

## Van der Waal forces

The various types of forces described above are fairly easy to understand, as they arise from the straightforward electrostatic interaction involving charged or polar molecules. But there is a further type of long-range force, the van der Waals force, which acts between totally neutral atoms and molecules such as helium, methane, carbon dioxide, etc. A rigorous analysis of VDW forces would lead us into the world of quantum theory, but for a semi-quantitative understanding of how these forces arise David Tabor has presented the following model based on the interaction between two Bohr atoms:

In the Bohr atom an electron is pictured as orbiting round a proton. The smallest distance between the electron and proton is known as the *first Bohr radius* and is given by

$$a_0 = e^2 / (8\pi\epsilon_0 h\nu) = 5.29 \times 10^{-11} \text{ m.} \quad (1)$$

Here  $e$  is the electronic charge ( $e = 1.602 \times 10^{-19} \text{ C}$ ),  $h$  is the Planck constant ( $h = 6.626 \times 10^{-34} \text{ J s}$ ),  $\epsilon_0$  is the permittivity of free space

$$(\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}),$$

and  $\nu$  is the orbiting frequency of the electron (for a Bohr atom  $\nu = 3.3 \times 10^{15} \text{ s}^{-1}$ ; so that  $h\nu = 2.18 \times 10^{-18} \text{ J}$ . This is the energy of an electron in the first Bohr radius, also known as the *first ionization potential*). The Bohr atom has no

permanent dipole moment, i.e. it is neutral. However, at any instant there exists an instantaneous dipole moment  $\mathbf{p}_1$  of order

$$\mathbf{p}_1 \approx a_0 e. \quad (2)$$

The field of this instantaneous dipole at a distance  $D$  from the atom will be of the order

$$E \approx \mathbf{p}_1 / (4\pi\epsilon_0 D^3) \approx a_0 e / (4\pi\epsilon_0 D^3). \quad (3)$$

If a second neutral atom is nearby it will therefore be polarized by this field and acquire an induced dipole moment of strength

$$\mathbf{p}_2 = \alpha E \approx \alpha a_0 e / (4\pi\epsilon_0 D^3) \quad (4)$$

where  $\alpha$  is the atomic polarizability of the second atom. Note that the atomic polarizability of an atom is proportional to its radius cubed, i.e. for a Bohr atom

$$\alpha \approx 4\pi\epsilon_0 a_0^3. \quad (5)$$

We therefore have two dipoles of moments  $\mathbf{p}_1$  and  $\mathbf{p}_2$  separated by a distance  $D$ , and the potential energy of interaction will therefore be of order

$$\left. \begin{aligned} U &\approx -\mathbf{p}_1 \mathbf{p}_2 / (4\pi\epsilon_0 D^3) \\ &\approx -\alpha a_0^2 e^2 / [(4\pi\epsilon_0)^2 D^6] && \text{using eqns. (2) and (4)} \\ &\approx -\alpha^2 h\nu / [(4\pi\epsilon_0)^2 D^6] && \text{using eqns. (1) and (5)} \end{aligned} \right\} \quad (6)$$

and the attractive force  $F$  (obtained by differentiating the energy  $U$  with respect to distance  $D$ ) therefore varies as  $1/D^7$ .

Except for a numerical factor, eqn. (6) is the same as that derived rigorously by London (1930) using quantum theory. London's expression for the VDW interaction energy between two identical atoms is

$$U = -(3/4)h\nu\alpha^2 / [(4\pi\epsilon_0)^2 D^6]. \quad (7)$$

From the above simple model we see that even two neutral atoms attract each other. The force arises from the *instantaneous* dipole moments of neutral atoms (a quantum mechanical phenomenon) though the subsequent interaction is still essentially electrostatic. Note that the VDW interaction is very similar to that between a polar molecule and a neutral atom, mentioned in item (6) above, and this force also has an inverse seventh power distance dependence.

Finally, we must not forget the stabilizing repulsive forces between all atoms that determine how closely two atoms may ultimately approach each other. These repulsive forces are of very short range and increase sharply as the interatomic distance decreases. If atoms are considered as hard spheres, that is, if we assume that the repulsive force suddenly becomes infinite at a certain interatomic separation, the radius of an atom is then called its *van der Waals radius*. The van der Waals radii of most atoms lie between 0.1 and 0.2 nm.

When atoms and molecules interact with each other in the solid, liquid or gaseous state, it is not uncommon for two or more of the above interactions to occur simultaneously. However, whereas there is no electrostatic force between neutral molecules VDW forces are always present and, except in the case of highly polar or charged molecules, usually dominate the interaction. For small atoms and molecules at room temperature their thermal energy  $kT$

is normally greater than their VDW energy, and such molecules (e.g. methane) are therefore gaseous at room temperature, but condense into van der Waals liquids and solids at lower temperatures. Larger molecules, such as the higher molecular weight hydrocarbons, have stronger VDW forces of attraction and are liquids or solids at room temperatures.