Chapter #4:
Vibrations in a Crystal

Lecture 2: Interatomic Potential and Harmonic Approximation

4-2 Harmonic Oscillators

We previously mentioned in Chapter 1 that the total energy of a crystal can be expressed in terms of interactions between atoms.

We assume that any pair of atoms separated by a distance r contributes an interaction energy ϕ. Therefore, the total potential energy of the crystal is:

$$U = \frac{1}{2}\sum_r \sum_{r'} \varphi(\vec{r} - \vec{r}\,') \qquad \text{when } T = 0\text{ K} \qquad (1)$$

The system is at equilibrium, so the total potential energy corresponds to the equilibrium configuration.

That is, the total potential energy of the crystal is the sum of the contributions from all isolated (pairwise) interactions.

- Each pair contributes energy
- The factor 1/2 avoids double-counting

- **Atomic Displacement**

At equilibrium, atoms sit at positions R.

However, if T ≠ 0, the crystal vibrates and atoms move slightly:

$$\vec{r}(\vec{R}) = \vec{R} + u(\vec{R})$$

The total potential is given by:

$$U = \frac{1}{2}\sum_r \sum_{r'} \varphi(\vec{r}(\vec{R}) - \vec{r}\,'(\vec{R})) \qquad (2)$$

We use R and R′ to label atoms by their equilibrium positions, and we use r and r′ to describe their actual positions after displacement.

u(R): displacement of atom at R

u(R′): displacement of atom at R′

With Displacement

$\vec{r}(\vec{R}) = \vec{R} + u(\vec{R})$

$\vec{r}(\vec{R}') = \vec{R}' + u(\vec{R}')$

$$U = \frac{1}{2}\sum_R \sum_{R'} \varphi((\vec{R} + u(\vec{R})) - (\vec{R}' + u(\vec{R}')))$$

$$= \frac{1}{2}\sum_R \sum_{R'} \varphi((\vec{R} - \vec{R}') + (u(\vec{R}) - u(\vec{R}'))) \quad (3)$$

❖ Taylor Expansion

To understand how energy changes with displacement, we expand the potential energy using the Taylor expansion.

Assuming small displacements:

$$\left|u(\vec{R}) - u(\vec{R}')\right| \ll \left|\vec{R} - \vec{R}'\right|$$

We expand using Taylor's theorem:

$$f(\vec{r} + \vec{a}) = f(\vec{r}) + (\vec{a}.\vec{\nabla})f(\vec{r}) + \frac{1}{2}(\vec{a}.\vec{\nabla})^2 f(\vec{r}) + other\ terms$$

Comparing with the energy expression, we identify:

$$f \leftrightarrow \varphi$$

$$r \leftrightarrow \vec{R} - \vec{R}'$$

$$a \leftrightarrow u(\vec{R}) - u(\vec{R}')$$

Then, we can rewrite eq. (3) as follows:

$$U = \frac{1}{2}\sum_R \sum_{R'} \left[\varphi(\vec{R} - \vec{R}') + \left(u(\vec{R}) - u(\vec{R}')\right).\vec{\nabla}\varphi(\vec{R} - \vec{R}') + \frac{1}{2}(u(\vec{R}) - u(\vec{R}')).\vec{\nabla}^2\,\varphi(\vec{R} - \vec{R}') + other\ terms\right] \quad (4)$$

Neglecting the terms that contain the third power means that we are using the harmonic approximation.

❖ Harmonic Approximation

🗣 We keep only terms up to second order.

👉 This is called: Harmonic approximation.

👉 The system behaves like **many coupled springs.**

***** Now, we will study each term separately *****

1st Term:

$$U_1 = \frac{1}{2}\sum_R \sum_{R'} \varphi(\vec{R} - \vec{R}') \qquad (5)$$

This is the equilibrium energy.

It is constant.

- This term depends only on equilibrium positions.

If we define: $\vec{R}'' = \vec{R} - \vec{R}'$

$$U_1 = \frac{1}{2}\sum_{\vec{R}''} \varphi(\vec{R}'')$$

That means the 1st term depends only on $\vec{R}''$.

$$U_1 = \frac{1}{2}\sum_{\vec{R}''} \varphi(\vec{R}'') = U_{equilibrium}$$

This represents the total potential energy at T=0 K.
For the same ion, we can choose:

$$\varphi(0) = 0$$

2nd Term:

$$U_2 = \frac{1}{2}\sum_R \sum_{R'} ((u(\vec{R}) - u(\vec{R}')).\vec{\nabla})\varphi(\vec{R} - \vec{R}')$$

$$= \frac{1}{2}\sum_R \sum_{R'} (u(\vec{R}).\vec{\nabla})\varphi(\vec{R} - \vec{R}') - \frac{1}{2}\sum_R \sum_{R'} ((u(\vec{R}').\vec{\nabla})\varphi(\vec{R} - \vec{R}') \qquad (6)$$

$$= \frac{1}{2}\sum_R u(\vec{R}).(\sum_{R'} \vec{\nabla}\varphi(\vec{R} - \vec{R}')) - \frac{1}{2}\sum_{R'} u(\vec{R}').(\sum_R \vec{\nabla}\varphi(\vec{R} - \vec{R}')) = 0$$

The term $\sum_{R'} \vec{\nabla}\phi(\vec{R} - \vec{R}')$ denotes the force on the ion at $\vec{R}$ due to all other ions at positions $\vec{R}'$.

Similarly, $\sum_{R} \vec{\nabla}\phi(\vec{R} - \vec{R}')$ denotes the force on the ion at $\vec{R}'$ due to all ions at $\vec{R}$.

✓ **At equilibrium, these forces vanish, since the net force on each atom is zero.**

3rd Term:

$$U_3 = \frac{1}{4} \sum_R \sum_{R'} (u(\vec{R}) - u(\vec{R}')).\vec{\nabla}^2 \varphi(\vec{R} - \vec{R}') = U_{harmonic}$$

$$U_{harmonic} = \frac{1}{4} \sum_R \sum_{R'} \sum_\mu \sum_\nu (u_\mu(\vec{R}) - u_\mu(\vec{R}'))\, \varphi''(\vec{R} - \vec{R}')\ (u_\nu(\vec{R}) - u_\nu(\vec{R}')\ (7)$$

$$\varphi''_{\mu\nu}(\vec{r}) = \frac{\partial^2 \varphi(\vec{r})}{\partial \mu\, \partial \nu} \qquad \text{and} \qquad \mu, \nu = x, y, z$$

$$U_{harmonic} = \frac{1}{4} \sum_R \sum_{R'} \sum_\mu \sum_\nu \frac{\partial^2 \varphi(\vec{r})}{\partial \mu\, \partial \nu} (u_\mu(\vec{R}) - u_\mu(\vec{R}'))\ \ (u_\nu(\vec{R}) - u_\nu(\vec{R}'))\ (8)$$

- ✓ Taylor expansion allows us to convert a complex interaction into a simple harmonic form.

In the harmonic energy expression, the multiple summations over $\vec{R},\vec{R}'$ and the Cartesian components μ,ν may appear complicated at first glance. However, their meaning is straightforward: the summation over $\vec{R},\vec{R}'$ accounts for all interacting pairs of atoms in the crystal, while the summation over μ,ν=x,y,z accounts for the contributions from all spatial directions. Thus, the expression simply represents the total energy arising from relative displacements between every pair of atoms in all directions.

In practice, these calculations are often simplified using symmetry, nearest-neighbor approximations, or by reducing the problem to lower dimensions. Moreover, in modern solid-state physics, such summations are efficiently handled using high-performance computing (HPC), where large-scale numerical methods allow us to evaluate interactions across millions of atoms with high accuracy. Therefore, while the expression is mathematically extensive, its physical meaning is clear, and its computation is manageable with modern computational tools.