Tutorial
Intermolecular Forces and Solids

Intermolecular Forces

The forces determine many physical properties of substances. The forces range from weak (i.e. dispersion type forces) to moderate (dipole-dipole, of which H-bonds are a specific case) to stron (e.g. forces involving ions).

e.g. in a sample of liquid Argon, what forces are holding the molecules to each other?

Argon exists as discreet atoms, which are spherically symmetrical. Thus, there are no dipoles present. The atoms are not charged, so no ionic forces exist. The only way for two Ar atoms to attract one another is through dispersion (London) forces.

e.g. in a sample of $HCl_{(g)}$, what forces exist between two HCl molecules?

HCl is a polar molecule, since the Cl is so much more electronegative than the H. Thus, there will be dipole-dipole forces, as well as the usual dispersion forces.

e.g. Fe^{+2}(aq) in $H_2O_{(l)}$

Fe^{+2} is an ion and H_2O is a polar molecule, so we expect ion-dipole forces, as well as the usual dispersion forces.

e.g. CH_3Cl in H_2O

CH_3Cl is polar, as is H_2O. We thus expect dipole-dipole interactions, as well as the usual dispersion forces.

CH_3F in H_2O

CH_3F is polar, as is H_2O. We thus expect dipole-dipole interactions, as well as the usual dispersion forces. You might be tempted to think that H-bonds are involved here, but note that the F atom is bound to the C atom. For H-bonds, we need the H to be bound to F, O or N.

e.g. $NH_{3(g)}$

Dispersion and dipole-dipole forces here. In fact, the dipole-dipole forces are H-bonds, since the H is bound to the N.

e.g. Arrange the following in increasing order of melting point: NaCl, Na_2O, He, Xe, H_2O

The one with the lowest MP will have the weakest intermolecular forces, i.e. dispersion forces only. He and Xe have only dispersion intermolecular forces. Xe is larger, therefore more polarizable, therefore has larger dispersion forces.

Thus, He < Xe

The next weakest forces are dipole-dipole. Only water has these forces, in the form of H-bonds

Thus, He < Xe < H_2O

Ionic forces are the largest. Both NaCl and Na_2O are ionic substances. The difference in electronegativities is greatest in NaCl, thus it has the higher melting point. The overall order is thus.

He < Xe < H_2O < Na_2O < NaCl

The order of boiling points will be the same.

2. Solids

(a) Simple cubic structures: these structures have 1/8 of an atom at each corner, for a toal of 1 atom per unit cell. To solve problems using a simple cubic unit cell, note that the length of one side of the unit cell = 2 x the radius of an atom.

(b) Body centred cubic structures: these structures have 1/8 of an atom at each corner, plus one complete atom at the centre of the unit cell, for a total of two atoms per unit cell. Note that the 1/8 atoms at the corners do not touch each other, so solving problems using the BCC structure is more complicated. You must realize that the atoms touch along the diagonal through the central atom, i.e. this diagonal has a length of 4r. There is an easier way to solve it - see below.

(c) Face centred cubic structures: these structures have 1/8 atom at each corner, plus ½ atom on each of the six faces for a total of 4 atoms per unit cell. To solve FCC problems, note that the diagonal of one face has a length of 4r.

e.g. Copper metal is FCC, and has a density, $\rho = 8.95 \text{ g cm}^{-3}$. Find the radius of a copper atom.

Approach: 1. Find $m_{\text{unit cell}}$
2. Find $V_{\text{unit cell}}$
3. find $l_{\text{unit cell}}$ (edge length)
4. find the length of the diagonal, and then r_{Cu}.

1. $m_{\text{unit cell}} = 4 \text{ atoms} \times (63.55 \text{ g/mol} / 6.022 \times 10^{23} \text{ atoms/mol}) = 4.22 \times 10^{-22} \text{ g}$

2. $V_{\text{unit cell}} = m_{\text{unit cell}} / \rho = 4.22 \times 10^{-22} \text{g}/8.95 \text{ g cm}^{-3} = 4.72 \times 10^{-23} \text{ cm}^3$

3. Since the cell is cubic, the edge length = cube root of the unit cell volume = $(4.72 \times 10^{-23} \text{ cm}^3)^{1/3} = 3.61 \times 10^{-8} \text{ cm}$

4. The diagonal of one face = 4r. Thus, using Pythagoras' theorem, $(4r)^2 = l^2 + l^2$, or $r^2 = l^2/8$. Solving, $r = 1.28 \times 10^{-8} \text{ cm} = 128 \text{ pm}$

e.g. Ba is BCC, $\rho = 3.62$ g/cm^3. Find r_{Ba}.

Here, l is unknown, since the atoms do not touch along the edges of the unit cell, but rather through the centre atom. To solve this one, remember that the packing efficiency is 68% in BCC structures.

Approach: 1. Convert density to volume per gram
2. Convert to volume per mole of Ba metal
3. Using the packing efficiency, convert to volume per mole of Ba atoms
4. Convert to volume per Ba atom
5. Assuming spherical atoms, find the radius of an atom.

1. Vol/g = $1/\rho_{Ba}$ = 1/3.62 g cm^{-3} = 0.276 cm^3 g^{-1}

2. Volume per mole Ba metal = 0.276 cm^3 g^{-1} x 137.3 g Ba/mol = 37.9 cm^3/mol

3. But! Ba metal = 68% atoms, 32% empty space. Thus, volume per mole Ba atoms = 37.9 cm^3/mol x 0.68 = 25.8 cm^3/mol Ba atoms

4. Volume per Ba atom = 25.8 cm^3/mol Ba atoms / 6.022 x 10^{23} atoms/mol = 4.28 x 10^{-23} cm^3/atom

5. Volume of a sphere = $4/3\ \pi\ r^3$. Solving for r, r = 2.17 x 10^{-8} cm = 217 pm.

e.g. Solid oxygen, $O_{2(s)}$, crystallizes in a simple cubic structure, with an edge length of 332 pm. Calculate the density of solid oxygen.

In this case we have an entire O_2 molecule at each lattice point. Since the cubic unit cell contains the equivalent of one molecule, the mass of a unit cell is 1 molecule x (32 g mol^{-1} /6.02 x 10^{23} mol^{-1}) = 5.32 x 10^{-23} g

$V_{unit\ cell} = l^3 = (332 \times 10^{-12}\ m)^3 = (332 \times 10^{-10}\ cm)^3 = 3.66 \times 10^{-23}\ cm^3$

$\rho = m_{unit\ cell} / V_{unit\ cell} = 5.32 \times 10^{-23} g / 3.66 \times 10^{-23}\ cm^3 = 1.45\ g\ cm^3$