

Condensed Matter Physics (phy 771)

HW # 7 - solution

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① for crystal with N atoms, the cohesive energy is

$$\mathcal{E} = 2NE \left[A_{12} \left(\frac{\sigma}{d_0} \right)^{12} - A_6 \left(\frac{\sigma}{d_0} \right)^6 \right] \dots (1)$$

where d_0 is NN distance given by $d_0 = \sigma \left(\frac{2A_{12}}{A_6} \right)^{1/6} \Rightarrow \frac{\sigma}{d_0} = \left(\frac{A_6}{2A_{12}} \right)^{1/6}$

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

$$\frac{\mathcal{E}^{bcc}}{\mathcal{E}^{fcc}} = \frac{A_{12}^{bcc} \left(\frac{\sigma}{d} \right)_{bcc}^{12} - A_6^{bcc} \left(\frac{\sigma}{d} \right)_{bcc}^6}{A_{12}^{fcc} \left(\frac{\sigma}{d} \right)_{fcc}^{12} - A_6^{fcc} \left(\frac{\sigma}{d} \right)_{fcc}^6} ; \text{ where } \left(\frac{\sigma}{d} \right)_{bcc}^{12} = \left(\frac{A_6^{bcc}}{2A_{12}^{bcc}} \right)^2$$

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

$$= \frac{(A_6^{bcc})^2 / 4A_{12}^{bcc} - (A_6^{bcc})^2 / 2A_{12}^{bcc}}{(A_6^{fcc})^2 / 4A_{12}^{fcc} - (A_6^{fcc})^2 / 2A_{12}^{fcc}}$$

$$= \frac{4.118 - 8.236}{4.3034 - 8.6068} = 0.96$$

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

②

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

for simple cube $\vec{a}_1 = a\hat{i}$, $\vec{a}_2 = a\hat{j}$, $\vec{a}_3 = a\hat{k}$, and

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 = a(n_1\hat{i} + n_2\hat{j} + n_3\hat{k})$$

$$R^2 = a^2(n_1^2 + n_2^2 + n_3^2)$$

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

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

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

$$A_6 = \sum_{n_1, n_2, n_3 \neq 0} \left(\frac{1}{n_1^2 + n_2^2 + n_3^2} \right)^3, \text{ now truncate the series}$$

after a certain number of terms $\Rightarrow$

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

$$\approx 8.4019$$

similarly for A_{12}

$$A_{12} = \sum_{n_1=-N}^N \sum_{n_2=-N}^N \sum_{n_3=-N}^N \frac{1}{(n_1^2 + n_2^2 + n_3^2)^6} \approx 6.2022$$

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

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n = (*Define the range of summation*) n = 20;

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(*Initialize the sums*)

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A6 = 0.0;

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A12 = 0.0;

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(*Sum over all lattice points*)

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Do[Do[Do[If[n1 == 0 && n2 == 0 && n3 == 0, Continue[]]; (*Skip the origin*) rSquared = n1^2 + n2^2 + n3^2;

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  A6 += 1 / (rSquared^3);

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  A12 += 1 / (rSquared^6);, {n3, -n, n}], {n2, -n, n}], {n1, -n, n}];

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(*Print the results*)

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Print["A6 for simple cubic: ", A6];

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Print["A12 for simple cubic: ", A12];

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A6 for simple cubic: 8.40163

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A12 for simple cubic: 6.20215

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③ Argon has an FCC structure with $E = 0.0104 \text{ eV}$, $\sigma = 3.4 \text{ \AA}$

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

energy per atom ϵ/N

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

Bulk modulus B

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

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

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

These values are the same as those recorded in table 11.5

④

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

where $k_e = 9 \times 10^9 \text{ N.m}^2/\text{C}^2$

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

$$\begin{aligned} \frac{\epsilon}{N} &= k_e \left[-\frac{\alpha e^2}{d_0} + \frac{e^2 \alpha}{12 d_0} \right] = \underbrace{-k_e \frac{\alpha e^2}{d_0}}_{\epsilon_{\text{Coulomb}}} + \underbrace{k_e \frac{e^2 \alpha}{12 d_0}}_{\epsilon_{\text{repulsive}}} \\ &= \epsilon_{\text{Coulomb}} + \epsilon_{\text{repulsive}} \end{aligned}$$

$$\begin{aligned} \Rightarrow \epsilon_{\text{Coulomb}} &= -k_e \frac{\alpha e^2}{d_0} = -9 \times 10^9 \times \frac{1.747 \times (1.602 \times 10^{-19})^2}{2.82 \times 10^{-10}} \\ &= -14.31 \times 10^{-19} \text{ J} = \frac{-14.31 \times 10^{-19}}{1.602 \times 10^{-19}} \text{ eV} = -8.93 \text{ eV} \end{aligned}$$

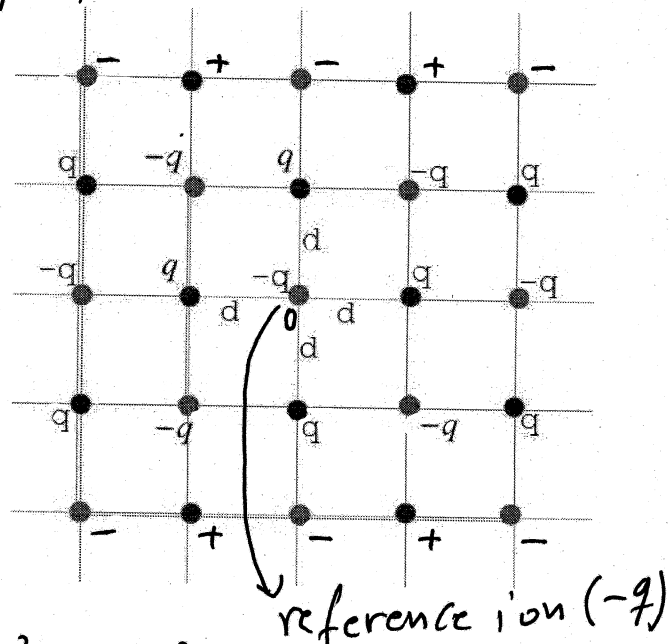
$$\begin{aligned} \epsilon_{\text{repulsive}} &= k_e \frac{e^2 \alpha}{12 d_0} = 9 \times 10^9 \times \frac{(1.602 \times 10^{-19})^2 \times 1.747}{12 \times 2.82 \times 10^{-10}} = 1.192 \times 10^{-19} \text{ J} \\ &= 0.744 \text{ eV} \end{aligned}$$

$$\Rightarrow \epsilon = -8.93 + 0.744 = -8.18 \text{ eV}$$

$\Rightarrow |\epsilon| = 8.18 \text{ eV}$ 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



$$\frac{\epsilon}{N} = -\frac{4e^2}{d} + \frac{4e^2}{\sqrt{2}d} + \frac{4e^2}{2d} - \frac{8e^2}{\sqrt{5}d} + \frac{4e^2}{\sqrt{8}d} - \dots$$

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

$$\Rightarrow \alpha \approx 1.334$$

now numerically,

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

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

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

alternates 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 ($L \rightarrow \infty$), but practically, one gets 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 $-n < n_1 < +n$, $-n < n_2 < +n$

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

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

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In[169]:= (*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

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