§3 – Cohesion

3.1 Crystal Binding

As we have shown in several previous modules, there are **four** main types of bond or binding, with different potential forms. The type of binding in a particular material depends mainly on its chemical properties. The four main binding types are:

1. Ionic – This is the usual binding between electro-negative and -positive elements e.g. a salt;
2. Metallic – This type of bond is most common in metal elements and alloys;
3. Covalent – Mainly occurs in non-metallic metals with similar electronegative e.g. H_2O, CH_4, C_2H_4;
4. Van der Waals – This is a very weak bonding and is only usually noticed in noble gases, where none of the other processes occur.

Definition:

The ***cohesive energy*** is the energy needed to break a solid apart into neutral free atoms.

We can measure the cohesion energy in eV. There are a wide range of of energies across the periodic table: $C=7.6\,eV\,;\;\;W=8.9\,eV\,;\;\;Ne=0.02\,eV$. C is covalent, W is metallic with some covalency, and Ne is van der Waals

There is a strong correlation between the melting point and cohesive energy, especially among the metals. The highest cohesion energy occurs in tungsten W, which has a melting point of 3700 K.

3.2 Noble Gas Crystals

Inert or ***noble gases*** are the last group in the periodic table, so they have a closed shell configuration. The former name tends not to be used any more as it is not strictly accurate: Kr and Xe have showed some reactivity in the laboratory.

These are namely: He, Ne, Kr, Ar, Xe, Rn.

The ionisation energy for the noble gases is very high, so positive ions would discharge in forming a crystal.

This closed shell structure remains in the crystal.

Only two major forces are present:

1. Core repulsion (due to Pauli exclusion principle);
2. Van der Waals interaction.

The Van der Waals interaction is also known as:

- London interaction
- Induced dipole-dipole interaction

a) Pauli Exclusion Principle

The Pauli exclusion principle states that no two identical fermions (e.g. electrons) may simultaneously occupy the same quantum state.

When two fermions with the same quantum numbers are brought together , they experience a repulsive force known as ***Pauli repulsion***. The strength the the Pauli repulsion is proportional to the overlap of their wavefunctions.

Closed shell structures have, by definition, all their electrons paired, so there is no possibility of covalent bonding.

b) London Dispersion (Induced Dipole-Induced Dipole Interaction)

An electron cloud can be displaced relative to the nucleus by an electric field.

This spontaneous fluctuation of the atom can induce a momentary dipole moment of magnitude, $p = e\,d$.

The interaction energy between a dipole and an electric field is proportional to the dipole moment. The electric field of a dipole is proportional to $1/r^3$.

If a second atom is placed in the vicinity of the first, a dipole can also be induced in this atom. This causes an attractive force proportional to $(r^{-3})(r^{-3}) = r^{-6}$. This fluctuation is driven by the dynamics of the electrons.

3.3 Lennard-Jones Potential

The Lennard-Jones potential models the force acting on neutral particles . It includes an attractive Van der Waals force and a repulsive Pauli repulsion force:

$$\boxed{U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] = \frac{A}{R^{12}} - \frac{B}{R^{6}}} \qquad (3.1)$$

The $1/R^{12}$ form of the repulsive term is completely ad-hoc, fitted from experimental data. The repulsive force could be exponential, but the choice of this function makes little difference to the result.

We can choose $A = 4\epsilon\sigma^{12};\ B = 4\epsilon\sigma^{6}$, without losing generality. We can then see that σ is a

distance similar in size to R.
We can see that at the minimum, $|B| \gg |A|$, so the form of A is not terribly important.

3.4 FCC Lennard-Jones Solid

$U(R)$ applies to every pair of atoms in the solid. We can neglect kinetic energy contributions, as they are approximately independent of structure.

Noble gases pack together as closely as possible, so have either fcc or hcp structure.

The cohesive energy is found by summing the Lennard-Jones potential over all pairs in the crystal. For a crystal of N atoms with nearest neighbour separation R, the cohesive energy is:

$$\boxed{U_{\text{tot}} = \frac{1}{2} N (4\epsilon) \left[\sum_j \left(\frac{\sigma}{p_j R} \right)^{12} - \sum_j \left(\frac{\sigma}{p_j R} \right)^{6} \right]} \tag{3.2}$$

Where: p_j is a dimensionless geometric factor giving the distance of the jth neighbour in the crystal.

These summations are a property of the lattice type only.

We can summarise the summations as:

	Fcc	**Hcp**
$\sum_j p_j^{-12}$	12.1319	12.1323
$\sum_j p_j^{-6}$	14.4539	14.4549

As can be seen, the repulsive term comes almost entirely from the 12 nearest neighbours, with the attractive term affected slightly by atoms further away.

We can see that the magnitude of the cohesive energy is slightly higher in the fcc structure, making this structure more favourable over the hcp structure.

The equilibrium distance, R_0 can be found by differentiating the energy with respect to R and setting it to zero:

$$\frac{d\,U_{\text{tot}}}{d\,R} = 2N\epsilon \left[-12(12.13)\frac{\sigma^{12}}{R_0^{13}} + 6(14.45)\frac{\sigma^{6}}{R_0^{7}} \right] = 0$$

This gives the equilibrium distance:

$$\boxed{R_0 = 1.09\,\sigma} \tag{3.3}$$

The value of σ can be measured from the gas phase properties of the material.

Some of the real ratios are shown below:

Table 3.1: Experimental Values of R_0/σ

	Ne	**Ar**	**Kr**	**Xe**
R_0/σ	1.14	1.11	1.10	1.09

The slight deviation from the theoretical value for lighter atoms is due to zero point quantum effects.

At zero pressure and absolute zero, the cohesive energy can simply be found by substituting the summations into equation (3.2) to give:

$$U_{\text{tot}} = -2.15(4N\epsilon) \quad .$$

This has a range $U_{\text{tot}} \sim 0.02 - 0.16\,\text{eV}$.

3.5 Ionic Crystals

The most obvious examples of ionic bonding are salts such as NaCl. These are formed by non-metals with nearly closed shells (such as halogens) and metals with nearly empty shells (such as alkali metals).

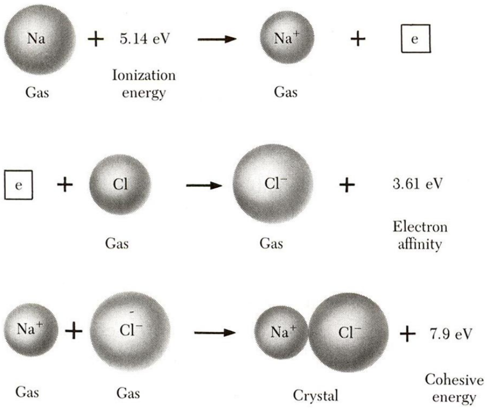

Figure 3.1: Diagram showing the process of formation of a sodium chloride crystal from free sodium and chlorine atoms.

The ionisation 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 unfavourable on their own. The lattice energy of a single NaCl molecule is 7.9 eV.

Thus, the cohesive energy of a single NaCl molecule is given by:

$$U=7.9+3.6-5.1=6.4\,\text{eV}$$

Note:

For charged ions, the effect of the Van der Waals force is dwarfed by the effect of the Coulomb force.

The computation of cohesive energy is more complicated for ionic compounds due to the differing signs.

The basic form will be a Coulomb attraction for nearest neighbours, however, we need to add an exponential repulsive term (this is even less important because of the R^{-2} dependence in the Coulomb term). We also have either repulsion or attraction for other neighbours:

$$U_j = \begin{cases} \lambda e^{-R/\rho} - \dfrac{q^2}{4\pi\varepsilon_0 R} & \text{nearest neighbours} \\ \pm \dfrac{q^2}{4\pi\varepsilon_0 \left(p_j R\right)} & \text{all other neighbours} \end{cases}$$

If we take the sum over j as before, we have:

$$\boxed{U_{\text{tot}}=N\left(z\lambda e^{-R/\rho}-\frac{\alpha q^2}{4\pi\epsilon_0 R}\right)} \qquad (3.4)$$

Where: z is the number of nearest neighbours.

We have also included a constant α, where:

$$\boxed{\alpha=\sum_j \frac{(\pm)}{p_j}\equiv\textbf{Madelung constant}} \qquad (3.5)$$

Again, we can differentiate to find the equilibrium distance:

$$\frac{dU_{\text{tot}}}{dR}=-\frac{Nz\lambda}{\rho}e^{-\frac{R}{\rho}}+\frac{N\alpha q^2}{4\pi\epsilon_0 R^2}=0$$

$R_0^2 \exp\left(\frac{-R_0}{\rho}\right) = \frac{\rho \alpha q^2}{4 \pi \epsilon_0 z \lambda}$, which can be solved to find R_0.

We also find that:

$$U_{\text{tot}} = \underbrace{-\frac{N \alpha q^2}{4 \pi \epsilon_0 R_0}}_{\text{Madelung energy}} \left(\underbrace{1}_{\text{Coulomb}} - \underbrace{\frac{\rho}{R_0}}_{\text{repulsion (<10\%)}} \right)$$

3.6 Madelung Sum

The first calculation of the coulomb energy constant α was executed by Madelung. A general method for calculating lattice sums was invented by Ewald.

The 1-dimensional case is fairly simple.

For the jth neighbour, the separation is $R_j = jR = p_j R$, $\Rightarrow$ $p_j = j$.

Clearly, the sum will look like a harmonic series, but with alternating signs and an additional factor of two, since we need to count in both directions:

$$\alpha = 2 \sum_{j=1} \frac{(-1)^{j-1}}{j}$$

Remember, the Taylor expansion of $\ln(1+x)$ is given by:

$\ln(1+x) = \sum_{j=1}^{\infty} \frac{x^j (-1)^{j-1}}{j}$, which is weakly convergent.

Thus, $\alpha = 2 \ln 2 \approx 1.386$.

The 3-dimensional case is **extremely** hard because the number of distant neighbours increases very rapidly. The Ewald method groups the terms into charge-neutral shells. Without this approach, the series will never converge.

Some typical values of α are shown below:

α(NaCl) = 1.748

α(CsCl) = 1.763

α(ZnSe)=1.638

3.7 Atomic and Ionic Radii

We have seen that sphere-packing plays an important part in determining the choice of structure. If all atoms are the same size, then close sphere-packing is possible.

However, if the basis contains atoms of two or more different radii, then other structures become available.

a) Alkali Halides

These are a type of salt formed from monovalent ions.

If we measure the electron density through X-ray diffraction, we find that they are (to a good approximation) spherical.

The majority of alkali halides have the NaCl structure, except the Caesium halides other than CsF.

We can approximate the ionic separation as the sum of the two ionic radii. This works well with NaCl structured compounds, with errors of a few %.

However, this approximation works less well for the other alkali halides.

The problem is that as the radius of the anions increase, they start to touch each other.

The crossover between these structures occurs when: $r^{+}+r^{-}=\sqrt{2}\,r^{-}$.

Rearranging, this corresponds to an anion to cation ratio of:

$$\boxed{\frac{r^{-}}{r^{+}}=\left(\sqrt{2}-1\right)^{-1}=2.414} \tag{3.6}$$

This crossover was originally employed by Pauling to determine the relative sizes of the anions and cations.

This method also works well for many oxides, except that we need to correct for the coordination number: more neighbours corresponds to a larger radius.

3.8 Covalent Crystals

For unfilled shells, the Pauli principle allows electrons from two different atoms to bind by overlapping their wavefunctions without being excited to a higher energy state.

The covalent bond therefore has strong directional properties.

Some of the possible bonding arrangements can be deduced from the chemical hybridization (number of shared electrons):

4 electrons: $s^{2}p^{2}\rightarrow 4\times s\,p^{3}$ **tetrahedral bonding**

3 electrons: $s^2 p \rightarrow 3 \times s\, p^2$ **hexagonal bonding**

The bond lengths are strictly constrained, giving an open "ball-and-stick" lattice structure. The density of the packing has little effect on the bond length.

There appears to be some crossover between ionic and covalent structures. Partial charging can appear at the ends of bonds.

Consider GaAs:

Ga $4s^2 4p^1 \rightarrow Ga^- \;\; 4 \times sp^3$

As $4s^2 4p^3 \rightarrow As^+ \;\; 4 \times sp^3$

These ions form a zincblende structure, with tetrahedral bond angles $\cos^{-1}\left(-\frac{1}{3}\right) = 109^\circ$.

To minimise the electrostatic potential energy, GaAs sites are rigidly defined in the lattice: there are no Ga-Ga or As-As bonds.

3.9 Metals

Metals are yet another configuration consisting of ions and "free" electrons. The electrons are kept apart by the Pauli exclusion principle. The electrons in the metal determine most of its properties.

If the electrons get too close, their overlap energy increases, whereas if they are spread too far apart, then some of the electrons must return to the ions, losing the benefit of sharing ions. The electrons can screen the ions from one other, so they do not feel the full force of the electric field.

The structure is determined by the maximum separation of the ions. The bond formed by conduction electrons is not very strong: the interatomic distances, especially in alkali metals, are relatively large, to minimise the kinetic energy of the conduction electrons, leading to weak bindings. Thus, close-packed structures are preferred (fcc and hcp).

There are cases where less dense structures form instead, especially in the transition metals. For example, *W*, *Mo* and *Ta* form bcc crystals. Transition metals (and those that follow) have additional binding from inner electrons shells. This is due to large *d*-orbital shells, causing an increase in binding energy which means that less dense structures are preferred.

These *d*-orbitals are also important in the higher group transition metals, where the ionic radius and the metallic radius are approximately equal. For example Au has an ionic/metallic ratio of 1.37/1.44.