VI. Lattice Vibrations

A. What is the problem?

By studying "lattice vibrations", we want to study the possible normal modes of oscillations of the atoms or ions. These atoms or ions are "connected" to each other by chemical bonds.

The crystal structure studied in previous chapters refers to the atoms/ions sitting at the equilibrium positions.

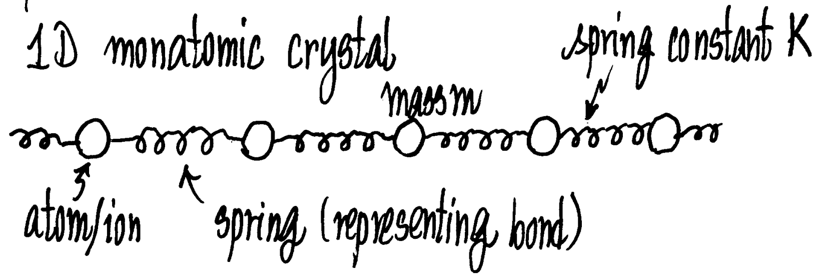
- How about small oscillations[+] about the equilibrium positions?

Thus, we are studying "excitations" of a solid.

[+] This problem is treated in undergraduate textbooks, e.g. Thornton and Marion, "Classical Dynamics of particles and systems".

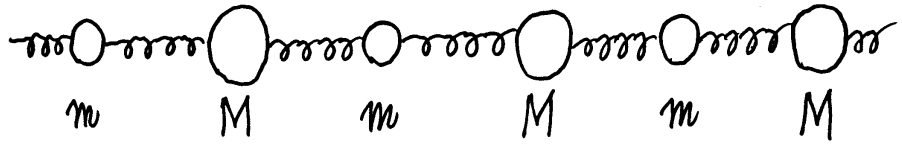
Examples

- 1D monatomic crystal



What are the normal modes?

- 1D crystal with a basis of two atoms



What are the normal modes?

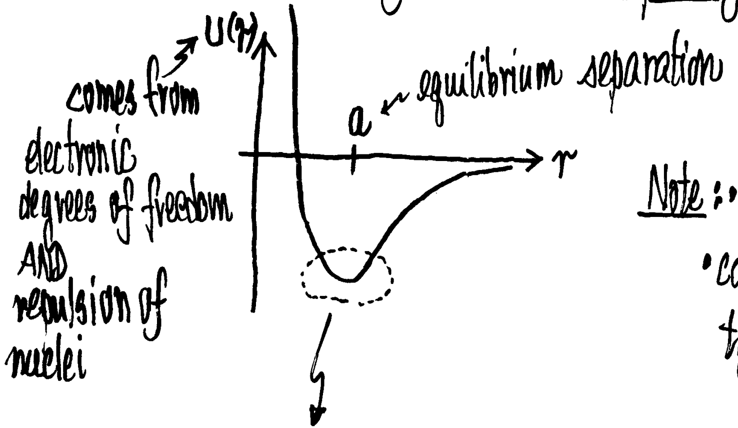
- 2D/3D crystals

These problems are not difficult to solve!

But before doing anything, let's consider:

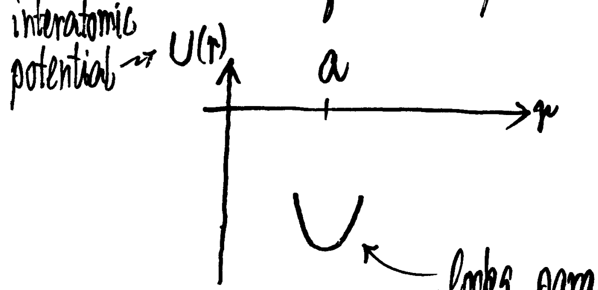
- why we can represent chemical bonds as elastic springs
- why we can handle lattice vibrations by treating a crystal as balls and springs.

- The existence of equilibrium positions implies that each atom/ion is under the influence of a potential energy as a function of <u>interatomic spacing</u> r of the form:



<u>Note</u>: this form is general
- could come from various types of bonding

<u>near</u> equilibrium position (i.e., near minimum)



looks parabolic (Taylor expansion and keep lowest non-vanishing term)

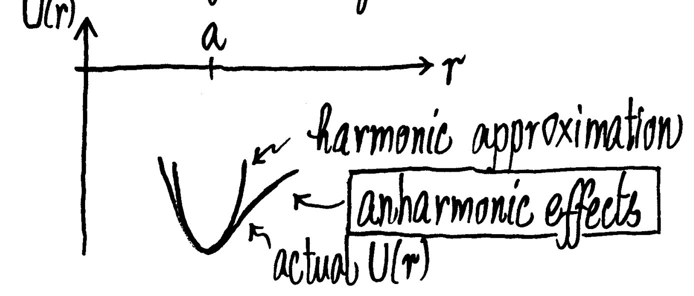
parabolic → harmonic

∴ The physics and mathematics are that of harmonic oscillators (classical/quantum/statistical mechanics)

$$U_0 + \frac{1}{2}K(r-a)^2 \text{ with } K = \left.\frac{d^2U}{dr^2}\right|_{r=a}$$

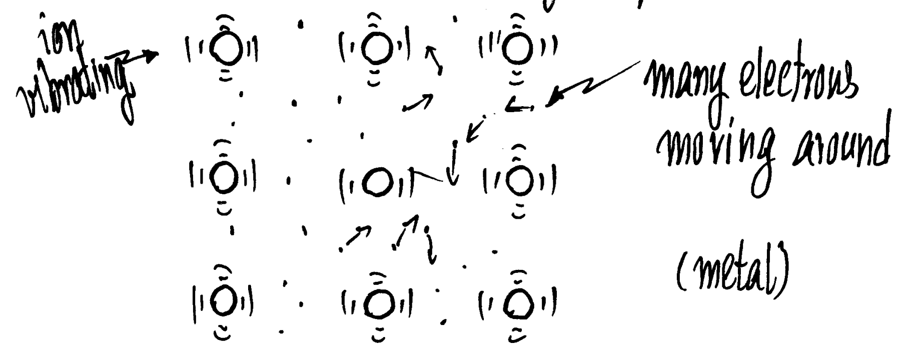
K (or $m\omega^2$) reflects property of bonding

Farther away from equilibrium position



- But there are ions and electrons in a crystal. What is giving rise to U(r) and where are the electrons in our problem?

The actual situation is <u>very complicated</u>!



Interactions: electron-ion, ion-ion, electron-electron

+ Deviations from parabolicity are called "anharmonic effects". Physical properties such as thermal expansion, thermal conductivity rely on anharmonic effects.

It is hard to imagine that the ions' motions can be "<u>decoupled</u>" from the electrons' motions!

Adiabatic Approximation⁺

- From molecular physics, we notice the key differences between the <u>ionic</u> and <u>electronic</u> parts.

$$M \gg m_e$$

m_e ← mass of electron

M ↑ mass of <u>ion</u> (nucleus + $\underbrace{\text{core electrons}}_{\text{those not involved in forming chemical bonds}}$)

$$\Delta \ll \delta$$

Δ ↑ a typical value of energy involved in <u>ionic</u> vibrations (e.g. $\underbrace{\text{vibrational spectrum}}_{\text{IR range}}$ of molecules) <u>IR range</u> (~0.01eV)

δ ← a typical value of energy involved in electronic transitions (e.g. Fermi energy of metals, hydrogen atom) <u>a few eV</u> or higher

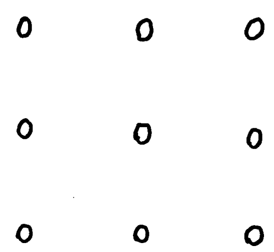
---

⁺ In molecular physics, this is called the <u>Born-Oppenheimer approximation</u>. Using it, you will get the vibrational spectrum of molecules.

<u>Key consequences</u>⁺ (<u>Adiabatic Approximation</u>)

(a) The nuclei move so slowly that the motion of the electrons can be determined on the assumption that the nuclei are fixed.

For an <u>electron</u>, it sees



an ordered array of ions

⇓

$U(\vec{r})$ = potential energy function $= U(\vec{r}+\vec{R})$ (periodic)

This gives rise to:

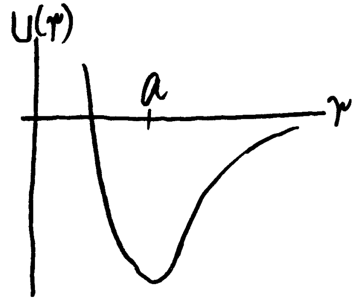
$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\vec{r}) + \underset{\text{periodic}}{U(\vec{r})}\psi(\vec{r}) = E\psi(\vec{r})$$

Schrödinger Equation

This is the starting point of <u>energy band theory</u>, which we will treat later.

(b) The nuclei can be thought of as moving in a potential energy function determined by the average motion of the electrons.

This gives rise to the $U(r)$ between two ions:



and thus the springs in the harmonic approximation.

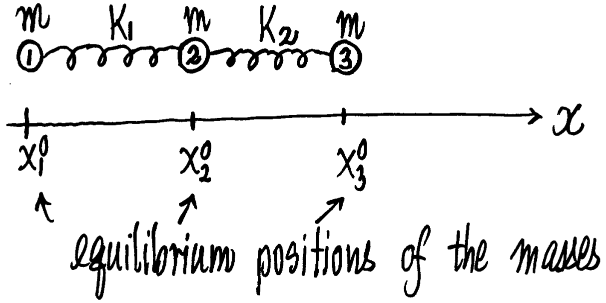
∴ We have our "lattice vibration" problem.

+ A full discussion on the approximations involved in the adiabatic approximation can be found in
G. Weinreich, "Solids: Elementary Theory for Advanced Students"
The derivation requires some quantum mechanics.

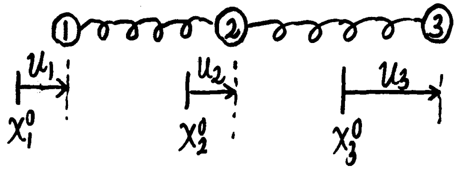
B. A Review: 3 identical masses and 2 springs

a linear molecule

at equilibrium positions



At an instant while ions are oscillating



Assume displacements along the chain, i.e. longitudinal motion.

$u_1(t)$, $u_2(t)$, $u_3(t)$: instantaneous displacements of the masses from equilibrium

K_1, K_2 : spring constants

Eq. of motion for mass 1:

$$F_1 = \text{force on mass } 1 = -K_1(u_1-u_2)$$

(Hooke's law, harmonic approx.)

$$m\frac{d^2u_1}{dt^2} = -K_1(u_1-u_2) \qquad (1)$$

+ One could put another spring to connect mass 1 and mass 3. The procedures that follow can still solve the normal modes.

<u>Eq. of motion for mass 2</u>:

$$F_2 = \text{force on mass } 2 = -K_1(u_2-u_1) - K_2(u_2-u_3)$$

$$m\frac{d^2u_2}{dt^2} = -K_1(u_2-u_1) - K_2(u_2-u_3) \qquad (2)$$

<u>Eq. of motion for mass 3</u>:

$$F_3 = \text{force on mass } 3 = -K_2(u_3-u_2)$$

$$m\frac{d^2u_3}{dt^2} = -K_2(u_3-u_2) \qquad (3)$$

Eqs. (1), (2), (3) form a set of coupled equations.

<u>Normal mode Solutions</u>

- We want to look for the characteristic frequencies of oscillations that such a system allows.
- Assume

$$u_i(t) = u_i\, e^{-i\omega t} \quad \text{for mass } i \qquad (4)$$

(i.e., each displacement has the same $e^{-i\omega t}$. Complex notation is used. The physical displacement is the real part.)

Substituting Eq. (4) into Eqs. (1)-(3):

$$(K_1 - m\omega^2)u_1 - K_2u_2 = 0$$

$$-K_1u_1 + (K_1+K_2-m\omega^2)u_2 - K_2u_3 = 0$$

$$-K_2u_2 + (K_2-m\omega^2)u_3 = 0$$

These equations can be written in <u>matrix form</u> as:

$$\begin{pmatrix} K_1-m\omega^2 & -K_2 & 0 \\ -K_1 & K_1+K_2-m\omega^2 & -K_2 \\ 0 & -K_2 & K_2-m\omega^2 \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = 0 \qquad (5)$$

- A trivial solution is $u_1 = u_2 = u_3 = 0$ (but no fun)
- Non-trivial solutions exist if

$$\begin{vmatrix} K_1-m\omega^2 & -K_2 & 0 \\ -K_1 & K_1+K_2-m\omega^2 & -K_2 \\ 0 & -K_2 & K_2-m\omega^2 \end{vmatrix} = 0 \qquad (6)$$

which is a cubic equation for ω^2

$\Rightarrow$ 3 roots for ω^2

(3 normal mode frequencies)

This is as expected from the <u>3 degrees of freedom</u> in the problem.

The 3 normal mode frequencies are: (Ex.)

$$\begin{aligned} \omega_1 &= 0 \\ \omega_2 &= \frac{1}{\sqrt{m}}\left[(K_1+K_2)-\sqrt{K_1^2+K_2^2-K_1K_2}\right]^{1/2} \\ \omega_3 &= \frac{1}{\sqrt{m}}\left[(K_1+K_2)+\sqrt{K_1^2+K_2^2-K_1K_2}\right]^{1/2} \end{aligned} \qquad (7)$$

- For each normal mode frequency, one can solve for u_1, u_2, u_3 (ratios of them)

$$\begin{array}{lccc} & \begin{pmatrix}u_1\\u_2\\u_3\end{pmatrix}_{\omega_1} & \begin{pmatrix}u_1\\u_2\\u_3\end{pmatrix}_{\omega_2} & \begin{pmatrix}u_1\\u_2\\u_3\end{pmatrix}_{\omega_3} \\ & \uparrow & \uparrow & \uparrow \\ & \text{corresponding to } \omega_1 & \omega_2 & \omega_3 \\ \text{time evolution:} & e^{-i\omega_1 t} & e^{-i\omega_2 t} & e^{-i\omega_3 t} \end{array}$$

- General motion (general solution) is a linear combination of these normal modes. The coefficients in the linear combination are fixed by some initial conditions.
- Transform from u_1, u_2, u_3 to normal coordinates, then we have a center-of-mass motion ($\omega_1=0$), and two independent harmonic oscillators with angular frequencies ω_2 and ω_3.

Things to learn from this simple review

- Mathematical structure of the problem

Eq.(5) is

$$\frac{1}{m}\underbrace{\begin{pmatrix} K_1 & -K_2 & 0 \\ -K_1 & K_1+K_2 & -K_2 \\ 0 & -K_2 & K_2 \end{pmatrix}}_{\overleftrightarrow{D}\ =\ \text{dynamical matrix}}\begin{pmatrix}u_1\\u_2\\u_3\end{pmatrix} = \omega^2\begin{pmatrix}u_1\\u_2\\u_3\end{pmatrix} \qquad (8)$$

(information of balls/springs syste

this is an eigenvalue problem

- ω^2 (normal mode frequencies) are the eigenvalues of $\overleftrightarrow{D}$
- for each allowed ω, there is an eigenvector $\begin{pmatrix}u_1\\u_2\\u_3\end{pmatrix}$
- the procedure of finding the normal mode-frequencies is thus of that of finding a transformation that diagonalizes the dynamical matrix, i.e., we start with coupled oscillators, after properly choosing new coordinates, the transformed $\overleftrightarrow{D}$ is diagonal, and we have independent oscillators, one for each allowed ω.

- 3 normal mode frequencies

  "3" because 3 degrees of freedom

  ↑ motion in $\hat{x}$-direction only, (3 masses)

  <u>Extension</u>:

  A solid with N unit cells and a basis of s atoms has $N \cdot s \cdot d$ normal mode frequencies.

  ↑ $d = 1$ (if motion in one direction only)
  $d = 2$ (if motion in two directions)
  $d = 3$ (if motion in all three directions)

  3D solids ($d = 3$)

- <u>All masses are involved</u> in each normal mode.

  "Collective excitations"

- The $\omega = 0$ mode is a translational mode.
  If the molecule (solid) is fixed, this mode is irrelevant.
  This is the motion of the center of mass.