

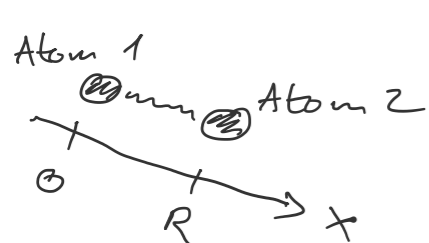
# Lecture notes

Wednesday, 21 March 2018 1:05 PM

Tasks for next week:

- Read chapter 4 (Kittel): Phonons/Lattice Vibrations

## Crystal bindings



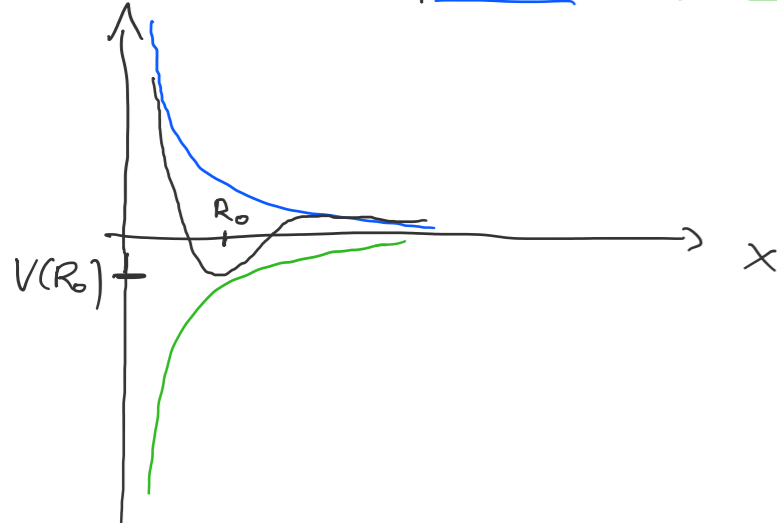
- There is repulsive interaction  $V_{repulsive}$
- Attractive interaction  $V_{attractive}$

$$V = V_{repulsive} + V_{attractive}$$

↑                    ↑  
potentials

→ Crystal: Many body problem:  $V_{total} \propto \sum_j V_{ij}$

$$V(x) = V_{repulsive} + V_{attractive}$$



$R_0$  "most favourable point for distance between atoms" → find  $\frac{dV(x)}{dx} = 0 \Rightarrow x = R_0$   
 $V(R_0)$  "binding potential" → binding energy

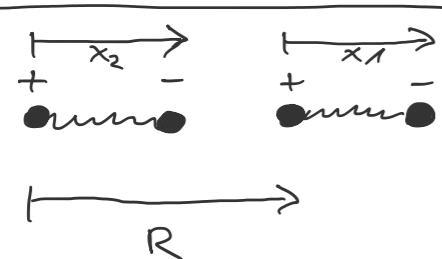
- Attractive Interactions:
- van der Waals
  - Ionic binding
  - covalent binding
  - metallic
  - What about hydrogen bonds?

Noble gases at very low temperature form crystals!

Binding force in noble gas crystal: van der Waals

↳ form fcc crystals

## Van der Waals interactions



Two dipoles

- both considered harmonic oscillators with spring constant  $C$  and  $\omega_0 = \sqrt{C/m}$

Hamiltonian:  $H_0 = \frac{p_1^2}{2m} + \frac{1}{2} C x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2} C x_2^2$  "uncoupled"

↳ Eigenstates of a harmonic oscillator:  $E = \hbar \omega_0 (n + \frac{1}{2})$   
 $\Rightarrow E_0 = \frac{1}{2} \hbar \omega_0$

Hamiltonian for the coupled system:

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}$$

Assumption:  $R \gg x_1, x_2$  "Distance between atoms much bigger than length of dipole"

↳ Taylor expansion:  $\frac{1}{1-x} = 1 + x + x^2 + \dots$

$$H_1 = \frac{e^2}{R} \left( 1 + \frac{1}{1-\frac{x_2-x_1}{R}} - \frac{1}{1-\frac{x_1}{R}} - \frac{1}{1-\frac{x_2}{R}} \right)$$

$$= \frac{e^2}{R} \left[ 1 + \left( 1 + \frac{x_2-x_1}{R} + \left( \frac{x_2-x_1}{R} \right)^2 \right) - \left( 1 + \left( -\frac{x_1}{R} \right) + \left( -\frac{x_1}{R} \right)^2 \right) - \left( 1 + \left( \frac{x_2}{R} \right) + \left( \frac{x_2}{R} \right)^2 \right) \right]$$

$$= \frac{e^2}{R} \left( -\frac{2x_1x_2}{R^2} \right) = -\frac{2e^2x_1x_2}{R^3}$$

Hamiltonian  $H = H_0 + H_1 = \frac{p_1^2}{2m} + \frac{1}{2} C x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2} C x_2^2 - \frac{2e^2x_1x_2}{R^3}$

Now use trick:  $x_b = \frac{x_1+x_2}{\sqrt{2}}$      $x_a = \frac{x_1-x_2}{\sqrt{2}}$

↳  $x_1 = \frac{x_b+x_a}{\sqrt{2}}$      $x_2 = \frac{x_b-x_a}{\sqrt{2}}$     → to add  $H_0$  and  $H_1$  together

For the momentum:  $p_1 = \frac{p_b+p_a}{\sqrt{2}}$      $p_2 = \frac{p_b-p_a}{\sqrt{2}}$

$$\Rightarrow H = \frac{(p_b+p_a)^2}{4m} + \frac{(p_b-p_a)^2}{4m} + \frac{(x_b+x_a)^2}{4} C + \frac{(x_b-x_a)^2}{4} C - \frac{e^2(x_b-x_a)^2}{R^3}$$

$$= \frac{p_b^2+p_a^2}{2m} + \frac{C(x_b^2+x_a^2)}{2} - \frac{e^2(x_b^2-x_a^2)}{R^3} = \frac{p_b^2}{2m} + x_b^2 \left( \frac{C}{2} - \frac{e^2}{R^3} \right) + \frac{p_a^2}{2m} + x_a^2 \left( \frac{C}{2} + \frac{e^2}{R^3} \right)$$

→ This is again the Hamiltonian of a harmonic oscillator

Frequency:  $\omega_{\pm} = \left[ C \pm \frac{2e^2}{R^3} \right] / m$      $\omega_0 = \sqrt{C/m}$     Taylor expansion

$$E_0 = 2 \cdot \frac{1}{2} \hbar \omega_0 = \hbar \omega_0$$

$$E = \frac{1}{2} \hbar (\omega_+ + \omega_-) = \frac{1}{2} \hbar \left[ 2\omega_0 - \frac{\omega_0}{4} \left( \frac{2e^2}{CR^3} \right)^2 \right]$$

Difference between the energy of the uncoupled and coupled dipole system - this is the binding energy

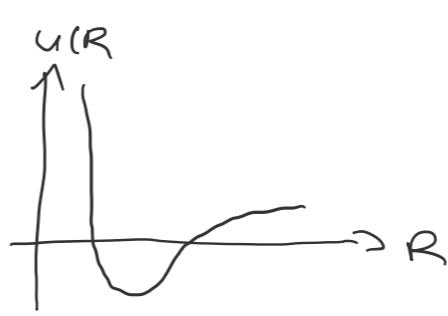
$$\Delta U = E - E_0 = \hbar \omega_0 - \frac{\hbar^2 \omega_0^3}{2C^2} \frac{1}{R^6} - \hbar \omega_0 = -\frac{\hbar^2 \omega_0^3}{2C^2} \frac{1}{R^6}$$

$$\Delta U \propto -R^{-6}$$

## Lennard-Jones Potential

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

where  $B = 4\varepsilon \sigma^{12}$  and  $A = 4\varepsilon \sigma^6$



## Full crystal

$$U_{total} = 4\varepsilon \frac{1}{2} \sum_j \left( \left( \frac{\sigma}{R_{ij}} \right)^{12} - \left( \frac{\sigma}{R_{ij}} \right)^6 \right)$$

Assumption: crystal so big that you can take only one atom and account for all its interactions

$N$  = # atoms

$R_{ij}$  = distance between atom  $i$  and  $j$

$R_1, R_2, R_3, \dots \equiv$  nearest, next-nearest, next-next-nearest, ... neighbour distance

$$x_j = \frac{R_j}{R_1}$$

$N_j$  = # numbers of neighbours of distance  $R_j$

with this  $\sum_j (R_{ij})^{-n} = \sum_j N_j \cdot R_j^{-n} = R_1^n \sum_j N_j x_j^{-n}$      $\underbrace{\sum_j N_j x_j^{-n}}_{A_n}$     They converge very fast!

Rewrite  $U_{total}$ :  $U_{total} = 2N\varepsilon \left[ A_{12} \left( \frac{\sigma}{R_1} \right)^{12} + A_6 \left( \frac{\sigma}{R_1} \right)^6 \right]$

$$\frac{dU_{total}}{dR_1} = 0 \Rightarrow \frac{R_1(\varepsilon)}{\sigma} = \left( \frac{2A_{12}}{A_6} \right)^{1/6}$$

→ This model gives the information of why noble gases condense to fcc