

Lecture 5.1

Bonding

Started course with observation that crystal is low entropy.

i.e. $\Delta S_{\text{crystal}} < 0$ during crystal formation

Therefore, since $dQ = TdS$ this means that heat leaves the crystal during formation.

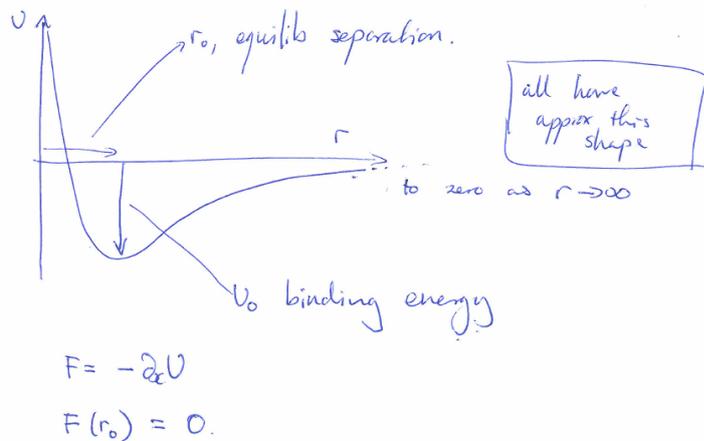
This energy comes from the atoms falling into a potential. i.e. atoms attract.

Call this potential holding atoms together the "bond".

The type of bond tells us about the crystal.

Look at a few types and some implications.

Atoms attract but not all the way to zero separation. As a generic model: long-range attraction and short-range repulsion.



Crystallisation happens when the temperature is sufficiently low that the thermal energy is small compared with the bonding potential. We observe that crystallisation happens at very different temperatures, and therefore we expect that there are different types of bond.

Substance	Phase change T/K
Argon	74
Nitrogen	63
Water	273
CO ₂	216
Methanol	179
Gold	1337
NaCl	1074
Si	1683

We will classify, but beware that these classifications are only approximations; e.g. van der Waals, which we'll meet first, is always present, but often other mechanisms are more significant.

Another example is solid nitrogen, where N₂ molecules (covalently bonded) form a crystal (van der Waals bonded).

van der Waals

Consider a noble gas atom i.e. closed shell.

We know that these freeze (and pack like hard spheres).

Atom is overall neutral, but made of charge constituent parts.

Classical picture: random fluctuation in charge distribution of one atom *induces* a dipole in a neighbouring atom. This induced dipole is attracted to the first atom. The force is attractive for any orientation of the original fluctuation. Quantum mechanical treatment (London dispersion force) gets the same answer (and, indeed, the QM description came first, with the ad hoc classical argument after).

The potential is very short range: $U \propto r^{-6}$.

The electron cloud of a van der Waals bonded atom in a crystal is hardly disturbed at all compared with the free atom. There are zero electrons donated to the lattice. Optical absorption is little different compared with the gas state, and optical branch phonons cannot be excited by light.

This is a very weak bonding. Typically, 0.1...0.2 eV/atom compared with ionization potential ~ 12 eV.

Ionic

Consider two atoms, one with closed shells plus a single outer electron (e.g. Na), and another which has a nearly closed shell with just one missing electron (e.g. Cl).

It is energetically favourable for the spare electron to migrate so that both atoms now have closed shells i.e. this overcomes the electrostatic energy necessary to make the ions.

We now have two ions which are electrostatically attracted.

This can be a very strong bond ~ 8 eV/atom. Essentially, we have noble gas ions which are electrostatically attracted.

Many crystals form FCC with a two-atom basis; can be seen as two offset FCCs (offset by half a conventional unit vector).

Electron density mapping

This simple picture of ionic bonds, of electron donation and consequent ion attraction, is backed up by *measurement* of the electron cloud distribution. One method of measuring this $\rho(\mathbf{r})$ is to revisit the integral over the crystal which we used to discuss diffraction

$$E'_0 \propto \int_{\text{crystal}} \rho(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}} dV = \sum_{\mathbf{n}} e^{i\Delta\mathbf{k}\cdot\mathbf{R}_n} \int_{\text{unit cell}} \rho(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}} dV.$$

We pulled out the summation by using the translational symmetry of ρ , and found that $\Delta\mathbf{k} = \mathbf{G}_m$ a reciprocal lattice vector. Now, we recognise that the integral over the unit cell is a 3D Fourier transform. We can measure $E'_0(\mathbf{k}')$ and then perform an inverse Fourier transform to recover $\rho(\mathbf{r})$.

The resulting electron density map shows that, indeed, one electron is almost fully donated from Na to Cl.

See, e.g., [https://doi.org/10.1016/S0081-1947\(08\)60216-7](https://doi.org/10.1016/S0081-1947(08)60216-7)

Covalent

Electron pair bond from chemistry.

Consider simplest system: two hydrogen-like atoms i.e. each as one outer electron.

At large separation, each electron associated with one nucleus.

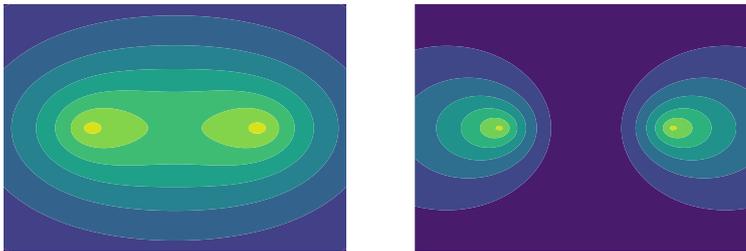
At arbitrary small separation, electrons would orbit as though helium.

At intermediate separation, make Born–Oppenheimer approximation: nucleus far heavier than electron, so essentially stationary as electron cloud redistributes.

Between the nuclei, the electrostatic potential is lower than outside. Therefore, electrons between the nuclei means lower energy.

The clouds can add *destructively* or *constructively*. If constructive, then more likely to find electron in region of lower electrostatic energy, which means we should expect these to bond.

Here's an illustration of the contours of probability for each of the possibilities.



Notes about covalent bonds

- They are directional
 - e.g. Silicon has 4 electrons involved, and forms tetrahedral bonds
- Depends on shape of atomic orbital (s,p,d,...)
- Charge distribution, and thus energy, depends on electron spin (via Pauli exclusion)
 - this *seems* like a dependence of the energy on the spin: "exchange interaction"
- Bonds range continuously from pure covalent (i.e. between identical atoms) to very, very ionic.

The optical phonon branch (in our 1D diatomic model) corresponds to neighbouring atoms moving in opposite directions. This can be excited by an oscillating electric field iff neighbouring atoms have a difference in charge. In covalent (and van der Waals) they do not, and therefore we cannot excite optical branch phonons in these materials.

Metallic

Picture as ions embedded in a fairly uniform density sea of free electrons, and bonding is the electrostatic attraction of this sea with the ions.

This is a good model for Group I (sodium, lithium, rubidium, ...) but not the full picture for other metals (e.g. iron), for which the inner electrons may be involved in some covalent bonding.

Group I metals are fairly soft (you can cut them with a knife, probably because your knife is made of steel). Iron and others are much harder metals, and this "metallic" bonding, with a sea of electrons, is not the full story.