

1 INTERACTION POTENTIALS BETWEEN MACROSCOPIC BODIES

In this section we shall relate the pair interaction between two molecules to the interaction between a molecule and a flat surface, between two spherical particles (or two curved surfaces), between a spherical particle and a flat surface, and between two flat surfaces.

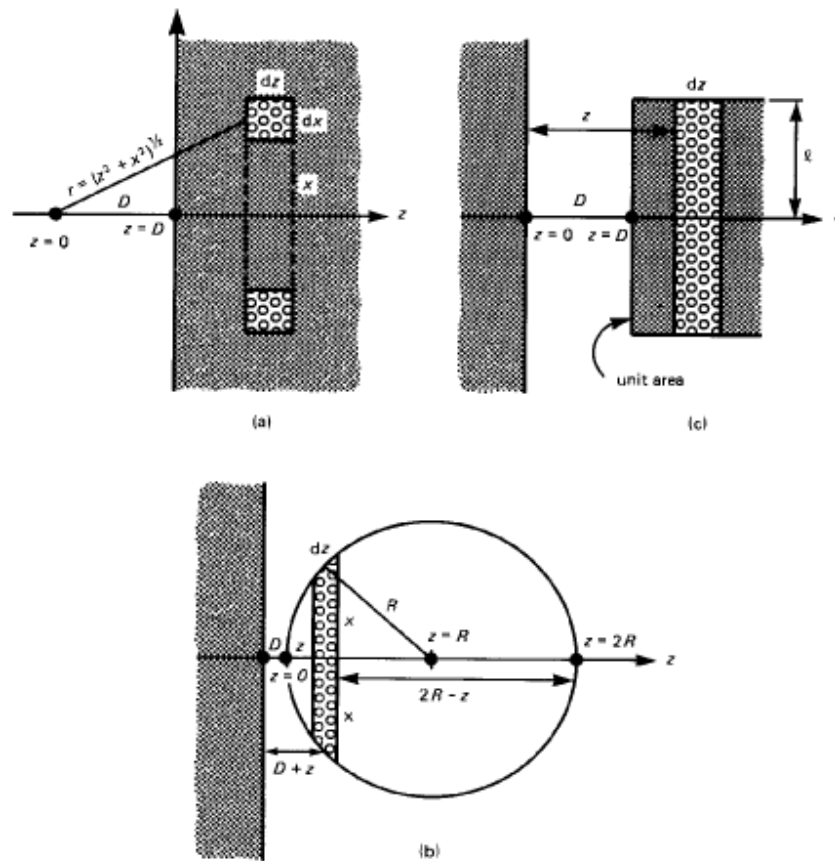


Fig. 10.2. Methods of summing (Integrating) the interaction energies between molecules in condensed phases to obtain the interaction energies between macroscopic bodies. (a) Molecule near a flat surface or 'wall'. (b) Spherical particle near a wall ($R \gg D$). (c) Two planar surfaces ($l \gg D$).

Figure 1: example caption

1.1 Molecule-surface interaction

Let us once again assume that the pair potential between two atoms or small molecules is purely attractive and of the form $w(r) = -C/r^n$. Then, with the further assumption of additivity, the net interaction energy of a molecule and the planar surface of a solid made up of like molecules (Fig. 10.2a) will be the sum of its interactions with all the molecules in the body. For molecules in a circular ring of cross-sectional area $dx dz$ and radius x , the ring volume is $2x dx dz$, and the number of molecules in the ring will be $2\pi\rho x dx dz$, where ρ is the number density of molecules in the solid. The net interaction energy for a molecule at a distance D away from the surface will therefore be

$$w(D) = -2\pi C\rho \int_{z=D}^{z=\infty} dz \int_{x=0}^{x=\infty} \frac{x dx}{(x^2 + z^2)^{n/2}} = \frac{2\pi C\rho}{n-2} \int_D^{\infty} \frac{dz}{z^{n-2}} = -\frac{2\pi C\rho}{(n-2)(n-3)D^{n-3}} \quad (1)$$

where we have used

$$\int_{x=0}^{x=\infty} \frac{x dx}{(x^2 + z^2)^{n/2}} = \frac{1}{2} \int_{x=0}^{x=\infty} \frac{dx^2}{(x^2 + z^2)^{n/2}} = \frac{1}{2} \int_{y=z^2}^{y=\infty} \frac{dy}{y^{n/2}} = -\frac{1}{2} \frac{z^{1-n/2}}{1-n/2} = \frac{1}{n-2} \frac{1}{z^{n-2}}$$

For $n = 6$ (van der Waals forces) becomes

$$w(D) = -\frac{\pi C\rho}{6} D^{-3}$$

The corresponding force could of course have been derived in a similar way by summing (integrating) all the pair forces resolved along the z axis.

1.2 Sphere-surface and sphere-sphere interaction

We can now calculate the interaction energy of a large sphere of radius R and a flat surface (Fig. 10.2b). First, from geometric considerations, with the variables defined in Fig. 1.2 we notice we can write

$$r^2 = R^2 + R^2 - 2R^2 \cos \theta \quad (2)$$

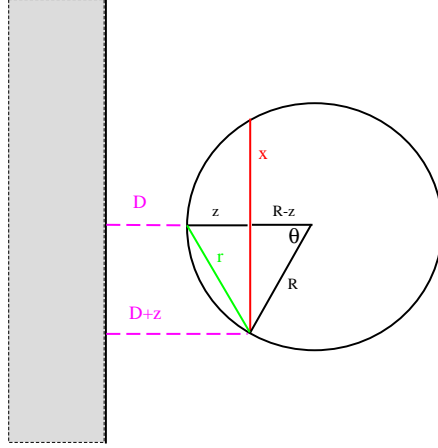
$$x^2 = r^2 - z^2 \quad (3)$$

$$(R - z) = R \cos \theta \quad (4)$$

such that (Chord equation)

$$x^2 = 2R^2 - 2R(R - z) - z^2 = 2Rz - z^2 = z(2R - z) \quad (5)$$

The volume of a thin circular section of area πx^2 and thickness dz is therefore $\pi x^2 dz = \pi(2R - z)z dz$, so that the number of molecules contained within this section is $\pi\rho(2R -$



$z)zdz$ where ρ is the number density of molecules in the sphere. Since all these molecules are at a distance $(D + z)$ from the planar surface, the net interaction energy is,

$$W(D) = -\frac{2\pi^2 C \rho^2}{(n-2)(n-3)} \int_{z=0}^{z=2R} \frac{(2R-z)z}{(D+z)^{n-3}} dz$$

For $D \ll R$, only small values of z ($z \approx D$) contribute to the integral, and we can extend the integration limit and neglect z with respect to $2R$ to obtain

$$\begin{aligned} W(D) &= -\frac{2\pi^2 C \rho^2}{(n-2)(n-3)} \int_0^\infty \frac{2Rz}{(D+z)^{n-3}} dz = -\frac{2\pi^2 C \rho^2}{(n-2)(n-3)} \int_0^\infty \frac{2R(t-D)}{t^{n-3}} dt \\ &= -\frac{4\pi^2 C \rho^2 R}{(n-2)(n-3)(n-4)(n-5)D^{n-5}} \end{aligned}$$

which for $n = 6$ (van der Waals forces) becomes

$$W(D) = -\frac{\pi^2 C \rho^2 R}{6D}$$

Note that the interaction energy is proportional to the radius of the sphere and that it decays as $1/D$, very much slower than the $1/r^6$ dependence of the intermolecular pair interaction.

For $D \gg R$, we may replace $(D + z)$ in the denominator by D , and we then obtain

$$W(D) = -\frac{2\pi^2 C \rho^2}{(n-2)(n-3)} \int_0^{2R} \frac{(2R-z)z}{D^{n-3}} dz = -\frac{2\pi C \rho (4\pi R^3 \rho / 3)}{(n-2)(n-3)D^{n-3}}$$

Since $4\pi R^3 \rho / 3$ is simply the number of molecules in the sphere, the above is essentially the same as the expression for the interaction of a molecule (or small sphere) with a surface.

It is left as an exercise for the interested reader to show that for two spheres of equal radii R whose surfaces are at a small distance D apart ($R \gg D$), their interaction energy is one half that we have calculated, while for two spheres far apart ($D \gg R$) the energy varies as $-1/D^n$ as for two molecules. At intermediate separations ($R \approx D$) the expression for the interaction potential is more complicated but remains analytic.

1.3 Surface-surface interactions

Let us now calculate the interaction energy of two planar surfaces a distance D apart. For two infinite surfaces, the result will be infinity, and so we have to consider the energy per unit surface area. Let us start with a thin sheet of molecules of unit area and thickness dz at a distance z away from an extended surface of larger area (Fig. 10.2c). From the previous calculations, the interaction energy of this sheet with the surface is $-2C\rho(\rho dz)/(n-2)(n-3)z^{n-3}$. Thus, for the two surfaces, we have

$$W(D) = -\frac{2\pi C\rho^2}{(n-2)(n-3)} \int_D^\infty \frac{1}{z^{n-3}} dz = -\frac{2\pi C\rho^2}{(n-2)(n-3)(n-4)D^{n-4}} \quad (6)$$

which for $n = 6$ becomes

$$W(D) = -\frac{\pi C\rho^2}{12D^2} \quad \text{per unit area.}$$

It is important to note that these two expressions are for unit area of one surface interacting with an infinite area of another surface. In practice this usually amounts to two unit areas of both surfaces, but it is strictly applicable only when D is small compared to the lateral dimensions of the surfaces.

2 INTERACTION ENERGIES AND INTERACTION FORCES: THE DERJAGUIN APPROXIMATION

So far we have been dealing mainly with interaction energies rather than the forces experienced by molecules and particles. This is because most experimental data on molecular interactions are of a thermodynamic nature and therefore more readily understood in terms of interaction energies. However, between macroscopic bodies it is the forces between them that are often easier to measure, and of greater interest, than their interaction energies. It is therefore desirable to be able to relate the force law $F(D)$ between two curved surfaces to the interaction free energy $W(D)$ between two planar surfaces. Luckily, a simple relation exists for the two geometries most commonly encountered, viz. two flat surfaces and two spheres (a sphere near a flat surface being a special case of two spheres with one sphere very much larger than the other). A glance at Eq. 1 shows that for the additive intermolecular

pair potential $w(r) = -C/r^n$, the value of $F(D)$ for a sphere near a flat surface (sphere of infinite curvature) is

$$F(D) = -\frac{\partial W(D)}{\partial D} = -\frac{4\pi^2 C \rho^2 R}{(n-2)(n-3)(n-4)D^{n-4}}$$

This force law can be seen to be simply related to $W(D)$ per unit area of two planar surfaces (Eq.6), by

$$F(D)_{\text{sphere-sphere}} = 2\pi R W(D)_{\text{plane-plane}}$$

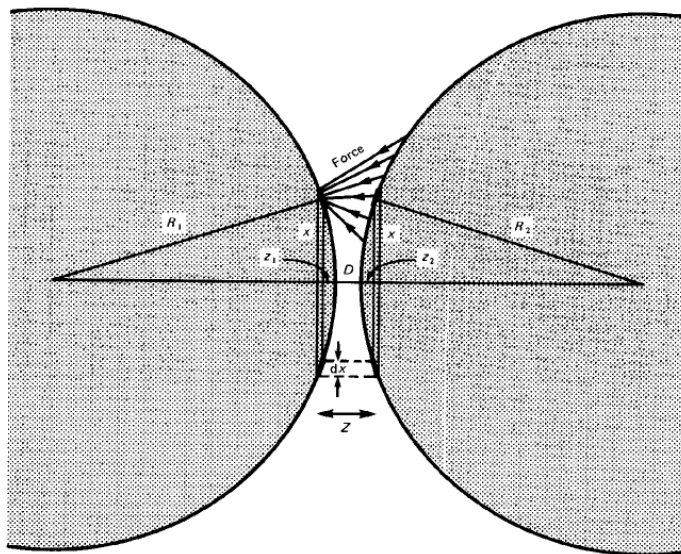


Fig. 10.3. The Derjaguin approximation (Derjaguin, 1934), which relates the force law $F(D)$ between two spheres to the energy per unit area $W(D)$ of two flat surfaces by $F(D) = 2\pi[R_1 R_2 / (R_1 + R_2)]W(D)$.

This is a very useful relationship, and while it was derived for the special case of an additive inverse power potential, it is in fact valid for any type of force law, as will now be shown. Assume that we have two large spheres of radii R_1 and R_2 a small distance D apart (Fig. 10.3). If $R_1 \gg D$ and $R_2 \gg D$, then the force between the two spheres can be obtained by integrating the force between elementary surfaces. Consider the surface of the left sphere as divided in small circular regions of area $2\pi x dx$. Each of these surface interact with the entire right sphere, which is considered as a planar interface (locally flat). The distance between the surface differential element and the planar interface is calculated along the line connecting the sphere-sphere centres, $Z = D + z_1 + z_2$ and it is identical for all elements composing the small circular region of area $2\pi x dx$

The net force between the two spheres (in the z direction) is therefore

$$F(D) = \int_{Z=D}^{Z=\infty} 2\pi x dx f(Z)$$

where $f(Z)$ is the normal force *per unit area* between two flat surfaces. Since from the Chord Theorem (Eq. 5), neglecting z_i respect to R_i , $x^2 = 2R_1z_1 = 2R_2z_2$, we have

$$Z = D + z_1 + z_2 = D + \frac{x^2}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

$$dZ = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) x dx$$

so that

$$F^{sphere-sphere}(D) = \int_D^\infty 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) f(Z) dZ$$

Now we note that if we had to calculate the interaction energy of an unit of surface, we would have integrated from infinity to D the force $f(Z)$. Hence

$$\begin{aligned} F^{sphere-sphere}(D) &= 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) W^{plane-plane,unit\ area}(D) \\ &\sim \int_0^D F^{plane-plane,unit\ area}(D') dD' \end{aligned}$$

which gives the force between two spheres in terms of the energy per unit area of two flat surfaces at the same separation D . Note also that the derivative of the sphere-sphere force is proportional to the plane-plane force.

The previous equation is known as the Derjaguin approximation (Derjaguin, 1934). It is applicable to any type of force law, whether attractive, repulsive or oscillatory, so long as the range of the interaction and the separation D is much less than the radii of the spheres. It is a useful theoretical tool, since it is usually easiest to derive the interaction energy for two planar surfaces (rather than for curved surfaces). It is also useful for interpreting experimental data and it has been well verified experimentally. From the Derjaguin approximation, we may deduce the following:

- (i) If one sphere is very large so that $R_2 \gg R_1$, we obtain $F(D) = 2\pi R_1 W(D)$, which is the same as we had calculated and corresponds to the limiting case of a sphere near a flat surface.
- (ii) For two equal spheres of radii $R = R_1 = R_2$, we obtain $F(D) = \pi R W(D)$, which is half the value for a sphere near a flat surface.

- (iii) For two spheres in contact ($D = \sigma$), the value of $W(\sigma)$ can be associated with 2γ , where γ is the conventional surface energy per unit area of a surface. The Derjaguin expression then becomes

$$F(\sigma) = F_{ad} = \frac{4\pi\gamma R_1 R_2}{R_1 + R_2}$$

which gives the adhesion force F_{ad} between two spheres in terms of their surface energy.

- (iv) Perhaps the most intriguing aspect of the Derjaguin approximation is that it tells us that the distance dependence of the force between two curved surfaces can be quite different from that between two flat surfaces even though the same type of force is operating in both. This is illustrated in Fig. 10.4, where we see that a purely repulsive force between two curved surfaces can be attractive between two planar surfaces (over a certain distance regime), with equilibrium at some finite separation (Fig. 10.4b). Conversely, a purely attractive force between curved surfaces can become repulsive between two planar surfaces (Fig. 10.4c).
- (v) Finally, it may be readily shown that for two cylinders of radii R_1 and R_2 crossed at an angle θ to each other, the Derjaguin approximation becomes

$$F(D) = \frac{2\pi\sqrt{R_1 R_2} W(D)}{\sin \theta} \quad \text{for } D \ll R_1, R_2$$

Note that for two cylinders of equal radii $R = R_1 = R_2$, crossed at right angles to each other ($\theta = 90, \sin \theta = 1$) the above reduces to the same result as for a sphere of radius R near a flat surface. In other words the interaction of two orthogonal cylinders is the same as that of a sphere and a wall if all three radii are the same.

3 VAN DER WAALS FORCES BETWEEN SURFACES

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

As we saw previously, 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

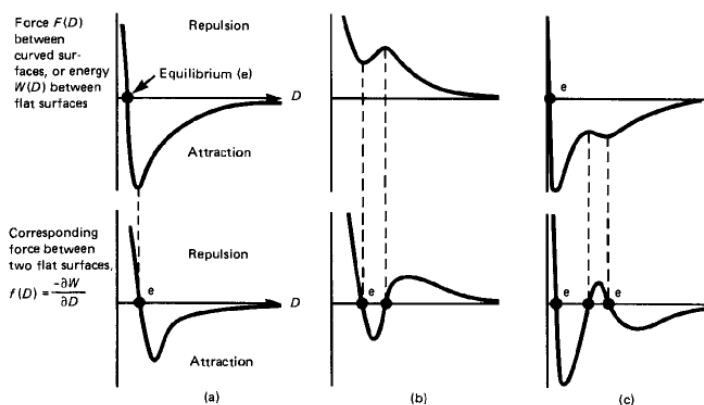


Fig. 10.4. Top row: force laws between two curved surfaces (e.g., two spherical particles). Bottom row: corresponding force laws between two flat surfaces. Note that stable equilibrium occurs only at points marked *e* where the force is zero ($f = 0$) and the force curve has negative slope; the other points where $f = 0$ are unstable.

Figure 2: example caption

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, for a sphere near a surface, or for two flat surfaces. 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

$$A = \pi^2 C \rho_1 \rho_2$$

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. The Hamaker constants of most condensed phases are found to lie in the range $(0.4 - 4) \cdot 10^{-19}$ J, to be compared with the value of $k_B T$ at ambient temperature $k_B T \approx 4 \cdot 10^{-21}$ J. Since the Hamaker constants are of the order of $k_B T$, two spheres of radius $R = 0.5 \mu\text{m}$ at distance of 0.5 nm interact with an energy of the order of $100 k_B T$, which means that these particles will aggregate.

To prevent aggregation, two different strategies are commonly adopted to add a repulsive interaction. One is to charge the particle surface (to add an electrostatic repulsive interaction) and the other is to graft the surfaces of the particle with non-absorbing polymers. The interaction between such surfaces will be discussed elsewhere.

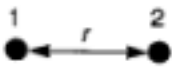

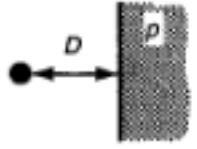
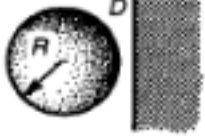
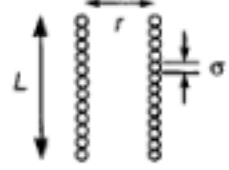
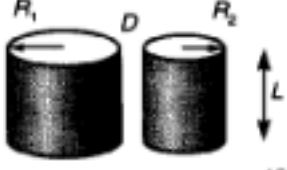
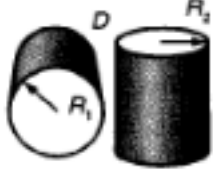
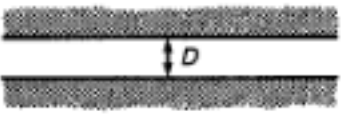
<p>Two atoms</p>  $w = -C/r^6$	<p>Two spheres</p>  $W = \frac{-A}{6D} \frac{R_1 R_2}{(R_1 + R_2)}$
<p>Atom-surface</p>  $w = -\pi C\rho/6D^3$	<p>Sphere-surface</p>  $W = -AR/6D$
<p>Two parallel chain molecules</p>  $W = -3\pi CL/8\sigma^2 r^3$	<p>Two cylinders</p>  $W = \frac{AL}{12\sqrt{2}} D^{3/2}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

3.2 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 we have given ignore the influence of neighbouring atoms on the interaction between any pair of atoms. First, as we saw 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. 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 where the atomic structure is ignored and the forces between large bodies, now treated as continuous media, are derived in terms of such bulk properties as their dielectric constants and refractive indices. However, before we proceed it is well to point out that all the expressions in Fig. 11.1 for the interaction energies remain valid even within the framework of continuum theories. The only thing that changes is the way the Hamaker constant is calculated. The original Lifshitz theory (Lifshitz, 1956; Dzyaloshinskii et al., 1961) requires a thorough working knowledge of quantum field theory for its understanding, and it is probably due to this that it was initially ignored by most scientists who persisted with the additivity approach of Hamaker. Later, Langbein, Ninham, Parsegian, Van Karopen and others, showed how the essential equations could be derived using much simpler theoretical techniques (for reviews see Israelachvili and Tabor, 1973; Parsegian, 1973; Israelachvili, 1974; Mahanty and Ninham 1976). Here we shall adopt the simplest of these using a modified additivity approach.

We have already seen that the van der Waals interaction is essentially electrostatic, arising from the dipole field of an atom 'reflected back' by a second atom that has been polarized by this field.

To evaluate the polarizability of atoms immersed in a material of known dielectric constant, we compare a case where we are able to solve the problem exactly. We consider a charge interacting with a polarizable molecule both of them in a medium of dielectric constant ϵ_3 . For this case, we have seen that the interaction energy of a charge with a polarizable molecule is given by

$$w(r) = -\frac{C}{r^n} = -\frac{Q^2\alpha_2}{2(4\pi\epsilon_3)^2r^4}$$

where α_2 is the excess polarizability of molecule 2 in medium 3.

Next consider the case in which molecules of type 2 occupy the volume at the right of a planar surface at distance D from the charge, with density ρ_2 . When molecule 2 is

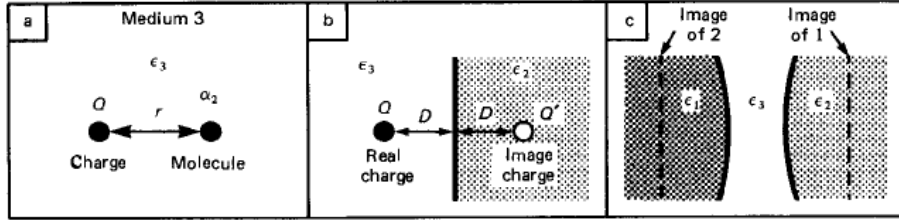


Fig. 11.2. (a) A charge interacts with a neutral molecule because of the field reflected by the molecule on becoming polarized. (b) Likewise, a charge interacts with a surface because of the field reflected by the surface. This reflected field is the same as if there were an 'image' charge Q' at a distance $2D$ from Q . Similarly, a dipole near a surface will see an image of itself reflected by the surface. If $\epsilon_2 > \epsilon_3$, the force is attractive; if $\epsilon_2 < \epsilon_3$, it is repulsive. (c) Two surfaces will see an image of each other reflected by the other surface that gives rise to the van der Waals force between them. In principle, the reflected or image fields are the same as occur when one looks at a glass surface or a mirror. Metal surfaces reflect most of the light falling on them, and the van der Waals force between metals is much stronger than that between dielectric media.

replaced by a medium the interaction between the charge in medium 3 and medium 2 may be obtained by the method of additivity, which gives $W(D) = -2\pi C\rho_2/(n-2)(n-3)D^{n-3}$. Inserting values for C and n from Eq. 1 gives

$$W(D) = -\frac{\pi Q^2 \rho_2 \alpha_2}{2(4\pi\epsilon_3)^2 D} \quad (7)$$

However, it is well known that a charge Q in a medium of dielectric constant ϵ_3 at a distance D from the plane surface of a second medium of dielectric constant ϵ_2 experiences a force as if there were an 'image' charge of strength $-Q \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right)$ at a distance D on the other side of the boundary, i.e., at a distance $2D$ away (Landau and Lifshitz, 1984, Ch. II). This force is therefore given by

$$F(D) = -\frac{Q^2}{4\pi\epsilon_3(2D)^2} \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right)$$

which corresponds to an interaction energy of

$$W(D) = -\frac{Q^2}{4(4\pi\epsilon_3)D} \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) \quad (8)$$

Equating the two expressions Eq. 7 and 8 we find that

$$\rho_2 \alpha_2 = 2\epsilon_3 \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right)$$

This is an important result, giving the excess bulk or volume polarizability of a planar dielectric medium 2 in medium 3 in terms of the purely macroscopic properties of the

media. The Hamaker constant for the interaction of two media 1 and 2 across a third medium 3 may now be expressed as

$$A = \pi^2 C \rho_1 \rho_2 = \frac{6\pi^2 k_B T \rho_1 \rho_2 \alpha_1 \alpha_2}{(4\pi \epsilon_3)^2}$$

$$= \frac{3}{2} k_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right)$$

A more precise (quantum mechanics based) derivation, accounting for the frequency dependence of the dielectric constant, gives

$$A = \frac{3}{2} k_B T \sum_{n=0,1,\dots}^{\infty} \left[\frac{\epsilon_1(i\nu_n) - \epsilon_3(i\nu_n)}{\epsilon_1(i\nu_n) + \epsilon_3(i\nu_n)} \right] \left[\frac{\epsilon_2(i\nu_n) - \epsilon_3(i\nu_n)}{\epsilon_2(i\nu_n) + \epsilon_3(i\nu_n)} \right]$$

Replacing the sum by the integral we end up with the expression for the Hamaker constant based on the Lifshitz theory

$$A \approx \frac{3}{4} k_B T \left[\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right] \left[\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right] + \frac{3h}{4\pi} \int_{\nu_1}^{\infty} \left[\frac{\epsilon_1(i\nu) - \epsilon_3(i\nu)}{\epsilon_1(i\nu) + \epsilon_3(i\nu)} \right] \left[\frac{\epsilon_2(i\nu) - \epsilon_3(i\nu)}{\epsilon_2(i\nu) + \epsilon_3(i\nu)} \right]$$

where ϵ_i are the static dielectric constants of the three media, $\epsilon(i\nu)$ are the values of ϵ at imaginary frequencies, $\nu_n = (2k_B T/h)n = 4 \cdot 10^{13} \text{ s}^{-1}$ at 300 K. The first term gives the zero-frequency energy of the van der Waals interaction and includes the Keesom and Debye dipolar contributions. The second term gives the dispersion energy and includes the London energy contribution. The previous equations are not exact but are only the first term in an infinite series for the non-retarded Hamaker constant. The other terms, however, are small and rarely contribute more than 5 %.

If a particle of dielectric constant ϵ_1 is immersed in two coexisting fluids of dielectric constant ϵ_2 and ϵ_3 it will behave in one of two ways depending on the relative values of the dielectric permittivities:

- (i) The particle will be attracted to the interface from either side of it (e.g. if ϵ_1 is intermediate between ϵ_2 and ϵ_3).
- (ii) The particle will be attracted towards the interface from one side and then repelled from the other side (e.g., if $\epsilon_1 > \epsilon_3 > \epsilon_2$)

Thus, in the absence of constraints or other forces the van der Waals interaction alone may promote the migration of small uncharged particles across liquid interfaces. Note that repulsion from both sides of the interface never occurs.