

van der Waals Forces: Part I

Dr. Pallab Ghosh
Associate Professor
Department of Chemical Engineering
IIT Guwahati, Guwahati–781039
India

Table of Contents

Section/Subsection	Page No.
3.1.1 Intermolecular and surface forces	3
3.1.2 van der Waals EOS	4
3.1.3 Mie and Lennard-Jones potentials	6
3.1.4 Types of van der Waals force	8
3.1.5 Retardation effect	10
3.1.6 Relation between London force constant and the van der Waals EOS parameters	10
3.1.7 van der Waals force between two macroscopic bodies	11
3.1.8 Derjaguin approximation	14
3.1.9 Hamaker constant	15
Exercise	20
Suggested reading	22

3.1.1 Intermolecular and surface forces

- ◆ The forces of Nature can be broadly classified into four categories: (i) strong and weak interactions which occur between the constituents of atoms, (ii) electromagnetic, and (iii) gravitational forces.
- ◆ The first two forces act between electrons, protons, neutrons and other elementary particles. Their range of operation is very small, within $\sim 10^{-14}$ m. The electromagnetic and gravitational forces operate over a much wider range. The electromagnetic forces are the source of all intermolecular interactions and they are responsible for the properties of matter in pure state as well as in solution. The gravitational forces are also very important in interface science, e.g., capillary rise and the related phenomena.
- ◆ The attraction and repulsion between particles and surfaces have enormous significance in the adsorption of surfactants at interfaces, adhesion, stability of colloids and micellization of surfactants. Some of the most important forces are van der Waals forces, electrostatic double layer force, solvation and steric forces.
- ◆ The van der Waals forces involve momentary attraction between molecules and atoms. They are different from covalent and ionic bonds. Since their origin is in the atomic level, they are important in all aspects involving materials. They are not as strong as Coulomb or hydrogen bonding forces, but they are omnipresent. The van der Waals forces are responsible for coagulation of colloids and coalescence of drops and bubbles.
- ◆ The electrostatic double layer force at the fluid–fluid and liquid–solid interfaces becomes important when charged molecules are present at the interfaces. The charge may arise due to the adsorption of a charged ion (such as an ionic surfactant or a polyelectrolyte) at the interface, or dissociation of an ionizable surface group (e.g., the dissociation of $-\text{COOH}$ or $-\text{SiOH}$ groups present on the surface of a solid).
- ◆ The dissociated group attached to the surface attracts the counterions by Coulomb force. On the other hand, osmotic pressure forces the counterions away from the surface and from each other. The dispersion of the counterions is

thermodynamically favorable because it increases the entropy. A balance between the Coulomb attraction and osmotic repulsion maintains the double layer. Two similarly-charged surfaces encounter osmotic repulsion when they approach each other due to the reduction in entropy.

- ◆ The double layer force is very important in the stabilization of emulsions, foams, and colloids. The combined effect of van der Waals and double layer forces between two surfaces is described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.
- ◆ At very small separations between the surfaces or particles (say, a few nanometers), the non-DLVO forces such as the solvation forces and hydrophobic interaction forces become important. The contribution from such forces can be very large, even greater than the DLVO forces.
- ◆ The solvation forces arise mainly due to the ordering of the solvent molecules into discrete layers between the surfaces in a highly restricted space. The repulsion can be caused by the hydrated groups at the surfaces when they approach each other. In this case too, the repulsion has entropic origin. It has been found that the solvation forces stabilize certain soap films and gas bubbles in salty media.
- ◆ Another example of repulsion caused by the reduction in entropy is the polymeric steric force. When two surfaces on which polymer molecules are adsorbed approach each other, they encounter this type of repulsion. The polymer brushes overlap when two polymer-covered surfaces come into very close proximity of each other. The repulsive osmotic force develops due to the unfavorable entropy that happens due to the confinement of the chains trapped between the surfaces of the particles.

3.1.2 van der Waals EOS

- ◆ In 1873, van der Waals pointed out that real gases do not obey the ideal gas law, $PV = mRT$. He suggested that two correction terms should be included to improve the accuracy of the ideal gas law.

- ◆ In ideal gas law, intermolecular attraction and the space occupied by the gas molecules were ignored. According to van der Waals, there should be correction terms for pressure (due to the attraction between the molecules, which is valid for polar as well as nonpolar molecules), and volume (due to the finite size of the molecules, which act as hard spheres during collision).
- ◆ The equation proposed by van der Waals was,

$$\left(P + \frac{m^2 a}{V^2}\right)(V - mb) = mRT \quad (3.1.1)$$

- ◆ The van der Waals constants, a and b , are different for different gases. Two types of forces were proposed by van der Waals: (i) the short-range repulsive forces which give rise to the excluded volume constant, b , and (ii) the long-range attractive forces which lead to the constant a . The values of these constants for some gases are presented in Table 3.1.1.

Table 3.1.1 van der Waals constants a and b for some gases

Gas	a ($\text{m}^6 \text{ Pa/mol}^2$)	$b \times 10^5$ (m^3/mol)
Hydrogen	0.0247	2.7
Oxygen	0.1378	3.2
Nitrogen	0.1408	3.9
Carbon dioxide	0.3638	4.3
Ammonia	0.4225	3.7
Methane	0.2280	4.3
Argon	0.1368	3.2
Helium	0.0034	2.4

- ◆ The constant, a , varies with temperature. The attractive force decreases with the rise of temperature. The effect of temperature on b is comparatively small (b decreases slightly with rise in temperature for some gases).

3.1.3 Mie and Lennard-Jones potentials

- ◆ The two correction terms proposed by van der Waals are related to the interaction energy between the gas molecules. In the early part of the twentieth century, a few semi-empirical correlations were proposed for the interaction energy. For example, Mie (1903) gave the following correlation.

$$\phi = -\frac{A}{s^p} + \frac{B}{s^q} \quad (3.1.2)$$

- ◆ The first term represents attraction and the second term represents repulsion between two molecules separated by a distance s . The force is given by,

$$F = -\frac{d\phi}{ds} \quad (3.1.3)$$

- ◆ Another correlation was proposed by Lennard-Jones in 1925, which can be considered as a special case of the correlation proposed by Mie.

$$\phi = -\frac{A}{s^6} + \frac{B}{s^{12}} \quad (3.1.4)$$

- ◆ The interaction energy, ϕ , given by this equation is also known as *L-J potential* or *6-12 potential*. Equations (3.1.2) and (3.1.4) were developed based on the hypothesis that the pair of molecules is subject to two distinct forces in the limits of large and small separations, viz. an attractive force at the long ranges and a repulsive force at short ranges. The attraction is due to the dispersion interactions. The short-range repulsion term is due to the overlap of the molecular orbitals (known as *Pauli repulsion* or *Born repulsion*).
- ◆ Although the Lennard-Jones equation was proposed semi-empirically, it still finds wide use among the scientists, especially in molecular dynamics simulations. The following example illustrates the energy profile as per the Lennard-Jones equation.

Example 3.1.1: The Lennard-Jones parameters for argon are: $A = 1.022 \times 10^{-77} \text{ J m}^6$ and $B = 1.579 \times 10^{-134} \text{ J m}^{12}$. Draw the energy profile. Calculate the distance at which the energy will be minimum. Calculate the minimum energy.

Solution: Putting the values of A and B in Eq. (3.1.4) we get,

$$\phi = -\frac{1.022 \times 10^{-77}}{s^6} + \frac{1.579 \times 10^{-134}}{s^{12}}$$

This equation is represented graphically in Fig. 3.1.1.

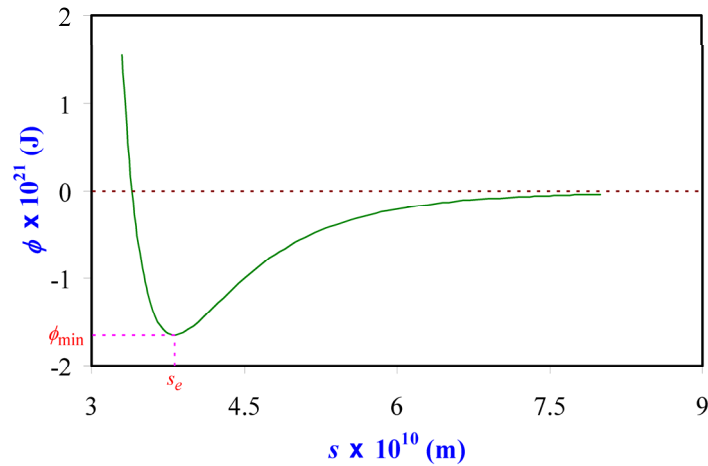


Fig. 3.1.1 Variation of interaction energy with distance.

The energy will be minimum when $d\phi/ds = 0$. This occurs at $s = s_e$. Therefore,

$$\frac{6A}{s_e^7} = \frac{12B}{s_e^{13}}$$

$$\therefore s_e = (2B/A)^{1/6}$$

Putting the values of A and B in the above equation we get, $s_e = 3.816 \times 10^{-10}$ m.

The minimum energy is,

$$\phi_{\min} = \phi|_{s_e} = -\frac{A^2}{2B} + \frac{A^2}{4B} = -\frac{A^2}{4B}$$

$$\therefore \phi_{\min} = -\frac{(1.022 \times 10^{-77})^2}{4 \times 1.579 \times 10^{-134}} = -1.651 \times 10^{-21} \text{ J}$$

s_e and $\phi_{\min}$ are indicated in the above figure.

3.1.4 Types of van der Waals force

- ◆ The total van der Waals interaction between molecules has three components: (i) interaction between two induced dipoles, which is known as *London dispersion force*, (ii) interaction between two permanent dipoles, which is known as *Keesom orientation force*, and (iii) interaction between one permanent dipole and one induced dipole, which is known as *Debye induction force*.
- ◆ Interestingly, each of these contributions varies with s^{-6} . The dispersion forces were explained by Fritz London in 1930. These forces exist between all atoms and molecules, even the non-polar molecules. At any given instant, a non-polar molecule will have a dipole moment because of the fluctuations in the distribution of the electrons in the molecule. This dipole creates an electric field that polarizes another molecule located nearby, and an induced dipole results. The interaction between these dipoles leads to the attractive energy. The time-averaged dipole moment of each molecule is zero but the time-averaged interaction energy is finite due to these temporarily interacting dipoles. The molecules of hydrocarbons and liquefied gases are held together mainly by these forces.
- ◆ The main features of dispersion forces can be summarized as follows.
 - (i) They are long-range forces and depending on the situation, can be effective from large distances (> 10 nm) down to interatomic spacings.
 - (ii) These forces can be repulsive or attractive, and in general the dispersion force between two molecules or large particles does not follow a simple power law.
 - (iii) Dispersion forces not only bring molecules together, but also tend to mutually align or orient them, though this orienting effect is usually weak.
 - (iv) The dispersion interaction of two bodies is affected by the presence of other bodies nearby. This is known as the *non-additivity* of the interaction.
- ◆ In addition to the London force, additional interactions exist between polar molecules. The Keesom interaction involves interaction between permanent

dipoles, and the Debye interaction involves permanent dipole–induced dipole interaction.

- ◆ Since each of these three interactions has energy which varies with the inverse sixth power of the distance, the total van der Waals interaction energy for two dissimilar polar molecules is given by,

$$\phi_{\text{vdW}} = -\frac{A_{\text{vdW}}}{s^6} = -\frac{A_L + A_K + A_D}{s^6} \quad (3.1.5)$$

The details of each of these three components of total van der Waals interaction energy have been discussed in detail by Israelachvili (1997).

- ◆ The expression for ϕ_{vdW} in terms of molecular parameters is given by,

$$\phi_{\text{vdW}} = -\left[\frac{1}{(4\pi\epsilon_0)^2 s^6} \right] \left[\left\{ \frac{3\alpha_1\alpha_2 h\nu_1\nu_2}{2(\nu_1 + \nu_2)} \right\} + \left(\frac{\mu_1^2 \mu_2^2}{3kT} \right) + (\mu_1^2 \alpha_2 + \mu_2^2 \alpha_1) \right] \quad (3.1.6)$$

where μ is the dipole moment, α is the polarizability, h is Planck's constant, ν is the orbiting frequency of electron, k is Boltzmann's constant and ϵ_0 is the permittivity of the free space. The subscripts 1 and 2 refer to the two molecules.

- ◆ The dispersion forces are probably the most important of the three forces which constitute the total van der Waals force. They are always present, but the presence of the other two types depends upon the properties of the molecules. The dispersion forces play very important roles in adhesion, adsorption, wetting, physical properties of gases and liquids, thin films, coagulation, coalescence and many other phenomena.

Example 3.1.2: Estimate the London dispersion force constant (A_L) for neon using the following data: $h\nu = 3.46 \times 10^{-18}$ J, and $\frac{\alpha}{4\pi\epsilon_0} = 3.9 \times 10^{-31}$ m³.

Solution: The London constant is given by,

$$A_L = \frac{3}{4} \left(\frac{\alpha}{4\pi\epsilon_0} \right)^2 h\nu$$

Inserting the values of $h\nu$ and $\alpha/(4\pi\epsilon_0)$ in the above equation, we get,

$$A_L = \frac{3}{4} \times (3.9 \times 10^{-31})^2 \times 3.46 \times 10^{-18} = 3.95 \times 10^{-79} \text{ J m}^6$$

3.1.5 Retardation effect

- ◆ If the distance between two molecules is large, the time taken by the electric field issued from the instantaneously-polarized molecule to reach the second molecule can be longer than the time period of the fluctuating dipole. The oscillating dipole induced by the second molecule re-radiates an electromagnetic field that is propagated back to the first molecule. Therefore, when the latter field reaches the first molecule, it may find that the orientation of the instantaneous dipole of the first molecule has changed from the original, and may be unfavorable for attractive interaction.
- ◆ Therefore, the dispersion energy may decay at a rate that is faster than $1/s^6$. The dispersion force between molecules at large separations is known as *retarded force*, and the effect is known as *retardation effect*.
- ◆ In free space, the retardation effect becomes important when the distance between the molecules is ~ 5 nm. In media where the speed of light is slower, the retardation effect can occur at smaller separations. Only the dispersion force encounters such retardation, the orientation and induction forces are not affected.

3.1.6 Relation between London force constant and the van der Waals EOS parameters

- ◆ The London dispersion force constant can be correlated with the parameters of the van der Waals equation of state (i.e., a and b). The relationship is given by (Israelachvili, 1997),

$$A_L = \frac{9}{4} \frac{ab}{\pi^2 N_A^3} \quad (3.1.7)$$

where N_A is Avogadro's number.

Example 3.1.3: Calculate the value of the London dispersion force constant for methane using the constants of the van der Waals equation of state.

Solution: The values of a and b for methane are (Table 3.1.1),

$$a = 0.228 \text{ m}^6 \text{ Pa mol}^{-2}$$

$$b = 4.3 \times 10^{-5} \text{ m}^3/\text{mol}$$

$$A_L = \frac{9}{4} \frac{ab}{\pi^2 N_A^3} = \frac{9 \times 0.228 \times 4.3 \times 10^{-5}}{4\pi^2 \times (6.023 \times 10^{23})^3} = 1.02 \times 10^{-77} \text{ J m}^6$$

3.1.7 van der Waals force between two macroscopic bodies

- ◆ The procedure to calculate the van der Waals interaction energy *in vacuo* between two bodies having simple geometry was developed by H. C. Hamaker (1937).
- ◆ It is assumed that the interaction is additive as well as non-retarded. These two assumptions will make the treatment approximate for the reasons discussed earlier.
- ◆ The (attractive) London interaction energy between two atoms or small molecules is $-A_L/s^6$.
- ◆ Let us first consider the interaction between a molecule and a solid body of infinite extent bounded by a plane surface (i.e., a planar half-space) which is made of the same molecules, as shown in Fig. 3.1.2.

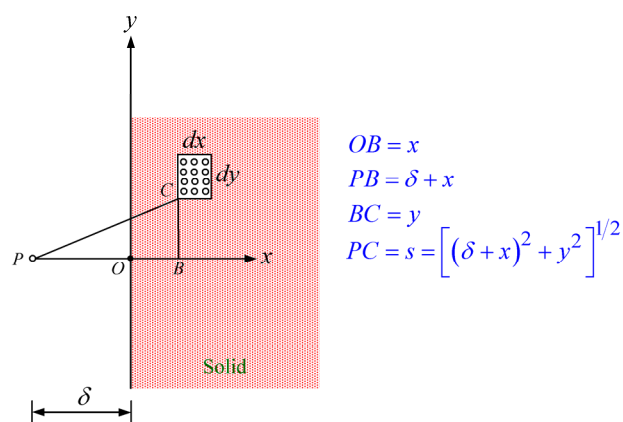


Fig. 3.1.2 Interaction between a molecule and a planar half-space.

- ◆ The net interaction will be the sum of the interactions of this molecule with all the molecules in the body. The volume of the circular ring of radius y and cross sectional area $dx dy$ containing the molecules shown in Fig. 3.1.2 is $2\pi y dx dy$. The number of molecules in the ring is $2\pi n y dx dy$, where n is the number of molecules per unit volume of the solid. The net interaction energy of the molecule P at a distance δ away from the surface is,

$$\phi = -2\pi n A_L \int_0^\infty dx \int_0^\infty \frac{y dy}{\left[(\delta + x)^2 + y^2\right]^{3/2}} = -\frac{\pi n A_L}{6\delta^3} \quad (3.1.8)$$

The force is given by,

$$F = -\frac{d\phi}{d\delta} = -\frac{\pi n A_L}{2\delta^4} \quad (3.1.9)$$

- ◆ Following a similar procedure, we can derive the expressions for the interaction energy for some simple shapes which are of importance in interfacial engineering. The analytical solution is possible for a few cases only. For example, the van der Waals interaction energy per unit area between two blocks of the same material at distance δ apart is given by,

$$\phi = -\frac{\pi n^2 A_L}{12\delta^2} \quad (3.1.10)$$

- ◆ The quantity, $\pi^2 n^2 A_L$, is known as *Hamaker constant* (A_H) (Hamaker, 1937). If the interaction between the molecules of type 1 and type 2 is being considered then,

$$A_H = \pi^2 n_1 n_2 A_L^{1,2} \quad (3.1.11)$$

where $A_L^{1,2}$ is the London constant for molecules of types 1 and 2, and n_1 and n_2 are the number of molecules per unit volumes of the two types of material, respectively.

- ◆ Therefore, Eq. (3.1.10) can be written in terms of Hamaker constant as,

$$\phi = -\frac{A_H}{12\pi\delta^2} \quad (3.1.12)$$

The van der Waals interaction energies between two bodies having simple geometries calculated by the additive procedure discussed above are presented in the Table 3.1.2.

Table 3.1.2 van der Waals interaction energies between two bodies

System	Interaction energy
Sphere and sphere (radii = R_{s1} and R_{s2})	$\phi = -\frac{A_H}{6\delta} \left(\frac{R_{s1}R_{s2}}{R_{s1} + R_{s2}} \right), \quad R_{s1}, R_{s2} \gg \delta$
Sphere (radius = R_s) and planar half-space	$\phi = -\frac{A_H R_s}{6\delta}, \quad R_s \gg \delta$
Parallel cylinders (radii = R_{c1} and R_{c2})	$\phi = -\frac{A_H}{12\sqrt{2}\delta^{3/2}} \left(\frac{R_{c1}R_{c2}}{R_{c1} + R_{c2}} \right)^{1/2} \text{ (per unit length),}$ $R_{c1}, R_{c2} \gg \delta$
Crossed cylinders (radii = R_{c1} and R_{c2})	$\phi = -\frac{A_H (R_{c1}R_{c2})^{1/2}}{6\delta}, \quad R_{c1}, R_{c2} \gg \delta$
Plane parallel half-spaces	$\phi = -\frac{A_H}{12\pi\delta^2} \text{ (per unit area)}$

- ◆ The ratio of the van der Waals force between a sphere and planar half-space, and the interaction energy (per unit area) between plane parallel half-spaces can be correlated with the radius of the sphere as follows.
- ◆ The van der Waals interaction energy between a sphere and planar half-space is,

$$\phi_{sp} = -\frac{A_H R_s}{6\delta} \quad (3.1.13)$$

where R_s is the radius of the sphere and δ is the separation between the surfaces.

The force of interaction is given by,

$$F_{sp} = -\frac{d\phi_{sp}}{d\delta} = -\frac{A_H R_s}{6\delta^2} \quad (3.1.14)$$

The interaction energy per unit area between plane parallel half-spaces (ϕ_{pp}) is,

$$\phi_{pp} = -\frac{A_H}{12\pi\delta^2} \quad (3.1.15)$$

Therefore,

$$\frac{F_{sp}}{\phi_{pp}} = 2\pi R_s \quad (3.1.16)$$

3.1.8 Derjaguin approximation

- ◆ For macroscopic bodies with curved surfaces, the interaction is not significant until the distance of closest approach is small compared to the radii of curvature of the bodies. Equation (3.1.16) shows that the van der Waals force between a curved surface and a planar half-space can be easily correlated with the interaction energy per unit area between plane parallel half-spaces (ϕ_{pp}) at the same separation.
- ◆ The latter is easier to determine than the interaction energy between curved surfaces. The forces between large spheres or crossed cylinders can be correlated easily with ϕ_{pp} . Another important fact is that such a simple relationship exists for any type of force law (e.g., attractive, repulsive or oscillatory) so long as δ is much less than the radii of the spheres.
- ◆ The force between two spheres can be expressed in terms of ϕ_{pp} as,

$$F_{ss} = 2\pi \left(\frac{R_{s1}R_{s2}}{R_{s1} + R_{s2}} \right) \phi_{pp}, \quad \delta \ll R_{s1}, R_{s2} \quad (3.1.17)$$

It can be seen that if $R_{s2} \gg R_{s1}$, Eq. (3.1.16) is obtained.

- ◆ Derjaguin approximation for the crossed cylinders leads to the following relationship,

$$F_{cc} = 2\pi (R_{c1}R_{c2})^{1/2} \phi_{pp} \quad (3.1.18)$$

- ◆ These results are very useful to interpret the experimental data. ϕ_{pp} can be determined by measuring the force between crossed cylinders. However, the

accuracy of the approximation dwindles as the radius decreases and the separation between the bodies increases.

3.1.9 Hamaker constant

- ◆ Equation (3.1.11) can be used to calculate the Hamaker constant. The pairwise-summation method described in Section 3.1.7 is expected to be least in error when the molecules are far from one another so that the individual pair-interactions are relatively unaffected by the other molecules. Because complete additivity of the intermolecular forces was implicit in the concept of the Hamaker constant (A_H), only the London dispersion forces need be considered. The Debye and Keesom interactions can be important in interfacial phenomena but their range of action is very small. That is why the Hamaker equations are more appropriate where the interactions occur over a separation which is larger than the molecular dimensions.
- ◆ The London dispersion constant can be calculated by the methods illustrated in the Examples 3.1.2 and 3.1.3. The number of molecules per unit volume can be calculated from the knowledge of the molecular diameter (which can be obtained by the acoustic methods or methods using the refractive index data). The Hamaker constants of some materials interacting *in vacuo* are given in Table 3.1.3.

Table 3.1.3 Hamaker constants of some materials interacting *in vacuo* (or air)

Material	$A_H \times 10^{20}$ J	Material	$A_H \times 10^{20}$ J
<i>n</i> -C ₅ H ₁₂	3.75	Ethanol	4.20
<i>n</i> -C ₆ H ₁₄	4.07	Fused quartz	6.50
<i>n</i> -C ₇ H ₁₆	4.32	Fused silica	6.55
<i>n</i> -C ₈ H ₁₈	4.50	Gold	45.30
<i>n</i> -C ₉ H ₂₀	4.66	Iron oxide	21.00
<i>n</i> -C ₁₀ H ₂₂	4.82	Mica	13.50
<i>n</i> -C ₁₁ H ₂₄	4.88	Natural rubber	8.58

$n\text{-C}_{12}\text{H}_{26}$	5.04	Polymethyl methacrylate	7.11
$n\text{-C}_{13}\text{H}_{28}$	5.05	Polystyrene	6.58
$n\text{-C}_{14}\text{H}_{30}$	5.10	Polyvinyl chloride	7.78
$n\text{-C}_{15}\text{H}_{32}$	5.16	Rutile	43.00
$n\text{-C}_{16}\text{H}_{34}$	5.23	Sapphire	15.60
Acetone	4.17	Silicon carbide	44.00
Alumina	15.40	Silver	39.80
Benzene	5.00	Teflon	3.80
Calcite	10.10	Toluene	5.40
Calcium fluoride	7.20	Water	3.70
Carbon tetrachloride	5.50	Zirconia	27.00
Cyclohexane	5.20		

- ◆ When two interacting bodies (represented by the superscripts 1 and 2) are separated by a third medium (represented by the superscript 3), the Hamaker constant can be calculated by the following equation (Gregory, 1969).

$$A_H^{1,3,2} = A_H^{1,2} + A_H^{3,3} - A_H^{1,3} - A_H^{3,2} \quad (3.1.19)$$

where $A_H^{i,j}$ represents the Hamaker constant for the interacting materials i and j *in vacuo*.

- ◆ Equation (3.1.19) can be derived as follows. From Eq. (3.1.11) we have,

$$A_H^{1,2} = \pi^2 n_1 n_2 A_L^{1,2} \quad (3.1.20)$$

where $A_L^{1,2}$ is the London constant for molecules of types 1 and 2, and n_1 and n_2 are the number of molecules per unit volumes of the two types of material.

- ◆ Let us consider two particles constituted of different substances designated by 1 and 2, and embedded in a medium, which is designated as 3. This is illustrated in Fig. 3.1.3.

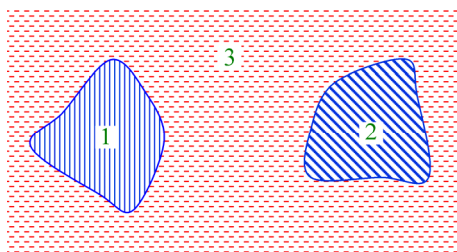


Fig. 3.1.3 Hamaker constant for interaction between two bodies (1 and 2) in a medium (3).

In evaluating the energy variations in this system, we have to take into account the two particles 1 and 2, and also the particles of same size constituted of medium 3. Let us denote the interaction energy between the particles 1 and 2 *in vacuo* as ϕ_{12} , the interaction energy between particle 1 and particle 3 *in vacuo* as ϕ_{13} , the interaction energy between particle 2 and particle 3 *in vacuo* as ϕ_{32} , and the interaction energy between the two particles of medium 3 *in vacuo* as ϕ_{33} .

- ◆ These energies will be functions of the distances between the particles. If ϕ_1 represents the energy of particle 1 in the medium at infinity, this particle, when brought in the neighborhood of the particle 2 will possess an energy $(\phi_1 + \phi_{12} - \phi_{13})$. While bringing the particle 1 towards the particle 2, we have at the same time to remove a particle of medium 3 towards infinity. This will correspond to a change in energy from $(\phi_3 + \phi_{32} - \phi_{33})$ to ϕ_3 when ϕ_3 is the energy of the particle of medium 3 at infinity.
- ◆ Since ϕ_1 and ϕ_3 are constants, the energy changes associated with the variations in the distance between the particles 1 and 2 will be,

$$\phi = \phi_{12} - \phi_{13} - (\phi_{32} - \phi_{33}) = \phi_{12} + \phi_{33} - \phi_{13} - \phi_{32} \quad (3.1.21)$$

- ◆ This expression is independent of the nature of the forces of interaction. It is, however, inherent in this argument that the energy of interaction of one particle with the medium shall be unaffected by the presence or absence of the other particle. This can be a severe limitation if the interaction between the particles and medium 3 is accompanied by an orientation of the molecules of medium 3. In

such cases, we may consider the total energy to be made up of two parts: a part independent of the orientation of the medium molecules, and an additional amount due to this orientation. Whenever the latter part is only a small fraction of the total, it is justified to assume that the conclusions drawn from Eq. (3.1.21) will be correct.

- ◆ Let us represent the interaction energy between two particles of same substance *in vacuo* as,

$$\phi = -A_H \phi_y(x) \quad (3.1.22)$$

where $\phi_y(x)$ is a function of the geometrical data (i.e., diameter and distance), and A_H is equal to $\pi^2 n^2 A_L$. If the two particles are composed of two different substances 1 and 2, the Hamaker constant will be given by Eq. (3.1.20). If these two particles are embedded in medium 3, then from Eqs. (3.1.21) and (3.1.22) we get,

$$\begin{aligned} A_H^{1,3,2} &= \pi^2 \left[n_1 n_2 A_L^{1,2} + n_3^2 A_L^{3,3} - n_1 n_3 A_L^{1,3} - n_3 n_2 A_L^{3,2} \right] \\ &= A_H^{1,2} + A_H^{3,3} - A_H^{1,3} - A_H^{3,2} \end{aligned} \quad (3.1.23)$$

- ◆ The presence of a third medium does not change the distance-dependence of the van der Waals force, but its magnitude is affected by the modified value of the Hamaker constant $(A_H^{1,3,2})$. From Eq. (3.1.19) is apparent that,

$$A_H^{1,3,2} < A_H^{1,2}, \quad \text{if} \quad A_H^{3,3} < A_H^{1,3} + A_H^{3,2} \quad (3.1.24)$$

The condition given in Eq. (3.1.24) holds quite often, which indicates that the Hamaker constant is likely to be reduced in presence of the third medium.

- ◆ Several combining relations are available which can be used to calculate the approximate value of the Hamaker constant in terms of the known values. For example,

$$A_H^{i,j} = \sqrt{A_H^{i,i} A_H^{j,j}}, \quad i \neq j \quad (3.1.25)$$

- ◆ Therefore, from Eqs. (3.1.23) and (3.1.25) we can obtain the following equation for $A_H^{1,3,2}$.

$$A_H^{1,3,2} = \left(\sqrt{A_H^{1,1}} - \sqrt{A_H^{3,3}} \right) \left(\sqrt{A_H^{2,2}} - \sqrt{A_H^{3,3}} \right) \quad (3.1.26)$$

- ♦ Note that the Hamaker constant for air is zero.

Exercise

Exercise 3.1.1: Determine the van der Waals interaction between two blocks of the same material at distance δ apart. The blocks have planar surfaces but have infinite extension.

Exercise 3.1.2: The London dispersion constant for CCl_4 is $1520 \times 10^{-79} \text{ J m}^6$. If the number of molecules per unit volume is $0.6 \times 10^{28} \text{ m}^{-3}$, calculate the Hamaker constant.

Exercise 3.1.3: Derive the equation: $A_H^{1,3,2} = \left(\sqrt{A_H^{1,1}} - \sqrt{A_H^{3,3}} \right) \left(\sqrt{A_H^{2,2}} - \sqrt{A_H^{3,3}} \right)$.

Exercise 3.1.4: Calculate the Hamaker constants for the following systems.

- (i) A polystyrene surface and a mica surface interacting across water
- (ii) A fused quartz surface and a Teflon surface interacting across water

Exercise 3.1.5: Answer the following questions clearly.

- (a) Explain the various forces present in Nature with examples.
- (b) Explain the importance of the interfacial forces.
- (c) What are the most important interfacial forces?
- (d) What are DLVO forces?
- (e) What are the main reasons, according to van der Waals, for gases to deviate from ideality?
- (f) What is Lennard-Jones potential? Explain the terms of the Lennard-Jones equation.
- (g) What are the forces which constitute the total van der Waals force?
- (h) What is the origin of London dispersion force?
- (i) Explain the importance of dispersion force.
- (j) What is retardation effect?
- (k) Explain how the London dispersion force constant can be calculated from the parameters of the van der Waals equation of state.
- (l) What is Hamaker constant?

- (m) What are the assumptions behind pairwise additivity?
- (n) What is Derjaguin approximation?
- (o) Explain how you will calculate the Hamaker constant of two materials across water.

Suggested reading

Textbooks

- ◆ P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1997, Chapter 10.
- ◆ P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapter 5.
- ◆ R. J. Hunter, *Foundations of Colloid Science*, Oxford University Press, New York, 2005, Chapter 11.

Reference books

- ◆ G. J. M. Koper, *An Introduction to Interfacial Engineering*, VSSD, Delft, 2009, Chapter 4.
- ◆ J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1997, Chapters 4–6.
- ◆ V. A. Parsegian, *van der Waals Forces*, Cambridge University Press, New York, 2006, Level 1.

Journal articles

- ◆ F. London, *Z. Physik.*, **63**, 245 (1930).
- ◆ H. C. Hamaker, *Physica*, **4**, 1058 (1937).
- ◆ J. Gregory, *Adv. Colloid Interface Sci.*, **2**, 396 (1969).
- ◆ J. Visser, *Adv. Colloid Interface Sci.*, **3**, 331 (1972).