Ionic

(20)

Attractive

$$-\frac{q^2}{p_{ij}R}$$ for some p_{ij}

(SI: $\frac{1}{4\pi\epsilon_0}\frac{q^2}{r}$ ★ CGS: $\frac{q^2}{r}$)

Repulsive

$$+\frac{q^2}{p_{ij}R}$$ for some other p_{ij}

$\lambda e^{-R/\rho}$ for Pauli exclusion (nearest neighbors) λ, ρ = empirical parameters

(reference = negative charge)

$$U_{tot} = N\left(z\lambda e^{-R/\rho} - \sum_i \frac{(\pm)q^2}{p_{ij}R} \right)$$

z ↓ nearest neighbors

Why not $N/2$?

because N = # pairs, i.e. # ions = $2N$

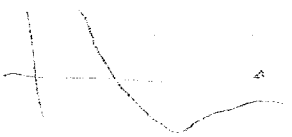
$\frac{-q^2}{R}\sum_i \frac{(\pm)}{p_{ij}}$

$\sum_i \frac{(\pm)}{p_{ij}} = \alpha$; Madelung constant

calculate very similar to VdW stuff in last section

NaCl structure $\alpha = 1.7475645$
CsCl $\alpha = 1.7626755$
ZnS $\alpha = 1.6381$

$$U_{tot} = N\left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right)$$



same deal $\frac{\partial U}{\partial R} = 0$ gives R_0 (transcendental eqn, numerical soln)

then $U_{tot}(R=R_0)$ → total lattice energy

has analytic:

$$U_{tot} = -\frac{N\alpha q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right)$$

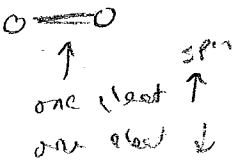
$\frac{\rho}{R_0}$ ← repulsive; "Madelung"

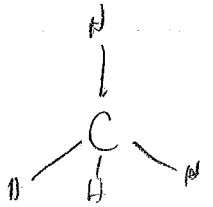
Cohesive energy a few eV, ~10× larger than VdW noble gases

★ table 7 pg 66 nice agreement!

Covalent Crystals

Ex: H_2





CH_4

diamond structure (I can't draw)

Merton textbook 222 diamond problem

comes from QM - orbitals (?)

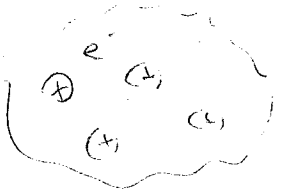
Hard to analyze quantitatively from first principles

Metals

Some electrons free (valence elect of atom → Cond. electrons)

↓

but lowered in energy (due to quantum (?))



← Some

a Weaker binding (ductile, malleable) → still crystalline on microscopic level

. close packed

↳ strong for transition metals though

Table 1 pg 50

↳ weaker than ionic

Compare kcal/mol to Table 7 pg 66

Hydrogen bonds

- already discussed

return

Atomic Radii

- basically, no such thing for universal case

distances between atoms depend strongly on structure

but can get approx ← vdW
ionic (modification of vdW)
covalent
metallic

Table 9 pg 71
Table 10 pg 72
that's all I'll say

Elastic Strains

From Physics 121

stress = Force/area

strain = $\Delta L / L$

Young's modulus Y = stress/strain

Crystals: difference between eg [100] and [111] directions complicates things!

Goals: • Find generalization of Y, called "stiffness constants" (tensor)

- for cubic crystals, get wave eqn for long wavelength waves
  → properties like wave speed (transverse + long.)
  in [100], [110], [111] (for this) } directions in terms of stiffness constants

Vibrational Modes in a Solid

molecules
- 3 translational d.f
- 2-3 rotational d.f
- ? vibrational d.f

Looking ahead

Solid ⇒ can use translational symmetry to simplify vibrational problem

- longitudinal vs transverse
- long wavelength (solid like homogeneous medium) → but not isotropic → rest of this chapter
- vs. short wavelength (must consider microscopic structure) → Next two chapters

Reminder: matrix multiplication. Change a vector into 3 new vector components

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}' = \begin{pmatrix} b \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

$$a_i' = \sum_{j=1}^{3} b_{ij} a_j$$

To turn a matrix into a ~~new matrix~~ components?

$$b_{jk}' = \sum_{l} \sum_{m} C_{jklm} b_{lm}$$

b_{jk}: "rank 2 tensor" → 9 components

Cijklm: rank 4 tensor → 81 components