

# Existence of a New Force in Colloidal Systems – Hydrophobic Attraction Between Macroscopic Surfaces

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## Keywords

Colloids, hydrophobic effect, surface force apparatus, DLVO theory, nanoparticles, van der Waals interaction.

Colloids play an important role in our modern lives. In this article, we briefly discuss various forces that are known to operate between colloidal particles and then take the reader through the discovery of a new, strong and long ranged force operating between hydrophobic particles/surfaces. Characteristics of the new force and some promising theories proposed in the literature to explain its origin are also discussed; the origin of the new force is not yet resolved, however.

Colloidal systems, also known as colloids, generally refer to a dispersion of fine particles in the size range of 10 nm upwards in a fluid medium. They are encountered extensively in day to day life, both in natural and man-made settings. Some common examples of natural colloids can be found in our body itself: blood consists of colloidal sized red blood corpuscles (RBC) which provide the vital oxygen to all the body tissues. Fat from the food we consume is assimilated by the body by converting it into colloidal sized globules, called chylomicrons. Milk is another example of a natural colloid. In addition, many important synthetic products such as perfluorocarbon based artificial blood, inks, paints, suspension and emulsion based medicines, modern foods including ice-cream, asphalt emulsions for repairing road, cosmetics, health care products, and other very large number of emulsion based products are all colloids. Colloids play a significant role in many natural phenomenon – the formation of clouds is due to condensation of water vapour on colloidal sized dust particles suspended in the atmosphere. In fact, this mechanism is used to create artificial rain by deliberately seeding the atmosphere with colloidal particles of silver iodide. Further, deltas



The field of colloids, started by Thomas Graham, and nurtured by Smoluchoski, Overbeek, Deryaguin and Fuchs entered a new phase with the development of surface force apparatus by Israelachvili and coworkers.

are formed near sea because the salt present in the sea induces coagulation and settling of colloidal matter contained in rivers flowing into the sea.

In the last few decades colloids have also entered the materials field. A novel method, called colloidal processing, is extensively used to make nano-sized particles which are helpful in bringing down material processing temperatures and loads, thereby effecting substantial cost savings and also for making ductile and machinable ceramics. Further, these nanoparticles (consisting of just a couple of thousand of molecules) have many interesting properties significantly different from the bulk materials and are useful in various advanced applications such as self-assembled composite structures, high energy density batteries and high resolution display panels.

The unique applications of colloidal systems depend on our ability to control dispersion and coagulation of the particles in the fluid medium. This requires an understanding of the nature of the forces acting between the particles in the presence of the fluid. Efforts to study colloidal systems started as early as 1860 by Thomas Graham, a Scottish inorganic and physical chemist. In fact, he coined the name 'colloid'. A successful quantitative theory called the DLVO theory, that explained the stability of colloidal systems in terms of attractive and repulsive forces between particles, was developed in the middle of the 20th century. However, significant interest was generated in this field when Jacob Israelachvili and Adams built an apparatus called the Surface Force Apparatus in 1976 that could directly measure the very small forces between surfaces in the presence of a fluid at separations down to angstrom level. This apparatus, while confirming the validity of DLVO theory, also revealed the existence of new types of forces not considered in the development of the DLVO theory. These and some other already known forces not included in the original DLVO theory are called as non-DLVO forces; the important ones among them are the solvation, steric, and hydrophobic forces.



The non-DLVO forces play a major role in many industrially important colloidal systems and are therefore extensively studied. Among these forces the hydrophobic (which literally means ‘water-fearing’) force, has attracted a lot of interest primarily because of two reasons. Firstly, it is significantly longer ranged than the others; its interaction length can be as long as about 100 nanometers whereas that of others normally does not exceed 5 nanometers. Secondly, there is no satisfactory explanation for its long range nature. For instance, as will be detailed later, some theories require a change in structure of water layers in contact with a hydrophobic surface to extend to what is considered to be an unaccountably large range of hundreds of water layers away from the surface. Whereas, some other theories require the presence of gas bubbles of nanometer sizes over timescales of microseconds!

A large class of surfactants known as non-ionic surfactants, used very widely in industrial products impart stability through non-DLVO steric repulsive force.

In order to bring out the brief journey that hydrophobic force has undertaken so far, after it was discovered just about twenty years ago, we first put it in proper perspective with an outline of the forces present in colloidal systems, followed by a brief introduction to the DLVO forces. We then address current status of hydrophobic force, along with the major theories proposed to explain it.

### Forces in Colloidal Systems

A number of forces such as steric repulsion, depletion attraction, double layer repulsion, van der Waals attraction, repulsion between undulating surfaces in close proximity, and hydration force are known to operate between particles/surfaces present in colloidal systems. Although they appear to have significantly different properties, the origin of most of these forces can be explained on the basis of the familiar repulsion/attraction between similar/dissimilar charges or the comparatively less known entropic or osmotic pressure. While the former is self-evident, let’s consider an example of the latter. Consider two containers, one containing pure water and the other with salt solution, connected through an ‘only water permeable membrane’. The

A large number of forces are known to operate between colloidal particles while some of those are obvious, others have counter-intuitive origins.



Osmotic pressure manifests in many different and interesting ways in colloidal systems.

water transports from the pure side to the salt side to increase the chemical potential of water (or somewhat equivalently to increase entropy of ionic species). The net transport of water can be stopped only if the salt side is pressurised; the extent of pressure needed is the osmotic pressure. It is for this reason that honey is not spoiled by bacteria or fungus; water in the bacterial cells diffuses out, across the cell membrane, to dilute the honey (sugar solution), thereby causing the death of cells.

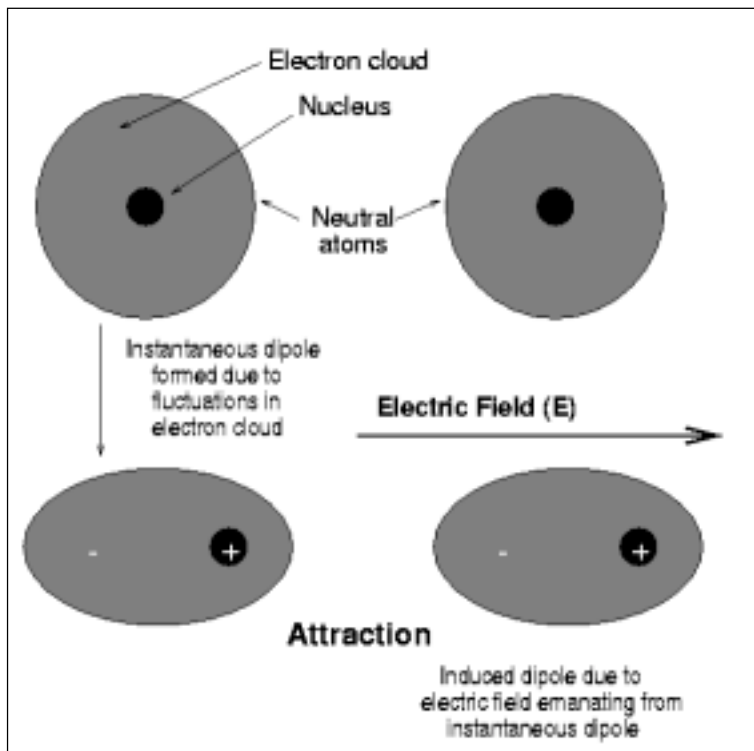
When two particles with long chain molecules adsorbed on them are brought together, the concentration of chain segments in the region between the two particles increases. This sets up increased osmotic pressure in the region between the particles. A non-uniform osmotic pressure around the particles results in a net repulsive force acting on them. On the other hand, if the long chain molecules do not adsorb on particle surfaces, the concentration of chain segments between the particles at smaller separations reduces due to the geometrical constraints. The decreased concentration of chain segments in this region sets up lower osmotic pressure which results in attraction between the particles.

The absence of such molecules from the system should lead to particles neither repelling nor attracting each other, and black ink should form upon dispersion of fine carbon particles in a solvent. The experiments, however, show that ink is never formed; the carbon particles aggregate and settle at the bottom of the container.

### DLVO Theory

Could there be a link between the aggregation of carbon particles in a solvent and condensation of gases to form liquid nitrogen, liquid oxygen, etc? van der Waals proposed that the condensation of gases occurs due to an attraction between gas molecules. An explanation for the origin of this attraction, however, had to await developments in quantum mechanics. London in 1937 showed that a fluctuation in electron cloud of a molecule induces a dipole in a neighbouring molecule. The





*Figure 1. One of the three components of van der Waals attraction between atoms/molecules is attraction between instantaneous dipole due to fluctuations in electron cloud and dipole induced by it in a neighbouring molecule. The other two components are: interaction between permanent dipoles and a permanent dipole and induced dipole.*

fluctuating dipole in one and the induced dipole in the other molecule lead to attraction between them, as shown in *Figure 1*. It is now easy to see the connection between condensation of gases and aggregation of carbon particles. Just as the molecules of gases attract each other, the molecules in particles also attract each other, giving rise to macroscopically observable phenomena such as sticking of dirt particles to cloth. A comprehensive theory to predict attraction between two macroscopic bodies in a medium, due to Landau and Lifshitz, is available. The theory makes use of properties such as refractive index which you might think has nothing to do with forces between bodies. When the properties of the medium are intermediate between those of the two interacting particles, the van der Waals interaction between two such particles can become repulsive too.

In general, van der Waals interaction between two particles of same material is nearly always attractive. There must be a repulsive force that prevents the particles from coming together

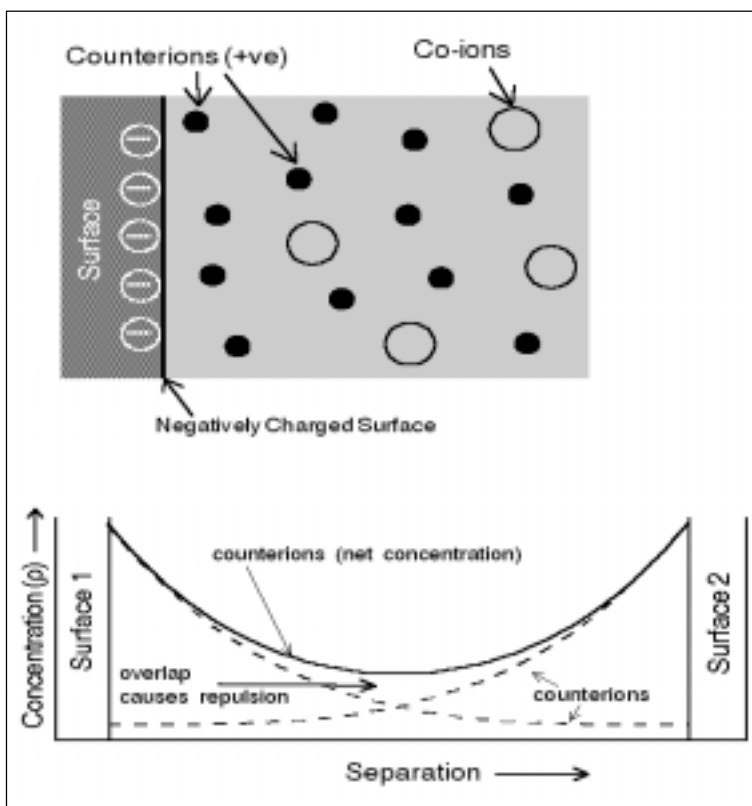
Theories often make interesting predictions. One such in the context of colloids predicts that if the refractive index of dirt particles were to be same as that of air, our clothes would not get dirty as soon as they do.



Particles acquiring similar charge in solutions repel each other, but not due to coulombic repulsions.

and stabilises the system. This force arises when the particle surfaces become charged through either the dissociation of the surface groups or selective adsorption of one type of ions from the medium. One may be tempted to attribute this repulsive force to repulsion between similarly charged bodies. The correct answer, however, is quite counter-intuitive. A charged particle is surrounded by a diffused layer of oppositely charged counterions. These counterions screen the electric field emanating from the charged particle. Thus, a charged particle with its diffused layer of counterions (also known as electrical double layer) appears like a neutral particle from a distance. Consequently, two similarly charged particles, when far away from each other do not experience any repulsion. In the event of overlap of the cloud of counter-ions, the concentration of counterions in between the particles increases, as shown in *Figure 2*. This sets up repulsion between them through osmotic pressure.

**Figure 2.** A schematic of double layer repulsion between two charged surfaces. Each surface is surrounded by its diffused cloud of counterions and other ionic species.

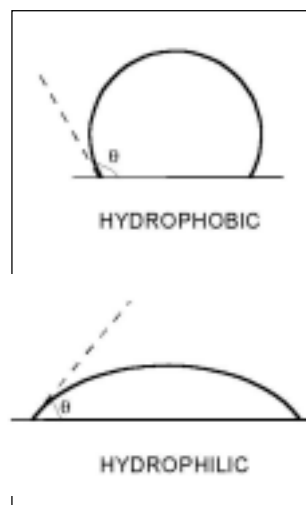


To summarise, attraction between two *neutral* particles has an *electrostatic* origin, and the repulsion between *charged* particles surrounded by the counterions has an *entropic* origin through osmotic pressure gradient around the particle. Around the second world war, Deryaguin and Landau in USSR and Verwey and Overbeek in Netherlands independently put these two forces together to quantitatively explain the stability of colloidal dispersions, particularly the strong destabilising effect of addition of multivalent salts – concentration of a divalent salt needed to destabilise (coagulate) a colloidal dispersion is  $2^6$  times smaller than that of a monovalent salt. This theory is now known as DLVO theory; letters in DLVO stand the names of the four scientists mentioned above.

## A New Force

DLVO theory has quantitatively explained a large number of experimental findings on stability of colloids and stands as a monument in the landscape of colloid science. Some glaring omissions were, however, reported. This prompted researchers to verify the existence of the forces involved in DLVO theory directly which was made possible with the surface force apparatus (SFA), developed in 1976 by Israelachvili and Adams (*Nature*, Vol. 262, pp. 774-776, 1976). More details on the surface force apparatus are provided in Box 1. A very unusual discovery was soon made by Israelachvili and Pashley (*Nature*, Vol. 300, pp. 341-342, 1982) when they measured the force between two hydrophobic surfaces in water. Hydrophobic surfaces are defined as those not wetted by water. A quantitative measure of hydrophobicity is *contact angle*, which is the angle between the solid surface and the air-water interface at the contact point, as shown in Figure 3. A surface with contact angle greater than 90 degrees (like wax coated paper) is hydrophobic. The hydrophobic surfaces used in these experiments were obtained by adsorbing on hydrophilic mica hexadecyltrimethylammonium bromide (CTAB), a cationic surfactant with a hydrocarbon chain. The attractive force, was found to be an order of magnitude stronger than the attractive van der Waals force.

**Figure 3.** The angle made by drops of a liquid sitting on a solid at the contact line is known as contact angle  $\theta$ . For completely wetting and completely non-wetting surfaces, this angle takes values  $0^\circ$  and  $180^\circ$ , respectively.

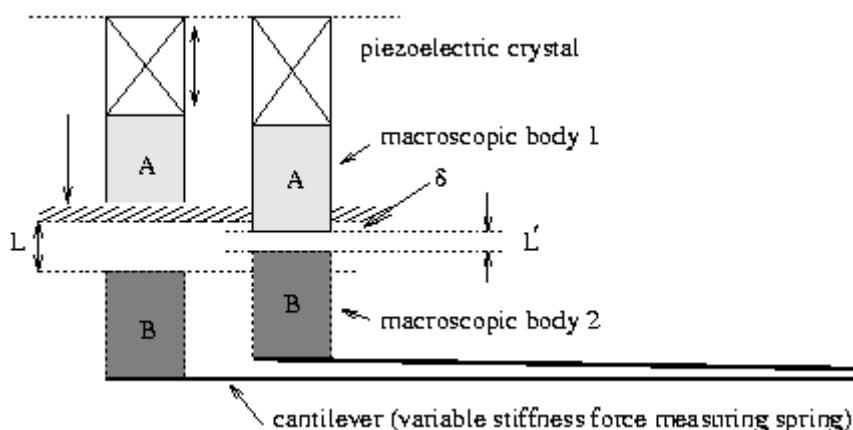


**Box 1. Surface Force Apparatus**

Surface force apparatus (SFA) is routinely used to measure force between two surfaces in air or liquids. The broad principle used by Israelachvili and Adams is shown in *Figure A*. Consider two surfaces *A* and *B* at separation  $L$ ; surface *B* is mounted on a cantilever and surface *A* can be moved in and out to change gap width between *A* and *B*. If surface *A* is now moved by a known distance  $\delta$ , for non-interactive surfaces, the gap will reduce to  $L - \delta$ . However, if the surfaces attract each other, the new gap  $L'$  will be less than  $L - \delta$ . The movement of the cantilever which is  $L - (L - \delta)$  can be multiplied with spring constant  $k$  to obtain the increase in force when the separation between the surfaces is decreased from  $L$  to  $L'$ .

Israelachvili and Adams used the above principle to measure surface forces of the order of  $10^{-8}$  N (equivalent to one microgram weight) between surfaces separated by distances as small as a nanometer. The gap thickness in their apparatus could be measured with an accuracy of 0.1 nm using multiple beam interference fringes, called Fringes of Equal Chromatic Order. The separation between the surfaces could be varied with an accuracy of 0.1 nm using a three stage mechanism employing rod (for micron scale movement), helical spring (for nanometer scale movement), and piezoelectric tubes (for sub-nanometer range) as shown in *Figure B*. The forces were measured between two crossed cylinders, and by using cantilevers of appropriately chosen spring constants. The forces between other geometries can be worked out from this data itself.

A similar principle has also been used to develop atomic force microscope (AFM) which can measure even smaller forces. AFM is used to investigate two dimensional surfaces with atomic resolution, for example, to understand structure of surfactant monolayers on solid surfaces.

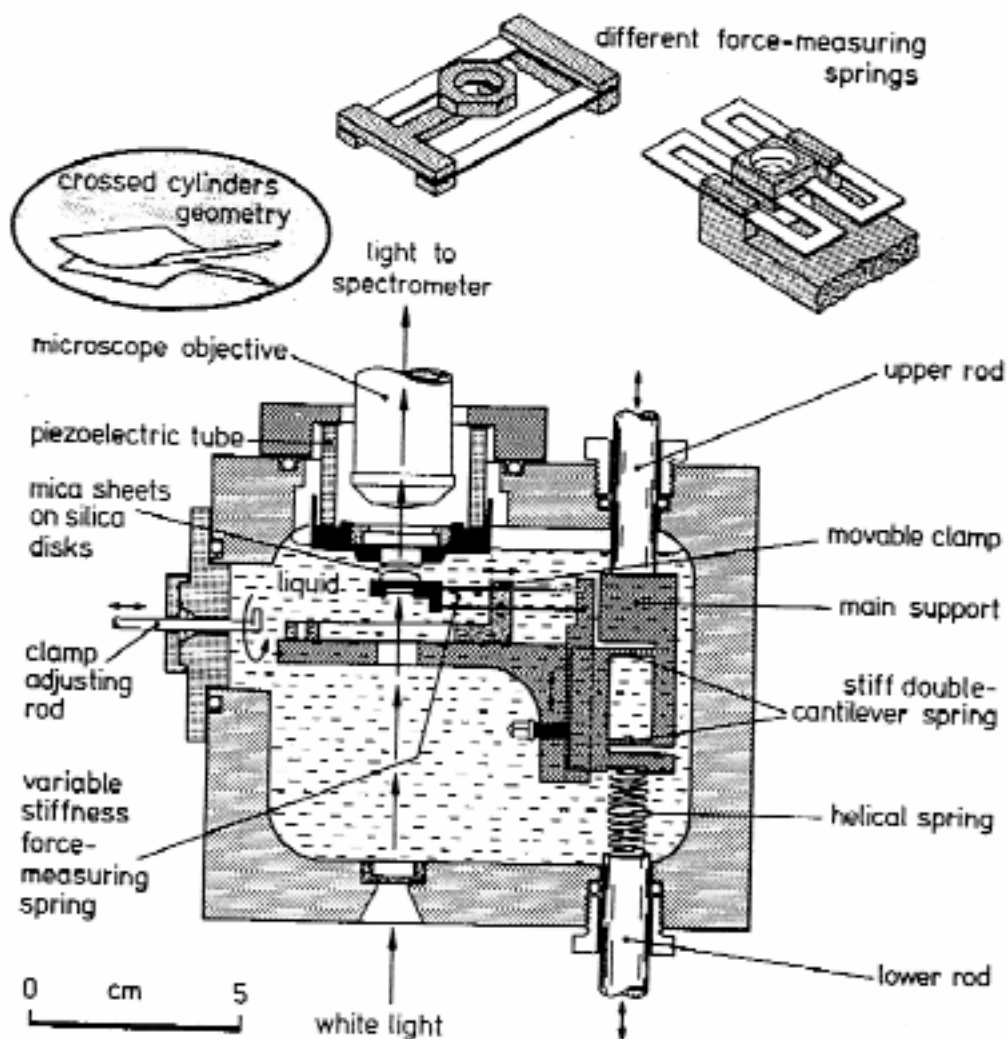


**Figure A. Principle used in SFA to measure force between macroscopic bodies.**

*Box 1. continued ...*



Box 1. continued...



**Figure B.** Surface force apparatus developed by Israelachvili and coworkers (Israelachvili, *Intermolecular and Surface Forces*, 2nd edition, Academic Press, 1991).

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No sooner than a new finding is made, a theory becomes available to explain it. A subsequent painstaking scrutiny of this theory in the light of new experimental evidence and theoretical objections often leads to a completely different but only more credible theory for the same finding. The truth may still be farther away.

### *Origin and Characteristics of the New Force*

The discovery of the new long ranged attractive force reconciled some of the deficiencies of the DLVO theory, but the focus soon shifted from DLVO theory to characteristics and origin of the new force. Israelachvili and Pashley considered the new force to be large scale manifestation of the familiar *hydrophobic effect* (see *Box 2*) between hydrophobic molecules. The latter is responsible for unusually high surface tension of water, formation of bilayers in cells, and many other self-assembled structures in biological systems. Water molecules around such hydrophobic molecules adopt a cage like structure, like that in ice, with decreased density as compared to that of the bulk water. The decreased density (concentration) due to the structuring of water between hydrophobic surfaces causes a decrease in entropy, and sets up an osmotic pressure, hence an attractive force between hydrophobic surfaces. An approximate calculations provided by the authors corroborated their claim about the origin of this force, hence the name *attractive hydrophobic force* for the new force.

Subsequently, many more experimental measurements under different conditions were reported. All these measurements have verified the presence of an additional attraction between hydrophobic surfaces and shown it to be quite strong and long ranged, as shown in *Figure 4*. While Israelachvili and Pashley found it to be an order of magnitude stronger than the van der Waals force but with the same range (10 nm), the new data reveal that this force can be ten times longer in range and about 100 times stronger than the van der Waals force. It is now established that the difference in data are due to the use of different methods of surface preparation.

The new measurements, obtained with surfaces covered with strongly hydrophobic surfactants (dimethyl dioctadecyl-ammonium bromide) having two chains, show that the measured force is best correlated by two exponential functions:

$$F(D) = C_1 \exp(-D/D_{10}) + C_2 \exp(-D/D_{20}),$$

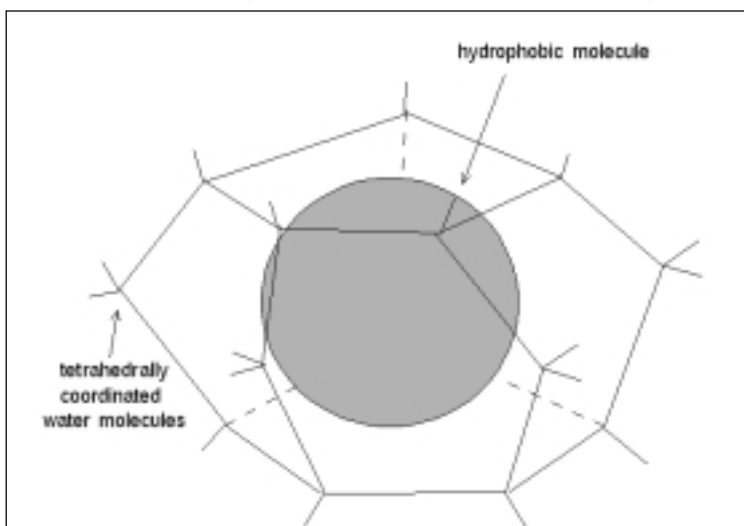


### Box 2. Hydrophobic Effect

Ability of water molecules to form H-bonds is responsible for many of the unusual properties of water. Strength of H-bond is responsible for high boiling and melting points and latent heat of vapourisation. Highly directional nature of H-bond is responsible for decrease in density and increase in dielectric constant upon solidification, exactly opposite to the behaviour of most liquids. The directional nature of H-bonds requires water molecules to adopt a short ranged tetrahedral structure (like that of diamond), in which a reference molecule is surrounded by four neighbours. Continuous jiggling of molecules, however, reduces the number of neighbours from 4 to 3.5.

When an inert or hydrophobic molecule is introduced into water, one expects some H-bonds to break to accommodate this molecule, and heat should be absorbed. Measurements, on the other hand, show that heat is liberated indicating formation of more H-bonds. The picture that has emerged over the years is that water molecules orient and order themselves around the inert molecule in *cage* like structures (shown in Figure C) in which water molecules make four H-bonds but at the cost of decreased jiggling (entropy).

It is because of these effects (known as hydrophobic effect) that surfactant molecules which consist of hydrocarbon chain(s) and polar head, are preferentially located on the air-water interface. By expelling the hydrophobic portion of the surfactant molecule out of water, entropically unfavourable contact between hydrocarbon and water is minimised. When the concentration of such molecules in water exceeds a certain concentration (known as critical micelle concentration), the surfactant molecules come together



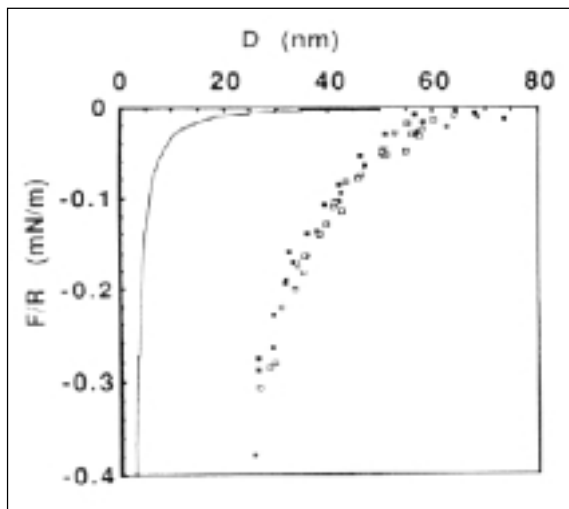
**Figure C. A schematic of highly ordered structure (*cage*) of water molecules around an inert body. Tetrahedral structure of water allows it to make more H-bonds than in bulk water.**

to form a new structure in which their hydrophobic hydrocarbon chains are shielded from water. The simplest structure with these features is a spherical micelle in which the polar heads cover the entire surface area and the tails are kept buried in the core.

Some researchers believe that hydrophobic effect is responsible for the beginning of life on the earth. As the small organic molecules came together in water, they grew bigger and developed two hydrocarbon tails. The hydrophobic tails of these molecules were so bulky that they could not be con-

tained in the core of spherical micelles. These molecules instead aggregated to form sheets with the polar heads on either side and the hydrophobic segment in-between (called bilayers), shielded from water. These sheets folded onto themselves to form cells, with some water trapped inside, isolated from the water outside. The life sustaining machinery of cells gradually evolved in them.





**Figure 4.** Experimental data showing the presence of a strong long range attractive force between two dimethyldioctadecylammonium bromide covered mica surfaces in water. The solid line shows the expected force, if only van der Waals attraction operated between the two surfaces. (Claesson and Christenson, *J. Phys. Chem.*, 92, pp.1650-1655, 1988). Reproduced with permission from ACS, Washington, USA.

where  $D_{10} = 2-3$  nm and  $D_{20} = 13-16$  nm. The first term represents strong short range hydrophobic attraction whereas the second term represents somewhat weak, long range attraction. A clear separation of two length scales, according to some researchers, is indicative of a different mechanism for each of them.

These experiments seem to indicate that making a surface more hydrophobic increases the strength and the range of the new force. Experiments with surfaces having contact angle smaller than 90 degrees

(hydrophilic surfaces) show that even these surfaces can experience weak hydrophobic attraction. Similar experiments with mica surfaces covered with surfactants having fluorinated and hydrocarbon chains, which display different contact angles show that the strength of hydrophobic attraction is approximately the same. These and other findings show that the hydrophobicity of a surfactant covered surface as manifested by contact angle does not correlate with the strength of the attractive hydrophobic force.

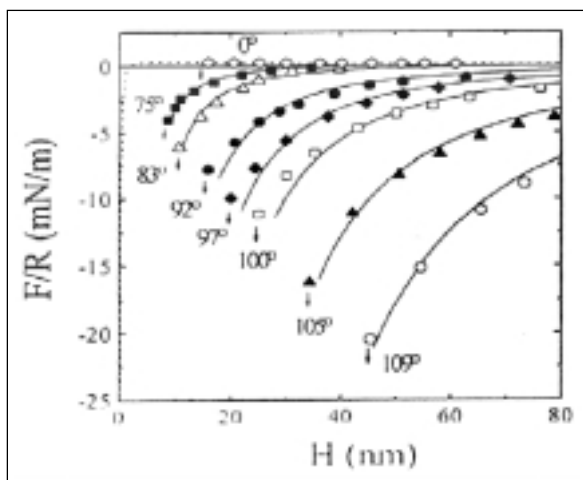
After the strength of the attractive force was found to be uncorrelated with contact angle, the explanation proposed by Israelachvili and Pashley also came under scrutiny. For their explanation to hold, the altered structure of water in the vicinity of a hydrophobic surface should propagate to distances as large as 200-300 times the diameter of a water molecule. Molecular scale order propagating to such large length scales is hard to believe and has also not been borne out by molecular simulations carried out in our group and also by others which indicate that the structure of water approaches that of the bulk water just a couple of water layers away from a hydrophobic surface.

While the theoreticians struggled with their efforts to explain the origin of the new force, the experimentalists forged ahead



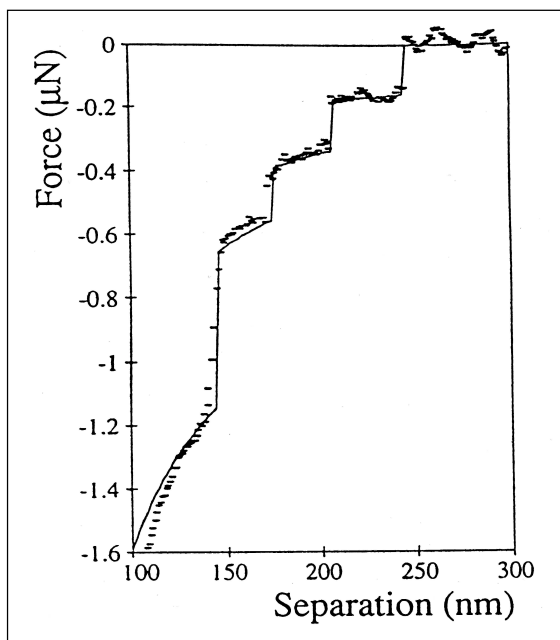
and produced more puzzling results. When one of the two hydrophobic surfaces was replaced by a hydrophilic surface (clean mica, glass or silica), the hydrophobic force, instead of becoming weaker became stronger! While the experiments with surfactant coated surfaces showed salts to sensitively affect the hydrophobic force, the same force between the surfaces obtained by reacting glass with fluorocarbon silanes remained nearly unchanged with the addition of salt. A slight increase in hydrophobic force with an increase in salt concentration was of the same order as the increase in surface tension of water due to the addition of salt. Interestingly, the strength of the hydrophobic attraction between these surfaces is found to be uniquely decided by contact angle, as shown in *Figure 5*. An increase in contact angle from 81 to 109 degrees increases the decay length (in exponential function) from 2 to 32 nm. Addition of alcohol to water substantially decreases the strength of hydrophobic force; the decrease in strength correlates well with the decrease in surface tension of water. All these results are exactly opposite to those found in studies with surfactant covered surfaces. Surface preparation seems to hold the key to these conflicting findings.

A recent theory considers attractive force to arise due to metastability of water film between hydrophobic surfaces. As in the original theory of Israelachvili and Pashley, this theory also



**Figure 5.** Effect of contact angle on hydrophobic attraction between silanated glass sphere with contact angle of 109° and silanated silica plates of different contact angles – increasing contact angle increases hydrophobicity of a surface (Yoon and others, *J. Coll. Int. Sci.*, 185, pp.363-370, 1997).

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**Figure 6. Experimental data showing jumps in measured force between hydrophobic surfaces were obtained by reacting glass spheres with (tridecafluoro-1,1,2,2-tetrahydrooctyl) dimethylchlorosilane. Solid lines are obtained by assuming six hemispherical cavities attached to surfaces, one each at  $r = 13, 16, 18$ , and three at  $19 \text{ nm}$  off the central axis (Parker and others, *J. Phys. Chem.*, **98**, pp.8468-8480, 1994). Reproduced with permission from ACS, Washington, USA**

considers the decrease in water density between hydrophobic surfaces to be the cause for the hydrophobic force. The decrease in density is, however, explained as arising due to the presence of voids and cavities in the water film. Any condensed phase has some equilibrium number of voids (cavities) at a given temperature. These voids fluctuate in size because of thermal vibrations. In the presence of a hydrophobic surface, the fluctuations are amplified, in particular, the lateral vibrations are enhanced owing to the fact that water molecules would like to keep away from the hydrophobic surface. These lateral fluctuations decrease the water density in the inter-surface region and hence cause an attractive force.

In the extreme case, the water film can spontaneously cavitate and the two hydrophobic surfaces can jump into contact forming a vapour bridge between the two surfaces. Spontaneous cavitation is possible when the solid surfaces are so near each other that they can support a vapour-liquid interface with curvature large enough to balance atmospheric pressure on the liquid side and vapour pressure of water on the vapour side. Since the vapour pressure of water at room temperature is much smaller than the atmospheric pressure, the two particles experience a net attraction.

A slight variation of the above line of thinking is the formation of a large number of nanometer size bubbles on hydrophobic surface. As the surfaces come closer, more and more of these bubbles make bridging contacts between the two surfaces. If this hypothesis were to hold, the measured force should show jumps corresponding to the event of a vapour cavity bridging two surfaces. Experimental data indeed show such jumps (Figure 6). This theory also explains the correlation between the strength of the hydrophobic attraction and surface tension of

water (varied through addition of salt and alcohol) and changes in contact angle (introduced by varying the extent of surface treatment, as in *Figure 5*). A qualitative prediction of the theory that hydrophobic attraction between particles should decrease with decreasing gas content of water as the latter decreases the number of gas nuclei has also been verified.

## Conclusions

A new attractive force between hydrophobic surfaces has been discovered by Israelachvili and Pashley. The new force is 10-100 times stronger than the van der Waals attractive force between macroscopic bodies and can be measured at surface separations in excess of 100 nanometers. Presently, there is neither a widely accepted set of characteristics of this force (reproducibility across the laboratories is not yet at an acceptable level) nor a theory which can explain the origin of this force and make quantitative predictions.

The recognition that there is an additional hydrophobic attractive force between hydrophobic surfaces is also entering engineering/design considerations. For example, degassing of water which reduces the number of gas nuclei and hence reduces the strength of hydrophobic attraction according to one of the theories has already been shown to be an effective control strategy to reduce aggregation and subsequent removal of coal particles from suspensions. As years go by, we are likely to see many more situations in which hydrophobic force is identified to play an important role. The challenge will lie in our ability to effectively manipulate it.

## Suggested Reading

- [1] J N Israelachvili, *Intermolecular and Surfaces Forces*, second edition, Academic Press, 1991.
- [2] J L Parker, P M Claesson, and P Attard, Bubbles, cavities, and the long ranged attraction between hydrophobic surfaces, *J. Phy. Chem.*, Vol. 98, pp. 8468-8480, 1994.

Water devoid of any impurity requires tension equal to hundreds of atmosphere and will require a temperature exceeding 300°C to boil at atmospheric pressure.

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