Introduction

There are four forces in nature. The strong and the weak interactions act between electrons, protons, neutrons and other elementary particles and do not concern us. We do not know of any normal material whose properties (melting point, for example) depend on the magnitude of these forces. The two other forces are gravitational and electromagnetic.

Gravitational forces account for large scale phenomena such as tides, and seasons, and together with intermolecular forces, decide the length of a giraffe’s neck. We shall not discuss gravitation.

All interactions that are important for solids, should in principle, come out as solutions of the Schrödinger equation (SE). Unfortunately, solutions of the SE are hard to come by for many real systems, and even if they were available, their utility would not be assured. We therefore continue to propagate the useful fiction that cohesive interactions in materials can be classified as belonging to one of four categories – van der Waals, ionic, covalent or metallic.¹ We keep in mind that these are not very easily distinguished from one-another in many solids.

For a delightfully readable text on the nature of cohesion between molecules, and between molecules and surfaces, look at J. N. Israelachvili, *Intermolecular and Surface Forces*.

The superconducting compound, Y$_2$C$_2$Br$_2$ is a beautiful illustration of how complex the interactions in a solid can be, despite it’s deceptively simple formula:


¹Hydrogen bonds are somewhere between being ionic and covalent and we do not see a good reason to place them in a class by themselves.
van der Waals

The simplest solids are perhaps those obtained on cooling down a noble gas – He, Ne, Ar, Kr or Xe. He does not form a solid at ambient pressure. All the other noble gases do.

The interactions between noble gas atoms (which have closed shells of electrons) is of the van der Waals type (note: van der Waals, not van der Waal’s!) which means that the interaction is between instantaneous dipoles formed because the atoms “breathe” and this breathing causes the centers of positive and negative charges to, from time to time, not coincide. The forces are therefore also referred to as induced dipole-induced dipole interactions, or London dispersion forces (after F. W. London).

![Diagram of electron cloud and nucleus](image)

If we were to believe the above scheme, it should come as no surprise that the largest noble gas atom should be the most polarisable and therefore the most cohesive. The boiling points (often better indicators of cohesion than melting points) testify to this:

<table>
<thead>
<tr>
<th>Atom</th>
<th>(T_M) (K)</th>
<th>(T_B) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>24</td>
<td>27</td>
</tr>
<tr>
<td>Ar</td>
<td>84</td>
<td>87</td>
</tr>
<tr>
<td>Kr</td>
<td>116</td>
<td>120</td>
</tr>
<tr>
<td>Xe</td>
<td>161</td>
<td>165</td>
</tr>
</tbody>
</table>

Other columns of elements in the periodic table don’t follow this simple trend. For example:

<table>
<thead>
<tr>
<th>Atom</th>
<th>(T_M) (K)</th>
<th>(T_B) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1353</td>
<td>2833</td>
</tr>
<tr>
<td>Ag</td>
<td>1235</td>
<td>2433</td>
</tr>
<tr>
<td>Au</td>
<td>1333</td>
<td>3133</td>
</tr>
</tbody>
</table>

The interaction between noble gas (and other atoms or molecules that have no charge and are approximately spherical) can be most simply represented as hard spheres with the following potential:

\[
U(r) = \begin{cases} 
\infty & \text{if } r < r_0 \\
0 & \text{if } r \geq r_0 
\end{cases}
\]

This is the hard sphere potential and the only variable in it is the equilibrium distance between atoms \(r_0\). Surprisingly, the hard sphere potential can be quite useful. However, it is effectively describes atoms at infinite temperature, and cannot be condensed unless pressure is applied.

A much better description of the atomic interaction is the Lennard-Jones (after Sir John Edward Lennard-Jones) potential:

\[
U(r) = 4\epsilon \left[ \left( \frac{r}{\sigma} \right)^{-12} - \left( \frac{r}{\sigma} \right)^{-6} \right]
\]
\( \sigma \) is the diameter of the atom, and \( \epsilon \) is the depth of the well. The second part, that describes the attraction between neutral molecules, stems from an analytical result for London dispersion (formula from Israelachvili):

\[
U_{\text{Attr}}(r) = -\left( \frac{3}{4} \right) \hbar v a^2 \left( \frac{4\pi \epsilon_0}{3} \right)^2 r^6
\]

There is no good reason for the first, repulsive part to have the \( r^{-12} \) form, except that it is mathematically convenient: Once one calculates \( (\sigma/r)^6 \), the calculation of \( (\sigma/r)^{12} \) is trivial. This is useful if you are doing it a billion times (as in a computer simulation).

It is important to note that uncharged pair-potentials having an exponent \( n \) in \( U(r) \sim r^{-n} \) require that \( n > 3 \). Else, in a fluid, the interactions between some central atoms and atoms that are far will dominate over the interactions between the central atom and atoms that are near (See Israelachvili).

Noble gases when cooled, form solids that are cubic close packed (except He which is possessed of a complex phase diagram). This is actually surprising since one would actually expect them to hexagonal close packed on the basis of energetics — hcp has a slight edge. A possible explanation for the preference for the fcc structure is that fcc stacking can accommodate *stacking faults* more readily. Stacking faults are inevitable at finite temperature. The fcc preference is therefore *entropy* driven.

**Ionic**

As a good thumb rule, atoms at the two ends of the electronegativity scale either give up their valence electrons very easily to form stable cations (ions with small values of electronegativity) or take up electrons very easily to form anions (ions with large electronegativities).
The process of giving up electrons (in the case of cations) and of taking electrons (anions) permits the ion to achieve a stable electronic configuration such as that of a noble gas: For example, Na\(^+\) and F\(^-\) have the Ne configuration the d\(^{10}\) configuration: Ga\(^{3+}\) takes this up the s\(^2\) configuration: Pb\(^{2+}\) and Bi\(^{3+}\) take this up

Once they have done this, they can pair up suitably to form ionic solids that are held together by Coulombic interactions


Ions pairs: Consider the reaction between two anions in the gas phase:

\[
M^{z+}(g) + X^{z-}(g) \rightarrow MX(g)
\]

The charges on the ions are \(z_+e\) and \(z_-e\) where \(e\) is the charge on an electron. The decrease in internal energy caused by bringing the ions near one-another is the Coulombic attraction holding the ion pair together:

\[
\Delta U_{\text{Att.}} = -\left(\frac{|z_+| |z_-| e^2}{4\pi \epsilon_0 r}\right)
\]

The lowering of energy is used to accomplish the following:

\[
M(s) \rightarrow M(g) \text{ and } X(s) \rightarrow X(g)
\]

\[
M(g) \rightarrow M^{z+}(g) + ze^- \text{ and } X(g) + ze^- \rightarrow X^{z-}(g)
\]

The Madelung potential — Coulombic interactions on a lattice:
Let the cations and the anions in the figure above have charges of $e^+$ and $e^-$. Then the Coulombic potential between some central ion (say a cation) and its neighbors is:

$$\Delta U_{\text{Att.}} = -\frac{e^2}{4\pi\epsilon_0 r} \left[ +\frac{2}{1} - \frac{2}{2} + \frac{2}{3} - \frac{2}{4} \cdots \right]$$

The summand within brackets is the geometric Madelung constant $A$ which varies according to crystal type.

<table>
<thead>
<tr>
<th>Lattice Type</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.7476</td>
</tr>
<tr>
<td>CsCl</td>
<td>1.7627</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>1.6413</td>
</tr>
<tr>
<td>Zinc Blende</td>
<td>1.6381</td>
</tr>
<tr>
<td>Fluorite</td>
<td>2.5194</td>
</tr>
<tr>
<td>Rutile</td>
<td>2.408</td>
</tr>
<tr>
<td>Cadmium Iodide</td>
<td>2.355</td>
</tr>
</tbody>
</table>

The Madelung constant in 3D is often non-trivial to sum up (because successive terms are larger and larger). One need to perform the summation in reciprocal space using a technique called the Ewald Summation.

For any ionic crystal, the attractive Coulombic part (per mole) is therefore:

$$\Delta U_{\text{Att.}} = -\left( \frac{L A |z_+||z_-|e^2}{4\pi\epsilon_0 r} \right)$$

$L$ is the Avogadro number.

The repulsive part arises because atoms and ions behave nearly like hard spheres. This is a consequence of the Pauli exclusion principle which says that no two electrons in a system can have all four quantum numbers the same.

The repulsion can be approximated by the expression:

$$\Delta U_{\text{Rep.}} = \frac{LB}{r^n}$$

where $B$ is called the repulsion coefficient and $n$ is the Born exponent. $n$ is normally around 8 or 9.

The two terms add:

$$\Delta U(0 \text{ K}) = -\frac{L A |z_+||z_-|e^2}{4\pi\epsilon_0 r} + \frac{LB}{r^n}$$

At equilibrium (after the structure has relaxed) we can write $r = r_0$ and set $d\Delta U/dr = 0$. We can thus eliminate $B$ and write the Born-Lande equation:

$$\Delta U(0 \text{ K}) = -\frac{L A |z_+||z_-|e^2}{4\pi\epsilon_0 r_0} \left( 1 - \frac{1}{n} \right)$$

The Born-Haber cycle, Hess's law, Kapustinskii equation: Please see the handout.
Covalent bonding

- Covalent bonds are formed between non-metallic (usually) atoms of similar electronegativity. \( s \) or \( p \) orbitals are used.

For example, the 1s orbitals on two hydrogen atoms combine to form the molecular orbitals \( \sigma(1s) \) which is bonding and \( \sigma^*(1s) \), which is antibonding. The two electrons occupy the bonding level and leave the antibonding level empty. In the following depiction, the circles are the 1s orbitals:

Covalent bonding in an extended solid is very similar: Consider a chain of H atoms:

Why is covalent bonding strongly directional? The example of sp\(^3\) hybrids in diamond and Si:
Hybrid orbitals are obtained from linear combinations of atomic orbitals on the same atom. These hybrid orbitals can then overlap with similar hybrid orbitals on neighboring atoms, just as the 1s orbitals do in the hydrogen chain.

**Metallic bonding**

This is a special case of covalent bonding where all the states are not filled up. We will come back to this in a later class, when we discuss energy bands.

**Colloids**

The source for the material that follows is: J. Prost and F. Rondelez, *Structures in colloidal physical chemistry*, Nature Supplement 350 (18th April 1991) 11-23. Also see Israelachvili.

Colloids are systems with a characteristic length scale between 10 nm and 1,000 nm.

For experiments on colloidal interactions, a nice system to work with are cross-linked polymer spheres of uniform size. Usually, these particles are modified so that they have ionizable surface groups.

The Deryaguin-Landau-Verwey-Overbeek \(^2\) (DLVO) theory describes suspended colloidal particles in solution based on the principal interactions which are:

**The van der Waals attraction**: Usually written \(-H/r^6\) where \(r\) is the distance between two particles and \(H\) is the so-called Hamaker constant. \(H\) is related to the polarizability of the material.

**The Coulomb repulsion**: Since the particles have like charges, they repel. However, ions in the solvent medium screen the repulsion so it does not take the usual \(1/r\) form, but instead, takes the form \(\exp(-r/\lambda)/r\), where \(\lambda\) is the Debye screening length, and comes from the Debye-Hückel theory for electrolytes. The complete DLVO potential looks something like:

\[
U(r) = \frac{z^2e^2}{\epsilon} \left[ \frac{\exp(\lambda a)}{1 + \lambda a} \right]^2 \frac{\exp(-r/\lambda)}{r} - \frac{H}{r^6}
\]

Where \(z\) is the number of charges, \(a\) is the radius of the sphere within which the charge resides (approximated to the radius of the particle) and \(\epsilon\) is the dielectric constant of the solvent.

By tuning \(\lambda\) through changing the concentration of salt in the solution, the interaction potential can be tuned.

The system of polymer spheres in water is characterized by three parameters, \(d\), \(a\) and \(\lambda\):

\(d/\lambda \gg 1; d/a \approx 1\) The system behaves like a collection of hard spheres of radius equal to the screening length \(\lambda\). When the system crystallizes, the structures formed are typical of hard spheres (e.g., hcp, fcc).

\(d/a \gg 1; d/\lambda \ll 1\) The system behaves like a one-component plasma in a uniform background of neutralizing charges. The system crystallizes as a bcc array.

The DLVO theory explains why rivers (fresh water) silt up at the mouths (water is salty). Colloidal clay particles attract, but in fresh water, the repulsive Coulombic forces dominate. When the amount of salt in the water increases, the Debye screening length \(\lambda\) becomes very small, and the particles no longer repel as strongly. The van der Waals attraction dominates and the particles coagulate, and then precipitate.