

Lecture 3: Crystal binding energy

Kit Matan

Mahidol University

In the previous two chapters, we have learned that atoms do not like to be isolated and prefer forming a periodic structure of crystals. In the chapter, we will attempt to answer the question of why atoms prefer such an arrangement. Some of you might be able to guess the answer and you are right; it has everything to do with minimizing energy and it has to do with one of the four fundamental forces in nature, that is, electromagnetic force. It turns out the attractive force between electrons and nucleus is what holds crystal together. This electromagnetic force can reveal itself in different form of binding energy such as exchange energy, van der Waals force, and covalent bond, all of which are fundamentally related to the electromagnetic force. In this case, the binding energy or cohesive energy is the energy required to separate atoms in the crystal. The more the binding energy is, the more the energy is required to separate atoms. The cohesive energy listed below ranges from the weakest bonding between neutral atoms of inert gases to the strongest covalent bond seen in, for example, the diamond crystal.

1. Molecular crystal and inert gas (van der Waals attraction)
2. Hydrogen -bonded crystal
3. Ionic crystal (Coulomb attraction)
4. Metallic crystal (electron delocalization)
5. Covalent crystal (covalent bond)

To get a sense of all of the above bonding types in crystals, one can consider the energy of two atoms as a function of separation between them. For all types of bonding, one can divide this plot into two regions (the detail of the curve could be different but the main features are the same). For the short-distance region (small \vec{r} region where \vec{r} is the separation between any two atoms), there is a short-range repulsion between atoms preventing the two atoms from collapsing and fusing into each other. The energy is positive and goes to infinity as \vec{r} goes to zero. For the long-distance region (large \vec{r} region), there is long-range attraction. The energy is negative and goes to zero when \vec{r} goes to infinity. Therefore, there must be an intermediate \vec{r} at which the global minimum in energy is achieved. This global minimum point defines the mean distance (or equilibrium separation) between two nearest atoms in the crystal. Therefore, one can write the total energy between any two nucleuses as

$$U(r) = U_{\text{repulsive}}(r) - U_{\text{attractive}}(r), \quad (3.1)$$

where $U_{\text{repulsive}}(r)$ is a short-range repulsion, which is most likely due to Pauli exclusion principle that prevent the overlapping of electron (one could make an analogy with a hard-sphere repulsion), and $U_{\text{attractive}}(r)$ is a long-range attraction, which is due to other physics such as dipole-dipole interaction in the case of van der Waals force, Coulomb attraction between opposite charges in the case of ionic crystals, and delocalization of electrons, which lowers the kinetic energy, in the case of metallic crystals and covalent bond..

3.1 Cohesive forces in crystals

We will first focus on the attractive forces that cause atoms or molecules to crystallize. In this class, we will discuss in detail only two of our five crystals listed above; the first one is the van der Waals attraction and the second one is the Coulomb attraction in the ionic crystal.

3.1.1 van der Waals attraction

The van der Waals attraction is weaker than the Coulomb force that dominates in the charge particles. Therefore, it only becomes a prominent force in the neutral atoms or molecules with no charge nor permanent dipole moment. However, the nature of this force is in fact electromagnetic and the force is the attraction between two fluctuations or induced dipole.

We know that at a finite temperature both nucleus and electron clouds of atoms and molecules do not remain static but fluctuate around their mean positions. These fluctuations cause a momentary dipole moment, which in turn induces dipole moment in nearby atoms or molecules. The two dipoles then interact through the dipole-dipole interaction. In order to get this cohesive energy as a function of the separation distance between two induced dipoles, we can assume first that the fluctuations cause the dipole \vec{p}_1 at \vec{r}_1 that generates the electric field $\vec{E} \propto \frac{\vec{p}_1}{|\vec{r}_1 - \vec{r}_2|^3}$ at \vec{r}_2 . This field induces the dipole \vec{p}_2 where $\vec{p}_2 \propto \vec{E} \propto \frac{\vec{p}_1}{R^3}$, where $R = |\vec{r}_1 - \vec{r}_2|$. The dipole-dipole interaction between \vec{p}_1 and \vec{r}_2 gives the energy

$$U(R) \propto \frac{\vec{p}_1 \cdot \vec{p}_2}{R^3} \propto \frac{1}{R^6}$$

We then combine this attractive potential with the repulsive one, which is empirically proportional to $\frac{1}{R^{12}}$. This $\frac{1}{R^{12}}$ dependence was determined from the experiment on the inert gases. Therefore, the total energy for the neutral atoms or molecules is:

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right], \quad (3.2)$$

which is known as the Lennard-Jones potential. The parameters ϵ and σ indicate the strength of attraction and repulsion as determined from experimental data of the inert atoms in the gaseous state.

Now we will use the Lennard-Jones potential of the inert gas to explain the properties of the solid state of the inert atoms. In the solid state, atoms of the inert gases forms a Bravais lattice. The total energy of the solid is the sum over all atoms in the lattice. In order to simplify the calculations, we will write the lattice vector \vec{R} as a dimensionless parameter $\alpha(\vec{R})$ times the nearest-neighbor distance r , that is, $R \equiv |\vec{R}| = \alpha(\vec{R})r$. We can rewrite the Lennard-Jones potential for the solid inert gases as

$$\begin{aligned} u &= \frac{1}{2} \sum_{\vec{R} \neq 0} U(\vec{R}) \\ &= 2\epsilon \left[\sum_{\vec{R} \neq 0} \left(\frac{\sigma}{\alpha(\vec{R})r} \right)^{12} - \sum_{\vec{R} \neq 0} \left(\frac{\sigma}{\alpha(\vec{R})r} \right)^6 \right] \\ &= 2\epsilon \left[\left(\sum_{\vec{R} \neq 0} \frac{1}{\alpha(\vec{R})^{12}} \right) \left(\frac{\sigma}{r} \right)^{12} - \left(\sum_{\vec{R} \neq 0} \frac{1}{\alpha(\vec{R})^6} \right) \left(\frac{\sigma}{r} \right)^6 \right] \\ &= 2\epsilon \left[A_{12} \left(\frac{\sigma}{r} \right)^{12} - A_6 \left(\frac{\sigma}{r} \right)^6 \right], \quad (3.3) \end{aligned}$$

where the **lattice sum** A_n is equal to

$$A_n = \sum_{\vec{R} \neq 0} \frac{1}{\alpha(\vec{R})^n}.$$

The constants A_n (Table 3.1) depends on the type of the Bravais lattices and the exponent n . If n is large, all large $\alpha(\vec{R})$ terms are negligible and only nearest neighbor distance $\alpha(\vec{R}) = 1$ contributes to the sum as $n \rightarrow \infty$. On the other hand, for small n large $\alpha(\vec{R})$ will contribute more to the sum. Therefore, A_{12} dominates the short-range region while A_6 dominates the long-range region.

Table 3.1: The lattice sums A_n for the three cubic Bravais lattices taken from Ref. [ashcroft]

n	sc	bcc	fcc
≤ 3	∞	∞	∞
4	16.53	22.64	25.34
5	10.38	14.76	16.97
6	8.40	12.25	14.45
12	6.20	9.11	12.13
≥ 17	$6 + 12(1/2)^{n/2}$	$8 + 6(3/4)^{n/2}$	$12 + 6(1/2)^{n/2}$

Equilibrium separation From Eq. 3.3, one can calculate the equilibrium separation of atoms giving the values of A_{12} and A_6 and knowing that at the equilibrium separation $r_0 \left. \frac{\partial u}{\partial r} \right|_{r_0} = 0$. One obtains

$$r_0 = \left(\frac{2A_{12}}{A_6} \right)^{1/6} \sigma$$

Equilibrium cohesive energy By substituting the value of r_0 back to Eq. 3.3, we get the equilibrium cohesive energy

$$u_0 = -\frac{\epsilon A_6^2}{2A_{12}}.$$

3.1.2 Ionic crystals

For the ionic crystals, the Coulomb attraction is much stronger than the van der Waals force, which contributes only a few percents to the cohesive force in the ionic crystals. Therefore, we will ignore the van der Waals attraction and only focus our calculations on the Coulomb force between charged ions. Furthermore, we will also modify the repulsive force. Instead of using the empirical repulsive potential of the $\frac{1}{R^{12}}$ form that we have used for the inert gas, we will use the exponential potential for the ionic crystals. The reason is simply because this exponential form gives better agreement with experimental data. We can write the two-particle energy of the interaction between two ions as:

$$U_{ij}(\vec{R}) = \begin{cases} \lambda e^{-r/\rho} - \frac{q^2}{r} & \text{nearest neighbor} \\ \pm \frac{1}{\alpha_{ij}(\vec{R})} \frac{q^2}{r} & \text{otherwise} \end{cases}$$

Note that we have written the Coulomb term in the CGS unit, in which $\frac{1}{4\pi\epsilon} = 1$. As we can see, this potential is consisted of two parts. The first part acts only on the nearest neighbors (short-range) and is dominated by the hard-core repulsive energy whereas the second part is the long-range interaction and is dominated by the Coulomb attractive energy. The \pm sign implies that there are both attractive force for opposite charges and repulsive force for same charges.

From this two-particle potential, we can get the total energy by summing all ions, which gives:

$$U_{\text{total}} = N \left(z\lambda e^{-r/\rho} - A \frac{q^2}{r} \right),$$

where $2N$ is the total number of ions (negative and positive ions), z is a number of the nearest-neighbors, and A is the **Madelung constant**, which is equal to:

$$A \equiv \sum_{i \neq j} \frac{\pm 1}{\alpha_{ij}(\vec{R})}.$$

The Madelung constant is similar to the lattice sum we defined for the inert gases in which it also depends on the crystal structure and how the ions with different charges arrange themselves with respect to one another. We will come back and evaluate this constant for the simplest case of one-dimensional lattice later. For now, we will calculate the equilibrium separation and equilibrium energy similar to what we have done in the case of the inert cases.

Equilibrium separation At the equilibrium, we will require that $\frac{dU_{\text{total}}}{dr} = 0$. Therefore, we have:

$$\frac{dU_{\text{total}}}{dr} = N \left[-\frac{z\lambda}{\rho} e^{-r/\rho} + A \frac{q^2}{r^2} \right] = 0.$$

which gives the following equation for the equilibrium separation r_0 :

$$r_0^2 e^{r_0/\rho} = \frac{\rho A q^2}{z\lambda}.$$

From this equation one can calculate r_0 if the constants ρ and λ are known. Normally, these constants are determined from the experimental data. However, unlike in the case of the inert gases where the constants are obtained from the data of the gaseous state, for ionic crystal, these constants are obtained from the solid state.

Equilibrium energy In order to calculate the equilibrium energy, we can substitute r_0 back into the equation for the total energy, which gives:

$$U_{\text{total}} = -\frac{NAq^2}{r_0} \left(1 - \frac{\rho}{r_0} \right)$$

The first term $-\frac{NAq^2}{r_0}$ is the **Madelung energy**, which is an attractive energy, whereas the second term is the short-range repulsive energy, which is in the order of 10% of the Madelung energy ($\rho \approx 0.1r_0$).

Calculation of the Madelung constant We will start with the simplest lattice, that is, the ionic one-dimensional lattice where ions form a line with alternate charges. We will let the nearest neighbor distance \bar{r} be the distance between nearest ions with opposite charge. Therefore, we can write the expression for the Madelung constant A as:

$$A = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right].$$

If the sum is finite, the right hand side depends heavily on the last term. Therefore, we will assume that we have infinite lattice and ignore the condition at the boundary. It is multiplied by 2 because we have ions extended both to the left and to the right.

In order to evaluate this sum, we have to remember that

$$\log(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

For $x = 1$, the right hand side of both equations become the same, which means:

$$A = 2 \log 2.$$

In three dimensions, we can construct similar series for the Madelung constant. However, the way each term is arranged will play a crucial role in evaluation. We will not attempt to try to calculate it here. Instead, we will give the values of the Madelung constants for common lattices in the cubic system (Table 3.2).

Table 3.2: Madelung constants of common lattices in the cubic system taken from Ref. [ashcroft]

structure	Madelung constant A
Sodium chloride	1.747565
Cesium chloride	1.762675
Zincblende	1.6381

3.1.3 Covalent and metallic bonds

The detail theory behind these two cohesive energies is beyond the scope of this class and we will not discuss it here. However, we will point out that the cohesive force in both of these cases has the same underlying principle, that is, the delocalization of electrons. For the covalent bond, the electrons on the most outer shell of atoms can become delocalized by sharing their energy level with electrons from the nearby atoms. It turns out this delocalization of electrons will lower the kinetic energy of electrons and therefore decrease the overall total energy, even though the bonding causes the nucleus to be closer and increases the nucleus-core-to-nucleus-core repulsion (potential) energy. But the decrease in the kinetic energy is more than enough to compensate for the increase in the potential energy. Similarly for the metallic crystal, the fact that electrons can move around freely inside the crystal lowers the kinetic energy of the system giving rise to the cohesive energy.

We could think of the decrease of the kinetic energy from the delocalization of electrons in term of the Heisenberg uncertainty principle. When electrons become delocalization, their positions are not well defined, that is, Δx is large. Therefore, from the uncertainty principle, their uncertainty in the momentum Δp must be small. Hence, their kinetic energy must also be small or smaller than when the electrons are localized.

References

- [1] Kittel, C.: Introduction to Solid State Physics 7th Edition (Chapter 3), John Wiley & Sons, Inc. (1996).
- [2] Ashcroft, N. W. and Mermin, N. D.: Solid State Physics (Chapter 20), Thomson Learning, Inc. (1976).