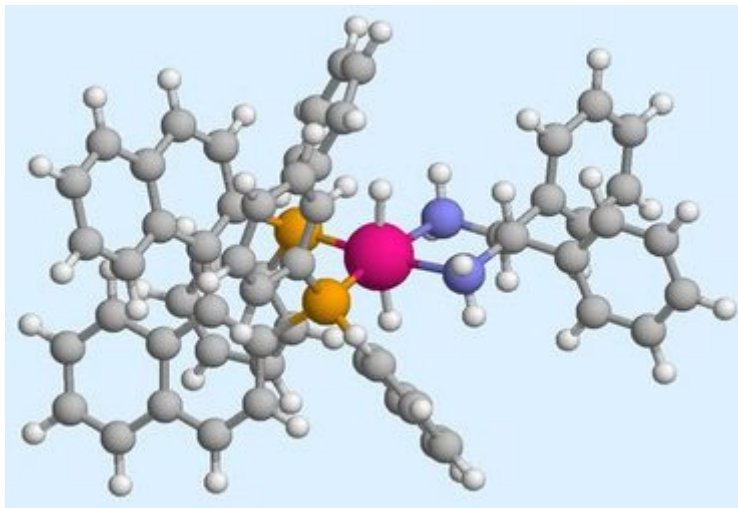


Chapter #3: Crystal Binding

Lecture 1: General Introduction and Crystal Stability



3.1 Introduction

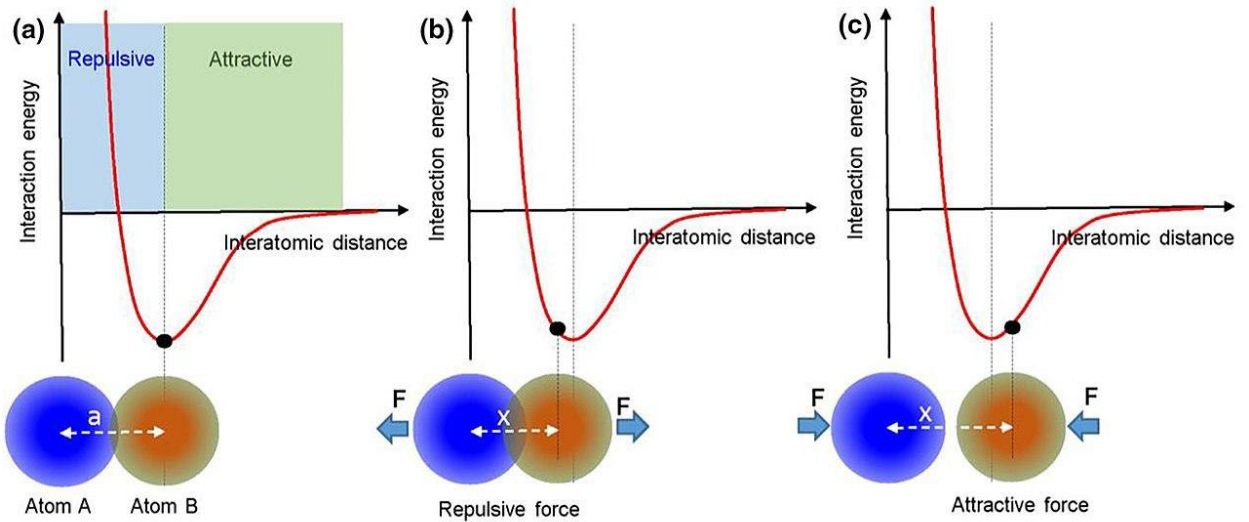
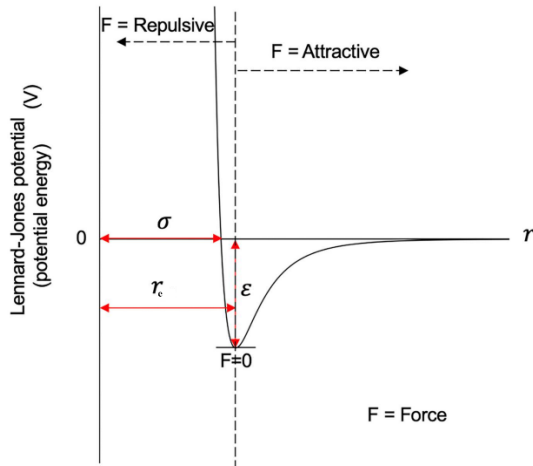
What makes atoms bind together in a crystal?

Solids are stable structures due to the existence of interactions that hold or bind atoms together inside the crystal.

For example, a sodium chloride crystal (NaCl) is more stable than isolated Na and Cl atoms.

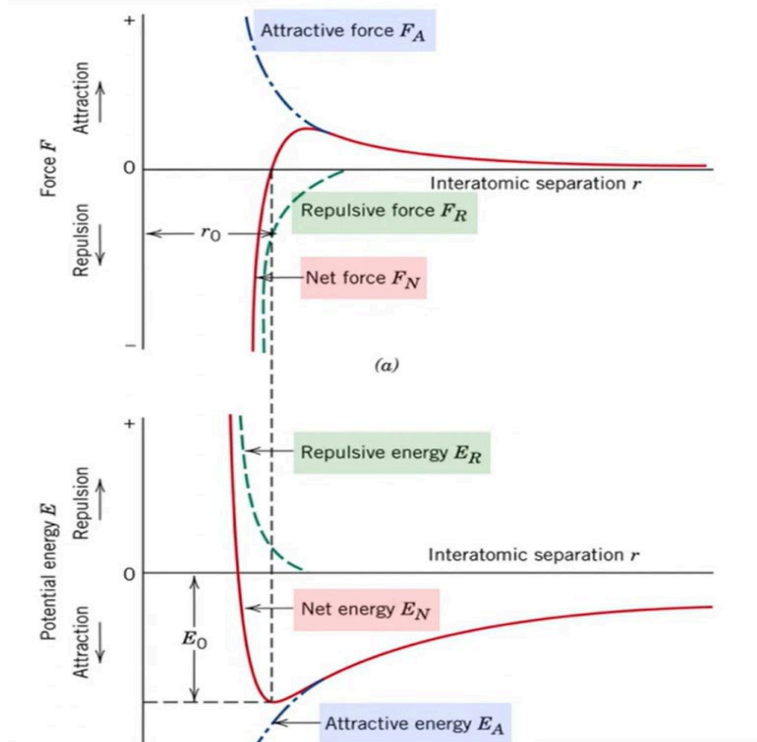
This indicates that when free atoms (of the same or different types) come together, **they bind under the influence of forces of varying nature and strength. Materials are usually classified according to the type of bonding.**

3.2 Interatomic Distance and Stability



The binding energy is directly related to the depth of the potential well:

$$E_{\text{binding}} = |U(r_e)|$$



At a large distance:

“Atoms attract each other because electrons are attracted to the nuclei of neighboring atoms.”

At a short distance:

“When atoms get too close, their electron clouds overlap, and strong repulsion appears due to electron–electron repulsion and the Pauli principle.”

At equilibrium:

“At this point, attraction and repulsion balance each other.”

➤ **A deeper well means stronger bonding and a more stable crystal.**

$$F = - \frac{dU}{dr}$$

- At equilibrium:

$$\frac{dU}{dr} = 0$$

- Stability requires:

$$\frac{d^2U}{d^2r} > 0$$

Binding is due to the interaction of the electrons and the nuclei

- Negative electrons and positive nuclei *attract* each other.
- There must also be *repulsion* for the solid (or liquid) to be stable at some density.
- All types of bonding arise from the *balance* between attractive and repulsive interactions.

Important definitions:

- **Bond length/equilibrium distance r_e**
- **Nearest-neighbor distance**

At equilibrium:

$$F=0$$

This means:

- Attractive force = Repulsive force
- Potential energy is minimum

• Condition of Stability

For a stable system:

$$\frac{dU}{dr} = 0 \quad \text{and} \quad U \Rightarrow \text{minimum}$$

From the diagram:

- At large distance \rightarrow weak attraction
- At short distance \rightarrow strong repulsion
- At $r=r_e \rightarrow$ equilibrium

• Nature of Forces

- Attractive force \rightarrow negative
- Repulsive force \rightarrow positive

Repulsive forces are **short-range forces**.

3.3 Cohesive Energy

The cohesive energy of a solid is the energy required to disassemble it into its constituent parts — i.e., its binding energy.

In fact, the cohesive energy corresponds to the depth of the potential well

Suppose we have a lattice with lattice constant a , and the system has total energy (E_1):

$$E_1 = PE + KE$$

Now, increase the lattice constant to *infinity* so the system becomes gaseous. Let its energy be E_2 .

$E_1 = E_{\text{crystal}}$ (energy of atoms in the solid)

$E_2 = E_{\text{free atoms}}$ (energy when atoms are infinitely separated)

- If $E_2 < E_1 \rightarrow$ atoms prefer the gaseous state.
- If $E_2 > E_1 \rightarrow$ atoms prefer the solid state.

Therefore, for a solid to form, the total energy of atoms in the solid must be less than that of free atoms.

Cohesive Energy: $E_c = E_2 - E_1$

$$E_c = \frac{E_{\text{free-atoms}} - E_{\text{crystal}}}{N}$$

Then state clearly:

Cohesive energy is defined **per atom**.

- N = number of atoms in the system
- Units: **eV/atom**

The cohesive energy describes crystal stability. The larger E_c , the more stable the crystal.

Exercise:

The figure shows the variation of potential energy $U(r)$ with interatomic distance for three different interactions (blue, orange, and green curves).

Which curve represents the strongest bond? Justify your answer based on the physical meaning of the graph.

