

CHAPTER 11

VAN DER WAALS FORCES BETWEEN SURFACES

11.1 THE FORCE LAWS FOR BODIES OF DIFFERENT GEOMETRIES:
THE HAMAKER CONSTANT

As we saw in Part I, van der Waals forces play a central role in all phenomena involving intermolecular forces, for while they are not as strong as Coulombic or H-bonding interactions, they are always present. When we come to consider the long-range interactions between macroscopic particles and surfaces in liquids we shall find that the three most important forces are the van der Waals, electrostatic and steric-polymer forces, and that at shorter distances (below 1 to 3 nm) solvation and other types of steric forces often dominate over both.

Let us begin by deriving the van der Waals interaction energies in vacuum for pairs of bodies of different geometries. Starting at the simplest level we shall assume that the interaction is *non-retarded* and *additive*. In Chapter 10 we saw that for an interatomic van der Waals pair potential of the form $w(r) = -C/r^6$, one may sum (integrate) the energies of all the atoms in one body with all the atoms in the other and thus obtain the 'two-body' potential for an atom near a surface (Eq. (10.2)), for a sphere near a surface (Eq. (10.5)), or for two flat surfaces (Eq. (10.8)). This procedure can be carried out for other geometries as well. The resulting interaction laws for some common geometries are shown in Fig. 11.1, given in terms of the conventional Hamaker constant

$$A = \pi^2 C \rho_1 \rho_2 \quad (11.1)$$

after Hamaker (1937), who together with Bradley (1932), Derjaguin (1934), and de Boer (1936), did much of the earlier work that advanced understanding of the forces between macroscopic bodies.

Typical values for the Hamaker constants of condensed phases, whether solid or liquid, are about 10^{-19} J for interactions across *vacuum*. For example,

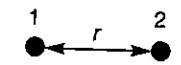

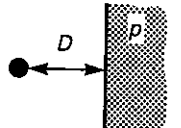
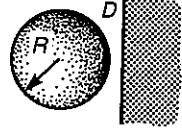
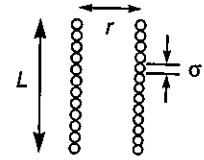
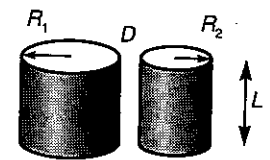
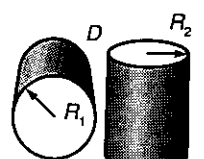
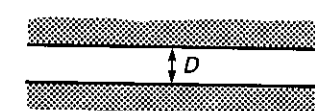
<p>Two atoms</p>  $w = -C/r^6$	<p>Two spheres</p>  $W = \frac{-A}{6D} \frac{R_1 R_2}{(R_1 + R_2)}$
<p>Atom-surface</p>  $w = -\pi C p / 6D^3$	<p>Sphere-surface</p>  $W = -AR/6D$
<p>Two parallel chain molecules</p>  $W = -3\pi CL/8\sigma^2 r^5$	<p>Two cylinders</p>  $W = \frac{AL}{12\sqrt{2} D^{3/2}} \left(\frac{R_1 R_2}{R_1 + R_2} \right)^{1/2}$
<p>Two crossed cylinders</p>  $W = -A\sqrt{R_1 R_2} / 6D$	<p>Two surfaces</p>  $W = -A/12\pi D^2 \text{ per unit area}$

Fig. 11.1. Non-retarded van der Waals interaction free energies between bodies of different geometries calculated on the basis of pairwise additivity (Hamaker summation method). The Hamaker constant A is defined as $A = \pi^2 C \rho_1 \rho_2$ where ρ_1 and ρ_2 are the number of atoms per unit volume in the two bodies and C is the coefficient in the atom-atom pair potential (top left). A more rigorous method of calculating the Hamaker constant in terms of the macroscopic properties of the media is given in Section 11.3. The forces are obtained by differentiating the energies with respect to distance.

if each body is composed of atoms for which $C = 10^{-77} \text{ J m}^6$ (cf. Table 6.1) and of number density $\rho = 3 \times 10^{28} \text{ m}^{-3}$ (corresponding to atoms of radius $\sim 0.2 \text{ nm}$), the Hamaker constant is

$$A = \pi^2 10^{-77} (3 \times 10^{28})^2 \approx 10^{-19} \text{ J } (10^{-12} \text{ erg}).$$

Let us consider three cases more specifically. First, for hydrocarbons, treating them as an assembly of CH_2 groups, we have $C \approx 5 \times 10^{-78} \text{ J m}^6$ and $\rho = 3.3 \times 10^{28} \text{ m}^{-3}$ per CH_2 group, from which we obtain $A \approx 5 \times 10^{-20} \text{ J}$. This is shown in Table 11.1 together with similarly calculated estimates for carbon tetrachloride and water.

TABLE 11.1 Hamaker constants determined from pairwise additivity, Eq. (11.1).

Medium	C (10^{-79} J m^6)	ρ (10^{28} m^{-3})	A (10^{-19} J)
Hydrocarbon	50	3.3	0.5
CCl_4	1500	0.6	0.5
H_2O	140	3.3	1.5

Note that all three Hamaker constants are similar even though the media are composed of molecules differing greatly in polarizability and size. This is not a coincidence. It arises because the coefficient C in the interatomic pair potential is roughly proportional to the square of the polarizability α , which in turn is roughly proportional to the volume v of an atom (Section 5.1). And since $\rho \propto 1/v$ we see that $A \propto C\rho^2 \propto \alpha^2 \rho^2 \propto v^2/v^2 \propto \text{constant}$. Of course, this is a gross oversimplification; nevertheless, the Hamaker constants of most condensed phases are found to lie in the range $(0.4\text{--}4)10^{-19} \text{ J}$.

11.2 STRENGTH OF VAN DER WAALS FORCES BETWEEN BODIES IN VACUUM OR AIR

Taking $A = 10^{-19} \text{ J}$ as a typical value, we can now estimate the strength of the van der Waals interaction between macroscopic bodies in vacuum (or air). Thus, for two spheres of radius $R = 1 \text{ cm} = 10^{-2} \text{ m}$ in contact at $D \approx 0.2 \text{ nm}$, their adhesion force will be

$$\begin{aligned} F &= AR/12D^2 = (10^{-19} \times 10^{-2})/12(2 \times 10^{-10})^2 \\ &= 2 \times 10^{-3} \text{ N (or } 0.2 \text{ g),} \end{aligned}$$

while at $D = 10 \text{ nm}$ the force will have fallen by a factor of 2500 to about 10^{-6} N , or 0.1 mg . Note that these forces are easily measurable using conventional methods.

Turning now to the interaction *energy*, at $D = 10 \text{ nm}$ the energy is $-AR/12D \approx -10^{-14} \text{ J}$, or about $2 \times 10^6 kT$, and even for particles with radii as small as $R = 20 \text{ nm}$ their energy exceeds kT at $D = 10 \text{ nm}$.

For two planar surfaces in contact ($D \approx 0.2 \text{ nm}$), the adhesive pressure will be

$$P = A/6\pi D^3 \approx 7 \times 10^8 \text{ N m}^{-2} \approx 7000 \text{ atm},$$

while at $D = 10 \text{ nm}$ the pressure is reduced by a factor of about 10^5 to a still-significant 0.05 atm . At contact the *adhesion energy* will be $-A/12\pi D^2 \approx -66 \text{ mJ m}^{-2}$, which corresponds to a surface energy of $\gamma = 33 \text{ mJ m}^{-2}$. This is exactly of the order expected for the surface energies and tensions of van der Waals solids and liquids, discussed later. We see, therefore, that the van der Waals interaction between macroscopic particles and surfaces is large, and not only when the bodies are in contact. Later we shall see that in a medium the interaction strength is reduced by about an order of magnitude, and that under certain conditions it can become repulsive.

11.3 THE LIFSHITZ THEORY OF VAN DER WAALS FORCES

The assumptions of simple pairwise additivity inherent in the formulae of Fig. 11.1 and the definition of A of Eq. (11.1) ignore the influence of neighbouring atoms on the interaction between any pair of atoms. First, as we saw in Section 5.7 the effective polarizability of an atom changes when it is surrounded by other atoms. Second, recalling our earlier simple model of the dispersion interaction between two Bohr atoms 1 and 2, if a third atom 3 is present, it too will be polarized by the instantaneous field of atom 1, and its induced dipole field will also act on atom 2. Thus, the field from atom 1 reaches atom 2 both directly and by reflection from atom 3. The existence of multiple reflections and the extra force terms to which they give rise is a further instance where straightforward additivity breaks down, and the matter becomes very complicated when many atoms are present (see Problem 6.2). In rarefied media (gases) these effects are small, and the assumptions of additivity hold, but this is not the case for condensed media. Further, the additivity approach cannot be readily extended to bodies interacting in a medium.

The problem of additivity is completely avoided in the *Lifshitz theory*