Intro. to Electro-physics **Crystal vibration (1**st)

Jaesang Lee Dept. of Electrical and Computer Engineering Seoul National University (email: jsanglee@snu.ac.kr)



Introduction

- Major reasons for the failure of Drude's and Sommerfeld's models ullet
 - Free-electron approx.: the ignorance of the effects of ions on electrons
 - Lack of understanding of microstructure of crystalline solids
- Main theme of the part IV = The effects of the periodic lattice & crystal vibrations •



Quantized crystal vibrations = phonons



Diatomic

Simple 1D atomic model



General properties of 1D atomic model (1/3)

Covalent bonding in 1D •

V(x): The potential between two neighboring atoms

- x : The distance between atoms
- Taylor expansion around its minimum at $x = x_{eq}$:

$$V(x) \approx V\left(x_{eq}\right) + \frac{\kappa}{2}\left(x - x_{eq}\right)^2 - \frac{\kappa^3}{3!}\left(x - x_{eq}\right)^2$$

When the deviation of *x* from $x_{eq} \left(\delta x_{eq} \triangleq x - x_{eq} \right)$ is small:

$$V(x) \approx V\left(x_{eq}\right) + \frac{\kappa}{2}\left(x - x_{eq}\right)^2$$

Quadratic potential based on Hooke's law









General properties of 1D atomic model (2/3)

• A force to compress the system (i.e., a pressure to 1D system)

$$F = -\frac{\partial V}{\partial x} = -\kappa \left(x - x_{eq} \right) = -\kappa \left(\delta x_{eq} \right)$$

(Isothermal) compressibility

$$\beta = -\frac{1}{V}\frac{\partial V}{\partial P} \xrightarrow{1}_{1D} \beta = -\frac{1}{L}\frac{\partial L}{\partial F} = \frac{1}{\kappa x_{eq}} = -\frac{1}{\kappa x_{eq}} = -\frac{1}$$

Speed of sound

$$v = \sqrt{\frac{B}{\rho}} = \sqrt{\frac{1}{\rho\beta}}, \quad \begin{cases} \rho : \text{mass density of a} \\ B \triangleq \frac{1}{\beta} = -V\frac{\partial P}{\partial V} : B_V \end{cases}$$

In a 1D solid,
$$\rho = \frac{m}{a}$$
.

$$\therefore v = \sqrt{\frac{1}{\frac{m}{a} \cdot \frac{1}{\kappa a}}} = 0$$

 $|V(x) \approx V\left(x_{eq}\right) + \frac{\kappa}{2}\left(x - x_{eq}\right)^2|_{1}$

Positive pressure reduces the distance between atoms!



Compressibility:

A measure of the instantaneous relative volume change of a fluid or solid in response to a pressure

matter

ulk modulus

Bulk modulus (stiffness):

- A measure of how resistant to compression that the matter is
- The ratio of the infinitesimal pressure increase to the resulting relative decrease of the volume







General properties of 1D atomic model (3/3)

- Thermal expansion at T > 0 (K)
 - The atoms oscillate around x_{eq} between $[x_{min}, x_{max}]$

Since
$$\left| x_{max} - x_{eq} \right| > \left| x_{min} - x_{eq} \right|$$
,
 $\therefore \langle x \rangle > x_{eq}$ Thermal expansion!







Vibrations of a 1D monatomic chain (1/2)

1D monatomic chain ullet

A chain of identical atoms of mass m, where the equilibrium spacing between atoms is a (i.e., lattice constant)

- The position of the n-th atom : x_n
- The equilibrium position of the *n*-th atom : $x_n^{eq} \triangleq na$
- The deviation from the equilibrium position : $\delta x_n \triangleq x_n x_n^{eq}$
- Total potential energy of the chain (i.e., stored energy in springs) At low T, the interatomic potential holding atoms together is "quadratic":

$$V_{tot} = \sum_{i} V(x_{i+1} - x_i) = \sum_{i} \frac{\kappa}{2} \left[(x_{i+1} - x_i) - a \right]^2 = \sum_{i} \frac{\kappa}{2} \left[\left(x_{i+1} - x_{i+1}^{eq} \right) - \left(x_i - x_i^{eq} \right) \right]^2$$
$$= \sum_{i} \frac{\kappa}{2} \left(\delta x_{i+1} - \delta x_i \right)^2$$

















































Vibrations of a 1D monatomic chain (2/2)

• The force on the n—th atom of the chain

$$F_{n} = -\frac{\partial V_{tot}}{\partial x_{n}} = -\frac{\partial}{\partial x_{n}} \left[\frac{\kappa}{2} \left(\dots + \left(\delta x_{n} - \delta x_{n-1} \right)^{2} + \left(\delta x_{n+1} - \delta x_{n} \right)^{2} + \dots \right) \right]$$
$$= \kappa \left(\delta x_{n+1} - \delta x_{n} \right) + \kappa \left(\delta x_{n-1} - \delta x_{n} \right) = \kappa \left(\delta x_{n+1} - 2\delta x_{n} + \delta x_{n-1} \right)$$

Newton's equation of motion •

$$m\delta \ddot{x}_n = F_n = \kappa \left(\delta x_{n+1} - 2\delta x_n + \delta x_{n-1}\right)$$

- Educated solution

$$\delta x_n = A e^{j(\omega t - kx_n^{eq})} = A e^{j(\omega t - kna)} \begin{cases} A : Am \\ \omega : free \\ k : way$$

For any coupled system, a normal mode is defined as

a collective oscillation where all particles move at the same frequency ω



- nplitude of oscillation
- quency
- ve number

Dispersion relation

- Educated solution ($\omega \ge 0$) $-m\omega^2 A e^{i(\omega t - kna)} = \kappa A e^{i\omega t} \left[e^{-ik(n+1)a} + e^{-ik(n-1)a} - 2e^{i\omega t} \right]$

$$-m\omega^{2}Ae^{i(\omega t - kna)} = \kappa Ae^{i\omega t} \left[e^{-ik(n+1)a} + e^{-ik(n-1)a} - 2e^{-ikna} \right]$$
$$-m\omega^{2} = \kappa \left[e^{-jka} + e^{jka} - 2 \right] \longrightarrow m\omega^{2} = 2\kappa \left(1 - \cos ka \right) = 4\kappa \sin^{2} \left(\frac{ka}{2} \right)$$

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

Dispersion $(\omega \text{ vs. } k)$ relation

A relationship between a frequency (ω) (energy) and a wavevector (k) (momentum)

The equation of motion

$$m\delta \ddot{x}_{n} = \kappa \left(\delta x_{n+1} - 2\delta x_{n} + \delta x_{n}\right)$$
$$\delta x_{n} = A e^{j(\omega t - kna)}$$







Reciprocal lattice and Brillouin zone

- **Reciprocal lattice** \bullet
 - A periodic system in real space with a periodicity a (i.e., $x \rightarrow x + a$)
 - = A periodic k-space (or "reciprocal space") with a periodicity $2\pi/a$ (i.e., $k \rightarrow k + 2\pi/a$)

$$\omega = 2\sqrt{\frac{\kappa}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$
 (Dispersion relation)

- Important terminologies
 - **Brillouin zone** : The periodic unit cell in k-space -
 - The first Brillouin zone : A unit cell centered around k = 0
 - **Brillouin zone boundaries** : $k = \pm \pi/a$

repeated in $k \rightarrow k + 2\pi/a$)





Real vs. reciprocal lattices

Meaning of the periodic dispersion relation
$$(k \to k + 2\pi/a)$$

$$\delta x_n = Ae^{j(\omega t - kna)} = \left[Ae^{j\left(\omega t - \left(k + \frac{2\pi}{a}\right)na\right)} = Ae^{j(\omega t - kna)} \cdot e^{-j2\pi n} = Ae^{j(\omega t - kna)}\right]$$

- $\therefore k$ and $k + 2\pi/a$ represent physically equivalent oscillation modes!

$$G_m$$
 is a member of reciprocal lattice
if and only if $\exp(iG_m x_n) = 1$ is true
for all $x_n \rightarrow \therefore G_m = \frac{2\pi}{a}m$

: k and $k + 2\pi p/a$ represent physically equivalent oscillation modes! (For any integer p, since $e^{-2\pi np} = 1$) Direct (real-space) lattice: the periodic set of points in real space with a periodicity a, $(x_n = na)$

Reciprocal lattice: the periodic set of points in k-space that are physically equivalent to the point k = 0 (G_m)





Intro. to Electro-physics Crystal vibration (2nd)

Jaesang Lee Dept. of Electrical and Computer Engineering Seoul National University (email: jsanglee@snu.ac.kr)



Review of last lecture

- 1D monatomic chain
 - A chain of identical atoms of mass *m*, where the equilibrium spacing between atoms is a (i.e., lattice constant)
 - Each atom vibrates with respect to the equilibrium position
 - A collective vibration of atoms at the same frequency = "Normal mode"
- Dispersion relation for a vibrational wave (ω vs. k relation)

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

Periodic in k-space with a periodicity $2\pi/a$

The dispersion in 1st Brillouin zone $\begin{vmatrix} \pi & \pi \\ -\frac{\pi}{a}, \frac{\pi}{a} \end{vmatrix}$ only matters!



* Brillouin zone : The periodic unit cell in k-space * 1st Brillouin zone : The unit cell around k = 0





Number of normal modes

- Number of normal modes (= allowed k values)
 - Assumption: a 1D system consists of *N* atoms in a row with a periodic boundary condition such that $x_{n+N} = x_n$

$$\delta x_n = A e^{j(\omega t - kna)} = A e^{j(\omega t - k(n + N)a)} -$$

- k is quantized as being:

 $kNa = 2\pi p$, where p : integer.

- The number of modes in the First Brillouin zone

Range of k	$2\pi/a$
Spacing between neighboring k 's	$2\pi/Na$

: One normal mode per particle in the system

= One normal mode per "degree of freedom" in the whole system







Phonon

- Vibrational wave of crystals in terms of quantum mechanics
 - The vibrational wave with a given k-value $\triangleq \psi_k(x)$
 - The wave satisfies Schrödinger's equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(x)\right)\psi_k(x) = E_k\psi_k(x), \text{ where } V$$

- The eigenstate $(\psi_k(x))$ yields the corresponding energy :

$$E_k = \hbar \omega_k \left(n + \frac{1}{2} \right) \ (n = 0, 1, 2, \cdots)$$

- At a given ω_k , there are many possible quantized energy levels
- ω_k determined by k: Dispersion relation
- [Quantum] Higher E_k (or higher n) = [Classic] Oscillations of increasing amplitude
- The discrete quantum of vibrational energy at a given $\omega_k = Phonon$



Eigenstates and eigenvalues

for quantum harmonic system



Vibrations of a 1D diatomic chain

D diatomic chain

A chain of two alternating atoms of masses m_1 and m_2 (e.g. NaCl, GaAs, …)

- Important terminologies
 - Unit cell : The smallest repeated unit in the structure (* Definition of the unit cell is non-unique)
 - Lattice constant : The length of the unit cell
 - Lattice : A periodic set of reference points inside each unit cell
 - Basis : All of the atoms in the unit cell located with respect to the lattice point —



Basis -

- : at 3/10a left to the reference
- : at 3/10a right to the reference
- The reference lattice point in n—th unit cell $(r_n = an)$

•
$$\mathbf{O}: x_n^{eq} = r_n - 3/10a$$

•
$$\mathbf{O}: y_n^{eq} = r_n + 3/10a$$



Normal modes of the 1D diatomic chain

Simplifying assumption

 $m_1 = m_2, \ \kappa_1 \neq \kappa_2$ (a.k.a. alternating chains)

• Newton's equation of motion for the deviations of the n-th atoms w.r.t. the n-th lattice point :

$$\begin{cases} m \dot{\delta x}_n = \kappa_2 \left(\delta y_n - \delta x_n \right) + \kappa_1 \left(\delta y_{n-1} - \delta x_n \right) \\ m \dot{\delta y}_n = \kappa_1 \left(\delta x_{n+1} - \delta y_n \right) + \kappa_2 \left(\delta x_n - \delta y_n \right)' \end{cases}$$

Educated solution:
$$\begin{cases} \delta x_n = A_x e^{j(\omega t - kna)} \\ \delta y_n = A_y e^{j(\omega t - kna)} \end{cases}$$

 $\rightarrow m\omega^2 = (\kappa_1 + \kappa_2) \pm \kappa_1 + \kappa_2 e^{3}$

$$\therefore \omega_{\pm} = \sqrt{\frac{\kappa_1 + \kappa_2 e^{jka}}{m}} = \sqrt{(\kappa_1 + \kappa_2 e^{jka})(\kappa_1 + \kappa_2 e^{-jka})}.$$



where
$$\begin{cases} \delta x_n \triangleq x_n - x_n^{eq} \\ \delta y_n \triangleq y_n - y_n^{eq} \end{cases}$$



Dispersion relation of 1D diatomic chain

- General characteristics
 - The periodic system with *a* in real space yields

the periodic dispersion relation with $\frac{2\pi}{a}$ in reciprocal space Only the 1st Brillouin zone $\left(-\frac{\pi}{a} \le k < \frac{\pi}{a}\right)$ matters

- The system has N unit cells with a periodic B.C. $(x_{n+N} = x_n)$

$$k$$
: quantized in units of $\frac{2\pi}{Na}\left(k = \frac{2\pi}{Na}p\right)$

- The number of allowed k values within the 1st B.Z. : N
- Two atoms per unit cell (i.e., total 2N atoms)
 - = Two degrees of freedom per unit cell

= **Two** possible normal modes per each k value

The Dispersion relation

$$\omega_{\pm} = \sqrt{\frac{\kappa_1 + \kappa_2}{m} \pm \frac{1}{m}} \sqrt{\left(\kappa_1 + \kappa_2\right)^2 - 4\kappa_1\kappa_2\sin^2}$$



Total N different k-values

Total 2N different modes



Acoustic phonon

- Low-energy branch (ω_{-}): Acoustic phonon •
- High-energy branch (ω_+) : Optical phonon
- Characteristics of the acoustic phonon (ω_{-}) •
 - As $k \to 0$: linear dispersion like a sound wave (i.e., $\omega = vk$)

$$v = \frac{d\omega_{-}}{dk} = \sqrt{\frac{a^2 \kappa_1 \kappa_2}{2m \left(\kappa_1 + \kappa_2\right)}} \text{ (HW!)}$$

- Why sound wave? -
 - The density of the chain : 2m/a►
 - $\kappa_1 \kappa_2$ The effective spring constant : $\tilde{\kappa} =$ $\kappa_1 + \kappa_2$
 - Compressibility of the chain : $\beta = 1/\tilde{\kappa}a$

The speed of sound : $v = \sqrt{\frac{B}{\rho}} = \sqrt{\frac{1}{\rho\beta}} = \sqrt{\frac{a^2\kappa_1\kappa_2}{2m(\kappa_1 + \kappa_2)}}$

The low-energy branch $\int \frac{\kappa_1 + \kappa_2}{m} - \frac{1}{m} \sqrt{\left(\kappa_1 + \kappa_2\right)^2 - 4\kappa_1 \kappa_2 \sin^2\left(\frac{ka}{2}\right)}$ $\omega_{-} = 1$



$$\frac{\kappa_1 \kappa_2}{\kappa_1 + \kappa_2}$$



Optical phonon

• Characteristics of the optical phonon (ω_{+})

- At k = 0

. Momentum : $v_g = \frac{d\omega}{dk} = 0 \implies p = mv_g = 0$

Energy:
$$\omega = \sqrt{\frac{2(\kappa_1 + \kappa_2)}{m}} \neq 0 \longrightarrow \varepsilon = \hbar\omega \neq 0$$

- Photons at k = 0
 - Momentum : $p = \hbar k = 0$ ►
 - Energy : $\varepsilon = \hbar \omega \neq 0$
- Such oscillation modes only possible via absorption of photon -
 - \rightarrow Fluctuations in displacement between atoms
 - = Fluctuation of electrical polarization that couples to EM wave
 - = "Optical phonon"

The high-energy branch $\omega_{+} = \sqrt{\frac{\kappa_{1} + \kappa_{2}}{m} + \frac{1}{m}} \sqrt{\left(\kappa_{1} + \kappa_{2}\right)^{2} - 4\kappa_{1}\kappa_{2}\sin^{2}\left(\frac{ka}{2}\right)}$







Acoustic vs. optical phonons

• In the derivation of dispersion relation (as $k \rightarrow 0$),







Phonons in 3D

- Number of modes
 - M atoms per unit cell in $\mathbf{1D} \rightarrow M$ distinct modes per each k value
 - The number of acoustic mode : 1 ($\omega = 0$ at k = 0)
 - The number of optical modes : M 1 ($\omega \neq 0$ at k = 0)
 - M atoms per unit cell in **3D** \rightarrow 3M distinct modes per each k value (:: 3 degrees of freedom per atom)
 - The number of acoustic mode : 3 ($\omega = 0$ at k = 0 along x, y, z)
 - The number of optical modes : 3(M-1) ($\omega \neq 0$ at k=0)



Energy gap



Two modes per k value

- Above is when $\kappa_1 \neq \kappa_2$ and $\kappa_1 < \kappa_2$
- The case of $\kappa_1 = \kappa_2$
 - A simple monatomic chain with a lattice constant a/2—

The 1st Brillouin zone :
$$\left[-\frac{2\pi}{a}, \frac{2\pi}{a}\right]$$

One mode per k value

- When the two atoms are only slightly different
 - A small perturbation applied to a situation where all atoms are identical
 - Due to the perturbation, a small energy gap opens up at the zone boundary, but the rest of the dispersion mostly looks alike that of the monatomic chain!

