van der Waals Forces (Part II)
&
Electrostatic Double Layer Force (Part I)

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3.2.1 Drawbacks of the Hamaker summation method

- The *pairwise-additivity* method has been quite popular among the scientists because of the simplicity involved in its calculations. However, this approach ignores the influence of the neighbor molecules on the interaction between a pair of molecules.
- The effective polarizability of a molecule changes when it is surrounded by other molecules. As discussed in Lecture 1 of Module 3, a neighbor molecule is also polarized when the electric field of a molecule polarizes a second molecule and the electric field of the first molecule reaches the second molecule directly as well as through the reflection from this neighbor molecule.
- Because of the contribution from these forces, the pairwise-additivity method does not remain straightforward and the calculations become very complicated. The pairwise-additivity method is applicable in gases. However, in condensed phases, this method can be inaccurate.
- The second most important drawback of the Hamaker approach is the neglect of the retardation effect. The retardation effect becomes important when surfaces interact in a liquid medium.
- Hamaker equations are based on the assumption that the summation over all interacting pairs of molecules may be replaced by an integration procedure. For this assumption to be valid, the separation between the bodies must be large enough so that the interacting materials may be treated as continuous media and not arrays of discrete molecules. Therefore, these equations do not apply at separations less than a few molecular diameters where the 'graininess of matter' can be an important factor.

Example 3.2.1: Calculate the Hamaker constant for the fused quartz (1) − air (2) − tetradecane (3) system. Compare your results with the experimental value of -0.5×10^{-20} J.

Solution: The Hamaker constants for interaction *in vacuo* are taken from Table 3.1.3.

$$A_H^{1,1} = 6.5\times10^{-20}\ \text{J}$$

$$A_H^{2,2} = 0\ \text{J}$$

$$A_H^{3,3} = 5.1\times10^{-20}\ \text{J}$$

Therefore,

$$A_H^{1,3,2} = \left(\sqrt{A_H^{1,1}} - \sqrt{A_H^{3,3}}\right)\left(\sqrt{A_H^{2,2}} - \sqrt{A_H^{3,3}}\right) = \left(\sqrt{6.5} - \sqrt{5.1}\right)\left(0 - \sqrt{5.1}\right)\times10^{-20}$$

$$= -0.66\times10^{-20}\ \text{J}$$

This value agrees well with the experimental value.

3.2.2 Lifshitz theory of van der Waals interaction

- The Lifshitz theory of van der Waals interactions was derived entirely from the considerations of the macroscopic properties of the media. Pairwise additivity was completely avoided in this theory. The attraction was assumed to be due to a fluctuating electromagnetic field in the gap which arises due to the spontaneous electric and magnetic polarizations within the media.
- It was implicit in this theory that the gap must be larger than molecular dimensions. The media were treated as continuous and the force between the macroscopic bodies was derived in terms of the dielectric constants and refractive indices. This theory is particularly suitable when we want to calculate the Hamaker constant for the interaction of the media 1 and 2 across medium 3.
- As per this theory, the Hamaker constant can be calculated from the following equation (Israelachvili, 1997).

$$A_H = \frac{3kT}{4}\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h\nu_e}{8\sqrt{2}}\left[\frac{\left(\eta_1^2 - \eta_3^2\right)\left(\eta_2^2 - \eta_3^2\right)}{\left\{\left(\eta_1^2 + \eta_3^2\right)\left(\eta_2^2 + \eta_3^2\right)\right\}^{1/2}\left\{\left(\eta_1^2 + \eta_3^2\right)^{1/2} + \left(\eta_2^2 + \eta_3^2\right)^{1/2}\right\}}\right] \tag{3.2.1}$$

In Eq. (3.2.1), $\varepsilon_i\ (i = 1,2,3)$ are the dielectric constants and $\eta_i\ (i = 1,2,3)$ are the refractive indices. ν_e is the main electronic absorption frequency in the ultra violet region. Its value usually lies between 3×10^{15} s^{-1} and 5×10^{15} s^{-1}. k is Boltzmann's constant ($\equiv 1.381\times10^{-23}$ J/K), T is temperature and h is Planck's constant ($\equiv$ 6.626×10^{-34} J s).

- The first term in Eq. (3.2.1) is termed *zero frequency contribution* and the second term is termed *non-retarded dispersion energy contribution*. The first term includes contributions from the Debye and Keesom interactions.
- From Eq. (3.2.1), we can observe that for two identical bodies (i.e., $\varepsilon_1 = \varepsilon_2$ and $\eta_1 = \eta_2$) the Hamaker constant is positive and the van der Waals force is always attractive.
- However, for two different bodies ($\varepsilon_1 \neq \varepsilon_2$ and $\eta_1 \neq \eta_2$), the Hamaker constant can be positive or negative, depending on the medium between them.
- Therefore, it is apparent that the van der Waals force is not always attractive but it can be repulsive also.
- The values of dielectric constant and refractive index *in vacuo* or air are unity, i.e., $\varepsilon_3 = 1$ and $\eta_3 = 1$. Therefore, the van der Waals force between two bodies will always be attractive *in vacuo* or air.

Example 3.2.2: Calculate the Hamaker constant for two Teflon bodies *in vacuo* at 298 K. Given: $\varepsilon_1 = 2.1$, $\eta_1 = 1.359$ and $\nu_e = 2.9\times10^{15}$ s^{-1}.

Solution: For two Teflon bodies *in vacuo*, Eq. (3.2.1) simplifies to,

$$A_H = \frac{3kT}{4}\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}}\frac{\left(\eta_1^2-\eta_3^2\right)^2}{\left(\eta_1^2+\eta_3^2\right)^{3/2}}, \qquad \varepsilon_3 = 1,\ \eta_3 = 1$$

Substituting the values of ε_1, η_1, k, T, h and ν_e in the above equation, we obtain,

$$A_H = \frac{3\times1.381\times10^{-23}\times298}{4}\left(\frac{2.1-1}{2.1+1}\right)^2 + \frac{3\times6.626\times10^{-34}\times2.9\times10^{15}}{16\sqrt{2}}\frac{\left[(1.359)^2-(1)^2\right]^2}{\left[(1.359)^2+(1)^2\right]^{3/2}}$$

Therefore, $A_H = 3.8863 \times 10^{-22} + 3.8039 \times 10^{-20} = 3.8428 \times 10^{-20}$ J

- Some values of the Hamaker constant calculated using Eq. (3.2.1) are presented in Table 3.2.1.

Table 3.2.1 Hamaker constants for two media interacting across another medium (calculated from the Lifshitz theory)

System	$A_H \times 10^{20}$ J
Air (1) – Water (3) – Air (2)	3.7
Alumina (1) – Pentane (3) – Alumina (2)	3.9
Fused quartz (1) – Water (3) – Fused quartz (2)	0.6
Mica (1) – Tetradecane (3) – Mica (2)	0.9
Mica (1) – Water (3) – Mica (2)	2.0
Octane (1) – Water (2) – Air (2)	–0.2
Octane (1) – Water (3) – Octane (2)	0.4
Polystyrene (1) – Water (3) – Polystyrene (2)	1.3
Teflon (1) – Water (3) – Teflon (2)	0.3
Water (1) – Pentane (3) – Air (2)	0.1

- A comparison between the data on interaction through a medium and through vacuum reveals that the intervening medium has a very significant effect on the van der Waals attraction between two macroscopic bodies.
- In the extreme instance, two bodies which attract *in vacuo* may not attract when immersed in another medium. Bergström (1997) has presented an extensive compilation of Hamaker constants for a variety of inorganic materials, which demonstrates the effect of medium on Hamaker constant.

Example 3.2.3: Estimate the van der Waals force between two sapphire spheres of 1 mm radius which are 1 nm apart *in vacuo*.

Solution: The van der Waals interaction energy between two spheres of radius R_s at separation δ is given by,

$$\phi = -\frac{A_H R_s}{12\delta}$$

The van der Waals force between the spheres is given by,

$$F = -\frac{d\phi}{d\delta} = \frac{A_H R_s}{12\delta^2}$$

$$A_H = 15.6\times10^{-20} \text{ J}$$

Given, $R_s = 0.001$ m, $\delta = 1\times10^{-9}$ m

Therefore, $$F = \frac{15.6\times10^{-20}\times0.001}{12\times\left(1\times10^{-9}\right)^2} = 1.3\times10^{-5} \text{ N}$$

3.2.3 Estimation of surface tension from Hamaker constant

- Surface properties such as surface energy can be determined from the Hamaker constant. According to Fowkes (1964), the surface tension of a non-polar liquid is equal to the surface energy due to the dispersion interactions γ^d (i.e., $\gamma = \gamma^d$). The calculation of γ^d from the dispersion interactions can be carried out quite easily.
- Let us imagine two semi-infinite blocks of hydrocarbon of unit area being brought from infinity to a separation where they are almost going to touch each other. The separation between them is δ_c. The surface tension (or surface energy) is then given by,

  $$\gamma = \gamma^d = -\frac{\phi_{pp}}{2} = \frac{A_H}{24\pi\delta_c^2} \tag{3.2.2}$$

  where the interaction energy per unit area between the plane parallel half-spaces at separation δ_c is expressed as ϕ_{pp}. In other words, the surface energy is equal to half the energy required to separate two flat surfaces from contact to near-infinity.

- Israelachvili (1997) has shown that Eq. (3.2.2) can be simplified for non-hydrogen bonding and non-polar liquids by putting $\delta_c \approx 0.165$ nm, i.e.,

$$\gamma = \frac{A_H}{2.1\times10^{-18}} \tag{3.2.3}$$

The surface tensions of some liquids calculated by using Eq. (3.2.3) are presented in Table 3.2.2. This equation can also be used to estimate surface energies of many solid materials.

Table 3.2.2 Surface tensions of some liquids calculated from Eq. (3.2.3)

Substance	$A_H \times 10^{20}$ J	Surface tension from Eq. (3.2.3) (N/m)	Experimental surface tension (N/m)
Benzene	5.00	0.024	0.029
Carbon tetrachloride	5.50	0.026	0.027
Cyclohexane	5.20	0.025	0.026
Ethyl alcohol	4.20	0.020	0.022
n-Decane	4.82	0.023	0.024
n-Heptane	4.32	0.021	0.020
n-Hexane	4.07	0.019	0.018
n-Octane	4.50	0.021	0.022
n-Pentane	3.75	0.018	0.016

3.2.4 van der Waals force in electrolyte solutions

- The effect of electrolytes present in the medium on van der Waals force can be important. The major effect of the presence of electrolyte occurs on the zero-frequency term [i.e., the first term on the right side of Eq. (3.2.1)]. This term can make a significant contribution to the Hamaker constant in some systems.
- The zero-frequency term represents an electrostatic interaction. In a medium which contains salt, the electrostatic field gets screened due to the polarization of

the charges. The dispersion contribution [i.e., the second term on the right side in Eq. (3.2.1)] is not affected by the presence of electrolytes in the medium.

- The screened electric field decays with distance as, $2\kappa\delta\exp\left(-2\kappa\delta\right)$ (where $1/\kappa$ is the *Debye length*, which will be discussed in detail in Lecture 3 of Module 3). The screening of the zero-frequency interaction occurs at a very short distance (say, 1 nm).
- It has been found that the Hamaker constant for uncharged lipid bilayers decreased from 7×10^{-21} J in water to 3×10^{-21} J in 200 mol/m^3 aqueous NaCl solution (Marra, 1986).

3.2.5 Disjoining pressure

- The concept of 'disjoining pressure' was originated by the Russian scientist B. V. Derjaguin (ca. 1936) on the basis of experiments with thin aqueous layers formed between two flat mica covered surfaces.
- Derjaguin and his co-workers measured the separation between two surfaces in water, and found that the separation was dependent on the applied external pressure. The thickness versus pressure profile was considered as an evidence of the presence of repulsive force between the surfaces. The effect was called a *disjoining pressure*. They presumed that the observed disjoining effect might be caused by electrostatic and/or solvation forces.
- The attractive disjoining pressure due to van der Waals force between two plane parallel half-spaces separated by a distance δ is given by $\Pi_{\mathrm{vdW}} = A_H \big/ 6\pi\delta^3$. The disjoining pressure due to electrostatic double layer or steric forces (discussed later) is repulsive. The net disjoining pressure is the resultant of the attractive and repulsive disjoining pressures.

3.2.6 Experimental determination of van der Waals force

- Hamaker constant can be determined experimentally by various techniques such as flocculation of colloidal particles, interaction of metal wires in electrolyte solutions, measurement of thickness of thin liquid films, surface tension and rheological measurements, and solid−solid interactions. The details of these methods have been discussed by Visser (1972). It has been be noted that the values of Hamaker constant reported in many of these studies are inconsistent.

- Owing to the need to reach very small separation between the interacting bodies, there are chances of error in the measurement of van der Waals forces. In the early experimental works on the measurement of van der Waals force, Hamaker constants for quartz and Pyrex glass were determined for plate−plate and sphere−plate arrangements. Tabor and Winterton (1968) measured the attractive force between cleaved mica sheets at separations between 5 nm and 300 nm. Their work detected the retarded as well as non-retarded van der Waals forces. The values of Hamaker constant obtained from their experiments were in reasonable agreement with the values predicted by the Lifshitz theory.
- In the experiments involving the coagulation of colloid particles, polystyrene lattices have been widely used as model colloids (e.g., Watillon and Joseph-Petit, 1966). They have been commonly used because they can be obtained as spherical monodispersed particles.
- The soap films have been used in several studies to measure the interfacial forces (Sheludko, 1967). The soap film can be visualized as a system of two parallel flat plates between which van der Waals and electrostatic double layer forces act. When the film drains to an equilibrium thickness, the van der Waals and electrostatic double layer forces are balanced. At this stage, the thickness of the film can be between 5 nm and 100 nm. These films are known as *common black films* because they appear black by the reflected light (due to the very low intensity of the light resulting from the interfering reflections from the film surfaces). The concentration of electrolyte in the medium strongly influences the thickness of the film.
- The Hamaker constant has been estimated from the measurement of equilibrium thickness of common black films (Lyklema and Mysels, 1965), and kinetics of thinning of the film (Sheludko *et al*., 1965). Both of these techniques require

knowledge of the electrostatic double layer repulsion in the film since this force is also present in the film.

- Experimental techniques exist to measure the van der Waals force directly using the *surface force apparatus* (*SFA*). The studies using the SFA have reported measurements at very small separations such as 1.5 nm (Israelachvili, 1997). The experiments have been carried out with the surfaces placed *in vacuo*, air or liquids. The experimental results have been found to agree with the predictions from the Lifshitz theory.
- In the SFA, the force is measured by a variety of interchangeable springs. The distance between the surfaces is varied from 1 μm up to 1 nm. It is measured by an optical method using multiple beam interference fringes known as *fringes of equal chromatic order*. The distance is precisely controlled by a variety of subtle mechanisms. The typical precision in the measurement of distance is 0.1 nm, and the instrument can measure force as small as 10^{-8} N. In the surface force apparatus described by Israelachvili (1997), the force profile (i.e., the variation of force with separation between the surfaces) for two mica surfaces in crossed-cylinder configuration was measured.
- Mica has a very smooth surface, and it is also easy to handle. It has been extensively used in the surface force studies. Apart from mica, smooth sapphire and silica sheets have also been used. The SFA has been used to measure van der Waals, electrostatic double layer, steric and solvation forces. It has also been used to study the dynamic interactions and time dependent effects such as viscosity of liquids in thin films, shear and frictional forces, and fusion of lipid bilayers. The schematic of the SFA is shown in Fig. 3.2.1. The photograph of a commercial surface force apparatus is given in Fig. 3.2.2.
- The *atomic force microscopy* (*AFM*) is another technique that is widely used to measure the van der Waals and other forces. In this method, the force is measured between a fine tip and the surface. This procedure is quite sensitive to measure very small forces, e.g., 10^{-10} N. The diameter of the tip is $\sim 1\times 10^{-6}$ m or less.

AFM has been used to measure van der Waals force in biosurfaces (Hansma *et al*., 1988; Dufréne, 2001).

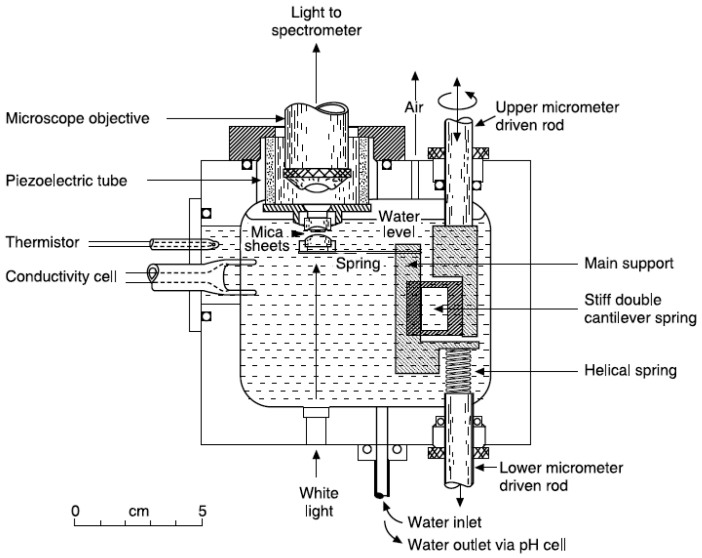

Fig. 3.2.1 Schematic of the surface force apparatus [Israelachvili and Adams, 1978 (reproduced by permission from The Royal Society of Chemistry © 1978); Israelachvili and Adams, 1976 (adapted by permission from Macmillan Publishers Ltd. ©1976)].

Fig. 3.2.2 Mark IV Surface Force Apparatus manufactured by The Australian National University (reproduced by permission from the Australian National University © 2009).

3.2.7 Electrostatic double layer force

- The electrostatic double layer force is one of the major repulsive forces which stabilize colloids. The surfaces of the particles can be charged by several mechanisms. One of the most common mechanisms of development of charge on a surface is the adsorption of ions (e.g., surfactants) from solution on the initially uncharged surface. Another possible mechanism is the ionization or dissociation of a surface group, e.g., dissociation of proton from a –COOH group by the mechanism: R–COOH → $\text{R–COO}^- + \text{H}^+$.
- From Coulomb's law, if two charges Q_1 and Q_2 are separated by a distance, s, the interaction energy between them is given by,

$$\phi = \frac{Q_1 Q_2}{4\pi\varepsilon\varepsilon_o s} \tag{3.2.4}$$

  where ε is the dielectric constant of the medium and ε_0 is the permittivity of the free space ($\equiv 8.854\times10^{-12}$ $\text{C}^2\ \text{J}^{-1}\ \text{m}^{-1}$).
- If we use Eq. (3.2.4) to calculate the interaction energy between two ions having valence z_1 and z_2, it becomes,

$$\phi = \frac{z_1 z_2 e^2}{4\pi\varepsilon\varepsilon_o s} \tag{3.2.5}$$

  where e is the electronic charge ($\equiv 1.602\times10^{-19}$ C).
- The Coulomb force is given by,

$$F = -\frac{d\phi}{ds} = \frac{z_1 z_2 e^2}{4\pi\varepsilon\varepsilon_0 s^2} \tag{3.2.6}$$

- The quantity, $1/4\pi\varepsilon_0$, is known as *electrostatic constant* or *Coulomb's constant*. Its value is 9×10^9 J m C^{-2}.
- If z_1 and z_2 are of the same sign, the interaction energy and force both are positive, which indicates repulsion between the ions (e.g., repulsion between two cations or anions). On the other hand, if z_1 and z_2 are of opposite sign, there will be attraction between the ions (e.g., between a cation and an anion).

- The dielectric constant of the medium plays an important role on Coulomb interaction. The following example illustrates the difference in magnitude of the Coulomb force for two ions in air and water. The dielectric constants differ widely in these two media (i.e., 1 and 78.5, respectively).
- The Coulomb force of attraction between two ions decreases in water due to the high dielectric constant of the medium. The high dielectric constant of water allows the dissociation of Na^+ and Cl^- ions to occur. In air or non-polar liquids (such as hexane), this dissociation does not occur. The dielectric constant is a measure of the extent to which the reduction in electric field would occur. The dielectric constants of some liquids are presented in Table 3.2.3.

Table 3.2.3 Dielectric constants of some liquids at 298 K

Liquid	Dielectric constant	Liquid	Dielectric constant
Acetic acid	6.2	Heptane	1.9
Acetone	20.7	Hexane	1.9
Acetonitrile	37.5	Liquefied air	1.5
Aniline	7.3	Liquefied hydrogen	1.2
Benzene	2.3	Methanol	32.6
Carbon tetrachloride	2.2	Methyl ethyl ketone	18.4
Chlorobenzene	5.6	*m*-Xylene	2.4
Chloroform	4.8	*n*-Butanol	17.8
Cyclohexane	2.0	Nitrobenzene	35.7
Cyclohexanol	15.0	*n*-Propanol	20.2
Dichloromethane	9.1	Octane	2.0
Dodecane	2.0	*o*-Xylene	2.6
Dodecane	2.0	Phenol	5.2
Dowtherm	3.4	Propionic acid	3.1
Ethanol	24.3	*p*-Xylene	2.3
Ethyl acetate	6.0	Pyridine	12.5
Ethyl ether	4.3	Silicone oil	2.8
Ethylene glycol	40.7	Toluene	2.4

Formic acid	58.1	Water	78.5
Glycerol	42.5		

3.2.7.1 Capacitor model of electrostatic double layer

- One of the earliest models of electrostatic double layer was the *capacitor model* in which the double layer was considered as a parallel plate condenser in which two parallel plates are separated by a nonconducting medium (i.e., a *dielectric*) with a potential difference between them. It is schematically shown in Fig. 3.2.3.

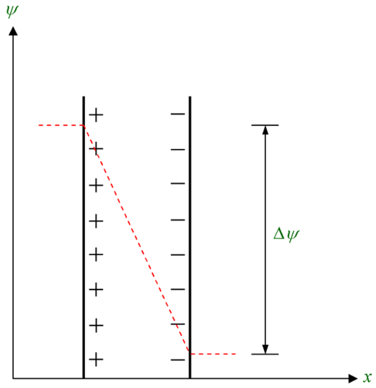

Fig. 3.2.3 The parallel capacitor model of electrostatic double layer.

- The potential drop across two locations separated by a small distance (which is of the order of molecular diameters) is depicted in the above figure. Suppose that the interface is positively charged (which is represented by the left plate) and the atmosphere of the negatively charged counterions is represented by the right plate.
- This visualization of the ionic atmosphere near a charged interface originated the term *electrostatic double layer*. This is, however, a highly simplified picture of the double layer as evident from the present day experimental observations and theories. A more realistic description of the double layer involves the diffuse part of the double layer extending into the solution as discussed in Lecture 3 of Module 3.

Exercise

Exercise 3.2.1: Calculate the Hamaker constants for the following systems.

(i) two polystyrene surfaces interacting across water

(ii) two fused quartz surfaces interacting across water

(iii) two carbon tetrachloride surfaces interacting across water

Calculate the Hamaker constants by using the Lifshitz theory.

Exercise 3.2.2: Derive the expression for van der Waals interaction energy between a sphere of radius R_s and a planar half-space at a separation δ. Assume that the radius of the sphere is much larger than the separation.

Exercise 3.2.3: Calculate the Coulomb force of attraction between a sodium ion and a chloride ion which are 0.3 nm apart in (a) air and (b) water.

Exercise 3.2.4: Answer the following questions clearly.

(a) What are the main drawbacks of the Hamaker theory?

(b) Explain how the Hamaker constant may be calculated from the Lifshitz theory.

(c) Explain the situations under which the Hamaker constant may be negative.

(d) Explain how surface tension can be calculated from the Hamaker constant.

(e) How does an electrolyte influence van der Waals force in aqueous medium?

(f) What is disjoining pressure?

(g) Mention three experimental methods for the determination of van der Waals force.

(h) Explain how an electrostatic double layer is created at the solid–liquid and liquid–liquid interfaces.

(i) Explain Coulomb's law of electrostatic interaction. Explain the importance of dielectric constant on Coulomb interaction.

(j) Explain the *capacitor model* of electrostatic double layer.

Suggested reading

Textbooks

- P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1997, Chapter 11.
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