

The hydrophobic interaction between macroscopic surfaces

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Abstract. The aim of this paper is to review our current level of knowledge of the interaction between hydrophobic surfaces immersed in water. The strong attractive forces observed between such surfaces have generally been referred to as "the hydrophobic interaction". Although the precise origin of this force has not yet been determined, we will examine recent experimental studies and relate them to other phenomena like cavity formation and repulsive hydration forces.

Keywords. Hydrophobic interaction; hydrophobic force; cavitation; surfactant monolayers; force measurements; hydration force.

1. Introduction

The hydrophobic nature of solute molecules often determines their solution properties; for example, it provides the driving force for molecular self-assembly of amphiphilic molecules into micelles, vesicles and bilayers (Tanford 1973; Franks 1973, Israelachvili *et al* 1976). The hydrophobic interaction also plays a crucial role in determining the detailed conformation of proteins in solution (Kauzmann 1959). Co-operative surfactant adsorption onto surfaces is also largely due to hydrophobic interaction between the hydrocarbon regions of the molecules (Cases and Mutaftschiev 1968; Herder *et al* 1987).

Although the hydrophobic force between solute molecules is used to explain solution behaviour this force has, until recently, seldom been considered important when discussing surface interactions. The reason for this is that solute-solvent interactions, in contrast to electrical double-layer and van der Waals forces, are believed to be of very short-range, decaying over a few diameters of solvent molecules at most. That the hydrophobic effect between macroscopic surfaces is of significant range and strength, however, was clearly illustrated some years ago by Laskowski and Kitchener (1969). These authors pointed out that although surface methylation of silica does not alter the van der Waals interaction or the electrical charge at the silica-water interface, the macroscopic wetting properties of the surface are drastically changed. The Derjaguin-Landau-Verwey-Overbeck (DLVO) theory applied to water films on silica predicts wetting for both surfaces (Pashley and

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Kitchener 1979), which is clearly not the case. Laskowski and Kitchener conclude, therefore, that some other structural or solvation effect must occur at the methylated surface and that this effect must extend some distance from the interface in order to overcome van der Waals and double-layer forces.

Blake and Kitchener (1972) attempted to estimate the range of the hydrophobic interaction on methylated silica by observing the rupture of an aqueous film produced on compressing an air bubble against the surface. They found an upper limit to the range of about 64 nm. Above this thickness the films were stabilized by repulsive double-layer forces.

More recently, a series of experiments has been carried out in an attempt to quantitatively measure the strength and range of the hydrophobic interaction between solid surfaces. The development of a remarkable surface forces apparatus (Israelachvili and Adams 1978) has made it possible to directly measure such forces. This apparatus measures the force as a function of separation between two mica surfaces in a crossed-cylinder configuration with a distance resolution of 0.1–0.2 nm and a sensitivity of 0.1 μN . The measured force F_c is related to the free energy of interaction between parallel, flat surfaces (G_f) (Derjaguin 1934),

$$F_c/R = 2\pi G_f, \quad (1)$$

where R is the local geometric mean radius of curvature of the interacting surfaces.

In these experiments the muscovite mica surfaces were made hydrophobic either by adsorption of surfactants from solution or by deposition of Langmuir-Blodgett films. The forces measured between hydrophobic surfaces have in all cases been much more attractive than can be explained by a combination of van der Waals and double-layer forces (the DLVO-theory).

The strength of this attraction is the cause of the stronger cohesion between hydrophobic surfaces in water than in air (Shchukin *et al* 1981), despite the fact that the van der Waals attraction should be larger in air (Hough and White 1980). Furthermore, this strong hydrophobic interaction appears to be long-range and will thus play a crucial role in many systems including the interaction of biologically important molecules in solution.

The hydrophobic force is of direct relevance to froth flotation where air bubbles, which are inherently hydrophobic ($\gamma_{sv} = 72 \text{ mJm}^{-2}$) interact with hydrophobed mineral particles across an aqueous surfactant solution during particle approach and attachment. The subtle control of this attachment process is the key to efficient mineral separation with this widely used technique. It should be pointed out that the van der Waals force between a mineral particle and an air bubble interacting across water is always repulsive and the occurrence of bubble attachment therefore indicates the presence of an additional, attractive force.

There are many other technically important areas in which hydrophobic interaction is involved in critical processes, for instance oil recovery, detergency, food emulsification, paint production and in the deposition of well-defined multimolecular Langmuir-Blodgett films for use in electronic devices (eg LEDs).

In the following section we will review some of the recent experiments carried out on the direct measurement of the hydrophobic interaction between macroscopic surfaces.

2. Direct measurements of the macroscopic hydrophobic interaction

The first direct evidence for the presence of a strong, long-range interaction between hydrophobic surfaces was obtained when forces between mica surfaces coated with an adsorbed monolayer of cetyltrimethylammonium ions (CTA^+) were measured (Pashley and Israelachvili 1981; Israelachvili and Pashley 1982, 1984). These surfaces were found to be highly charged and only moderately hydrophobic, with a water contact angle of about 60° . There was an exponential double-layer repulsion between the surfaces as illustrated in figure 1. At small separations attractive van der Waals forces should produce a force maximum at a separation of about 2 nm and an adhesive primary minimum at $D = 0$. However, the force maximum observed was at much larger distances and, in addition, the final primary minimum adhesion was much stronger than for the mica/water case.

In the theoretical curve in figure 1 the van der Waals force was assumed to be given by a simple non-retarded Hamaker equation: $F/R = A/D^2$, where the Hamaker constant A was taken to be $2 \times 10^{-20} \text{ J}$. This value is, if anything, an overestimate and is still insufficient to cause the attraction observed.

The hydrophobic force law was determined in this system from the analysis of a series of experiments carried out under different CTAB solution conditions. In order to do so the theoretical DLVO curve (obtained by a fit to the measured forces at larger separations) was subtracted from the total force to obtain an estimate of the range and magnitude of the interaction. The force law obtained in

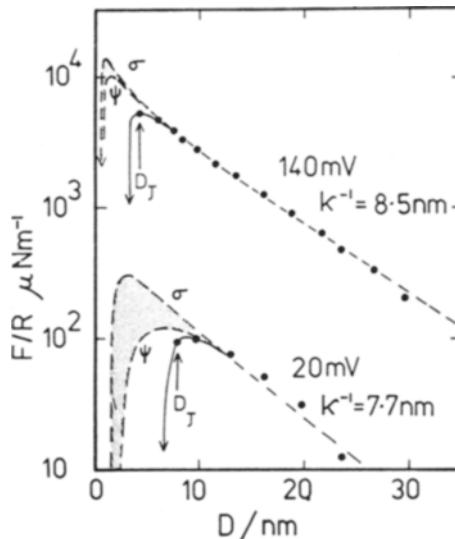


Figure 1. Measured repulsive force (normalized by radius) between two CTA^+ -coated surfaces in aqueous solutions of KBr. The upper force curve was measured at $\text{pH} \sim 5.6$ and a CTAB concentration of $2.5 \times 10^{-5} \text{ M}$ (plus KBr at $1.3 \times 10^{-3} \text{ M}$). The lower force curve was measured at $\text{pH} \sim 9.0$ and a CTAB concentration of 10^{-4} M (in addition to $1.5 \times 10^{-3} \text{ M}$ KBr). The dashed lines are the theoretical DLVO force laws expected where a *nonretarded* Hamaker constant of $A = 2 \times 10^{-20} \text{ J}$ has been assumed. Note that the force barriers occur much farther out than expected, indicating the existence of a strongly attractive force at these distances where the van der Waals force should be almost negligible.

this way could be fitted by an exponential function with a decay length of about 1 nm (see figure 2). These experiments clearly demonstrate that the hydrophobic interaction is much stronger than the expected van der Waals interaction and extends to at least 10 nm.

More recent experiments on the mica-CTAB system using carefully purified surfactant (Christenson and Claesson, unpublished results), have produced surfaces of almost zero charge and with a water contact angle close to 90°. The attractive force observed is qualitatively similar but extends to even larger distances. This recent result in fact is in closer agreement with results using double-chain surfactant monolayers to be discussed below.

Strongly hydrophobic surfaces were obtained by depositing a monomolecular layer of dioctadecyldimethylammonium (DDOA⁺) ions onto the mica surface using the Langmuir-Blodgett procedure. The deposited layer is stable in aqueous solutions up to several days due to the strong electrostatic bonds between the negatively charged mica surface (one negative lattice charge per ~0.5 nm²) and the cationic headgroups as well as due to the strong cohesive forces between the hydrophobic tails. The area per molecule in the deposited layer was found to be about 0.5 nm² as determined by ESCA and transfer ratio measurements (Claesson *et al* 1986a). The advancing water contact angle on such a 2 nm thick surfactant layer is about 94°. Direct force measurements showed that the surfaces were only

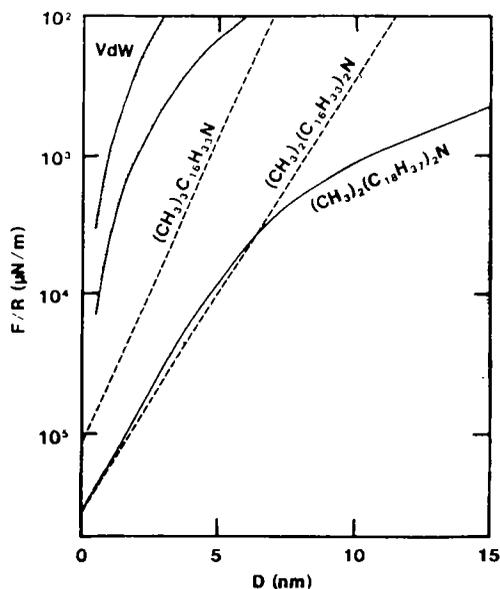


Figure 2. A comparison between the magnitude of the hydrophobic interaction measured in three different systems and the nonretarded van der Waals force, plotted on a logarithmic scale. The limits of the van der Waals force have been calculated using Hamaker constants of 2.2×10^{-20} J (as for mica/water/mica) and 5×10^{-21} J (as for hydrocarbon/water/hydrocarbon). The lines are for surfaces coated with cetyltrimethyl ammonium ions $((\text{CH}_3)_3(\text{C}_{16}\text{H}_{33})_2\text{N}^+)$ $\gamma_{\text{SL}} = 11$ mN/m, dihexadecyldimethylammonium ions $((\text{CH}_3)_2(\text{C}_{16}\text{H}_{33})_2\text{N}^+)$ $\gamma_{\text{SL}} = 34$ mN/m and dioctadecyldimethylammonium ions $((\text{CH}_3)_2(\text{C}_{18}\text{H}_{37})_2\text{N}^+)$ $\gamma_{\text{SL}} = 34$ mN/m. The first two surfaces were obtained by adsorption of the surfactant from solution, the third by Langmuir-Blodgett deposition.

weakly charged, but the dominant feature of the interaction was found to be a strong attractive force measurable out to separations of about 30 nm (Claesson *et al* 1986a). The experimental technique used in this particular case determines the slope of the force rather than the force itself. This slope is then, of course, proportional to the pressure between flat surfaces (taking the derivatives of equation (1)). Figure 3 shows a plot of the slope of the attraction (after subtraction of the weak double-layer repulsion) as a function of distance (see also figure 2).

Addition of potassium bromide to a concentration of 10^{-2} M reduced the range of the double-layer force, which made the total force purely attractive with the hydrophobic interaction dominant at all surface separations. The net hydrophobic interaction was only marginally reduced by the increased electrolyte concentration (see figure 3). This contrasts with the strong salt-dependence of attractive double-layer forces between one DDOA⁺-coated mica surface and one bare mica surface (Claesson *et al* 1987) and shows that the measured attraction is not due to the surfaces having opposite charge.

Surfaces having an even larger water contact angle of about 110° are obtained when a monolayer of a polyfluorinated double-chain cationic surfactant [N-(α -trimethylammonioacetyl)-0,0'-bis(1H,1H,2H,2H-perfluorodecyl)-L-glutamate chloride] is deposited onto mica. In figure 3 the slope of the hydrophobic force for this system shows that the attraction is even more long-range than for the hydrocarbon surfaces (Christenson *et al*, to be published). Clearly, the hydrophobic force is orders of magnitude stronger than the expected van der Waals force and seems to increase in strength with surface hydrophobicity as determined by the water contact angle.

A strong hydrophobic interaction has also been observed between mica surfaces coated with monolayers of a range of other surfactants including dodecylmethyl-

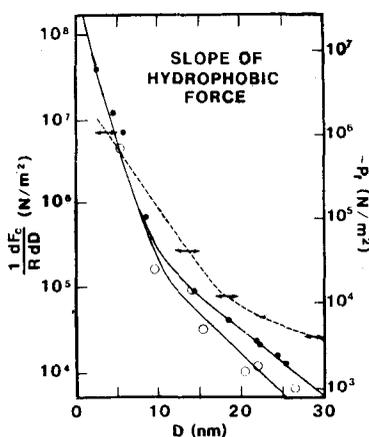


Figure 3. The slope of the hydrophobic interaction measured between dioctadecyl-dimethylammonium ion-coated mica surfaces (solid lines) and between fluorocarbon coated surfaces (dashed line). Filled circles are points obtained in conductivity water and open circles after addition of potassium bromide to 10^{-2} M. Any double-layer repulsion has been subtracted out. The slope of the force between curved surfaces is proportional to the pressure between flat surfaces, as shown on the right-hand ordinate. As can be seen, the effect of increasing the salt concentration 300 times is almost negligible. Note the logarithmic scale.

amine oxide and primary amines (Herder *et al.*, to be published), and dimethyldihexadecyl ammonium acetate (see figure 2) (Pashley *et al.* 1985). Hence, it is extremely unlikely that the strong attraction observed in all cases is due to some contamination present in all surfactant samples or in all the types of purified water used in these experiments.

Further support for the view that this attraction is a true hydrophobic interaction comes from the observation that it is completely removed on adsorption of a second surfactant layer with polar or ionic head groups facing the solution. This is illustrated in figure 4 for the case of pentaoxyethylenedodecyl ether (Claesson *et al.* 1986b) and is a general property of all the surfactants studied. Other compounds which have been shown to have a similar effect include primary amines and alkylamine oxide (Herder *et al.* to be published), quaternary amines (Pashley and Israelachvili 1981) and insulin (Claesson *et al.* to be published).

3. The hydrophobic force law

In this section we attempt to describe the distance dependence of the hydrophobic interaction between surfaces in a simple mathematical form. These expressions are useful for *estimating* the hydrophobic interaction expected between comparable hydrocarbon-coated surfaces and are a first step towards bridging the large gap between theory and experiment.

It appears that the hydrophobic interaction at distances less than about 7–8 nm can be reasonably well fitted with an exponential function. The free energy of interaction between flat surfaces can therefore be described roughly by the

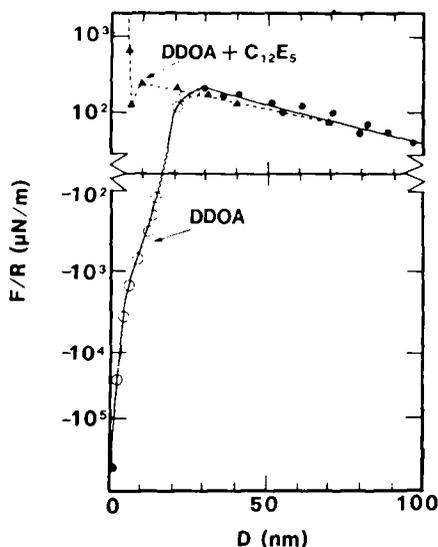


Figure 4. The total force measured between dioctadecyldimethylammonium ion-coated surfaces in water before (\circ) and after (\blacktriangle) addition of $6 \cdot 10^{-5}$ M pentaoxyethylenedodecyl ether ($C_{12}E_5$). The $C_{12}E_5$ adsorbs to the hydrophobic surfaces and completely removes the hydrophobic interaction, while the double-layer repulsion is unchanged.

relation:

$$G_f = -C \exp(-D/\lambda). \quad (2)$$

The decay constant, λ , is slightly above 1 nm. The other constant, C increases with surface hydrophobicity and is roughly equal to twice the solid-liquid interfacial energy (γ_{SL}) estimated from contact angle measurements. However, at lower distances, the observed hydrophobic interaction decays more slowly than that indicated by (2). One way of including the weaker tail in a simple manner is to use an exponential function with two decay constants. For instance the hydrophobic interaction between two DDOA-coated mica surfaces in 10^{-2} M KBr (see figure 3) is well described by the relation:

$$G_f = -5.8 \times 10^{-2} \exp(-D/1.2) - 1.0 \times 10^{-3} \exp(-D/4.5) \text{ (J/m}^2\text{)}, \quad (3)$$

where D is in nm. A power law function with a distance dependence of D^{-2} to D^{-3} can also be used to fit the measured hydrophobic interaction over a range of distances at least reasonably well.

4. Hydrophobic interaction and cavity formation

The possible formation of a cavity around two highly solvophobic surfaces in contact (the contact angle of the solvent on the surface should be larger than 90°) has been considered theoretically (Yaminsky *et al* 1983) and also observed experimentally between glass surfaces in mercury (Yushchenko *et al* 1983). It was shown that the creation of a vapour cavity between these surfaces is thermodynamically favoured when the surfaces are closer together than a certain critical distance, D_c , which depends among other things on surface hydrophobicity. However, the energy barrier for cavity formation is very large and no cavity should form until the surfaces are less than a few tenths of a nanometer apart. Once the cavity has formed the energy barrier for its disappearance is large. Consequently, the surfaces must be separated to distances considerably larger than D_c before the cavity disappears.

The main predictions of Yaminsky *et al* have in fact been nicely confirmed by recent measurements. Between fluorocarbon surfactant-coated mica surfaces many small and irregular shaped cavities do form once the surfaces are brought into contact, or about 1–2 nm from contact. These cavities remain between the surfaces upon separation until they suddenly disappear at separations of a few micrometers. However, it is important to note that during measurement of the hydrophobic attraction, prior to the surfaces coming into contact, *no* cavities between the surfaces have been observed.

Between less hydrophobic DDOA⁺-coated surfaces no detectable cavity forms between the surfaces when they are brought into contact. However, when separating the surfaces from molecular contact a cavity does form. This cavity is considerably smaller than those formed between fluorocarbon-coated surfaces, and upon separation, disappears at smaller surface separations.

Between CTA⁺-coated mica surfaces no cavity has yet been observed, but further investigations are under way to establish whether or not a cavity does form in this case. We would not expect cavity formation for surfaces with water contact angles significantly less than 90° .

We conclude that the measured hydrophobic interaction is not due to the presence or formation of small vapour cavities between the surfaces. However, the hydrophobic attraction and cavity formation are related to each other. Furthermore, the hydrophobic force measured between strongly hydrophobic surfaces is not a thermodynamic equilibrium force since in the true equilibrium state a cavity should be present between the surfaces. For all practical purposes, however, the force behaves as an equilibrium force in the sense that it is reproducible between experiments and between repeat measurements. The reason for this is, of course, that the energy barrier the system has to overcome in order to reach the thermodynamically stable state is too large and the system remains in its metastable state.

5. Speculations around the molecular mechanism underlying the hydrophobic interaction between macroscopic surfaces

The pressure, P , inside a liquid may be considered to be composed of one kinetic component, P_k , trying to separate liquid molecules and one cohesive component, P_c , acting so as to keep the liquid molecules held tightly together. For a simple liquid one has (Hill 1962):

$$P = P_k + P_c = nkT + \frac{n^2}{6} \int_0^{\infty} r \frac{du_2(r)}{dr} g_2(r, n, T) 4\pi r^2 dr, \quad (4)$$

where n is the number density of liquid molecules, g_2 the pair distribution function and u_2 the pair interaction potential. In water P_k is of the order of 1300 atmospheres or 1.3×10^8 N/m². Since P equals the external pressure of 1 atmosphere it follows that the cohesive pressure also is about 1300 atmospheres. Obviously one has two large contributions to the total pressure which together with the external pressure exactly balance each other. Let us assume that two hydrophobic surfaces in close proximity perturb the local balance of pressures. Clearly, this could potentially give rise to large forces comparable in strength to the measured hydrophobic attraction (figure 3). Take the hydrophobic interaction between DDOA⁺-coated mica surfaces as an example. At a surface separation of ~ 1 nm the attractive pressure is about 20 atmospheres and at 20 nm about 0.05 atmospheres. Clearly only a very small perturbation of the delicate balance between the kinetic and the cohesive pressures is sufficient to account for the observed hydrophobic interaction. Taking into account that cavities might form between hydrophobic surfaces in contact and that the hydrophobic interaction, at least for highly hydrophobic surfaces, is measured in a metastable state, it is easy to visualize perturbations of the balancing pressure terms occurring at larger distances. If this concept is correct, a hydrophobic interaction between surfaces occurs as a result of the system going in the direction of forming a cavity and this tendency will depend on the proximity of the two interacting surfaces.

A complementary "microscopic" view of the hydrophobic interaction may also be developed. Thus, we may assume that a hydrophobic surface will induce an increased, dynamic ordering of water molecules near the surface. The extensive hydrogen-bonding network of water will propagate this enhanced ordering out

from the surface until it has decayed to its bulk value. The approach of the two hydrophobic surfaces further enhances this dynamic ordering between the surfaces and displaces water molecules from the interlayer region to bulk solution. The overall effect of this is to decrease the free energy of the system thus giving rise to an attractive force. It is instructive to calculate the free energy gain per water molecule, g_t , transferred from the interlayer region to bulk, needed to account for the observed attraction. It is given by:

$$g_t = (\partial G_f / \partial D) / (\partial N / \partial D), \quad (7)$$

where N is the total number of water molecules between flat surfaces per unit area. This free energy gain for DDOA⁺-coated surfaces is shown as a function of surface separation in figure 5. Clearly, the large hydrophobic interaction observed corresponds to a free energy gain of only fractions of kT per water molecule. Thus, it cannot be expected that water between hydrophobic surfaces is different from bulk water in any way which could easily be detected using for instance Monte Carlo or molecular dynamics simulations. Once again, it appears that very minor differences between bulk water and water between two surfaces can give rise to enormous forces.

According to this view the attractive hydrophobic force is essentially of the same type as the repulsive hydration force observed between hydrophilic surfaces. One would thus expect a gradual change from a repulsive hydration force to an attractive hydration force (hydrophobic force) with increasing surface hydrophobicity (Israelachvili 1985). Some support for this hypothesis comes from an investigation of the temperature-dependent interaction between surfaces coated

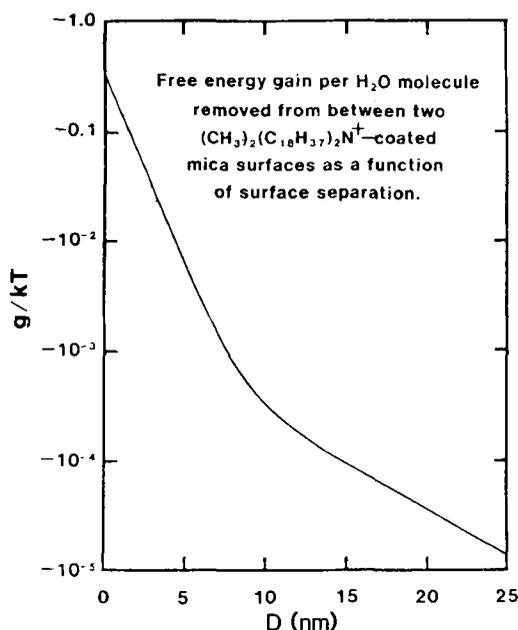


Figure 5. The free energy of transfer per molecule of water from between two hydrophobic surfaces to bulk. The values were calculated from the results of figure 3. As can be seen, the energy per water molecule is very small indeed.

with pentaoxyethylenedodecyl ether (Claesson *et al* 1986b). At low temperatures the hydration force between ethylene oxide units was found to be purely repulsive. However, as the temperature was increased part of the force curve turned attractive. This could be explained by assuming an essentially hydrophobic type of hydration around the ethyleneoxide chains. For the case of ethylene oxide the two large changes in ΔH_f and $T\Delta S_f$ and occurring on pushing the surfaces together nearly cancel each other in $\Delta G_f = \Delta H_f - T\Delta S_f$. Thus a small change in temperature changes the sign of ΔG_f and the repulsion turns into an attraction.

It is perhaps pertinent at this point to consider the oscillatory forces observed between mica surfaces in aqueous electrolyte solutions (Pashley and Israelachvili 1984). These forces have a periodicity close to the diameter of a water molecule and may be regarded as superimposed on the repulsive hydration force. However, these forces are not observed when the surface is rough on the molecular scale and are not seen between lipid bilayer-coated mica surfaces (Horn 1984; Marra and Israelachvili 1985). It is, therefore, likely that any such oscillations would be smeared out for the hydrophobic monolayer surfaces as well. In any case, the strong overall attraction present in these systems would make the detection of oscillatory forces, very difficult.

6. Future studies

There remains much to be done experimentally (as well as theoretically, of course). As an example, the temperature dependence of the hydrophobic interaction must be thoroughly investigated. Such a study would provide information about the changes in enthalpy and entropy involved when two hydrophobic surfaces come together in water. This in turn would give some clue as to the molecular origin of the hydrophobic force.

Another important study would involve the interaction between weakly hydrophobic surfaces. Such a study might clarify if a hydrophobic interaction arises suddenly at a given surface hydrophobicity or if there is a gradual change from a large repulsive hydration force, as observed between mica surfaces in concentrated electrolyte solutions, to (i) weakly repulsive and attractive hydration forces, as observed between ethylene oxide layers, and (ii) strongly attractive hydrophobic forces as observed between surfaces coated with surfactant monolayers.

A third area, not discussed here, involves the possibility of solvophobic forces in non-aqueous media. Do such forces exist in any other solvent or only in strongly hydrogen-bonding liquids or are they unique to water?

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