Condensed Matter Physics (Phy 771)

HW # 7 – Solution

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① for crystal with N atoms, the cohesive energy is

$$\mathcal{E} = 2N\epsilon\left[A_{12}\left(\frac{\sigma}{d_o}\right)^{12} - A_6\left(\frac{\sigma}{d_o}\right)^{6}\right] \quad \text{..... (1)}$$

where d_o is NN distance given by $d_o = \sigma\left(\frac{2A_{12}}{A_6}\right)^{1/6} \Rightarrow \frac{\sigma}{d_o} = \left(\frac{A_6}{2A_{12}}\right)^{1/6}$

and $A_6^{bcc} = 12.25$, $A_{12}^{bcc} = 9.11$, $A_6^{fcc} = 14.45$, $A_{12}^{fcc} = 12.13$ $\Rightarrow$

$$\frac{\mathcal{E}^{bcc}}{\mathcal{E}^{fcc}} = \frac{A_{12}^{bcc}\left(\frac{\sigma}{d}\right)_{bcc}^{12} - A_6^{bcc}\left(\frac{\sigma}{d}\right)_{bcc}^{6}}{A_{12}^{fcc}\left(\frac{\sigma}{d}\right)_{fcc}^{12} - A_6^{fcc}\left(\frac{\sigma}{d}\right)_{fcc}^{6}}$$

; where $\left(\frac{\sigma}{d}\right)_{bcc}^{12} = \left(\frac{A_6^{bcc}}{2A_{12}^{bcc}}\right)^2$ and $\left(\frac{\sigma}{d}\right)_{bcc}^{6} = \frac{A_6^{bcc}}{2A_{12}^{bcc}}$

$$= \frac{A_{12}^{bcc}\left(\frac{A_6^{bcc}}{2A_{12}^{bcc}}\right)^2 - A_6^{bcc}\left(\frac{A_6^{bcc}}{2A_{12}^{bcc}}\right)}{A_{12}^{fcc}\left(\frac{A_6^{fcc}}{2A_{12}^{fcc}}\right)^2 - A_6^{fcc}\left(\frac{A_6^{fcc}}{2A_{12}^{fcc}}\right)}$$

} similar relations for fcc structure

$$= \frac{(A_6^{bcc})^2/4A_{12}^{bcc} - (A_6^{bcc})^2/2A_{12}^{bcc}}{(A_6^{fcc})^2/4A_{12}^{fcc} - (A_6^{fcc})^2/2A_{12}^{fcc}} = \frac{4.118 - 8.236}{4.3034 - 8.6068} = 0.96$$

$\Rightarrow$ the fcc structure has higher cohesive energy and hence more stable than the bcc structure. Therefore, Neon (Ne) adapts the fcc structure.

(2)

$$A_\ell = \sum_{\vec{R}\neq 0} \left(\frac{d}{R}\right)^\ell$$

for simple cube $\vec{a_1} = a\hat{i}$, $\vec{a_2} = a\hat{j}$, $\vec{a_3} = a\hat{k}$, and

$$\vec{R} = n_1\vec{a_1} + n_2\vec{a_2} + n_3\vec{a_3} = a(n_1\hat{i} + n_2\hat{j} + n_3\hat{k})$$

$$\vec{R}^2 = a^2(n_1^2 + n_2^2 + n_3^2)$$

$$\Rightarrow A_\ell = \sum_{R\neq 0} \left(\frac{d^2}{R^2}\right)^{\ell/2}$$; for simple cube there are 6 NN with $d = a$

$$\Rightarrow A_\ell = \sum_{n_1,n_2,n_3} \left(\frac{a^2}{a^2(n_1^2+n_2^2+n_3^2)}\right)^{\ell/2} = \sum_{n_1,n_2,n_3} \left(\frac{1}{n_1^2+n_2^2+n_3^2}\right)^{\ell/2}$$

with $(n_1, n_2, n_3) = (0, 0, 0)$ is excluded

$$A_6 = \sum_{n_1,n_2,n_3\neq 0} \left(\frac{1}{n_1^2+n_2^2+n_3^2}\right)^3$$, now truncate the series after a certain number of terms $\Rightarrow$

$$A_6 = \sum_{n_1=-N}^{N} \sum_{n_2=-N}^{N} \sum_{n_3=-N}^{N} \frac{1}{(n_1^2+n_2^2+n_3^2)^3}$$; take $N = 20$

n1: -20 to 20 ; sum over 40 lattice points along a1 direction
n2: -20 to 20 ; sum over 40 lattice points along a2 direction
n3: -20 to 20 ; sum over 40 lattice points along a3 direction

overall, the sum is over 40*40*40 = 64,000 lattice points

≈ 8.4019

similarly for A_{12}

$$A_{12} = \sum_{n_1=-N}^{N} \sum_{n_2=-N}^{N} \sum_{n_3=-N}^{N} \frac{1}{(n_1^2+n_2^2+n_3^2)^6}$$

≈ 6.2022

the next mathematica code is for calculating A_6, A_{12} numerically.

```
In[1]:= (*Define the range of summation*)n = 20;

(*Initialize the sums*)
A6 = 0.0;
A12 = 0.0;

(*Sum over all lattice points*)
Do[Do[Do[If[n1 == 0 && n2 == 0 && n3 == 0, Continue[]]; (*Skip the origin*)rSquared = n1^2 + n2^2 + n3^2;
    A6 += 1 / (rSquared^3);
    A12 += 1 / (rSquared^6);, {n3, -n, n}], {n2, -n, n}], {n1, -n, n}];

(*Print the results*)
Print["A6 for simple cubic: ", A6];
Print["A12 for simple cubic: ", A12];
A6 for simple cubic: 8.40163
A12 for simple cubic: 6.20215
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(3) Argon has an FCC structure with $\epsilon = 0.0104\ eV$, $\sigma = 3.4\ \text{Å}$

NN distance $d_0 = \left(\frac{2A_{12}}{A_6}\right)^{1/6}\sigma = \left(\frac{2\times 12.1319}{14.4539}\right)^{1/6} \times 3.4\ \text{Å} = 3.71\ \text{Å}$

energy per atom E/N

$$E/N = -\frac{A_6^2}{2A_{12}}\epsilon = -\frac{(14.4539)^2}{2\times 12.1319} \times 0.0104\ eV = -0.089\ eV$$

Bulk modulus B

$$B = \frac{4\epsilon}{\sigma^3} A_{12}\left(\frac{A_6}{A_{12}}\right)^{5/2} = 0.019894\ \frac{eV}{\text{Å}^3}\ ;\ \text{using}$$

$1\ eV = 1.602\times 10^{-12}\ \text{dyne-cm}$ and $1\ \text{Å} = 10^{-8}\ \text{cm}$, we have

$$B = 0.019894 \times \frac{1.602\times 10^{-12}\ \text{dyne-cm}}{10^{-24}\ \text{cm}^3} = 3.18\times 10^{10}\ \frac{\text{dyne}}{\text{cm}^2}$$

These values are the same as those recorded in table 11.5

(4)

for NaCl crystal, $\frac{\mathcal{E}}{N} = k_e\left[-\frac{\alpha e^2}{d} + \frac{c}{d^{12}}\right]$ in SI units

where $k_e = 9\times10^9\ N.m^2/C^2$

at equilibrium, $d_0 = \left(\frac{12c}{e^2\alpha}\right)^{1/11} \Rightarrow \frac{c}{d_0^{12}} = \frac{e^2\alpha}{12d_0} \Rightarrow$

$$\frac{\mathcal{E}}{N} = k_e\left[-\frac{\alpha e^2}{d_0} + \frac{e^2\alpha}{12d_0}\right] = \underbrace{-k_e\frac{\alpha e^2}{d_0}}_{\mathcal{E}_{Coulomb}} + \underbrace{k_e\frac{e^2\alpha}{12d_0}}_{\mathcal{E}_{repulsive}}$$

$$= \mathcal{E}_{Coulomb} + \mathcal{E}_{repulsive}$$

$$\Rightarrow \mathcal{E}_{Coulomb} = -k_e\frac{\alpha e^2}{d_0} = -\frac{9\times10^9 \times 1.747 \times (1.602\times10^{-19})^2}{2.82\times10^{-10}}$$

$$= -14.31\times10^{-19}\ J = \frac{-14.31\times10^{-19}}{1.602\times10^{-19}}\ eV = -8.93\ eV$$

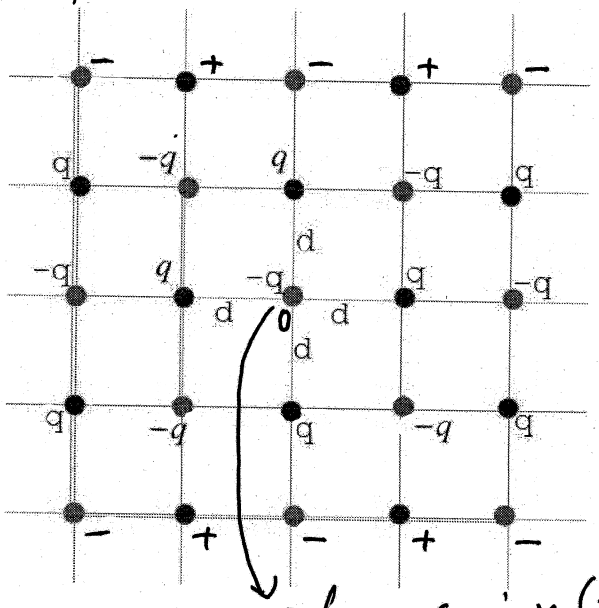
$$\mathcal{E}_{repulsive} = k_e\frac{e^2\alpha}{12d_0} = \frac{9\times10^9 \times (1.602\times10^{-19})^2 \times 1.747}{12\times2.82\times10^{-10}} = 1.192\times10^{-19}\ J$$

$$= 0.744\ eV$$

$$\Rightarrow \mathcal{E} = -8.93 + 0.744 = -8.18\ eV$$

$\Rightarrow |\mathcal{E}| = 8.18\ eV$ which is identical to the recorded value in table 11.8 of textbook. See that the contribution of the repulsive term is very small compared with the attractive (Coulomb) term.

(5) To calculate Madelung energy/molecule for an ionic 2D crystal, we sum the contributions from all ions (excluding the reference ion located at the origin (-q)). So the first five terms are



$$\frac{\mathcal{E}}{N} = -\frac{4e^2}{d} + \frac{4e^2}{\sqrt{2}d} + \frac{4e^2}{2d} - \frac{8e^2}{\sqrt{5}d} + \frac{4e^2}{\sqrt{8}d} - \cdots$$

$$= -\frac{e^2}{d}\left(4 - \frac{4}{\sqrt{2}} - 2 + \frac{8}{\sqrt{5}} - \frac{4}{\sqrt{8}} + \cdots\right) = -\frac{e^2}{d}(1.334) \equiv -\frac{e^2}{d}\alpha$$

$$\Rightarrow \alpha \approx 1.334$$

Now numerically,

$$\alpha = \sum_{\substack{n_1,n_2 \\ (n_1,n_2)\neq(0,0)}}^{\infty} \frac{\pm 1}{|\vec{R}|/d} \quad ; \text{ where } \vec{R} = n_1 d\hat{i} + n_2 d\hat{j} = d(n_1\hat{i} + n_2\hat{j})$$

$$|\vec{R}| = d\sqrt{n_1^2 + n_2^2}$$

$$= \sum_{\substack{n_1,n_2 \\ (n_1,n_2)\neq(0,0)}}^{\infty} \frac{(-1)^{n_1+n_2}}{\sqrt{n_1^2+n_2^2}} \quad ; \text{ the factor } (-1)^{n_1+n_2}$$

alternate the sign and the factor $\sqrt{n_1^2+n_2^2}$ is the distance of any ion relative to the reference ion (-q) located at the origin

Now the sum in α results in a negative value because attractive forces dominate repulsive forces. Thus, to align with the standard definition of α being a positive quantity, we take the absolute value. Technically, α is the value obtained when the size of the 2D crystal is infinite ($L \to \infty$), but practically, one get a good approximation by truncating the sum at large value of L. Let us assume a square box surrounding the ref ion $(-q)$ located at the origin $(0,0)$, with n ions in each direction, so $-n < n_1 < +n$, $-n < n_2 < +n$

$$\Rightarrow \alpha = \sum_{\substack{(n_1,n_2)=(-n,-n) \\ (n_1,n_2)\neq(0,0)}}^{(+n,+n)} \frac{(-1)^{n_1+n_2}}{\sqrt{n_1^2+n_2^2}}$$

, the next code takes $n = 1000$ and the obtained value of α is $\alpha = 1.6148$

In[166]:=
```
(*Define the cutoff radius*)n = 1000; (*Increase n for higher precision*)
(*Initialize the Madelung sum*)madelung = 0.0;

(*Sum over all lattice points (i,j) within radius n*)
Do[Do[If[n1 == 0 && n2 == 0, Continue[]]; (*Skip the origin*)
   term = (-1) ^ (n1 + n2) / Sqrt[n1 ^ 2 + n2 ^ 2];
   madelung += term;, {n2, -n, n}], {n1, -n, n}];

(*Take absolute value for the Madelung constant*)
madelung = Abs[madelung];

(*Print the result*)
Print["Madelung constant for square lattice: ", NumberForm[madelung, {6, 4}]];
```
```
Madelung constant for square lattice: 1.6148
```