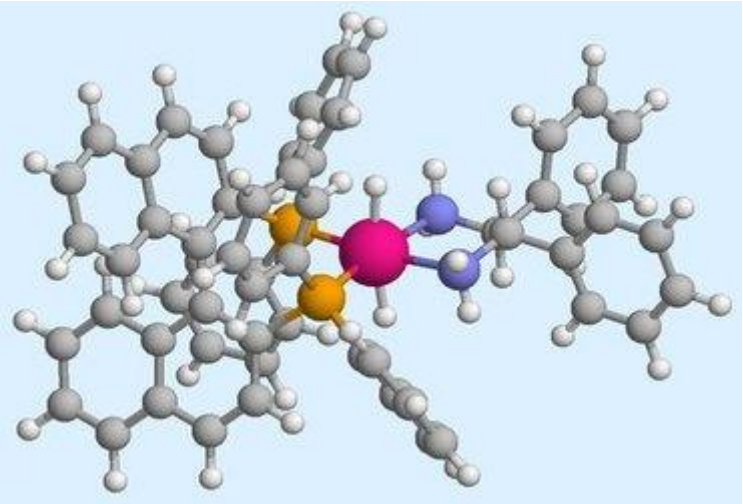
Chapter #3:
Crystal Binding

Lecture 1: General Introduction and Crystal Stability



3.1 Introduction

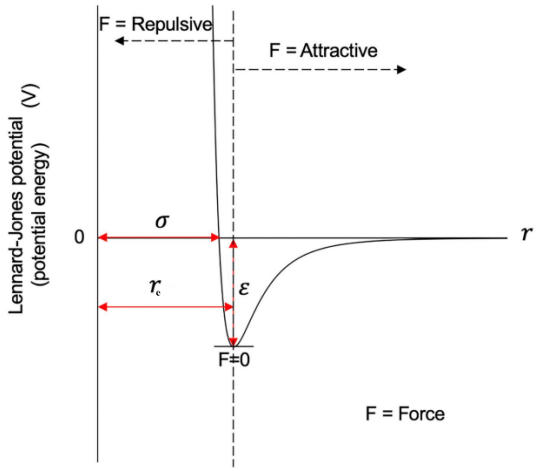
What makes atoms bind together in a crystal?

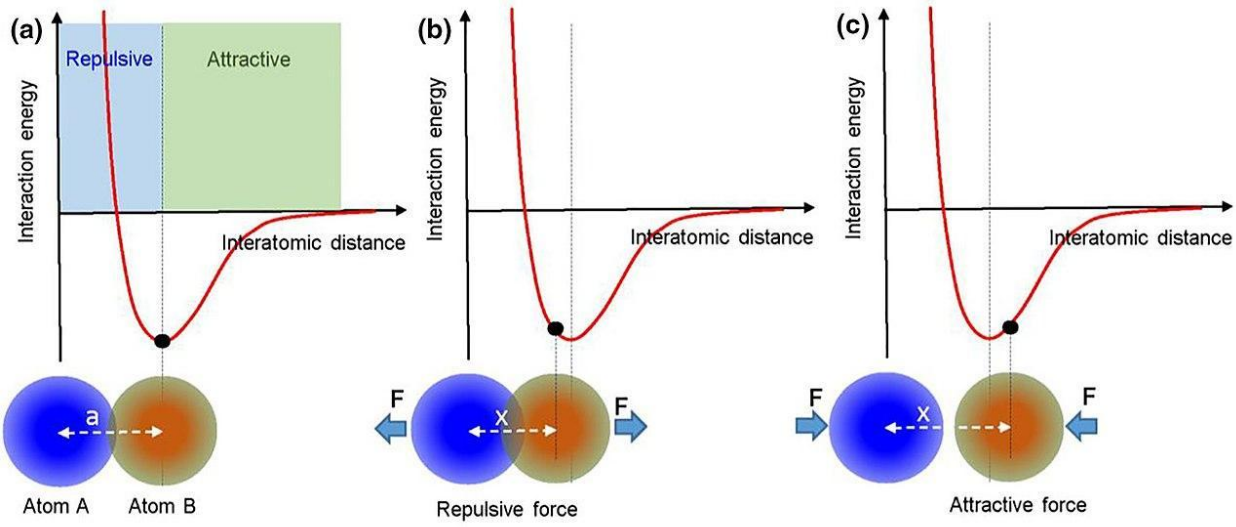
Solids are stable structures due to the existence of interactions that hold or bind atoms together inside the crystal.

For example, a NaCl crystal has a lower total energy than the corresponding separated neutral atoms.

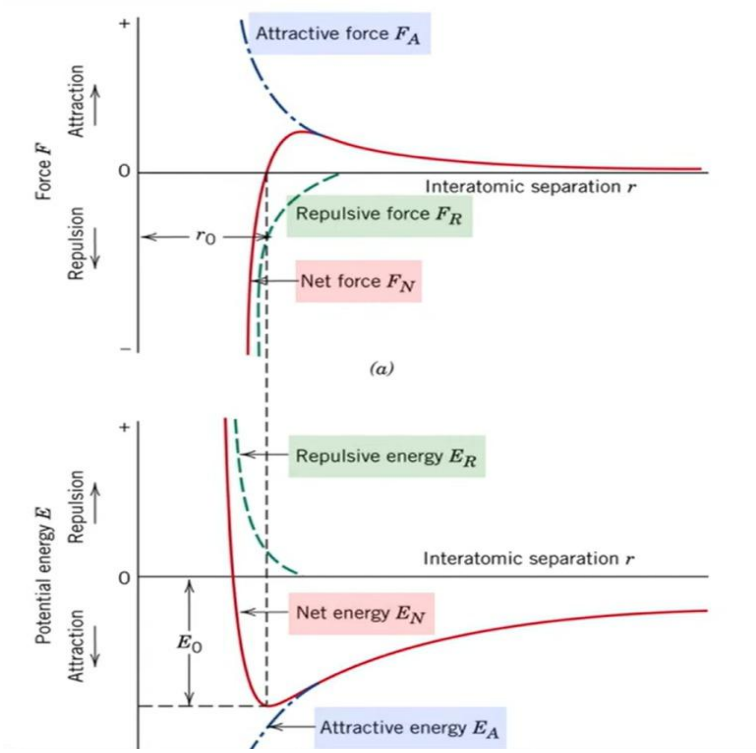
This indicates that when free atoms (of the same or different types) come together, **they bind under the influence of forces of varying nature and strength. Materials are usually classified according to the type of bonding.**

3.2 Interatomic Distance and Stability





The binding energy is directly related to the depth of the potential well:
$E_{binding} = |U(r_e)|$



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

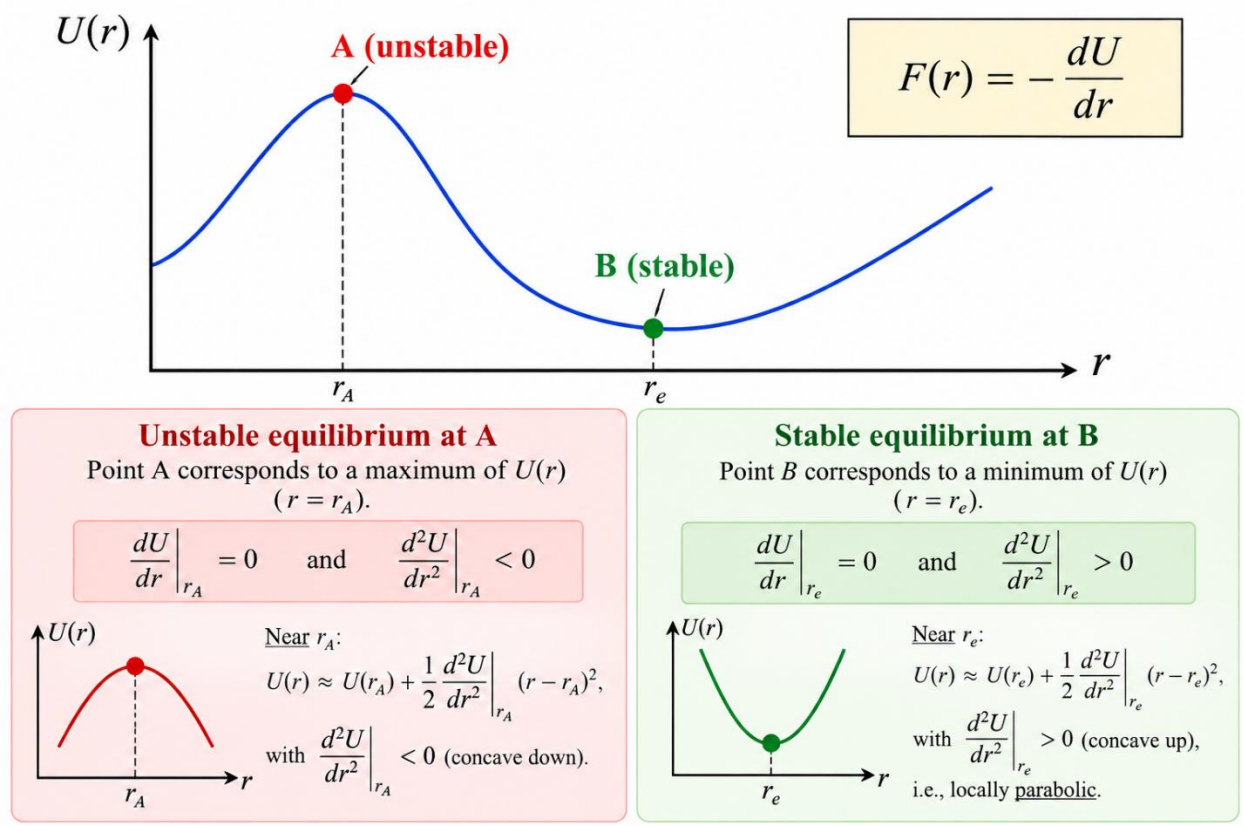
• Condition of Stability

For a stable system:

$\frac{dU}{dr} = 0$ and U == > minimum

From the diagram:

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



- ## Nature of Forces

- Attractive force → negative
- Repulsive force → 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.

$E_1=E_{crystal}$ (energy of atoms in the solid)
$E_2=E_{free\ atoms}$ (energy when atoms are infinitely separated)

- If $E_2 < E_1$ → atoms prefer the gaseous state.
- If $E_2 > E_1$ → 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: $E_c = E_2 - E_1$

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

Then state clearly:

Cohesive energy is defined **per atom**.

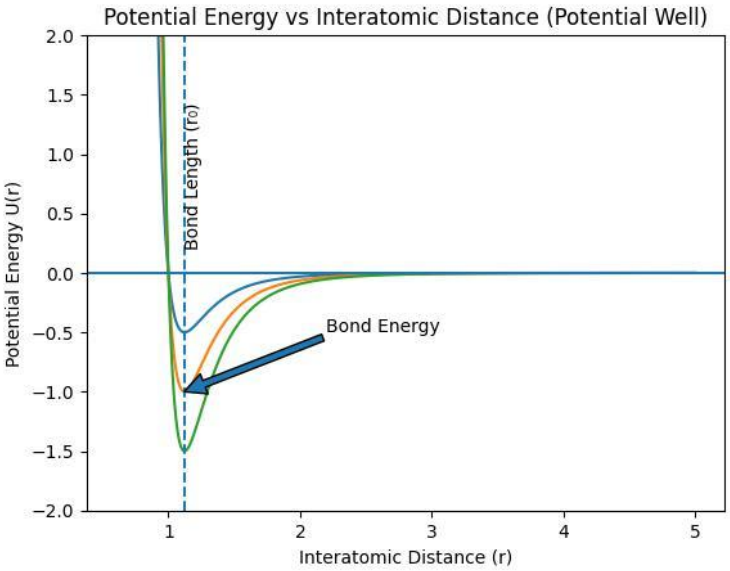
- N = number of atoms in the system
- Units: **eV/atom**
  - **The cohesive energy describes crystal stability. The larger E_c, the more stable the crystal.**
  - **In general, the cohesive energy (at T=0 K) of a compound AB is the difference between the energies of this crystal and the stable phases of the elements:**

$E_{cohesive} = (E_A + E_B) - E_{crystal}$

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.


Potential Energy vs Interatomic Distance (Potential Well)
Potential Energy U(r)
Interatomic Distance (r)
Bond Length (r_0)
Bond Energy
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
1
2
3
4
5