

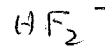
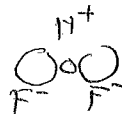
Starting Chapter 3 "Crystal Binding & Elastic Constants"

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



"It is believed that hydrogen bond is largely ionic in character"

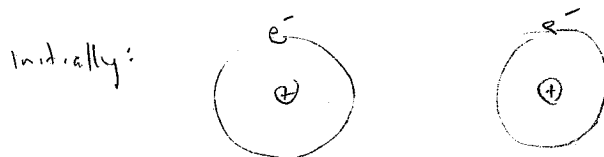
We'll only do mathematical models for

- van der Waals
- ionic

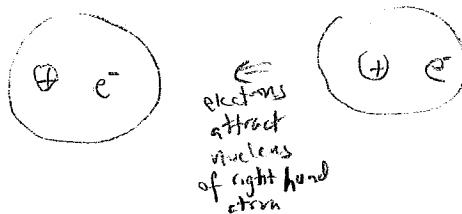
Van der Waals : "crystals of inert gases" section in book (noble gases)

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

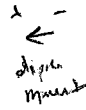
Strength of attraction?

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

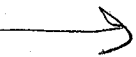
if were permanent dipole, $U \sim x^{-3}$

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"

More formulae: Kittel QM derivation on next page



Repulsion: what stops atoms from overlapping completely?

Pauli exclusion principle

Two models for repulsion

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

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

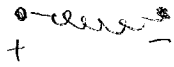
neither has very good theoretical basis. Pick what fits the data acceptably.

For this purpose, pick option (1).

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

(Can skip this page...)

Kittel's model



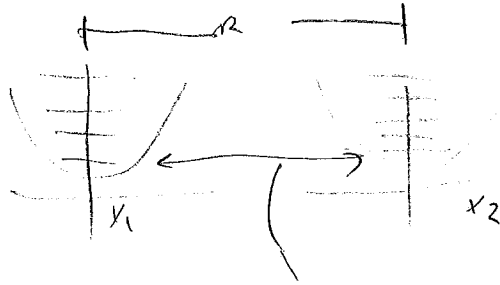
a charge SHO

$$E_n = (n + \frac{1}{2}) \hbar \omega_0 \quad n = 0, 1, 2, \dots$$

1 SHO

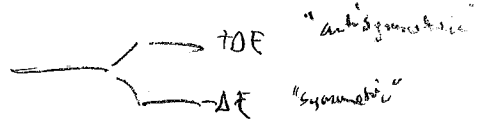


2 SHO near each other



interaction $x_1 x_2$

ground state splits



$$H_1 = \frac{p_1^2}{2m} + \frac{1}{2} k_1 x_1^2$$

$$H_2 = \frac{p_2^2}{2m} + \frac{1}{2} k_2 x_2^2$$

$$H_{tot} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{k}{2}(x_1^2 + x_2^2) - 2\lambda x_1 x_2$$

New coords $\Rightarrow x_s = \frac{x_1 + x_2}{\sqrt{2}}$
 $x_a = \frac{x_1 - x_2}{\sqrt{2}}$

dipole interaction $= -2 \frac{p_1 p_2}{R^3}$ } $p_i = -ex_i$
 $\Rightarrow \lambda = \frac{e^2}{R^3}$

$$H_{tot} = \frac{p_s^2}{2m} + \frac{1}{2} k_s x_s^2 + \frac{p_a^2}{2m} + \frac{1}{2} k_a x_a^2$$

$$k_s = k - 2\lambda$$

$$\omega = \sqrt{\frac{k_s}{m}}$$

$$\omega_s = \omega_0 - \text{a little}$$

$$k_a = k + 2\lambda$$

$$\omega_a = \omega_0 + \text{a little}$$

$\Delta E_{interaction} =$ new ground state - non-interacting ground state

$$= \frac{1}{2} \hbar \omega_s + \frac{1}{2} \hbar \omega_a - \left(\frac{1}{2} \hbar \omega_0 + \frac{1}{2} \hbar \omega_0 \right)$$

$$= \frac{\hbar \omega_0}{8} \left(\frac{2e^2}{kR^3} \right)^2 = \boxed{-\frac{A}{R^6}}$$

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

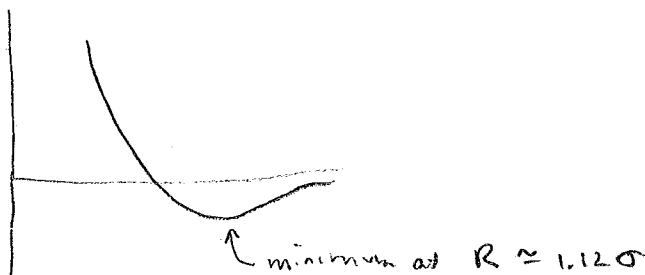
Called "Lennard-Jones potential"

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

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

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

Plot U vs R



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.

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

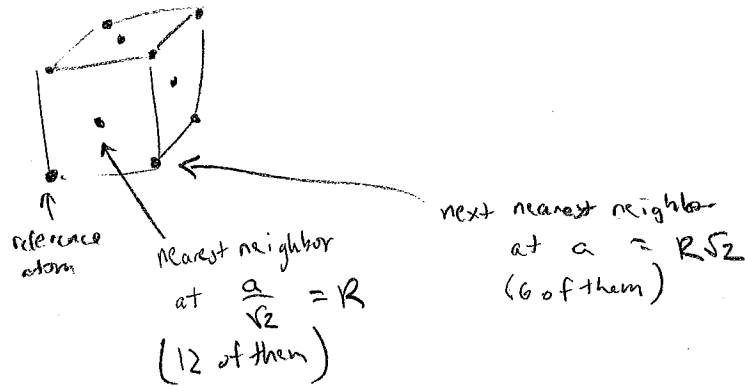
because each pair gets counted twice

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:

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

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

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

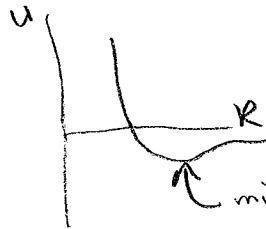
first two add to 12.094
infinite series adds to 12.13188

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

first two add to 12.75
infinite series adds to 14.45392

So, for fcc

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



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	2.8% 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.