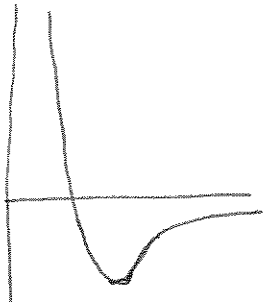
20 Cohesive Energy

Lennard-Jones potential: $\phi(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$.

$= 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

Molecular Crystals



Fits for Noble Gases

$u = \frac{1}{2}\sum_{R\neq 0}\phi(R)$ per particle

$u = 4\varepsilon\left[A_{12}\left(\frac{\sigma}{r}\right)^{12} - A_6\left(\frac{\sigma}{r}\right)^{6}\right]$

$R = \alpha(R)\cdot r$

r = nearest neighbor separation

$A_n = \sum_{R\neq 0}\frac{1}{\alpha(R)^n}$

$\frac{\partial u}{\partial r} = 0$ works $\rightarrow u(\text{equil.}) = -8.6\varepsilon$

$=$ cohesive energy

Bulk modulus also works well.

Ionic Crystals

$$U^{(r)} = U^{core}_{(r)} + U^{coulomb}_{(r)}$$

$r = a/2$ (Cubic)

$|R| = \alpha(R)\, r$

$|R+d| = \alpha(R+d)\, r$ — d transl. a/2

$$\frac{-e^2}{4\pi\varepsilon_0 r}\left\{\frac{1}{\alpha(d)} + \sum_{R\neq 0}\left(\frac{1}{\alpha(R+d)} - \frac{1}{\alpha(R)}\right)\right\}$$ 2 atombasis

$U = \frac{N}{2}$ "

$U^{coul} =$ " "

divide pairs ions (without 2)

Does not converge.

Depending on sum can get anything.

Sum so that Q, & surface charge.

Then decay $1/r^5$.

Ewald

$U^{Coul} = -\alpha\frac{e^2}{r}$, α = Madelung Constant

Dominant term = Coulomb

Need core-core repuls. to fine tune

Covalent Crystals & Metals

Tougher since valence electrons distorted

Need band structure.

Give my interpretation.

Metals

Electron K.E. + Coulomb

$$u^{coul} = -\frac{24.35}{(r_s/a_0)} \text{ eV/atom}$$

$$u^{kin} = \frac{3}{5}\varepsilon_F = \frac{30.1}{(r_s/a_0)^2} \text{ eV/atom}$$

$$u^{ex} = \frac{-12.5}{(r_s/a_0)} \text{ eV/atom}$$

$$\rightarrow \frac{r_s}{a_0} = 1.6$$

Alkali: $\frac{r_s}{a_0} = 2$ to 6

Not include ionic radius.