

## Simplified Derivation of the Van der Waal (VDW) Force

[Distillation of an article by Jacob Israelachvili that itself is based on an unreferenced article by David Tabor].

The van der Waals force acts between totally neutral atoms and molecules such as helium, methane, carbon dioxide, etc. A rigorous analysis of VDW forces requires quantum theory but a simplified derivation can be given in terms of the interaction between two Bohr atoms.

The first Bohr radius is given by

$$a_0 = \frac{e^2}{8\pi\epsilon_0 h\nu}, \quad (1)$$

where  $e$  is the electronic charge,  $h$  is Planck's constant,  $\epsilon_0$  the permittivity of free space, and  $\nu$  is the orbiting frequency of the electron. The Bohr atom has no permanent dipole moment but at any instant there exists an instantaneous dipole moment  $\mathbf{p}_1$  of order

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

The electric field of this instantaneous dipole at a distance  $r$  from the atom is of the order

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

If a second Bohr atom is nearby it will be polarized by this field and acquire an induced dipole  $\mathbf{p}_2$  given by

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

where  $\alpha$  is the polarizability of the second atom that for a Bohr atom is

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

The potential energy of two dipole moments  $\mathbf{p}_1$  and  $\mathbf{p}_2$  separated by a distance  $r$  is of order

$$U \approx \frac{\mathbf{p}_1 \mathbf{p}_2}{4\pi\epsilon_0 r^3} \quad (6)$$

$$\approx \frac{-\alpha a_0^2 e^2}{(4\pi\epsilon_0)^2 r^6} \quad (7)$$

$$\approx \frac{-\alpha^2 h\nu}{(4\pi\epsilon_0)^2 r^6}, \quad (8)$$

so that the attractive force (from  $dU/dr$ ) varies as  $1/r^7$ . Except for a numerical factor eq. (8) is the same as that rigorously derived by London (1930) using quantum theory:

$$U = -\left(\frac{3}{4}\right) \frac{\alpha^2 h\nu}{(4\pi\epsilon_0)^2 r^6}. \quad (9)$$

Thus two electrically neutral but polarizable atoms attract each other. VDW forces are always present but for small atoms and molecules at room temperature their thermal energy  $k_B T$  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 temperature.