta = G$$

since $G = 2\pi/a$ we get Bragg's Law

$$2d \sin\theta = n\lambda$$

For the SC the reciprocal lattice is SC, but for BCC, the reciprocal lattice is different...

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Chapter 2: cont'd

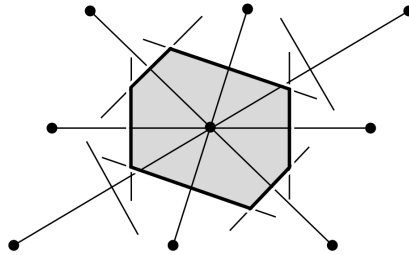**Wigner-Seitz primitive cell:** How to create the most symmetric primitive cell.

Figure 3.1: Wigner-Seitz Primitive Cell

Steps: Connect a given lattice point to all nearby lattice points. Bisect all lines. The area enclosed by the bisectors is the Wigner-Seitz primitive cell as shown in Figure 3.1.

Reciprocal Lattice of SC The lattice vectors (primitive translation vectors) are

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = a\hat{\mathbf{z}}$$

the reciprocal lattice vectors using the formula from last lecture are

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_c} = \frac{2\pi}{a}\hat{\mathbf{x}}, \quad \mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}, \quad \mathbf{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}$$

Reciprocal Lattice of BCC The lattice vectors are

$$\mathbf{a}_1 = \frac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

and the reciprocal lattice vectors are

$$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \quad \mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

Reciprocal Lattice of FCC The lattice vectors are

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

which is the same as the reciprocal space of BCC. Thus, the reciprocal lattice of FCC is BCC!

Brillouin Zone The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice.

Chapter 3: Crystal Binding and Elastic Constants

We are mostly interested in the E&M interaction between atoms on the energy scale of eV (e.g. the band gap of silicon is 1.2 eV).

There are 4 main types of bonds:

Metallic Bond Bonds between metals have weakly bound valence electrons. Hence the electrons move freely around like a fluid. This is why metals are good conductors.

Ionic Bond   Bonds between metals and non-metals (e.g. NaCl). The opposing charges attract each other where the electrons form full shells and hence less conductivity.

Covalent Bond   Bonds between non-metals (e.g. Si). The atomic orbitals defined by QM describes the bonds through the hybridization of the orbital wavefunctions (e.g. sp^3 in diamond). This is a very difficult problem to solve.

Van der Waals interaction   Inert gases... e.g. He is interesting as it is a liquid at very low temperatures, and it is a boson (He-4 superfluid) and fermion (He-3) depending on the number of neutrons.

Hydrogen Bonding   is very important in biology, but not in solid state physics.

Van der Waals interaction

Two types of energy to consider:

- Cohesive energy: Energy required to separate bound atoms. The cohesive energy of a solid is the sum of the cohesive energies of the bonds.

- Ionization energy: Energy required to remove an electron from an atom.

The ionization energy is larger because the Van der Waals interaction is a weaker bond. Given two inert gas atoms, there is no dipole or charge distribution contributing to the interactions between the atoms. In QM, there is no zero point energy, so we have to consider the atoms to not be perfect, but rather vibrate around a mean position. This is a dipole-dipole interaction.

dipole-dipole   Given two electrons spaced by a distance R in a 1D lattice, one atom fluxuates by x_2 and the other by x_1. The Hamiltonian of the unpertubed system is

$$H_o = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{1}{2}Cx_2^2$$

The Coulomb interaction:

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2}$$

Using Taylor expansion (2nd order) for small x_1 and x_2 we get

$$H_1 = -\frac{2e^2}{R^3}x_1 x_2$$

Since this has 2 degrees of freedom, we have a 2x2 matrix with 2 eigenvalues diagonlized by the normal mode transform. This results in 2 Canconical Modes:

$$x_s = \frac{1}{\sqrt{2}}(x_1 + x_2) \quad x_a = \frac{1}{\sqrt{2}}(x_1 - x_2)$$

THe total Hamiltonian is

$$H = \frac{1}{2m}\left[\frac{1}{2}(p_s + p_a)^2\right] + \frac{1}{2m}\left[\frac{1}{2}(p_s - p_a)^2\right] - 2\frac{e^2}{R^3} \cdot \frac{1}{2}(x_s^2 - x_a^2) + \frac{1}{2}cx_1^2 + \frac{1}{2}cx_2^2$$

$$= \left[\frac{p_s}{2m} + \frac{1}{2}\left(c - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{p_a}{2m} + \frac{1}{2}\left(c + \frac{2e^2}{R^3}\right)x_a^2\right]$$

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Chapter 3: cont'd

The momenta of the harmonic oscillators from last time are also in the ofmr 2 modes:

$$p_s = \frac{1}{\sqrt{2}}(p_1 + p_2) \quad p_a = \frac{1}{\sqrt{2}}(p_1 - p_2)$$

The matrix form

$$\begin{pmatrix} E_o & 0 \\ 0 & E_o \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \hbar\omega \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{vmatrix} E_o - \hbar\omega & \Delta \\ \Delta & E_o - \hbar\omega \end{vmatrix} = 0$$

solving for the eigenstates

$$\frac{1}{\sqrt{2}} \begin{pmatrix} a \\ b \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} a \\ -b \end{pmatrix}$$

The Hamiltonian of the single harmonic oscillator is

$$H_o = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

thus we can compare the frequencies of the harmonic oscillator and the Van der Waals interaction

$$\omega = \sqrt{\frac{c \pm \frac{2e^2}{R^3}}{m}}$$

and we know the *zero-point energy* $1/2\hbar\omega$ or in this case

$$\frac{1}{2}\hbar\Delta\omega = \frac{1}{2}\hbar[\Delta\omega_s + \Delta\omega_a]$$

From the uncoupled sum and using Taylor expansion

$$\omega = \omega_o \left[1 \pm \frac{1}{2}\left(\frac{2e^2}{R^3 c}\right) \pm \frac{1}{8}\left(\frac{2e^2}{R^3 c}\right)^2 + \dots \right]$$

thus we ge the interaction energy

$$\Delta U = \frac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = \frac{\hbar\omega_o}{2}\left[\frac{e^4}{c^2 R^6}\right] = -\frac{A}{R^6}$$

where the minus sign indicates an attractive force. We would expect the atoms to collapse, but this is not the case due to the Pauli exclusion principle (electrons cannot occupy the same state).

Pauli exclusion principle

As the atoms get closer, there is an overlap of the wavefunctions. If the wavefunctions are symmetric, the spin states must be anti-symmetric. Therefore anti-symmetric wavefunctions have symmetric spin states. This repulsive force from the Pauli exclusion principle is typically found empirically $\propto \frac{1}{R^{12}}$. Therefore the total potential is

$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right]$$

AKA the Lennard-Jones potential. We could find the equilibrium distance by minimizing the potential $\frac{dU}{dR} = 0$. This is fine for inert gases that are spherical, but other molecules are depend on more than the scalar distance R. This decays faster than the scale of Coulombs Law $\propto \frac{1}{R^2}$. The total energy for a crystal is

$$E = \frac{1}{2}N(4\epsilon)\left[\sum_j' \left(\frac{\sigma}{P_{ij}R}\right)^{12} - \sum_j' \left(\frac{\sigma}{P_{ij}R}\right)^6\right]$$

where the prime indicates that the sum is over the nearest neighbors. The fcc lattice

$$\sum_j' \left(\frac{1}{P_{ij}}\right)^{12} = 12.13188; \qquad \sum_j' \left(\frac{1}{P_{ij}}\right)^6 = 14.45392$$

for the 12 nearest neighbors. Solving for the minimum energy $\frac{dU}{dR} = 0$ we get

$$R_o/\sigma = 1.09$$

Ionic Crystal

The Coulomb interaction:

$$\pm\frac{q^2}{r_{ij}}$$

The short-term interaction

$$\lambda e^{-r_{ij}/\rho}$$

thus the potential is

$$U_{ij} = \lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}}$$

where at one site (one ion)

$$U_i = \sum_j' U_{ij}$$

and the total energy is

$$U = NU_i$$

For N molecules

$$U_{ij} = \begin{cases} \lambda e^{-r_{ij}/\rho} - \frac{q^2}{r_{ij}} & \text{nearest neighbor} \\ \pm\frac{q^2}{r_{ij}} & \text{otherwise} \end{cases}$$

and the total energy is

$$U_{tot} = N\left[ze^{-R/\rho} - \alpha\frac{q^2}{R}\right] \qquad \alpha = \sum_j' \frac{\pm}{p_{ij}}$$

where z is the number of nearest neighbors, and α is the Madelung constant. From this we can find the lattice constant by using

$$\frac{dU}{dR} = 0 \rightarrow R_o^2 e^{-R_o/\rho} = \alpha\rho\frac{q^2}{z\lambda}$$

solving for R_o and putting into the total energy equation we get

$$U_{tot} = -\frac{N\alpha q^2}{R_o}(1 - \frac{\rho}{R_o})$$

where we have a special term

$$-\frac{N\alpha q^2}{R_o}$$

known as the 'Madelung Energy'.

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Chapter 3: Bonds Bonds and Bonds

From last time:

$$U_{ij} = \begin{cases} \lambda e^{-R/\rho} - \frac{q^2}{R} & \text{nearest neighbor} \\ \pm \frac{q^2}{p_{ij}R} & \text{otherwise} \end{cases}$$

where $p_{ij}R = r_{ij}$ and the total energy (sum) is

$$U_{tot} = N\left[ze^{-R/\rho} - \alpha\frac{q^2}{R}\right]$$

where z is the number of nearest neighbors, N is the total ions, and α is the Madelung constant:

$$\alpha = \sum_j{}' \frac{\pm}{p_{ij}}$$

At the equilibrium seperation

$$\frac{\mathrm{d}U}{\mathrm{d}R} = 0 \rightarrow R_o^2 e^{-R_o/\rho} = \alpha\rho\frac{q^2}{z\lambda}$$

R_o is the equilibrium seperation (position). Substituting this back into the total energy we get the empirical formal for the equilibrium energy (ground state):

$$U_{tot} = -\frac{N\alpha q^2}{R_o}\left(1 - \frac{\rho}{R_o}\right)$$

where the first term outside the parenthesis is the Madelung energy
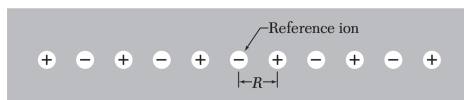
$$-\frac{N\alpha q^2}{R_o}$$

Figure 5.1: Line of ions with alternating charges

The Evaluation of Madelung Constant   Letting R denote the distance between the ions, we can write the Madelung constant for the 1D line of ions with alternating charges as.

$$\frac{\alpha}{R} = 2\left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R + \ldots}\right]$$
$$= \frac{2}{R}\left[1 - \frac{1}{2} + \ldots\right]$$
$$\alpha = 2\ln 2$$

Remember these numbers

- Bohr radius $a_o = 0.529A$

- fine structure constant $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$

For the covalent bond, we have to use QM because the electron distribution is homogenous like a sea of electrons. Sometimes we think of this as a homogenous electron gas. This is a very difficult problem to solve. So we move on to the Hydrogen bond. This is a very weak bond typically at the scale of meV—room temperature is around 25 meV. So the bonds can break easily.

Chatper 4: Phonons (lattice vibration)

First starting with the 1D case: evenly spaced atoms we can take the minimum energy energy at the atom and take the limit as it approaches zero or

$$\frac{\partial U}{\partial x} = 0$$

the first term is $V \propto x^2$ so we can approximate the potential as

$$U = \frac{1}{2} U'' x^2 = \frac{1}{2} c x^2$$

where c is the spring constant. So we can imagine that the atoms (u_{s-1}, u_s, u_{s+1}) are connected by springs. For 2 coupled springs in series we end up with 2 eigenmodes. But we look at each pair of atoms and sum up the forces. Using newton's second law we get the force of the s atom

$$F_s = c(u_{s+1} - u_s) + c(u_{s-1} - u_s) = c[u_{s+1} + u_{s-1} - 2u_s]$$

or as a differential equation

$$M \frac{\mathrm{d}^2 u_s}{\mathrm{d}t^2} = c[u_{s+1} + u_{s-1} - 2u_s]$$
$$u = u(\gamma) e^{-i\omega t}$$
$$\implies -M\omega^2 u_s = c[u_{s+1} + u_{s-1} - 2u_s]$$

this momentum of the crystal is not conserved but the Hamiltonian can still be written as

$$H(\gamma) H(\gamma + T)$$

where we discretize the translational symmetry, so we can write the periodic part of the atom as

$$u_s^k = u e^{-ik\gamma} \qquad u(\gamma) = u(\gamma + T)$$

where $k = 2\pi/L$ is the wavevector. So we can write the u_{s-1} and u_{s+1} as a translation of u_s:

$$u_{s-1} = u e^{-i(s-1)ka}$$
$$u_{s+1} = u e^{i(s+1)ka}$$
$$u_s = u e^{-iska}$$

where a is the lattice spacing. subbing this back in:

$$-M\omega^2 = c\left[e^{-ika} + e^{ika} - 2\right]$$
$$\omega^2 = 2\frac{c}{M}(1 - \cos(ka))$$

using the trig identity for half angles we get

$$\omega^2 = \frac{4c}{M} \sin^2\left(\frac{ka}{2}\right) \quad \text{or} \quad \omega = 2\sqrt{\frac{c}{M}} \left|\sin\left(\frac{ka}{2}\right)\right|$$

where $\omega = ck$ is the dispersion relation where we have boundaries at $\pm\pi/a$ and max $2\sqrt{c/m}$. The group velocity is

$$v_g = \frac{\partial \omega}{\partial k}$$

for $k \to 0$ we get the group velocity

$$v_g = a\sqrt{\frac{c}{M}}$$

we also get from the graph of ω is that the slope at the boundaries are zero.
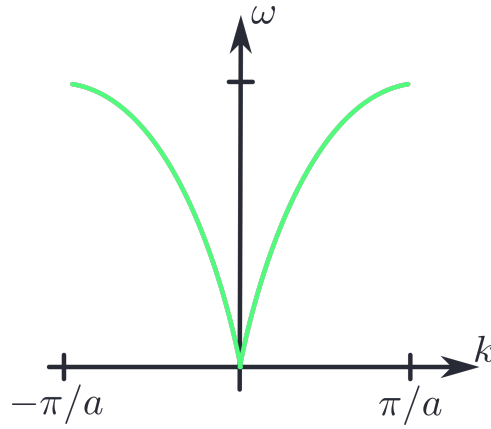
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Chapter 4: cont'd

Figure 6.1: Graph of ω vs k

Graphing ω vs k we get the graph in Figure 6.1. The slope at the boundaries is zero, and the maximum is $2\sqrt{c/M}$. But as $k \to 0$ we know that $\omega = 0$ and the energy is also zero. We can imagine the atoms are moving in phase (oscillating in the same direction) and amplitude. For $\omega = 2\sqrt{c/M}$ we have the atoms moving out of phase (moving in opposite of their neighbors with equal amplitude). At this point $k = \pi/a$ the potential is
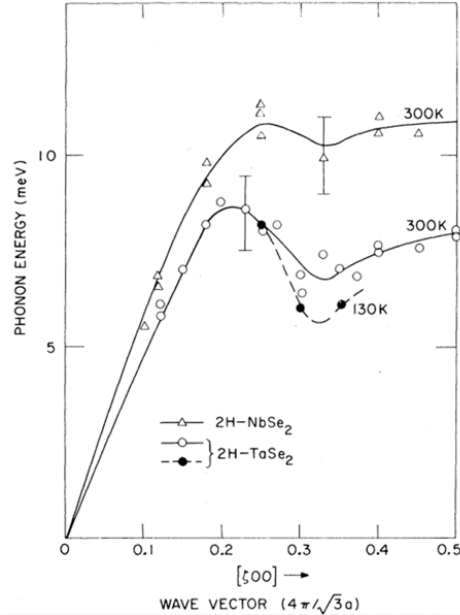
$$e^{i\pi/a \cdot a} \to e^{i\pi}$$

Figure 6.2: Graph of ω vs k for different material and temperature

Figure 6.2 shows the graph of ω vs k for neutron scattering observed in different materials and temperatures. We can see that the lower temperature has a low energy mode.

Aside: For phonons in low temperature, we see a double well potential, but for high temperatures, we see negative potential as shown in Figure 6.2.

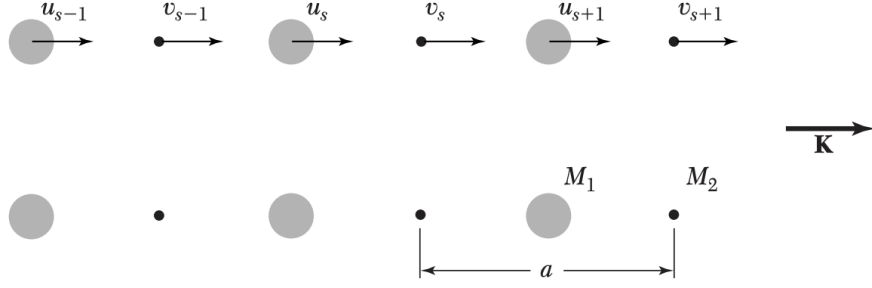**Two atom per unit cell** (primitive basis) For the 1D case again:

Figure 6.3: Two atom per unit cell

Using newton's second law

$$M_1 \ddot{u}_s = c[v_s + v_{s-1} - 2u_s]$$
$$M_2 \ddot{v}_s = c[u_s + u_{s+1} - 2v_s]$$

and the periodic nature of the lattice

$$u_s = u e^{iska} e^{-i\omega t}$$
$$v_s = v e^{iska} e^{-i\omega t}$$

from substitution we get

$$-M_1 \omega^2 u = cv[1 + ve^{-ika}] - 2u$$
$$-M_2 \omega^2 v = cu[1 + ue^{ika}] - 2v$$

or in matrix form

$$-\omega^2 \begin{pmatrix} M_1 & 0 \\ 0 & M_2 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = c \begin{pmatrix} -2c & c[1 + e^{-ika}] \\ c[1 + e^{ika}] & -2c \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} \tag{6.1}$$

to find the eigenvalues we solve the determinant of the matrix. We can only do this if the matrix is real (hermitian: complex conjugate is the same as the original). Solving for zero

$$A = \begin{vmatrix} -\omega^2 M_1 + 2c^2 & -c^2(1 + e^{-ika}) \\ -c^2(1 + e^{ika}) & -\omega^2 M_2 + 2c^2 \end{vmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = 0$$

and the determinant of A is

$$\omega^4 M_1 M_2 - 2c^2 \omega^2 (M_1 + M_2) + 4c^4 + c^2(1 + e^{-ika})(1 + e^{ika}) = 0$$
$$\omega^4 (M_1 M_2 - 2c^2 (M_1 + M_2) + 4c^4 - c^4[2 + 2\cos(ka)]) = 0$$

for $k = 0$ we get

$$M_1 M_2 w^4 - 2c[M_1 + M_2]\omega^2 = 0$$

we get the solutions

$$\omega_o = 0$$
$$\omega_1 = \sqrt{\frac{2c(M_1 + M_2)}{M_1 M_2}}$$

for $k = \pi/a$ we get

$$\omega^4 M_1 M_2 - 2c\omega^2 (M_1 + M_2) + 4c^4 = 0$$

Physically, the $k = 0$ mode there are two solutions, one where all basis move in the same direction, and the other where each atom moves in the opposing direction. For $k = \pi/a$ we have a solution where the basis pair move in the opposite direction of its neighbors. For this special case, we know that the Brillouin zone is half the size of the original zone, so the zone folds in half.

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Phonon modes For the $k = 0$, in the $\omega_o = 0$ case we know that $\lambda \to \infty$ and it is called an acoustic phonon, but for ω_1 this is an optical phonon. This is in the order of meV around the room temperature. For energy of the phonon,

$$E = \hbar\omega = pc \quad \text{and} \quad p = \hbar k$$

Raman scattering is related to the scattering of light from the optical phonon. The wavelength of incoming and outgoing light shift by the energy of the phonon.

3D Case: N atoms per unit cell. We have $3N$ branches of phonons. 3 acoustic and $3N - 3$ optical phonon.

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Chapter 4: cont'd

Raman Scattering & Infrared (THz) ~ 100 meV. For the 3D case, we have 3 acoustic modes and $3N - 3$ optical modes. FOr the acoustic mode.

$$k \to 0, \quad \omega \to 0$$

and for the optical modes

$$k \to 0, \quad \omega \to \infty$$

Chapter 5: Phonon properties

The heat capacity is in general

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

The proportionaly of heat capacity in different materials

- Metal: $C_v \propto I + QT^3$

- Insulator: $C_v \propto T^3$

The Energy of an N particle system is $E = Nk_BT$. and the heat capacity is

$$C_v = \frac{\partial E}{\partial T} = \omega k_B$$

The total energy is

$$U_{tot} = \sum k, p\hbar\omega_{k,p}\langle n_{k,p}\rangle$$

where $\langle n_{k,p}\rangle$ is the Bose-Einstein distribution

$$\langle n_\omega \rangle = \frac{1}{\exp\left(\frac{\hbar\omega}{k_BT}\right) - 1}$$

where there is no chemical potential. At low temperatures the constant goes to

$$\exp\left(\frac{\hbar\omega}{k_BT}\right)$$

or a boltzmann distribution.

$$U_{tot} \sum_{k,p} \frac{\hbar\omega_{k,p}}{\exp\left(\frac{\hbar\omega_{k,p}}{k_BT}\right) - 1}$$

or into an integral

$$\int \mathrm{d}k\, f(\omega) \to \int \mathrm{d}\omega\, f(\omega)\frac{1}{\frac{\mathrm{d}\omega}{\mathrm{d}k}}$$

We can compute this numerically from the phonon dispersion relation. For the Heat capacity of a solid, this T^3 term is in the order of 3 meV. We only need to take the acoustic modes into account for finding $\frac{\mathrm{d}\omega}{\mathrm{d}k}$ which approximately a constant C, so

$$\int_0^a \mathrm{d}\omega\, \frac{\hbar\omega^2}{\exp\left(\frac{\hbar\omega}{k_BT}\right) - 1}$$

where we can simplify using the substitution

$$x = \frac{\hbar\omega}{k_B T}$$

to change the integral from k space to ω space and the integral becomes

$$T^2 \int_0^\infty \mathrm{d}x \, \frac{x}{\exp(x) - 1}$$

where the T^2 term comes from substituting for ω twice. So the total energy is

$$U_{tot} = \sum_p \int \mathrm{d}\omega \, D_p(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

where $D_p(\omega)$ is the density of states. Using the substition for x we get

$$U_{tot} = \sum_p \int \omega \, \mathrm{d}\omega \, D_p(\omega) \frac{x}{e^x - 1}$$

and the heat capacity is

$$C_v = \frac{\partial U_{tot}}{\partial T} = k_B \sum_p \int \mathrm{d}\omega \, D_p(\omega) \frac{x^2 e^x}{(e^x - 1)^2}$$

The density of states (DOS) is given by

$$D(\omega) = \frac{\mathrm{d}N}{\mathrm{d}\omega}$$

where N is the number of states. For a 3D phonon gas, the total allowed states is

$$N = \frac{\frac{4}{3}\pi k^3}{\left(\frac{2\pi}{L}\right)^3}$$

Which is equivalent to the volume of a sphere for each unit volume. So the DOS is

$$D(\omega) = \frac{\mathrm{d}N}{\mathrm{d}\omega} = \frac{\mathrm{d}N}{\mathrm{d}k}\frac{\mathrm{d}k}{\mathrm{d}\omega} = \frac{V}{2\pi^2}\frac{k^2}{1}$$

and the heat capacity is

$$C_v \propto k_B \sum_p \in \mathrm{d}\omega \, \frac{k^2 V}{2\pi^2} \frac{1}{\frac{\mathrm{d}\omega}{\mathrm{d}k}} \frac{x^2 e^x}{(e^x - 1)^2}$$

and since $\omega = vk$ and $\frac{\mathrm{d}\omega}{\mathrm{d}k} = v$ we get

$$C_v \propto \sum_p \int_0^{\omega_D} \mathrm{d}\omega \, \frac{V}{1} \frac{\omega^2}{v^3} \frac{x^2 e^x}{(e^x - 1)^2}$$

so we get the number of states

$$N = \int_0^{\omega_D} \mathrm{d}\omega \, D(\omega)$$

where

$$\omega_D^2 = \frac{6\pi^2 N}{V}$$

the total energy is

$$U_{tot} = \int_0^{\omega_D} d\omega \, \frac{V\omega^2}{2T^2 v^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

and substituting for x we get

$$\propto T^4 \int_0^{x_D} dx \, x^2 \frac{x}{e^x - 1}$$

where we have four x terms that are substituted thus the T^4 term. We get Debye's law for the heat capacity

$$U_{tot} \propto T^4 f(x_D) \qquad C_v = \frac{\partial U}{\partial T} \propto T^3$$

for low temperature $T \to 0$, $x_D \to \infty$ so the $f(x_D) \to 1$ which will give us Debye's law. Some constants: ω_D is the Debye frequency and the Debye temperature is

$$\theta_D = \frac{\hbar\omega_D}{k_B}$$

Einstein Model

$$D(\omega) = N\delta(\omega - \omega_0)$$

so we get a simple expression for the total energy

$$U_{tot} \propto \frac{\hbar\omega_o}{\exp\left(\frac{\hbar\omega_o}{k_B T}\right) - 1}$$

and the heat capacity is

$$C_v = \frac{\partial U}{\partial T}\bigg|_{T\to 0} \propto \frac{1}{T} \frac{\exp\left(\frac{\hbar\omega_o}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega_o}{k_B T}\right) - 1\right)^2} \to T \exp\left(\frac{\hbar\omega}{k_B T}\right)$$

For the einstein model we get a wrong number because we assumed the density of states is a delta functions ,but it reality it is a constant.