

Starting Chapter 3 "Crystal Binding & Elastic Constants"

very different from each other, should have been 2 separate chapters

★ Crystal Binding

What types of bonds are there? (recall from Chemistry?)

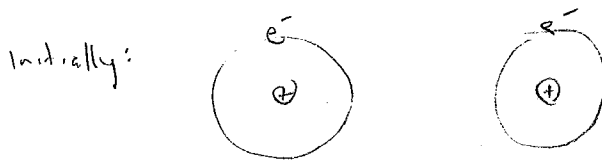
- van der Waals
- ionic
- covalent
- metallic
- hydrogen bond

We'll only do mathematical models for
- van der Waals
- ionic

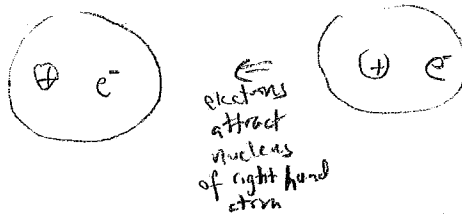
Van der Waals : "crystals of inert gases" section in book (noble gases)

Noble gases all "close packed", most fcc - Table 3, pg 20

Attraction Why do they stick together at all?



Random fluctuation leads to offset electron cloud



Now have a weak electrostatic attraction

Strength of attraction?

Book has detailed Quantum Mechanical derivation, pg 53-56

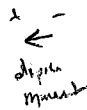
Result: $U_{\text{interaction}} \sim x^{-6}$

↓
potential energy

↘ distance between atoms

much easier way, although not as rigorous:

Each atom becomes small electric dipole



Energy of this dipole = $U = -\vec{p} \cdot \vec{E}$

↓
field from other dipole
 $E \sim x^{-3}$
along axis

if were permanent dipole, $U \sim x^{-3}$

But it's an induced dipole, so another factor of x^{-3}
because dipole field from one creates dipole in other

$$U \sim \frac{1}{R^6}$$

called the "London interaction"

Repulsion: what stops atoms from overlapping completely?

Pauli exclusion principle

Two models for repulsion

(1) $U \sim \frac{1}{R^{12}}$

(2) $U \sim e^{-R/\text{lengthscale}}$

} neither has very good theoretical basis. Pick what fits the data acceptably.

For this purpose, pick option (1).

(we'll use option (2) in our analysis of ionic crystals)

combine Attraction + Repulsion

$$U = \frac{C_1}{R^{12}} - \frac{C_2}{R^6}$$

Write as

$$U = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]$$

Use ϵ and σ as parameters instead of C_1 and C_2

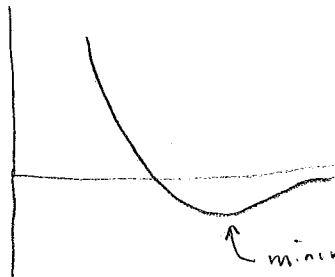
Called "Lennard-Jones potential"

I've no idea why the factor 4 is used convention, # guess

ϵ + σ relate to how atoms attract/repel each other

Kittel: "... can be obtained by gas phase data"

Plot U vs R



minimum at $R \approx 1.12\sigma$

If only two atoms, that would be equilibrium distance.

But, it's not the right distance when many atoms in a crystal structure.

U_{tot} : Must add up U for each pair of atoms. Call "i" = reference atom.

$$U_{tot} = \frac{1}{2} N (4\epsilon) \left[\sum_j' \left(\frac{\sigma}{p_{ij}R}\right)^{12} - \sum_j' \left(\frac{\sigma}{p_{ij}R}\right)^6 \right]$$

because each pair gets counted twice

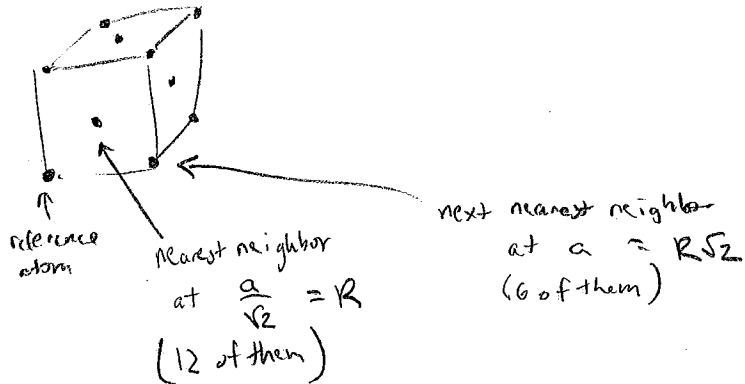
Sum over all atoms j . (The "prime" on the summation means you don't let $j=i$)

$p_{ij} \times R$ = distance between atoms i and j .

That is, p_{ij} = distance in terms of R (the nearest neighbor distance).
 p_{ij} = dimensionless

Note: this theory cannot predict structure directly, but given a structure, it can predict the energy

fcc structure



Summations are like this:

$$\begin{aligned} & \sigma^{12} \left[12 \times \frac{1}{(R)^{12}} + 6 \times \frac{1}{(R\sqrt{2})^{12}} + \text{third nearest neighbors} + \dots \right] \\ & - \sigma^6 \left[12 \times \frac{1}{R^6} + 6 \times \frac{1}{(R\sqrt{2})^6} + \text{third nearest neighbors} + \dots \right] \\ & = \frac{\sigma^{12}}{R^{12}} \left[\frac{12}{1^{12}} + \frac{6}{(\sqrt{2})^{12}} + \dots \right] \end{aligned}$$

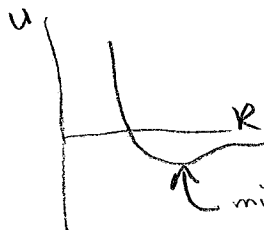
first two add to 12.094
infinite series adds to 12.13188

$$- \frac{\sigma^6}{R^6} \left[\frac{12}{1^6} + \frac{6}{(\sqrt{2})^6} + \dots \right]$$

first two add to 12.75
infinite series adds to 14.45392

So, for fcc

$$U_{\text{tot}} = \frac{1}{2} N(4\epsilon) \left[12.13188 \frac{\sigma^{12}}{R^{12}} - 14.45392 \frac{\sigma^6}{R^6} \right]$$



minimum at $R = 1.0902 \sigma = "R_0"$

(a little less than the expected value for 2 atoms)

Plug that distance back into energy equation,

$$U_{\text{tot}}(R=R_0) = -2.15 (4NE)$$

Compare with experiment:

| | R_0 | $U_{\text{tot}}(R=R_0)$ | $U_{\text{tot}}(R=R_0)$, with an additional quantum-mechanical correction related to "zero point energy" |
|----|--------------|-------------------------|---|
| Ne | 5% different | 28% different | 7% |
| Ar | 2% " | 10% " | ↓ |
| Kr | 1% " | 6% " | ↓ |
| Xe | 0% " | 4% " | 1% |

Again, no adjustable parameters other than gas-phase data!

Could do the same sort of calculation for other structures besides fcc, but the book doesn't bother.