Part III : MECHANICAL PROPERTIES

Chapter 11 : Cohesion of Solids

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What holds crystal together?.

Solids are stable structures, and therefore there exist interactions holding atoms in a crystal together. Forming a crystal implies that the energy of the crystal is lower than the energy of the free atoms. The amount of energy which is required to decompose the crystal into a set of free atoms is called the cohesive energy of the crystal, so

Cohesive energy = energy of free atoms – crystal energy

$\mathcal{E} = N\epsilon_{atom} - \mathcal{E}_{solid}(N)$; where ϵ_{at} is the energy of an isolated atom, $\mathcal{E}_{solid}(N)$ energy of the solid.

if $\mathcal{E} > 0$, solid is stable

$\mathcal{E} < 0$; solid is unstable and hence can't be formed.

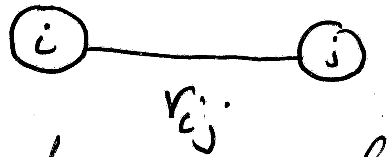
$\frac{\mathcal{E}}{N}$ varies for different solids from 1 to 10 eV/atom except inert gases in which $\mathcal{E}/N$ is $\sim$ 0.1 eV/atom.

The cohesive energy ($\mathcal{E}$) controls the melting temperature of a solid

11.2 : Van der waals bonding in inert gasses:

consider an inert gas crystal composed of N atoms. consider a pair of atoms separated by a distance r_{ij}, then the interaction energy between the tow atoms is given by $\phi(r_{ij})$

the total interaction (Potential) energy of all atoms is given by

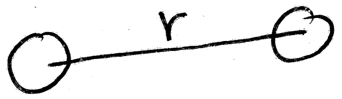


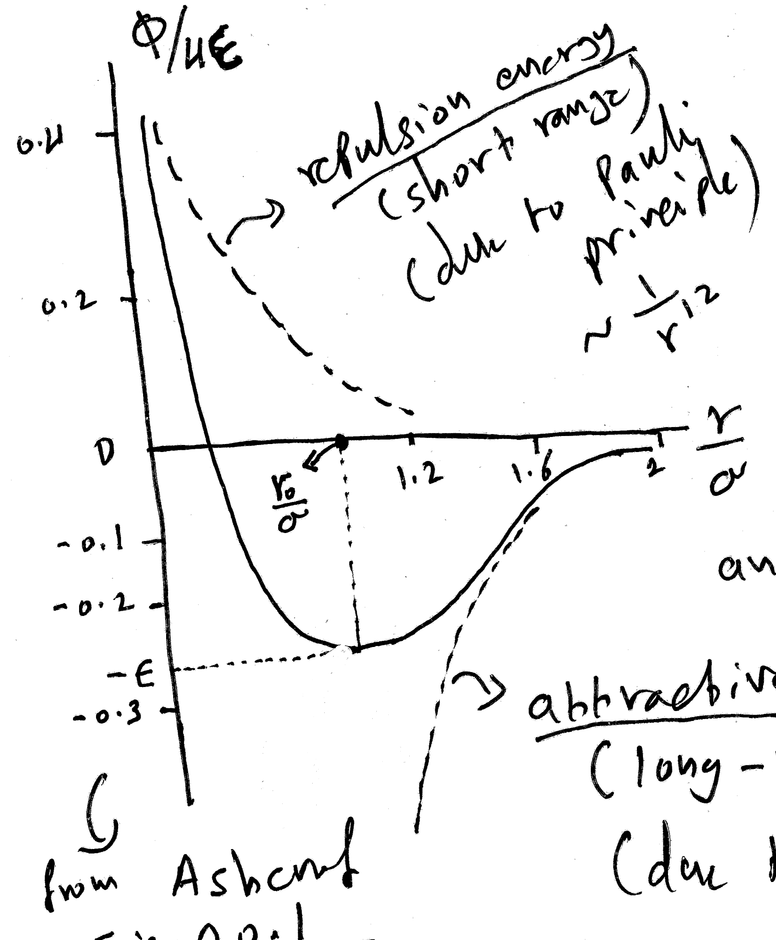
$$\mathcal{E} = N \sum_{\substack{ij \\ \to \text{ fix } i \text{ and run over } j}} \phi(r_{ij})$$; but Potential energy of atom $i \to j$ is the same as Potential energy of $j \to i$, so to avoid double counting, we divide by 2 $\Rightarrow$

$$\mathcal{E} = \frac{N}{2} \sum_{ij} \phi(r_{ij}) \; ; \text{ with } \underbrace{\phi(r) = -4\epsilon\left[\left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r}\right)^{12}\right]}_{\text{Lennard-Jones 6-12 Potential}}$$

where

σ = characteristic length
4ϵ = characteristic energy. } can be measured experimentally.





↳ from Ashcroft Fig 20.1

; to find equilibrium separation, r_0, set

$$\frac{d\phi}{dr} = 0 \Rightarrow r_0 = (2)^{1/6}\sigma \approx 1.12\sigma$$

and hence $\phi(r_0) = -\epsilon$

or $\frac{\phi(r_0)}{4\epsilon} = -0.25$

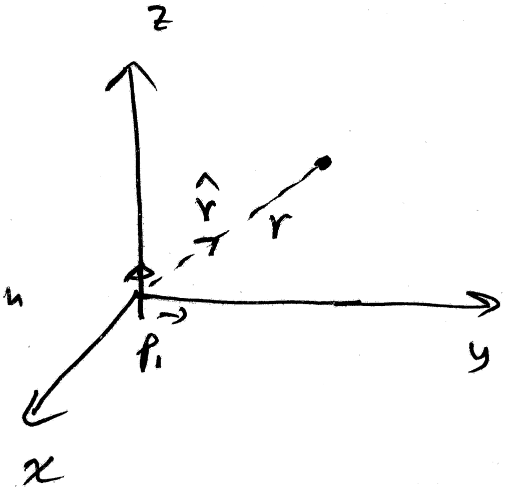
→ attractive energy
(long-range)
(due to dip-dipo interactions)
(van der waals)
$\sim -\frac{1}{r^6}$

so for large separation $r > r_0$, the force is attraction, tending to pull the atoms together. on the other hand, for $r < r_0$, the force becomes repulsive, tending to push the atoms apart. The repulsive and attractive forces cancel each other exactly at $r = r_0$ i.e $\vec{F}_A + \vec{F}_R = 0$, which is the equilibrium separation distance.

The origin of the repulsive force is mainly due to Pauli exclusion principle; two electrons can not occupy the same orbital. As atoms approach each other, the orbits of the electrons begin to overlap. That is forbidden by Pauli principle, as it increases the total energy of the system. Historically, this term was proposed to be $\sim \frac{1}{r^{12}}$ that quite well fits experimental data of inert gas crystals.

- the 2^{nd} term $\sim \frac{1}{r^6}$ originates from dip-dip interactions recall that the charge distribution in a single atom is spherically symmetric. hence its dipole moment $\vec{p} = 0$. However, at any moment of time, there may be non-zero electric dipole moment that is caused by fluctuations of the electronic charge around the atom. According to EM theory, this dipole moment produce an electric field given by

$$\vec{E}_{dip} = \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\left[3(\vec{p}_1\cdot\hat{r})\hat{r} - \vec{p}_1\right]$$

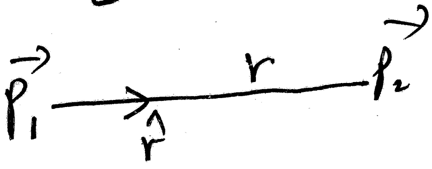


This field interacts with a second dipole placed at a distance r with an interaction energy (potential) given by

$$\Phi(\vec{r}) = -\vec{p}_2\cdot\vec{E}_{dip}$$

$$= -\frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\left[3(\vec{p}_1\cdot\hat{r})(\vec{p}_2\cdot\hat{r}) - \vec{p}_1\cdot\vec{p}_2\right]$$

$$= \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\left\{\vec{p}_1\cdot\vec{p}_2 - 3(\vec{p}_1\cdot\hat{r})(\vec{p}_2\cdot\hat{r})\right\}$$



↳ textbook uses Gaussian units (with $\frac{1}{4\pi\varepsilon_0} = 1$)

from the last expression, we see that the energy of interaction is proportional to the product of the dipole moments and inversely proportional to the cube of the distance ; i.e $\Phi \sim -\frac{p_1 p_2}{r^3}$

p_1 : electric dipole of atom ① caused by charge fluctuations

p_2 : electric dipole of atom ② which is induced by the field of the first dipole. Now $p_2 = \alpha_2 E'_{dip} \sim \alpha_2 \frac{p_1}{r^3}$ } time-average

$$\Rightarrow \Phi \sim -\alpha_2 \frac{p_1^2}{r^6}$$; Note that although $\langle p_1(t)\rangle = 0$, $\langle p_1^2(t)\rangle \neq 0$

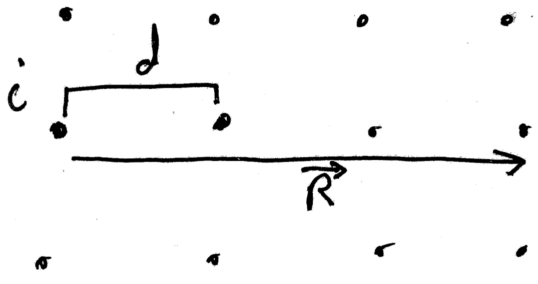
$\sim -\frac{1}{r^6} \Rightarrow$ for formal derivation, see Kittel chapter 3 coming back to L-J (6-12) potential given by

$$\phi(r) = -4\epsilon\left[\left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r}\right)^{12}\right]$$; σ, ϵ are measured experimentally for inert gases in the gaseous state and in the low density limit, and the corresponding values for inert gas crystals are deduced from these measurements.

Nobel gas	(hcp) He	(fcc) Ne	(fcc) Ar	(fcc) Kr	(fcc) Xe
ϵ (eV)	8.6×10^{-4}	0.0031	0.0104	0.0104	0.020
σ (Å)	2.56	2.74	3.4	3.65	3.98

Table 11.3 in text book.

Now consider an inert gas crystal with N atoms. Pick up an atom located at the origin ($\vec{R}=0$) and assuming that this atom interact with all other atoms ($\vec{R} \neq 0$) through L-J potential, then the total energy is given by



3D Bravais lattice of inert gas crystal

$\vec{R}$: Bravais lattice vector

d : nearest neighbor distance

$$\mathcal{E} = \frac{1}{2} N \sum_{\vec{R} \neq 0} \phi(\vec{R})$$

$$= \frac{1}{2} N \, 4\epsilon \sum_{\vec{R} \neq 0} \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

$\Rightarrow$ energy per atom

$$\frac{\mathcal{E}}{N} = 2\epsilon \sum_{R \neq 0} \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

This can be written as

$$\mathcal{E}/N = 2\epsilon \sum_{\vec{R}\neq 0}\left[\left(\frac{\sigma}{d}\right)^{12}\left(\frac{d}{R}\right)^{12} - \left(\frac{\sigma}{d}\right)^{6}\left(\frac{d}{R}\right)^{6}\right]$$

$$= 2\epsilon\left[\left(\frac{\sigma}{d}\right)^{12}\underbrace{\sum_{\vec{R}\neq 0}\left(\frac{d}{R}\right)^{12}}_{A_{12}} - \left(\frac{\sigma}{d}\right)^{6}\underbrace{\sum_{\vec{R}\neq 0}\left(\frac{d}{R}\right)^{6}}_{A_6}\right]$$

$$= 2\epsilon\left[A_{12}\left(\frac{\sigma}{d}\right)^{12} - A_6\left(\frac{\sigma}{d}\right)^{6}\right]$$; where

$A_l = \sum_{\vec{R}\neq 0}\left(\frac{d}{R}\right)^{l}$ lattice sum that can be calculated and then the energy depends only on the nearest-neighbor separation d

the A6 and A12 for simple cube are calculated in problem 2 in HW#7

Table 11.4:

crystal	fcc	bcc	hcp
A_6	14.4539	12.2537	14.4549
A_{12}	12.1319	9.1142	12.1323
$\frac{A_6^2}{2A_{12}}$	8.6102	8.2373	8.6111

Notice that A_{12} is dominated by the nearest neighbours (12 in fcc and hcp, and 8 in bcc) but more distant neighbours affect A_6. To find the equilibrium separation, d_0, we minimize $\mathcal{E}/N$

$$\frac{d}{dd}(\mathcal{E}/N) = 0 = 2\epsilon\left[A_{12}\cdot 12\cdot\left(\frac{\sigma}{d_0}\right)^{11}\left(\frac{-\sigma}{d_0^2}\right) + A_6\cdot 6\cdot\left(\frac{\sigma}{d_0}\right)^{5}\frac{\sigma}{d_0^2}\right]$$

$$\frac{d(\mathcal{E}/N)}{dd} = 0 = 12\epsilon\left[-2A_{12}\left(\frac{\sigma}{d_0}\right)^{12}\cdot\frac{1}{d_0} + A_6\left(\frac{\sigma}{d_0}\right)^{6}\cdot\frac{1}{d_0}\right]$$

$$= \frac{12\epsilon}{d_0}\left[A_6\left(\frac{\sigma}{d_0}\right)^{6} - 2A_{12}\left(\frac{\sigma}{d_0}\right)^{12}\right] = 0$$

$$\Rightarrow A_6\left(\frac{\sigma}{d_0}\right)^{6} = 2A_{12}\left(\frac{\sigma}{d_0}\right)^{12} \Rightarrow A_6 = 2A_{12}\left(\frac{\sigma}{d_0}\right)^{6}$$

$$\Rightarrow \frac{\sigma}{d_0} = \left(\frac{A_6}{2A_{12}}\right)^{1/6} \Rightarrow \boxed{d_0 = \left(\frac{2A_{12}}{A_6}\right)^{1/6}\sigma} \cdots\cdots\cdots (11.10)$$

so the cohesive energy at equilibrium separation is

$$\frac{\mathcal{E}}{N}(d=d_0) = 2\epsilon\left[A_{12}\left(\frac{A_6}{2A_{12}}\right)^{2} - A_6\left(\frac{A_6}{2A_{12}}\right)\right]$$

$$= 2\epsilon\left[\frac{A_6^2}{4A_{12}} - \frac{A_6^2}{2A_{12}}\right] = \frac{2\epsilon A_6^2}{A_{12}}\left[\frac{1}{4} - \frac{1}{2}\right]$$

$$\boxed{\frac{\mathcal{E}}{N} = -\frac{A_6^2}{2A_{12}}\epsilon} \;--- (11.11)$$

Typically $\underbrace{0.01 \text{ to } 0.1}$ eV/atom

see table 11.3 for values of ϵ, and table 11.4 for values of $A_6^2/2A_{12}$

- compressibility and Bulk modulus:

the compressibility K_T (or isothermal compressibility) is defined as $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. it measures the fractional volume change of a solid when pressure is applied. can be measured experimently.

the Bulk modulus B is the inverse of K_T

$$B = \frac{1}{K_T} = -V\left(\frac{\partial P}{\partial V}\right)_T$$

; B is a measure of the stiffness (or hardness) of the crystal now for any thermodynamic system, the internal energy $\mathcal{E} = \mathcal{E}(S, V, N) \Rightarrow$ or U = U (S, V, N) in other textbooks

$$d\mathcal{E} = dU = TdS - PdV + \mu dN$$

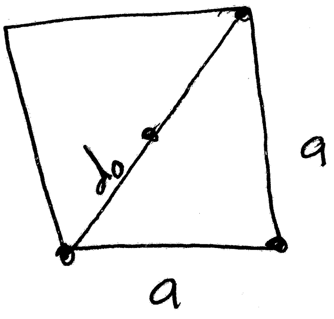
for fixed N and at $T = 0 \Rightarrow d\mathcal{E} = -PdV$

$$\Rightarrow P = -\left(\frac{\partial \mathcal{E}}{\partial V}\right) \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = -\frac{\partial^2 \mathcal{E}}{\partial V^2}$$

$\Rightarrow B = -V\left(\frac{\partial P}{\partial V}\right)_T = V\frac{\partial^2 \mathcal{E}}{\partial V^2}$; let us calculate B for an fcc lattice, that has 4 atom/unit cell

nearest-neighbour $d_0 = \frac{\sqrt{2}\, a}{2} \times \frac{\sqrt{2}}{\sqrt{2}}$

$$= \frac{\cancel{2}}{\cancel{2}\sqrt{2}}\, a = \frac{a}{\sqrt{2}}$$



now volume per atom $= \frac{a^3}{4} \equiv \frac{V}{N}$

$$\Rightarrow \frac{V}{N} = \frac{a^3}{4} = \frac{(\sqrt{2}\, d_0)^3}{4} = \frac{2^{3/2} d_0^3}{4} \Rightarrow d_0^3 = \frac{2^2}{2^{3/2}}\frac{V}{N}$$

$$= \sqrt{2}\,\frac{V}{N}$$

$\Rightarrow d_0 = 2^{1/6}\frac{V^{1/3}}{N^{1/3}}$, so

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

$$= 2N\epsilon\left[A_{12}\frac{\sigma^{12}N^4}{4V^4} - A_6\frac{\sigma^6 N^2}{2V^2}\right\}$$

$$\Rightarrow \frac{\partial^2 \mathcal{E}}{\partial V^2} = 2N\epsilon\left\{A_{12}\frac{20\sigma^{12}N^4}{4V^6} - A_6\frac{6\sigma^6 N^2}{2V^4}\right\}$$

$$\Rightarrow B = N\epsilon\left[A_{12}\,\frac{10\,\sigma^{12}N^4}{V^5} - A_6\,\frac{6\,\sigma^6 N^2}{V^3}\right]$$

but $V = Nv = N\left(\frac{V}{N}\right) = N\,\frac{a^3}{4} = \frac{N}{4}\left(\sqrt{2}\,d_0\right)^3$

$$= N\,\frac{2^{3/2}}{2^2}\,d_0^3 \quad ;\ \text{but} \quad \boxed{d_0 = \left(\frac{2A_{12}}{A_6}\right)^{1/6}\sigma} \text{ --(11.10)}$$

$$= N\,\frac{2^{3/2}}{2^2}\left(\frac{2A_{12}}{A_6}\right)^{1/2}\sigma^3 = N\left(\frac{A_{12}}{A_6}\right)^{1/2}\sigma^3$$

substitute back in B, we get

$$B = N\epsilon\left[10 A_{12}\sigma^{12}N^4 \times \frac{1}{N^5\sigma^{15}}\left(\frac{A_6}{A_{12}}\right)^{5/2} - 6A_6\sigma^6N^2 \times \frac{1}{N^3\sigma^9}\left(\frac{A_6}{A_{12}}\right)^{3/2}\right]$$

$$= N\epsilon\left[\frac{10\,A_6^{5/2}}{A_{12}^{3/2}N\sigma^3} - \frac{6\,A_6^{5/2}}{A_{12}^{3/2}N\sigma^3}\right] = \frac{4\,A_6^{5/2}\,\epsilon}{A_{12}^{3/2}\,\sigma^3}$$

$$\boxed{B = \frac{4\epsilon}{\sigma^3}\,A_{12}\left(\frac{A_6}{A_{12}}\right)^{5/2}} \text{ ... (11.13)}$$

To calculate the values of d_0, $\mathcal{E}/N$, B, use the values of A12, A6, σ, ϵ from tables 11.3 and 11.4

Table 11.5. Properties of noble gases compared with predictions of Lennard-Jones potentials

Noble Gas	Ne	Ar	Kr	Xe
Experimental d_0 (Å)	3.13	3.75	3.99	4.33
d_0 from Eq. (11.10) (Å)	2.99	3.71	3.98	4.34
Experimental $\mathcal{E}/N$ (eV/atom)	−0.02	−0.08	−0.11	−0.17
$\mathcal{E}/N$ from Eq. (11.11)	−0.027	−0.089	−0.120	−0.172
Experimental B (dyne/cm^2)	$1.1 \cdot 10^{10}$	$2.7 \cdot 10^{10}$	$3.5 \cdot 10^{10}$	$3.6 \cdot 10^{10}$
B from Eq. (11.13)	$1.81 \cdot 10^{10}$	$3.18 \cdot 10^{10}$	$3.46 \cdot 10^{10}$	$3.81 \cdot 10^{10}$

Results show agreement at roughly the 10% level. Source: Ashcroft and Mermin (1976), p. 401.

Ionic Bonding:

Crystals that can be pictured as formed by positive and negative ions are referred to as ionic crystals. An important quantity in the study of ionic crystals is the Coulomb interaction energy (Madelung energy) between ions of the crystals in the point ion approximation. The cohesive energy for an ionic crystal is the energy required to dissociate the lattice into positive and negative ions at infinite separation. Four common types of structures found in ionic crystals are NaCl structure which is face-centered cubic and CsCl which is body-centered cubic, zincblende structure, and the wurtzite structure. Let us now consider the case NaCl which is one of the best examples of an ionic compound. In the crystalline state, each Na atom loses its single valence electron to a neighboring Cl atom, producing Na^+ and Cl^- ions which have filled electronic shells. As a result an ionic crystal is formed containing positive and negative ions coupled by a strong electrostatic interaction.

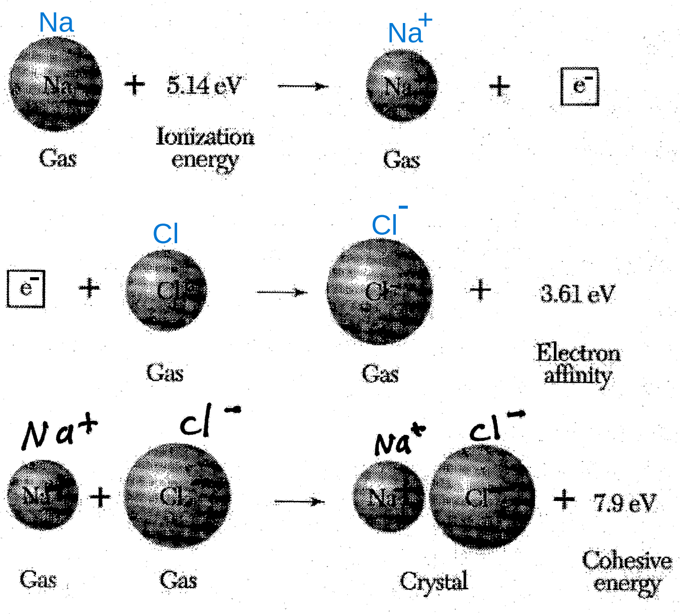


Fig 3.8 in Kittle

$\underset{11}{Na} : 1s^2/2s^2\,2p^6/\underbrace{3s^{①}}_{\text{valence shell}}$ ① valence electron

$\underset{11}{Na^+} : \underbrace{1s^2/2s^2\,2p^6/}_{\text{closed shell}}$ closed shell similar to Ne

---

$\underset{17}{Cl} : 1s^2/2s^2 2p^6/3s^2 3p^5$

$Cl^- : 1s^2/2s^2 2p^6/\underbrace{3s^2 3p^6/}$ close shell similar to Ar

Atom	Electron affinity (eV)	Atom	First ionization potential (eV)
H	0.75	Li	5.32
F	3.40	Na	5.14
Cl	3.61	K	4.34
Br	3.36	Rb	4.18
I	3.06	Cs	3.90

The ionization energy of Na is 5.1 eV and the electron affinity (the energy gained when the atom gains an electron) of a Cl atom is 3.6 eV. These events are unfavorable on their own.

The cohesive energy for one pair of NaCl is conventionally taken to be the energy needed to separate the ions of NaCl into free ions (Na+ and Cl-) at rest and at infinite separation.

In the NaCl crystal, the total cohesive energy results from two contributions: the long-range Coulomb interactions between the charged ions and the short-range core–core repulsion due to the Pauli principle prevents the crystal from collapsing

$$\mathcal{E} = \mathcal{E}(d)^{coul} + \mathcal{E}(d)^{core} \; ; \quad d: \text{nearest-neighbour distance} \quad ---(1)$$

net is attractive 90 %

repulsive 10 %

the cohesive energy per ion pair takes the form

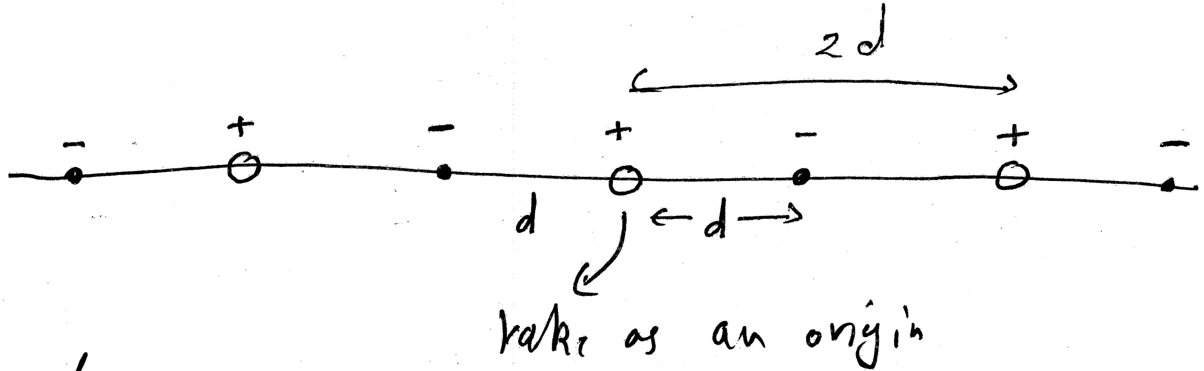
$$\frac{\mathcal{E}}{N_{\text{ion pair}}} = \underbrace{-\alpha\frac{e^2}{d}}_{\mathcal{E}^{\text{coul}}\text{ (Madelung energy)}} + \underbrace{\frac{C}{d^{12}}}_{\mathcal{E}^{\text{core}}}$$

; α is called Madelung constant (dimensionless)

$\mathcal{E}^{\text{core}}$ ($\frac{C}{d^{12}}$: based on experimental observations)

Now let us see how to find α

① 1D chain



$$\mathcal{E}^{\text{coul}} = \frac{-e^2}{d}\times 2 + \frac{e^2}{2d}\times 2 - \frac{e^2}{3d}\times 2 + \frac{e^2}{4d}\times 2 \cdots\cdots$$

$$= \frac{e^2}{d}\left[2\left(-1+\frac{1}{2}-\frac{1}{3}+\frac{1}{4}-\cdots\cdots\right)\right]$$

$$= -\frac{e^2}{d}\underbrace{\left[2\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\cdots\cdots\right)\right]}_{\alpha} = -\alpha\frac{e^2}{d}$$

where $\alpha = 2\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\cdots\right) = 2\ln 2 \simeq 1.386$

recall that $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} \cdots\cdots \Rightarrow$ let $x=1$

$\Rightarrow \ln 2 = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \cdots\cdots$. α always > 0

② 3D Lattice:

of 1st nn = 6 at adistance d

" 2n nn = 12 at distance $\sqrt{2}\,d$

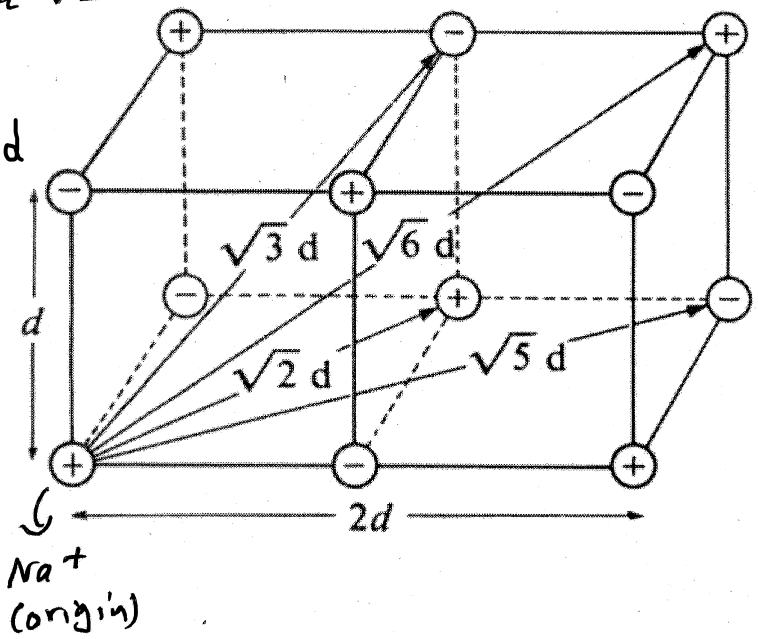
" 3d nn = 8 at $\sqrt{3}\,d$

" 4th nn = 6 at $\sqrt{4}\,d = 2d$

" 5th nn = 24 at $\sqrt{5}\,d$

and so on,

the coulomb energy of the Na+ ion placed at the origin is the sum



$$\mathcal{E}^{coul} = -\frac{6e^2}{d} + \frac{12e^2}{\sqrt{2}d} - \frac{8e^2}{\sqrt{3}\,d} + \frac{6e^2}{\sqrt{4}d} - \frac{24e^2}{\sqrt{5}\,d} + \cdots$$

$$= -\frac{e^2}{d}\underbrace{\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \cdots\right)}_{\alpha} = -\alpha\frac{e^2}{d}$$

the value of α is determined by the geometry of the lattice only and independent of the ionic radius and charge. The above $\mathcal{E}^{coul}$ is actually the coulomb energy of one pair of NaCl. The total coulomb energy is $\mathcal{E}^{coul}_{tot} = -N_{ion\ pairs}\frac{e^2}{d}\alpha$

Table 11.7. Madelung constants α for the most common ionic crystal structures

Structure	Madelung constant α
Cesium chloride	1.76268
Sodium chloride	1.74757
Wurtzite	1.638704
Zincblende	1.63806

$\because$ $\dfrac{\mathcal{E}}{N_{\text{ion Pairs}}} = -\dfrac{\alpha e^2}{d} + \dfrac{C}{d^{12}}$; let us find d_0 and $\dfrac{\mathcal{E}}{N_{\text{ion Pairs}}}$ at equilibrium distance

$$\Rightarrow \frac{d}{dd}\left(\mathcal{E}/N\right) = 0 = \frac{\alpha e^2}{d_0^2} - \frac{12C}{d_0^{13}} \Rightarrow d_0 = \left(\frac{12C}{e^2\alpha}\right)^{1/11}$$

$$\overset{\text{or}}{\Rightarrow} \text{ i.e } d_0^{11} = \frac{12C}{e^2\alpha} \Rightarrow \frac{C}{d_0^{11}} = \frac{e^2\alpha}{12} \Rightarrow \frac{C}{d_0^{12}} = \frac{e^2\alpha}{12d_0}$$

$$\Rightarrow \frac{\mathcal{E}}{N_{\text{ion-Pair}}} = -\frac{\alpha e^2}{d_0} + \frac{\alpha e^2}{12d_0} = \frac{\alpha e^2}{d_0}\left(\frac{1}{12} - 1\right) = -\frac{11}{12}\alpha\frac{e^2}{d_0} \quad \text{---} (11.26)$$

the results of this expression are compared with experimental data in Table 11.8

in SI units $\dfrac{\mathcal{E}}{N} = k_e\left[-\dfrac{\alpha e^2}{d} + \dfrac{C}{d^{12}}\right] = k_e\left[-\dfrac{\alpha e^2}{d_0} + \dfrac{e^2\alpha}{12d_0}\right]$

or $\dfrac{\mathcal{E}}{N} = k_e\left[-\dfrac{11}{12}\alpha\dfrac{e^2}{d_0}\right]$; where $k_e = 9\times10^9$

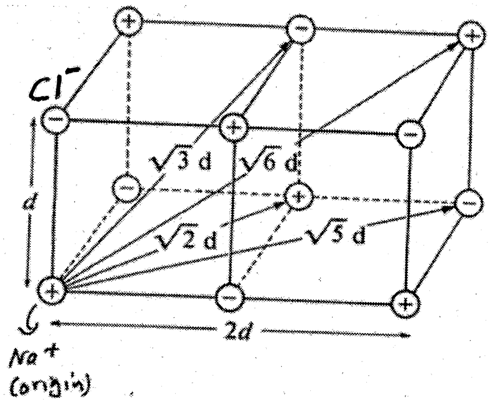
table 11.8

Compound	Experimental d_0 (Å)	Experimental $\mathcal{E}/N_{\text{ion pairs}}$ (eV)	Eq. (11.26) $\mathcal{E}/N_{\text{ion pairs}}$ (eV)
LiF	2.01	10.83	11.45
LiCl	2.57	8.85	8.98
LiBr	2.75	8.51	8.39
LiI	3.01	7.92	7.66
NaCl	2.82	8.18	8.18
NaF	2.32	9.62	9.96

for detailed calculation of cohesive energy per NaCl molecule, see problem 4 in HW#7

Calculation of Madelung constant for NaCl numerically :

Take the Na^+ as a reference ion located at the origin $(0,0,0)$. the Position vector $\vec{R}$ of any ion (but not the reference one) is



$$\vec{R} = n_1 d\,\hat{i} + n_2 d\,\hat{j} + n_3 d\,\hat{k}$$

$$= d(n_1\hat{i} + n_2\hat{j} + n_3\hat{k})$$; where d is the NN distance

$$\Rightarrow |\vec{R}| = d\sqrt{n_1^2+n_2^2+n_3^2} \Rightarrow \frac{|\vec{R}|}{d} = \sqrt{n_1^2+n_2^2+n_3^2}$$, with

$n_1, n_2, n_3 = \pm1, \pm2, \pm3, ----$. Note that the sign of each ion is given by $(-1)^{n_1+n_2+n_3}$, so the general definition of Madelung constant α is

$$\alpha = \sum_{\substack{n_1,n_2,n_3 \\ (n_1,n_2,n_3)\neq(0,0,0)}}^{\infty} \frac{\pm1}{|\vec{R}|/d} = \sum_{n_1,n_2,n_3}^{\infty} \frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2+n_2^2+n_3^2}}$$

See that the term $(-1)^{n_1+n_2+n_3}$ alternate the sign and the term $\sqrt{n_1^2+n_2^2+n_3^2}$ is the distance between any ion and the reference ion located at the origin.

α is defined such that the electrostatic Potential energy (Coulomb energy) is given by

$$\frac{\mathcal{E}_{coul}}{N} = -k_e \frac{e^2}{d}\alpha$$. α must be Positive quantity

but the sum in $\alpha = \sum_{n_1, n_2, n_3}^{\infty} \frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2+n_2^2+n_3}}$ often results in a negative value because attractive forces dominate repulsive forces. Thus to allign with the standard definition of $\alpha > 0$, we take the absolute value of α, in case it is negative. Technically, α is the value obtained when the size of crystal $L \to \infty$, but practically, one get a good approximation by truncating the sum at large value of L. let us assume a cubic box around the reference ion (Na^+) located at $(0,0,0)$, with n ions in each direction, so

$$-n < n_1 < +n \quad , \quad -n < n_2 < +n \quad , \quad -n < n_3 < n \Rightarrow$$

$$\alpha = \sum_{\substack{(n_1,n_2,n_3)=(-n,-n,-n) \\ (n_1,n_2,n_3) \neq (0,0,0)}}^{(+n,+n,+n)} \frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2+n_2^2+n_3^2}}$$

n1: -100 to 100 ; sum over 200 lattice points along a1 direction
n2: -100 to 100 ; sum over 200 lattice points along a2 direction
n3: -100 to 100 ; sum over 200 lattice points along a3 direction

overall, the sum is over 200*200*200 = 8,000,000 lattice points

the next mathematica code assumes $n = 100$ and the obtained value of α is

$\alpha = 1.7418$ very close to 1.7476 given in table 11.7 in textbook

```
In[210]:= (*Define the range of summation*)n = 100; (*Increase n for better accuracy*)
 (*Initialize the Madelung constant*)M = 0.0;

 (*Sum over shells of ions*)
Do[Do[Do[If[n1 == 0 && n2 == 0 && n3 == 0, Continue[]]; (*Skip the origin*)
    rSquared = n1^2 + n2^2 + n3^2;
    r = Sqrt[rSquared];
    charge = (-1)^(n1 + n2 + n3); (*Alternating charges*)M += charge / r;, {n3, -n, n}],
  {n2, -n, n}], {n1, -n, n}];
madelung = Abs[M];
(*Print the result*)
Print["Madelung constant for NaCl: ", madelung];
Madelung constant for NaCl: 1.74182
```