PHYS 0551 Lecture 8

VanderWaal and Ionic Bonding

As was stated previously, the electron-electron interactions have been completely ignored. Since the core electrons are concentrated near the nucleus, they and the nucleus can be considered a single entity. Hence the 1/R dependence of the nucleii must be modified greatly. For this, there exists no good exact analytic calculations. Hence for the repulsive interaction at short length scales we are reduced to an empirical formulation for this factor.

There are two common representations:

E(R) $= \lambda / R^n$ $\qquad$ $8 > n > l4$

or

E(R) $= \lambda exp(-R/\rho)$ $\qquad$ $0.3\ a_0 > \rho > a_0$ where a_0 is the Bohr radius

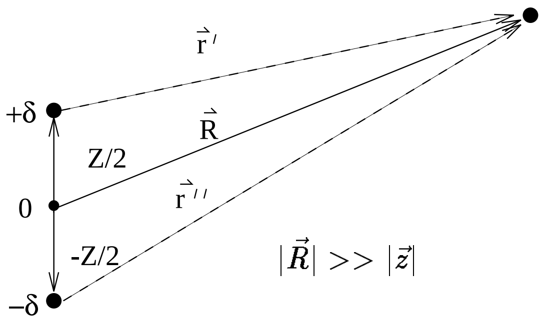
VanderWaal Bonding

VdW bonding occurs in all solids. However, this bonding is so weak that except for a limited number of systems it is completely overwhelmed by the other bonding types present. VdW bonding is the primary bonding in closed shell systems with no net charge transfer (i.e., neutral atoms or molecules).

Consider two neutral atoms separated by R. Assume atom 1 has dipole moment $\vec{p}_1$ at some instant in time.

$$\vec{E}_1(\vec{R}) = \frac{1}{4\pi\epsilon_0}\frac{1}{|\vec{R}^3|}(3\vec{p}_1 \cdot \hat{R}\hat{R} - \vec{p}_1)$$

$\vec{R} = x\hat{x} + y\hat{y} + z\hat{z} \qquad \vec{p}_1 = \delta\vec{z}$



$|\vec{R}| >> |\vec{z}|$

$$\Phi(\vec{R}) = \frac{1}{4\pi\epsilon_0}\left(\frac{\delta}{|\vec{r}\,'|} + \frac{-\delta}{|\vec{r}\,''|}\right)$$

$$\vec{r}\,' = \vec{R} - \vec{z}/2 \qquad \vec{r}\,'' = \vec{R} + \vec{z}/2$$

$$|\vec{r}\,'| = (\vec{r}\,' \cdot \vec{r}\,')^{1/2} = (R^2 - \vec{z}\cdot\vec{R} + z^2/4)^{1/2}$$

$$|\vec{r}\,''| = (\vec{r}\,'' \cdot \vec{r}\,'')^{1/2} = (R^2 + \vec{z}\cdot\vec{R} + z^2/4)^{1/2}$$

$$\frac{1}{|\vec{r}\,'|} = 1(R^2 - \vec{z}\cdot\vec{R} + z^2/4)^{1/2} = \frac{1}{R}\frac{1}{(1-\vec{z}\cdot\vec{R}/R^2 + z^2/4R^2)^{1/2}}$$

$$\frac{1}{|\vec{r}\,'|} \approx \frac{1}{R}(1-\vec{z}\cdot\vec{R}/2R^2)$$

by using a Taylor's series expansion

$$\frac{1}{|\vec{r}\,'|} \approx \frac{1}{R}(1-\vec{z}\cdot\vec{R}/2R^2)$$

so

$$\begin{aligned}\Phi(\vec{R}) &\approx \frac{1}{4\pi\epsilon_0}\delta\frac{1}{R}(\vec{z}\cdot\vec{R}/R^2)\\ &\approx \frac{1}{4\pi\epsilon_0}\vec{p}_1\cdot\vec{R}/R^3\end{aligned}$$

$$\vec{E}_1(\vec{R}) = -\bigtriangledown\Phi = \frac{1}{4\pi\epsilon_0}\frac{1}{|\vec{R}^3|}(3\vec{p}_1\cdot\hat{R}\hat{R} - \vec{p}_1)$$

$\vec{R} = |R|\hat{R}$

This electric field induces a dipole moment at atom 2.

$$\vec{p}_2 = \alpha\vec{E}_1(\vec{R}) \text{ where } \alpha \text{ is the polarizability of atom 2.}$$

$$U(\vec{R}) = -\vec{p}_2\cdot\vec{E}_1 = -\alpha\vec{E}\cdot\vec{E}$$

$$U(\vec{R}) = -\alpha\frac{1}{(4\pi\epsilon_0)^2}\frac{1}{R^6}[9(\vec{p}_1\cdot\hat{R})^2 - 6(\vec{p}_1\cdot\hat{R})^2 + p_1^2]$$

$$U(\vec{R}) = -\alpha\frac{1}{(4\pi\epsilon_0)^2}\frac{1}{R^6}[3(\vec{p}_1\cdot\hat{R})^2 + p_1^2]$$

$$\begin{aligned}\text{Notice:}\quad U(R) &< 0;\text{this implies an attractive force}\\ U(R) &\propto 1/R^6;\text{ which is very weak}\\ U(R) &\propto \text{time-average of } \vec{r}_1\\ & \quad \vec{p}_1\cdot\hat{R} = p_1\ cos\ \theta\\ & \quad < p_1^2\ cos\ ^2\theta > = \tfrac{1}{2} < p_1^2 > \quad \text{and} < p_1^2 > > 0\end{aligned}$$

so

$$< U(R) > = -\frac{5\alpha < p_1^2 >}{2(4\pi\epsilon_0)^2 R^6}$$

If $n = 12$ (the exponent of the repulsive force) then the interaction energy can be written in this standard form:

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

This form is known as the Lennard-Jones 6-12 potential.

In order to calculate the energy for a VdW solid (the "cohesive" energy), the

$$U_{total}(R) = \frac{1}{2}N4\epsilon\left[\sum_j\left(\frac{\sigma}{p_{ij}R}\right)^{12} - \sum_j\left(\frac{\sigma}{p_{ij}R}\right)^6\right]$$

By putting the sums in the above form, both σ and R can be removed from within the summation.

	FCC				BCC		
12	NN	1	12	8	NN	1	8
6	NNN	$\sqrt{2}$	$(\frac{1}{\sqrt{2}})^{12}$	6	NNN	$\frac{1}{(\frac{2}{\sqrt{3}})^{12}}$	6
24	NNNN	$\sqrt{3}$	$(\frac{1}{\sqrt{3}})^{12}$	12	NNNN	$\sqrt{3/8})^{12}$	12

$\sum_j p_{ij}^{-12} = 12.13$ $\quad\sum_j p_{ij}^{-6} = 14.45$ $\qquad\sum p_{ij}^{-12} = 9.11$ $\quad\sum_j p_{ij}^{-6} = 12$

The equilibrium structure can be determined;

$\frac{d\,U_{Total}}{dR} = 0$ and solve for R_0.

If $U_{Total}(R_0)$ is known, then the energy per atom is known. In general, the cohesive energy is a very difficult quantity to measure. However, a few bulk measurements can give a reasonable estimate of the cohesive energy.

$v = V/N$, volume per particle

$u = U/N$, energy per particle

$k \equiv$ isothermal compressibility = - $\frac{1}{V}(\partial V/\partial P)_T$

$dU = TdS - pdV$

$dU = -pdV$ (T= 0°K) or

$dU \approx -pdV$ (T> 0°K) since the change in entropy for a solid is a very slowly varying function.

$$\boxed{\frac{1}{k} = V \quad d^2U/dV^2L}$$

$$\frac{dU}{dV} = \frac{dU}{dr}\,\frac{dr}{dV}$$

$$\frac{d^2U}{dV^2} = \left(\frac{dr}{dV}\right)^2 \frac{d^2U}{dr^2} + \frac{d^2r}{dV^2}\,\frac{dU}{dr}$$

At equilibrium, $dU/dr = 0$

Thus

$$\boxed{\frac{d^2U(R)}{dV^2} = \left(\frac{dr}{dV}\right)^2 \frac{d^2U}{dr^2}}$$

$$V = Nr^3 \text{ or } 2Nr^3$$

and evaluate at $r = R_0$

So if R_0 and k are known, σ and ϵ can be determined.
In an ionic compound, the $1/R^6$ VdW bonding is completely lost in the background of the large Coulombic forces due to permanently charged species.

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

z = number of nearest neighbors

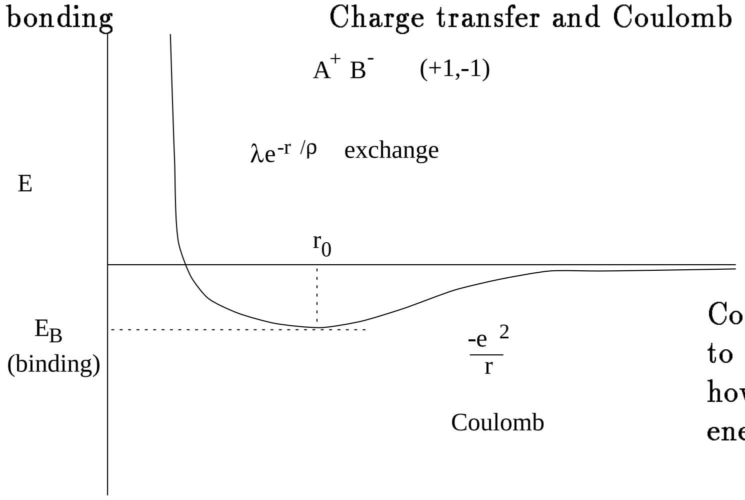
α = Malelung constant

λ strength of the interaction

ρ range of interaction

Ionic bonding

Charge transfer and Coulomb attraction



Cost energy
to transfer
however total
energy is lowered

In a crystal

$$
\begin{aligned}
U_{ij} &= \lambda\, e^{-r_{ij}/\rho} \pm q^2/r_{ij} \\
U_i &= \sum_j U_{ij} \\
U_{\text{Total}} &= NU_i \quad N \text{ is \# of ion pairs}
\end{aligned}
$$

The exchange term is short range so we need only consider nearest neighbor. We can rewrite $r_{ij} = p_{ij} r$ where r is the equilibrium distance.

$$
\begin{aligned}
U_{\text{Total}} &= N\left(z\lambda\, e^{-r/\rho} + \tfrac{q^2}{r}\textstyle\sum_j \pm\tfrac{1}{p_{ij}}\right) && \text{the Madelung constant and} \\
&\textstyle\sum_j \pm\frac{1}{p_{ij}} \equiv \alpha && \text{depends on the crystal structure}
\end{aligned}
$$

For NaCl (table salt)

$$\alpha = \left(\tfrac{6}{1} - \tfrac{12}{\sqrt{2}} + \tfrac{8}{\sqrt{3}} - + \ldots\right) = 1.747$$

NaCl is FCC with Cl [0, 0, 0],[1/2, 1/2, 0]
Na [1/2, 1/2, 1/2], [1, 1, 1/2], etc.

Note that this sum is *conditionally* convergent.