## Intro. to Electro-physics

## Crystal vibration (1st)

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

## Introduction

－Major reasons for the failure of Drude＇s and Sommerfeld＇s models
－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



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 $x=x_{e q}$ :

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



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

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



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)

$$
F=-\partial V / \partial x=-\kappa\left(x-x_{e q}\right)=-\kappa\left(\delta x_{e q}\right) \quad \text { Positive pressure reduces the distance between atoms! }
$$

- (Isothermal) compressibility

$$
\beta=-\frac{1}{V} \frac{\partial V}{\partial P} \underset{1 D}{\rightarrow} \quad \beta=-\frac{1}{L} \frac{\partial L}{\partial F}=\frac{1}{\kappa x_{e q}}=\frac{1}{\kappa a}
$$

## Compressibility:

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

- Speed of sound
$v=\sqrt{\frac{B}{\rho}}=\sqrt{\frac{1}{\rho \beta}},\left\{\begin{array}{l}\rho: \text { mass density of a matter } \\ B \triangleq \frac{1}{\beta}=-V \frac{\partial P}{\partial V}: \text { Bulk modulus }\end{array}\right.$


## 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

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

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

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

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

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


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

- 1D monatomic chain

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 : $x_{n}^{e q} \triangleq n a$
- The deviation from the equilibrium position : $\delta x_{n} \triangleq x_{n}-x_{n}^{e q}$

- Total potential energy of the chain (i.e., stored energy in springs)

At low $T$, the interatomic potential holding atoms together is "quadratic":

$$
\begin{aligned}
V_{t o t} & =\sum_{i} V\left(x_{i+1}-x_{i}\right)=\sum_{i} \frac{\kappa}{2}\left[\left(x_{i+1}-x_{i}\right)-a\right]^{2}=\sum_{i} \frac{\kappa}{2}\left[\left(x_{i+1}-x_{i+1}^{e q}\right)-\left(x_{i}-x_{i}^{e q}\right)\right]^{2} \\
& =\sum_{i} \frac{\kappa}{2}\left(\delta x_{i+1}-\delta x_{i}\right)^{2}
\end{aligned}
$$

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

$$
V_{t o t}=\sum_{i} \frac{\bar{\kappa}^{------}}{2}\left(\delta_{i+1}-\delta_{i}\right)^{2}
$$

- The force on the $n-$ th atom of the chain

$$
\begin{aligned}
F_{n}=-\frac{\partial V_{t o t}}{\partial x_{n}} & =-\frac{\partial}{\partial x_{n}}\left[\frac{\kappa}{2}\left(\cdots+\left(\delta x_{n}-\delta x_{n-1}\right)^{2}+\left(\delta x_{n+1}-\delta x_{n}\right)^{2}+\cdots\right)\right] \\
& =\kappa\left(\delta x_{n+1}-\delta x_{n}\right)+\kappa\left(\delta x_{n-1}-\delta x_{n}\right)=\kappa\left(\delta x_{n+1}-2 \delta x_{n}+\delta x_{n-1}\right)
\end{aligned}
$$

- 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

$$
\delta x_{n}=A e^{j\left(\omega t-k x_{n}^{e q}\right)}=A e^{j(\omega t-k n a)}\left\{\begin{array}{l}
A: \text { Amplitude of oscillation } \\
\omega: \text { frequency } \\
k: \text { wave number }
\end{array}\right.
$$

For any coupled system, a normal mode is defined as
a collective oscillation where all particles move at the same frequency $\omega$

## Dispersion relation

## iThe equation of motion

- Educated solution $(\omega \geq 0)$

$$
{ }^{1} \delta x_{n}=A e^{j(\omega t-k n a)}
$$

$-m \omega^{2} A e^{i(\omega t-k n a)}=\kappa A e^{i \omega t}\left[e^{-i k(n+1) a}+e^{-i k(n-1) a}-2 e^{-i k n a}\right]$
$-m \omega^{2}=\kappa\left[e^{-j k a}+e^{j k a}-2\right] \quad \longrightarrow \quad m \omega^{2}=2 \kappa(1-\cos k a)=4 \kappa \sin ^{2}\left(\frac{k a}{2}\right)$

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

Dispersion ( $\omega$ vs. $k$ ) relation
A relationship between a frequency ( $\omega$ ) (energy) and a wavevector $(k)$ (momentum)


## Reciprocal lattice and Brillouin zone

- Reciprocal lattice
- 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., $k \rightarrow k+2 \pi / a$ )
$\omega=2 \sqrt{\frac{\kappa}{m}}\left|\sin \left(\frac{k a}{2}\right)\right|$ (Dispersion relation repeated in $\left.k \rightarrow k+2 \pi / a\right)$
- 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 : $k= \pm \pi / a$



## Real vs. reciprocal lattices

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

$$
\delta x_{n}=A e^{j(\omega t-k n a)}=\left[A e^{j\left(\omega t-\left(k+\frac{2 \pi}{a}\right) n a\right)}=A e^{j(\omega t-k n a)} \cdot e^{-j 2 \pi n}=A e^{j(\omega t-k n a)}\right]
$$

$\therefore k$ and $k+2 \pi / a$ represent physically equivalent oscillation modes!
$\therefore k$ and $k+2 \pi p / a$ represent physically equivalent oscillation modes! (For any integer $p$, since $e^{-2 \pi n p}=1$ )

- Direct (real-space) lattice: the periodic set of points in real space with a periodicity $a,\left(x_{n}=n a\right)$
- Reciprocal lattice: the periodic set of points in $k$-space that are physically equivalent to the point $k=0\left(G_{m}\right)$
$G_{m}$ is a member of reciprocal lattice
if and only if $\exp \left(i G_{m} x_{n}\right)=1$ is true
for all $x_{n} \rightarrow \therefore G_{m}=\frac{2 \pi}{a} m$



# Intro. to Electro-physics 

Crystal vibration (2nd)

Jaesang Lee<br>Dept. of Electrical and Computer Engineering<br>Seoul National University<br>(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 ( $\omega$ vs. $k$ relation)

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

- Periodic in $k$-space with a periodicity $2 \pi / a$
- The dispersion in 1st Brillouin zone $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$ 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 $x_{n+N}=x_{n}$

$$
\delta x_{n}=A e^{j(\omega t-k n a)}=A e^{j(\omega t-k(n+N) a)} \quad \longrightarrow \quad e^{-j k N a}=1
$$

- $k$ is quantized as being:

$$
k N a=2 \pi p, \text { where } p: \text { integer. } \quad \therefore k=\frac{2 \pi}{N a} p
$$

- The number of modes in the First Brillouin zone
$\frac{\text { Range of } k}{\text { Spacing between neighboring } k^{\prime} \mathrm{s}}=\frac{2 \pi / a}{2 \pi / N a}=N$
$\therefore$ 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:

Interatomic

$$
\left(-\frac{\hbar^{2}}{2 m} \nabla^{2}+V(x)\right) \psi_{k}(x)=E_{k} \psi_{k}(x), \text { where } V(x) \stackrel{\downarrow}{=} \frac{1}{2} \kappa x^{2}
$$



Eigenstates and eigenvalues
for quantum harmonic system

- At a given $\omega_{k}$, there are many possible quantized energy levels
- $\omega_{k}$ 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


## Vibrations of a 1D diatomic chain

- 1D diatomic chain

A chain of two alternating atoms of masses $m_{1}$ and $m_{2}$ (e.g. NaCl, GaAs, $\cdots$ )

- 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 $3 / 10 a$ left to the reference
- O : at $3 / 10 a$ right to the reference
- The reference lattice point in $n$-th unit cell $\left(r_{n}=a n\right)$
- 
- $\bigcirc: y_{n}^{e q}=r_{n}+3 / 10 a$


## Normal modes of the 1D diatomic chain

- Simplifying assumption

$m_{1}=m_{2}, \quad \kappa_{1} \neq \kappa_{2}$ (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 :
$\left\{\begin{array}{l}m \ddot{\delta}_{n}=\kappa_{2}\left(\delta y_{n}-\delta x_{n}\right)+\kappa_{1}\left(\delta y_{n-1}-\delta x_{n}\right) \\ m \ddot{\delta}_{n}=\kappa_{1}\left(\delta x_{n+1}-\delta y_{n}\right)+\kappa_{2}\left(\delta x_{n}-\delta y_{n}\right)\end{array}\right.$, where $\left\{\begin{array}{l}\delta x_{n} \triangleq x_{n}-x_{n}^{e q} \\ \delta y_{n} \triangleq y_{n}-y_{n}^{e q}\end{array}\right.$
Educated solution: $\left\{\begin{array}{l}\delta x_{n}=A_{x} e^{j(\omega t-k n a)} \\ \delta y_{n}=A_{y} e^{j(\omega t-k n a)}\end{array}\right.$
$\rightarrow m \omega^{2}=\left(\kappa_{1}+\kappa_{2}\right) \pm\left|\kappa_{1}+\kappa_{2} e^{j k a}\right|$. Here, $\left|\kappa_{1}+\kappa_{2} e^{j k a}\right|=\sqrt{\left(\kappa_{1}+\kappa_{2} e^{j k a}\right)\left(\kappa_{1}+\kappa_{2} e^{-j k a}\right)}$.

$$
\therefore \omega_{ \pm}=\sqrt{\frac{\kappa_{1}+\kappa_{2}}{m} \pm \frac{1}{m} \sqrt{\left(\kappa_{1}+\kappa_{2}\right)^{2}-4 \kappa_{1} \kappa_{2} \sin ^{2}\left(\frac{k a}{2}\right)}}
$$

## Dispersion relation of 1D diatomic chain

The Dispersion relation
$\omega_{ \pm}=\sqrt{\frac{\kappa_{1}+\kappa_{2}}{m} \pm \frac{1}{m} \sqrt{\left(\kappa_{1}+\kappa_{2}\right)^{2}-4 \kappa_{1} \kappa_{2} \sin ^{2}\left(\frac{k a}{2}\right)}}$

- 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 $1^{\text {st }}$ Brillouin zone $\left(-\frac{\pi}{a} \leq k<\frac{\pi}{a}\right)$ matters
- The system has $N$ unit cells with a periodic B.C. $\left(x_{n+N}=x_{n}\right)$
. $k$ : quantized in units of $\frac{2 \pi}{N a}\left(k=\frac{2 \pi}{N a} p\right)$
- The number of allowed $k$ values within the $1^{\text {st }}$ B.Z. : $N$
- Two atoms per unit cell (i.e., total $2 N$ atoms)

= Two degrees of freedom per unit cell
= Two possible normal modes per each $k$ value

Total $N$ different $k$-values
Total $2 N$ different modes

## Acoustic phonon

- Low-energy branch ( $\omega_{-}$): Acoustic phonon

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

- High-energy branch $\left(\omega_{+}\right)$: Optical phonon
- Characteristics of the acoustic phonon ( $\omega_{-}$)
- As $k \rightarrow 0$ : linear dispersion like a sound wave (i.e., $\omega=v k$ )

$$
v=\frac{d \omega_{-}}{d k}=\sqrt{\frac{a^{2} \kappa_{1} \kappa_{2}}{2 m\left(\kappa_{1}+\kappa_{2}\right)}}(\mathrm{HW}!)
$$

- Why sound wave?
- The density of the chain : $2 m / a$
- The effective spring constant : $\tilde{\kappa}=\frac{\kappa_{1} \kappa_{2}}{\kappa_{1}+\kappa_{2}}$

- Compressibility of the chain : $\beta=1 / \tilde{\kappa} a$
. The speed of sound : $v=\sqrt{\frac{B}{\rho}}=\sqrt{\frac{1}{\rho \beta}}=\sqrt{\frac{a^{2} \kappa_{1} \kappa_{2}}{2 m\left(\kappa_{1}+\kappa_{2}\right)}}$


## Optical phonon

- Characteristics of the optical phonon $\left(\omega_{+}\right)$

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

- At $k=0$
- Momentum : $v_{g}=\frac{d \omega}{d k}=0 \longrightarrow p=m v_{g}=0$
. Energy : $\omega=\sqrt{\frac{2\left(\kappa_{1}+\kappa_{2}\right)}{m}} \neq 0 \longrightarrow \varepsilon=\hbar \omega \neq 0$
- 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"


## Acoustic vs. optical phonons

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

$$
m \omega^{2}\binom{A_{x}}{A_{y}}=\left(\begin{array}{cc}
\kappa_{1}+\kappa_{2} & -\kappa_{2}-\kappa_{1} e^{j k a} \\
-\kappa_{2}-\kappa_{1} e^{-j k a} & \kappa_{1}+\kappa_{2}
\end{array}\right)\binom{A_{x}}{A_{y}} \underset{k \rightarrow 0}{\longrightarrow} \quad \omega^{2}\binom{A_{x}}{A_{y}}=\frac{\kappa_{1}+\kappa_{2}}{m}\left(\begin{array}{cc}
1 & -1 \\
-1 & 1
\end{array}\right)\binom{A_{x}}{A_{y}}
$$

Acoustic mode $\left(\lim _{k \rightarrow 0} \omega \rightarrow 0\right)$
Eigenvector: $\binom{A_{x}}{A_{y}}=\binom{1}{1}$

$$
\text { Eigenvector: }\binom{A_{x}}{A_{y}}=\binom{1}{-1}
$$

*Two masses move in same direction


*Two masses move in opposite directions


## Phonons in 3D

- Number of modes
- $M$ atoms per unit cell in 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 $\rightarrow 3 M$ distinct modes per each $k$ value ( $\because 3$ 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



Reduced zone scheme
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 : $\left[-\frac{2 \pi}{a}, \frac{2 \pi}{a}\right]$

2nd B.Z.


## "Extended" zone scheme

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!

