

London-van der Waals Force

The London-van der Waals force, which is generally attractive in nature, is a short range force and decays rapidly to zero away from a surface. The origin of the London-van der Waals force lies in the instantaneous dipole generated by the fluctuation of electron cloud surrounding the nucleus of electrically neutral atoms. For a spherical particle of diameter d near a flat surface, the interaction energy is given by:

$$\phi = -\frac{A}{12} \left[\frac{1}{x} + \frac{1}{1+x} + 2 \ln \frac{x}{1+x} \right], \quad (1)$$

where $x=z/d$ and z is the distance of the sphere from the surface and A is the Hamaker constant. As the particle approaches the surface,

$$\phi \approx -\frac{Ad}{12z} \quad \text{as} \quad z \rightarrow 0. \quad (2)$$

Thus, the energy becomes infinite for $z=0$. Hence, the surface acts as a perfect sink for aerosol diffusion. The range of operation of the van der Waals force may be estimated by comparing the thermal energy with ϕ . Values of Hamaker constant A are in the range of 10^{-20} to 10^{-19} J. Thus,

$$z \leq \frac{Ad}{12kT} \approx 0.2d \quad \text{for} \quad A \approx 10^{-20}. \quad (3)$$

In Table 1 values for van der Waals force for a number of materials are listed and the values of van der Waals force is compared with the Stokes drag force acting on a particle that is moving with a velocity of 1 m/s in air and in water. It is seen that the van der Waals force in air is comparatively larger than that in water. Furthermore, van der Waals force is much larger than the drag force. The ratio of the van der Waals force to drag force in water is generally less than that in air.

Table 1. van der Waals force for a $1 \mu\text{m}$ particles. For comparison $U = 1 \text{ m/s}$ and a separation of $z_0 = 4 \text{ \AA}$ is assumed.

Particle	Surface	$F_v \times 10^8 \text{ N}$ (In air)	$\frac{F_v}{3\pi\mu dU}$	$F_v \times 10^8 \text{ N}$ (In water)	$\frac{F_v}{3\pi\mu dU}$
Polystyrene	Polystyrene	1.2-1.8	70-100	0.2	12
Si	Si	13.6-14.4	800-850	7	410
Cu	Cu	17	1000	9.8	580
Ag	Ag	18	1060	15.5	910

Table 2. Variation of Forces (N) versus particle diameter, d (μm), f or a flow velocity of $U_0 = 10 \text{ m/s}$					
	Van der Waals	Surface Tension	Added Mass	Drag/Lift	Basset
Diameter	$F_v \sim A_{123} \frac{d}{12z_0^2}$	$F_{st} \sim 2\pi\gamma d$	$F_{am} \sim \rho d^3 \frac{dV}{dt}$	$F_D \sim \rho^f d^2 V^2$	$F_B \sim \frac{\mu d^2 V}{\sqrt{vt}}$
Air					
d (μm)	F_v	F_{st}	F_{am}	F_D	F_B
0.2	3×10^{-8}	9×10^{-5}	10^{-18}	10^{-12}	4×10^{-15}
2	3×10^{-7}	9×10^{-4}	10^{-15}	10^{-10}	4×10^{-13}
20	3×10^{-6}	9×10^{-3}	10^{-12}	10^{-8}	4×10^{-11}
Water					
d (μm)	F_v	F_{st}	F_{am}	F_D	F_B
0.2	2×10^{-9}	—	8×10^{-16}	8×10^{-10}	10^{-12}
2	2×10^{-8}	—	8×10^{-13}	8×10^{-8}	10^{-10}
20	2×10^{-7}	—	8×10^{-10}	8×10^{-6}	10^{-8}

Values of van der Waals, surface tension, added mass, drag and Basset forces acting on a sphere of different sizes moving with a velocity of 10 m/s are shown in Table 2. For a particle in air, it is seen that the surface tension force is order of magnitudes larger than the other forces, which is followed by the van der Waals force. Among the hydrodynamic forces, drag is the dominating force and the virtual mass and the Basset forces are negligibly small. In water, the surface tension force is absent and the drag force acting on large particles becomes comparable with the van der Waals adhesion force.

van der Waals Force Near a Surface

The van der Waals for a sphere near a surface as shown in Figure 1 is given by

$$F = \frac{A_{132}d}{12z_0^2}, \quad (4)$$

where A_{132} is the Hamaker constant for substances “1” and “2” in presence of medium “3,” and z_0 is separation distance. For a particle attached to a wall, z_0 is about 4 to 10 \AA . Typically $z_0 = 4 \text{ \AA}$ is used.

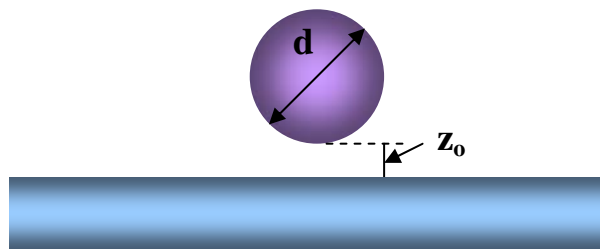


Figure 1. Schematics of a particle near a wall.

For cylinder-planar surface contacts shown in Figure 2,

$$\frac{F}{\text{length}} = \frac{A_{132}d^{1/2}}{16z_0^{5/2}}, \quad (5)$$



Figure 2. Schematics of a cylindrical particle near a wall.

For two planar surfaces shown in Figure 3,

$$\frac{F}{\text{area}} = \frac{A_{132}}{6\pi z_0^3}. \quad (6)$$

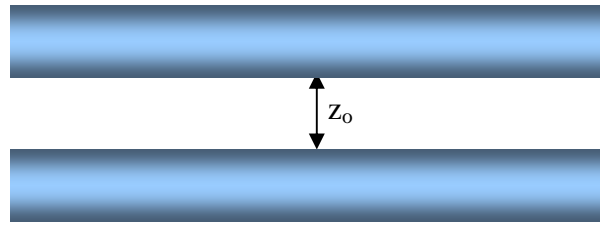


Figure 3. Schematics of a two planar surface at a separation distance of z_0 .

Hamaker Constants for Dissimilar Materials

For two dissimilar materials, the Hamaker constant may be estimated in term of Haymaker constant of each material. That is

$$A_{12} \approx \sqrt{A_{11}A_{22}} \quad (7)$$

or alternatively

$$A_{12} = \frac{2A_{11}A_{22}}{A_{11} + A_{22}} \quad (8)$$

For contact of two dissimilar materials in the presence of a third media,

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (9)$$

From Equation (8) it follows that

$$A_{131} = A_{11} + A_{33} - 2A_{13} = \frac{(A_{11} - A_{33})^2}{A_{11} + A_{33}} \simeq (\sqrt{A_{11}} - \sqrt{A_{33}})^2, \quad (10)$$

or

$$A_{132} \simeq (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}). \quad (11)$$

Lifshitz developed the “macroscopic theory” relating the Hamaker constant to dielectric constants of the materials. Accordingly,

$$A_{132} = \frac{3}{4\pi} h\bar{\omega}_{132} \quad (12)$$

Values of $h\bar{\omega}_{132}$ are given in Tables 3 and 4 for a number of materials. (Note that $1\text{ eV} = 1.602 \times 10^{-19}\text{ J}$.)

Table 3. Values of Lifshitz -van der Waals Constant $h\bar{\omega}_{131}$ for some materials (Visser, 1976).

Homogenous Combinations		
	$h\bar{\omega}_{131}$ (eV)	
Combinations	Vacuum	Water
Au-Au	14.3	9.85
Ag-Ag	11.7	7.76
Cu-Cu	8.03	4.68
Diamond-Diamond	8.6	3.95
Si-Si	6.76	3.49
Ge-Ge	8.36	4.66
MgO-MgO	3.03	0.47
KCl-KCl	1.75	0.12
KBr-KBr	1.87	0.18
KI-KI	1.76	0.20
Al ₂ O ₃ -Al ₂ O ₃	4.68	1.16
CdS-CdS	4.38	1.37
H ₂ O-H ₂ O	1.43	-
Polystyrene-Polystyrene	1.91	0.11

Table 4. Values of Lifshitz -van der Waals Constant $h\bar{\omega}_{131}$ for some materials (Visser, 1976).

Heterogeneous Combinations		
	$h\bar{\omega}_{131}$ (eV)	
Combinations	Water	Polystyrene
Au-Ag	-	8.27
Au-Cu	6.41	5.93
Au-Diamond	6.11	5.45
Au-Si	5.32	4.70
Au-Ge	6.50	5.93
Au-MgO	1.99	1.25
Au-KBr	0.73	0.0
Au-Al ₂ O ₃	-	2.60
Au-CdS	-	2.65
Au-Polystyrene	0.72	-

Tables 5 and 6 gives the values of Hamaker constant for a number materials in vacuum and in water.

Table 5. Values of Hamaker Constant for some materials.

A / 10 ⁻²⁰ J		
Materials	Vacuum	Water
Polystyrene	7.9	1.3
Hexadecane	5.4	-
Gold	40	30
Silver	50	40
Al ₂ O ₃	16.75	4.44
Copper	40	30
Water	4.0	-

Table 6. Values of Hamaker Constant for some materials.

A / 10 ⁻²⁰ J		
Materials	Vacuum	Water
Pentane	3.8	0.34
Decane	4.8	0.46
Hexadecane	5.2	0.54
Water	3.7	-
Quartz (Fused)	6.5	0.83
Quartz (Crystalline)	8.8	1.70
Fused Silica	6.6	0.85
Calcite	10.1	2.23
Calcium Fluoride	7.2	1.04
Sapphire	15.6	5.32
Poly (Methyl Methacrylate)	7.1	1.05
Poly (Vinyl Chloride)	7.8	1.30
Polyisoprene	6.0	0.74
Poly (tetrafluoroethylene)	3.8	0.33

London-van der Waals Surface Energy Between Particles

The London-van der Waals surface energy and force between two spherical particles of diameters d_1 and d_2 as show in Figure 4 was evaluated by Hamaker (1937). The corresponding surface energy is given as

$$\Phi = -\frac{A}{6} \left[\frac{d_1 d_2 / 2}{R^2 - \left(\frac{d_1 + d_2}{2}\right)^2} + \frac{d_1 d_2 / 2}{R^2 - \left(\frac{d_1 - d_2}{2}\right)^2} + \ln \frac{R^2 - \left(\frac{d_1 + d_2}{2}\right)^2}{R^2 - \left(\frac{d_1 - d_2}{2}\right)^2} \right] \quad (13)$$

where

$$R = \frac{d_1 + d_2}{2} + s \quad (14)$$

is the distance between particles center and s is the separation distance between surfaces.

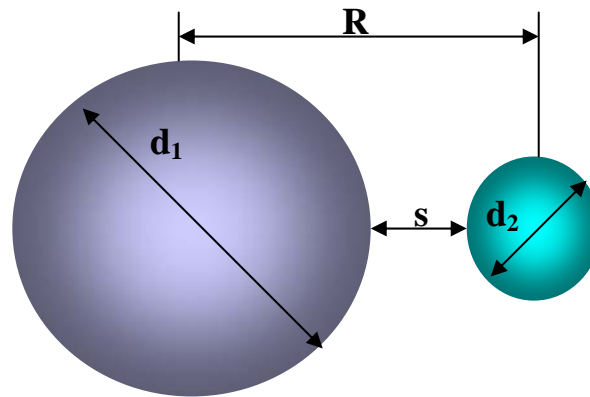


Figure 4. Schematics of contact of two dissimilar spheres.

For equal size particles, $d_1 = d_2 = d$, $r = d + s$, and

$$\Phi = -\frac{A}{6} \left[\frac{d^2}{2r^2} + \frac{d^2}{2(r^2 - d^2)} + \ln\left(1 - \frac{d^2}{r^2}\right) \right] \quad (15)$$

As noted before, A is typically of the order of 10^{-19} to 10^{-21} J and depends on the properties of particles (of composition 1) and suspending medium (composition 2). Accordingly, the effective Hamaker constant is given by

$$A_{121} = A_{11} + A_{22} - A_{12} \approx \sqrt{(A_{11} - A_{22})} \quad (16)$$