Solvation Forces and Liquid Structure, As Probed by Direct Force Measurements

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Introduction

An understanding of the magnitude and range of the various forces that exist between surfaces, particles, or solute molecules in a liquid (solvent) medium is essential for understanding many complex but everyday phenomena at the molecular level, ranging from the behavior of colloidal and biological systems to the efficient operation of technological and industrial processes as diverse as enhanced oil recovery techniques to ceramic processing.

Until recently only the attractive van der Waals and repulsive electrostatic "double-layer" forces were believed to be important. Thus if the former dominated, then two particles or surfaces would come together and adhere (variously referred to as "coagulation", "flocculation", or "precipitation"), while if the latter dominated they would be kept apart. Taken together the combined but opposing action of these two interactions form the basis of the celebrated "DLVO theory" (after its originators Derjaguin and Landau[1] and Verwey and Overbeek[2]), which since the 1950s has served as the main theoretical framework for analyzing the properties of colloidal and biocolloidal systems. The attractive van der Waals forces between two surfaces or particles have a power-law distance dependence whose strength depends on the dielectric properties (refractive index and optical absorption frequencies) of the interacting materials and the intervening medium. Repulsive electrostatic or "double-layer" forces arise in polar solvents whenever a surface becomes charged, either by the dissociation of surface ions (such as H^+ or Na^+) or by the adsorption of free ions from the solution. Theories of electrostatic interactions in ionic solutions are based on the so-called Poisson–Boltzmann equation[2,6] which shows that the electrostatic repulsion between two charged surfaces or particles is "screened" by the ions in the solution and that it decays roughly exponentially with the distance of separation between them. The characteristic decay length is known as the "Debye screening length", κ^{-1}, and is analogous to the Debye length characteristic of electron gases. The Debye length decreases with increasing salt concentration of the solvent (usually an aqueous salt solution) varying from about 30 nm in 10^{-4} M monovalent salt to 0.3 nm in 1 M salt. This length also provides a measure of the range of these electrostatic "double-layer" forces (see Figure 5 later).

In the DLVO theory since the van der Waals forces vary as $-1/D^n$ while the electrostatic forces vary as $e^{-\kappa D}$ it is expected that the van der Waals forces will always dominate, i.e. win out, at sufficiently small separations, D, giving a force at molecular contact that is attractive (i.e. adhesive). However, it has long been known that the interactions of certain colloidal particles, clay mineral surfaces, surfactant assemblies such as bilayers, and biological membranes in aqueous solutions, do not always obey the predictions of the DLVO theory. This occurs, for example, when colloidal particles in solution remain separated, i.e. the colloid is "stable", even in the absence of any net surface charge. It also occurs when two surfaces separate spontaneously (swell) from contact when immersed in a (usually aqueous) solvent medium, i.e. when they are hygroscopic.

For a long time the origin of these discrepancies remained a mystery: was the DLVO theory at fault, or was there some additional "third force" or "structural force"[3] of unknown origin (though invariably believed to be monotonically repulsive and to be somehow related to water structuring effects)? This issue remained highly controversial for a number of decades, during which time some very plausible (and often totally valid) explanations were presented which convincingly showed that the mere phenomenological observation of, say, stability of a colloidal suspension or clay swelling in the absence of any surface charge did not prove the existence of structural forces.[4] Only direct force vs distance measurements could provide this information.

With increasing theoretical attention and the advent of highly sensitive techniques for measuring these forces in the 1970s, it became clear that the whole situation is far from simple, that the intervening liquid medium could not be treated simply as a structureless continuum, and that, when the discrete molecular nature of the liquid medium (and of the surfaces) is taken into account, some very subtle and unexpected interactions can result, especially at small separations. Such forces are now commonly referred to as "solvation" or "structural" forces or, if the solvent medium is water, "hydration" forces. Here we shall first briefly outline one popular technique for directly measuring the forces between two surfaces and then proceed to review and assess some of the more interesting results that have

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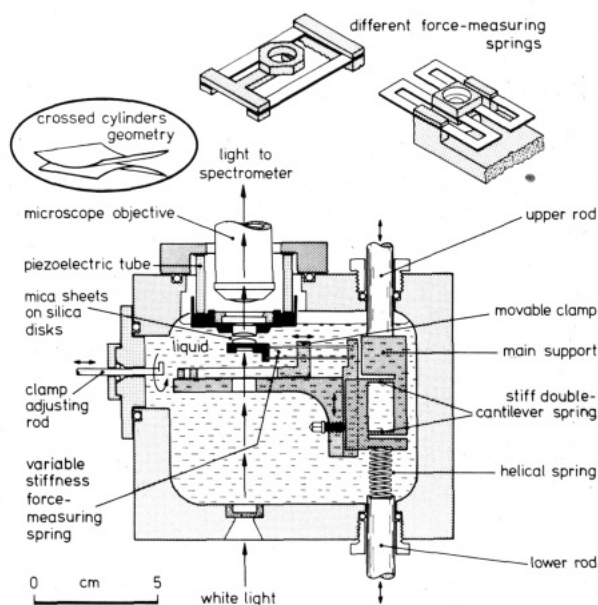(4) Israelachvili, J. N. *Chem. Scr.* 1985, *25*, 7.

Figure 1. Recently modified surface forces apparatus (SFA). The stiffness of the "variable-stiffness force-measuring spring" can be varied by shifting the position of the movable dove-tailed "clamp" using the "adjusting rod". A variety of interchangeable "force-measuring springs" (two shown on top) can be attached to the "main support" allowing greater versatility in measuring both repulsive or attractive forces over a range of more than 6 orders of magnitude. For further details and general applications of the SFA see ref 5 and 6. Reprinted with permission from ref 5. Copyright 1978 Royal Society of Chemistry.

emerged on solvation forces. We shall see how these studies have provided some unique insights into the fundamental interfacial interactions occurring at the molecular level both in simple liquids and in complex multicomponent fluid systems. But they also pose some new and intriguing questions concerning liquid structure and molecular ordering in bulk liquids and at surfaces.

The Surface Forces Apparatus

Figure 1 shows a force measuring apparatus with which the "force law" (force vs distance) between two curved molecularly smooth surfaces immersed in liquid or vapor can be directly measured.[5] The surfaces are usually bare mica, though these can have thin polymer or metal films, surfactant or lipid monolayers and bilayers, or some other surface film adsorbed (deposited) on them before they are installed into the apparatus. The distance between the two surfaces can be controlled and independently measured to better than 0.1 nm (1 Å), and the force sensitivity is about 10^{-8} N (10^{-6} g or 10^{-3} dyn).

The force is measured by expanding or contracting the piezoelectric crystal tube (which supports the upper surface) by a known amount and then measuring optically how much the two surfaces have actually moved; any difference in the two values when multiplied by the stiffness of the force-measuring spring gives the force difference between the initial and final positions. In this way both repulsive and attractive forces can be measured and a force law obtained over any distance regime.

Once the force F as a function of distance D is measured for the two curved surfaces of radius R (typically $R \approx 1$ cm), it can be shown that the force between any other two curved surfaces simply scales by R (i.e. by the total mutual curvature). Furthermore, it can also be shown that the corresponding interaction *energy* $E(D)$ per unit area between two flat surfaces is simply related to $F(D)$ by the so-called "Derjaguin approximation"[6]

$$F/R = 2\pi E \qquad (1)$$

It is therefore a straightforward matter to compare the results obtained for the forces between two curved surfaces, F, with theories of intersurface forces since these are usually formulated in terms of the interaction energies between two planar surfaces, E.

Short-Range (Oscillatory) Solvation Forces

Over the past few years many measurements have been made of the solvation forces in a variety of different liquids,[4,7] including inert nonpolar liquids,[7,8] polar liquids,[9] hydrogen-bonding liquids,[10,11] and aqueous electrolyte solutions.[4,12] In most situations the results show that when two smooth surfaces are separated by more than 5–10 solvent molecular diameters, the force laws are as expected from continuum theories;[6] viz. there is a monotonically attractive van der Waals force (described by the so-called "Lifshitz theory") and—if the surfaces are charged—a repulsive electrostatic "double-layer" force (described by the nonlinear Poisson–Boltzmann equation). At smaller separations, however, the force generally oscillates with distance (Figure 2), varying between attraction and repulsion, with a periodicity equal to the mean diameter of the liquid molecules. It is interesting to note that the strength of the final adhesion energy (or force) at molecular contact *is* often accurately given by the continuum Lifshitz theory, even though this theory fails to describe the way the force law varies with distance at larger separations.[6,8]

These short-range oscillatory solvation forces arise from the molecular geometry and local structure of the liquid medium, and they reflect the ordering of the liquid molecules into discrete but diffuse layers when constrained between two surfaces or particles (as illustrated in Figure 3). But the effect is more general and also occurs for liquid molecules constrained (confined) between any two boundaries, including two curved surfaces or even between two solute molecules in solution. The origin of the oscillatory forces between surfaces is now well understood theoretically,[6,13–16] and

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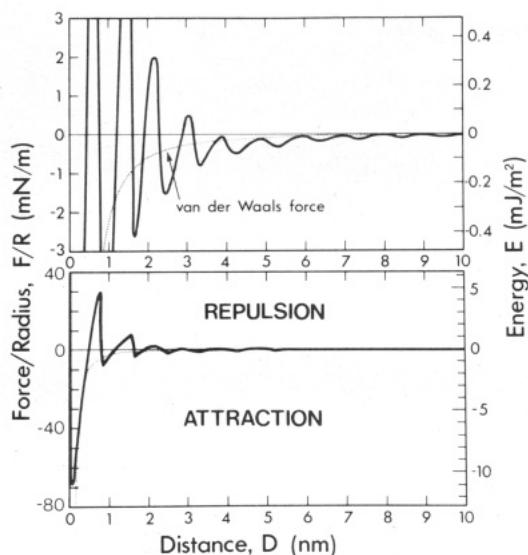
Figure 2. Measured forces between two curved mica surfaces in octamethylcyclotetrasiloxane (OMCTS:[$(CH_3)_2SiO]_4$),[8] a nonpolar liquid with nearly spherical molecules of diameter ~0.85 nm. By convention the force F is normalized by the radius R of the cylinders and plotted as F/R since this is proportional to the interaction energy E between the two surfaces (via eq 1). This convention also allows for results of different experiments with surfaces having different radii R to be shown on the same graph, and it also allows for the interaction energy E to be readily read off, as can be done here from the right-hand ordinate. Note that $F > 0$ corresponds to repulsion, while $F < 0$ to attraction. Dotted lines show the theoretically predicted van der Waals attraction, based on the continuum "Lifshitz theory". Such oscillatory force laws may be simply understood as follows: the attractive minima occur at separations where the molecules can pack comfortably into a discrete number of layers between the surfaces, while the repulsive maxima occur where each layer opposes being compressed or squeezed out (as must occur as the two surfaces approach each other). Such oscillatory forces laws are therefore seen to be primarily due to the *geometry* of molecules, and therein lies their origin and generality to all liquids. Note that on measuring such oscillatory forces there are regions of mechanical instability wherever the positive slope of the attractive "hills" exceeds the stiffness of the force measuring spring. This means that the exact shape of the force law linking a minimum to the adjacent maximum on the right cannot always be measured, especially for the very steep innermost oscillations which are here inferred (for more details on the question of the unstable regions of an oscillatory force law, see ref 8). Note, too, that as a consequence of the "Derjaguin approximation", eq 1, an oscillatory force between two flat surfaces does not become "smeared out" between two curved surfaces. Since one force law is simply the derivative of the other, and since the derivative of sin D is cos D, we see why oscillations will persist between surfaces with any curved geometry, as in the present case (but not between rough surfaces where if the roughness is random this *will* smear out the oscillations—see text). Data are from ref 8.

it is recognized that the exponentially decaying oscillatory force profiles characteristic of these solvation forces are related to, and have the same origin as, the "radial distribution functions" and oscillatory "potentials of mean force" which are the basis for theoretical descriptions of molecular interactions in pure liquids and liquid mixtures.

Sufficient experiments have now been done with a variety of different liquids to make some broad conclusions concerning the role of molecular size, shape, internal bond flexibility, dipole moment, hydrogen bonding, temperature, and surface roughness in de-
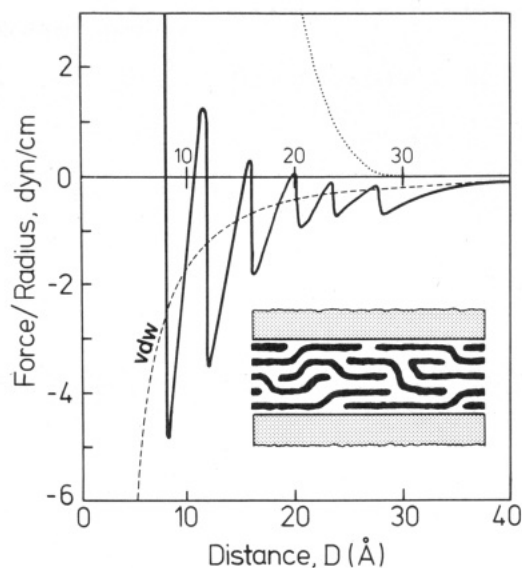
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Figure 3. Forces between two mica surfaces in liquid tetradecane ($C_{14}H_{30}$) at 21 °C. The mean periodicity of the decaying oscillations of 4.2 ± 0.3 Å is very close to the molecular diameter of the alkane chain and shows that there is a preferential alignment (ordering) of the chains parallel to the surfaces as drawn in the inset. The lower dashed curve shows the van der Waals attraction expected from the continuum Lifshitz theory, which lies roughly halfway between the maxima and minima. Also shown is the result of a calculation based on Flory's (mean-field) rotational isomeric state model of hydrocarbon chains (upper dotted curve). This predicts a repulsion far stronger than any of the measured forces. Experimental results obtained with other alkanes up to liquid hexadecane were very similar[20] and suggest that even when confined into a restricted space (e.g. a micelle) hydrocarbon chains in the fluid state retain their bulk liquidlike behavior much more than has been previously supposed. Data are from ref 20.

termining the oscillatory solvation (and adhesion) forces between surfaces in pure liquids. For example, the results show that the magnitude and range of oscillatory force laws are not particularly sensitive to molecular shape asymmetry (for small quasi-spherical or ellipsoidal molecules) nor to molecular dipole moment or temperature.[7,17] In the case of interacting charged surfaces in a polar medium of high dielectric constant, such as water, the oscillatory solvation force does not seem to be particularly modified but simply additive with the electrostatic "double-layer" force.[9–12] However, the range (and presumably the local liquid structure) is particularly sensitive to three things: (1) the roughness of the surfaces,[18] (2) the rigidity or "fluidity" of the liquid molecules, and (3) the presence of other components[6,8,19] (e.g. whether the solvent is a binary mixture). Thus, the oscillatory solvation force law has been found to be much reduced between two rough surfaces, even when the roughness is only a few angstroms,[18] which presumably is enough to smear out the oscillations. Similarly, when the solvent molecules have a high degree of intramolecular rotational bond flexibility, i.e. for more "fluidlike" molecules such as isooctane, the oscillations are much suppressed. In both cases what remains is a smoothly varying (monotonic) van der Waals-like attractive force at all separations right down to the last one or two molecular diameters. Given that

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most surfaces are rough (at least at the angstrom or molecular level), it is indeed a quirk of fate that the long-range attractive interaction forces in liquids *will* often be of the continuum van der Waals type, but for the wrong reasons. In the case of miscible mixtures Christenson[19] has found that the range of the oscillatory forces is reduced from that of either pure component.

For highly asymmetric linear molecules such as liquid alkanes[20] (paraffins) or short-chained polymers[21] (polymer melts), recent results have shown that the short-range interaction is still dominated by a decaying oscillatory function of distance of periodicity equal to the *width* of the chains. In other words, the force laws in such liquids remain qualitatively very similar to those occurring in simple isotropic liquids. An example of this phenomenon is illustrated in Figure 3, which shows the measured force law in tetradecane. Results obtained with other alkanes, from hexane to hexadecane, are very similar to each other[20] and, moreover, qualitatively similar to those occurring in simple isotropic liquids, as shown in Figure 2, as well as polar and hydrogen-bonding liquids (after the distance is appropriately scaled by the molecular diameter). Only for much higher segment numbers does the interaction begin to go over to that expected for "polymers" (discussed below).

Long-Range (Monotonic) Solvation Forces

There are a number of situations in which the fundamental oscillatory solvation force becomes perturbed and transformed into a smoothly varying (monotonic) function of surface separation. The resulting solvation force can be attractive or repulsive and short ranged or long ranged, and it is usually an exponentially decaying function of distance. Such solvation forces appear to have more than one origin, i.e. to fall into a number of distinct categories, which we shall now consider.

Steric Forces. Surfaces with long-chained polymers attached to them interact with each other not directly but via the flexible and highly mobile polymer segments that protrude from them like seaweeds.[6,22] This type of interaction is normally repulsive and can be of very long range, so that it usually dominates over the other types of interactions discussed so far. Indeed, polymer additives have long been used to "sterically stabilize" colloidal dispersions, i.e. prevent the suspended particles from aggregating (in paints and inks, for example). For high molecular weight polymers in the pure liquid form (polymer melts), or adsorbed into surfaces from solution, the interaction force can still be oscillatory at small separations (below a few molecular chain diameters as in Figure 3), but there is now a longer range monotonic tail to the interaction which extends out to distances of the order of (and often well beyond) the "radius of gyration", R_g, of the polymer. Such interactions are sometimes referred to as entropic or steric interactions, or "steric forces", and for these long-chained flexible molecules they can be described in terms of "scaling concepts" and "mean-field theories"[27] which are not appropriate to short-chained polymers, alkanes, or small molecules.

Steric forces are not normally considered as a subset of solvation forces, but their origin is conceptually the same, i.e. both types of interactions arise from the reordering or realignment of molecules constrained between two surfaces or confined within some restricted space (as in micelles or lipid bilayers). Furthermore, direct force measurements on the steric interactions occurring in a variety of different systems[21-26] have provided valuable information on the conformations of polymers both in bulk and at surfaces (information not easily obtainable by other techniques), which can then be compared, often favorably, with theory.[27] In the remainder of this review we shall not further consider these very interesting steric interactions (which are at present receiving much experimental and theoretical attention).

Entropic Undulation or Fluctuation Forces. Another type of interaction that falls into the broader category of steric forces occurs when the interacting surfaces are fluidlike, i.e. mobile, in particular as occurs between structures or aggregates made up of amphiphilic molecules. Amphiphilic molecules (commonly known as surfactants or lipids) are characterized by having a hydrophilic (water loving) part and a hydrophobic (water fearing) part. The hydrophilic part is usually a polar or ionic group, such as a sulfate or ammonium group, while the hydrophobic part is usually a long hydrocarbon chain (or chains) (typically with 10–20 CH_2 groups) attached to the hydrophilic "head-group". When dissolved in water these molecules self-assemble into a variety of structures such as small spherical or cylindrical "micelles", extended sheetlike "bilayers", or closed spherical bilayer "vesicles", where the head-groups are exposed to the aqueous phase and the hydrocarbon chains confined to the micellar or bilayer interiors (see ref 6, part 3).

Amphiphilic aggregates are usually fluidlike and their surfaces are consequently thermally mobile. Thus any oscillatory component that may be intrinsic to the solvation (or hydration) force is now smeared out, partly because of the "roughness" of these interfaces but mainly because of the thermal fluctuations of the head-groups. This leaves only an effectively monotonic (again usually exponentially decaying) repulsive "hydration-undulation" force between the surfaces, which was first investigated in detail by Rand, Parsegian, and co-workers.[28,29] Such forces are also believed to stabilize very thin soap films and were, indeed, first measured quantitatively in such systems.[30] As might be expected, the strength of the repulsion increases with

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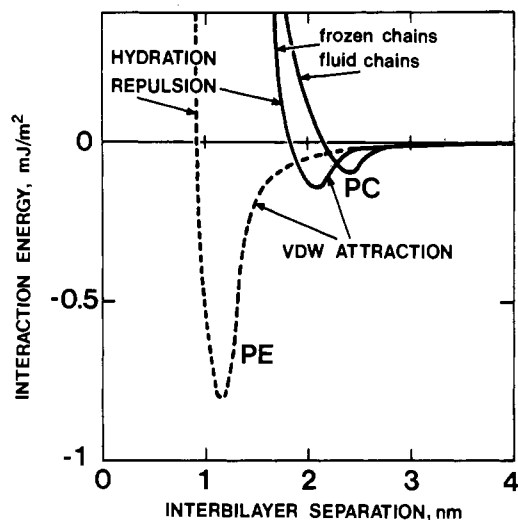(31) Marra, J.; Israelachvili, J. N. *Biochemistry* **1985**, *24*, 4608.

Figure 4. Solid curves are measured interaction energies between two lipid bilayers (supported on mica) composed of phosphatidylcholine or "lecithin" (PC) in water, showing the effect of interfacial mobility (fluidity) in enhancing the monotonically repulsive hydration-fluctuation force between the bilayers. Dashed curve is the measured interaction between two phosphatidylethanolamine (PE) bilayers whose head-groups are smaller, less hydrated, and less mobile than those of PC, resulting in a much reduced hydration repulsion and increased adhesion. [PC has a dipolar head-group of $-PO_4^--CH_2-CH_2-N^+(CH_3)_3$ while PE has a smaller dipolar head-group of $-PO_4^--CH_2-CH_2-NH_3^+$. The full chemical formulas and molecular structures of these double-chained biological lipids are given in ref 6, Chapter 15.] Data are from ref 31.

(i) the hydrated size of the head-groups,[4] (ii) the mobility of the head-groups (Figure 4), and (iii) the fluctuations or "undulations" of the fluidlike interfaces[32] (which for planar bilayers increase with decreasing bending modulus).

Such short-range interactions are difficult to separate into their pure solvation (hydration) and steric (fluctuation) components, which act together to give the total interaction potential. These short-range stericlike interactions between amphiphilic structures such as bilayers are sometimes referred to as "undulation forces" after Helfrich,[32] who first investigated their theoretical origin and suggested their importance. Their existence is confined not only to aqueous solutions but also to bilayers interacting in other polar media.[33]

However, not all surfactant or lipid aggregates (whether bilayers, micelles, or soap films) exhibit these short-range hydration repulsions even when the head-groups are charged or polar. Thus Marra[34] found that the interactions between negatively charged lipid bilayers of phosphatidylglycerol in both 1:1 and 2:1 electrolytes are well accounted for by the DLVO theory with no indication of any additional repulsion right down to separations below 15 Å and, in the presence of Ca^{2+} ions, with strong adhesion at contact. This was also found for the interactions between certain positively charged bilayers.[35] In some bilayer systems, for example, with the dipolar (zwitterionic) phosphatidyl-

ethanolamines, the range of the hydration force is between 4 and 11 Å (at most); i.e. it is of very short range indeed.

The elucidation of the nature of these hydration-undulation forces remains a challenge to both experimentalists and theoreticians. The theory of Helfrich[32] predicts a power law decay for the long-wavelength "undulation force" contribution (force $\propto 1/D^3$ between planar interfaces) whereas only exponential decays have so far been measured between bilayers. However, there are other contributions to the total hydration-entropic-fluctuation force between bilayers,[31] and these may well have an exponential distance dependence which dominates at smaller separations. This issue is currently highly topical and controversial.

The repulsive forces at short range are especially important in determining the adhesion strength of two surfaces in equilibrium "contact" with each other, viz. sitting at the bottom of their potential well (cf. Figure 4). Clearly, the shorter the range of these repulsive forces the closer the surfaces will come at equilibrium and the stronger will be their adhesion. Servuss and Helfrich[36] have recently shown that fluid lecithin bilayers that are totally free (flaccid) do not adhere to each other, whereas bilayers that are somehow restricted from undergoing free thermal undulations can adhere quite strongly. This occurs, for example, when bilayers are under tension, e.g. when bilayers or vesicles are stretched or swollen osmotically. Thus Evans and Metcalfe[51] found an adhesion energy of about 10^{-2} mJ/m^2 between lecithin vesicles under a tension of 10^{-2}–10^{-1} mN/m in good agreement with theoretical predictions.[36] The extreme case of totally immobilized bilayers occurs when they are frozen or supported on a rigid solid surface such as glass or mica. In such cases the range of their repulsive fluctuation force decreases even further and their adhesion correspondingly increases (e.g. to about 0.1 mJ/m^2 for lecithin bilayers, as shown in Figure 4).

Water: Monotonically Repulsive (Hydration) Forces and Attractive (Hydrophobic or Electrostatic) Forces in Water. Water appears to have some particularly unusual solvation forces which have been much studied and which have caused much confusion, consternation, and controversy since the 1920s. The unusual, if not unique, physical properties of water are well documented[37] and are now known to derive from the ability of water molecules to bind tetrahedrally to each other and thereby form a sort of loose three-dimensional association even in the liquid state. Such liquids are known as "associated liquids", and they have the possibility of longer range ordering effects than would be typical of simpler nonassociating liquids or even liquids with large dipole–dipole interactions.

Thus between two smooth, rigid surfaces in water (or in aqueous electrolyte solutions) there is the expected attractive van der Waals and repulsive double-layer force (the two DLVO forces) as well as a short-range oscillatory solvation (hydration) force (Figure 5). But in general there can also be an additional smoothly varying (i.e. monotonic) repulsive or attractive solvation

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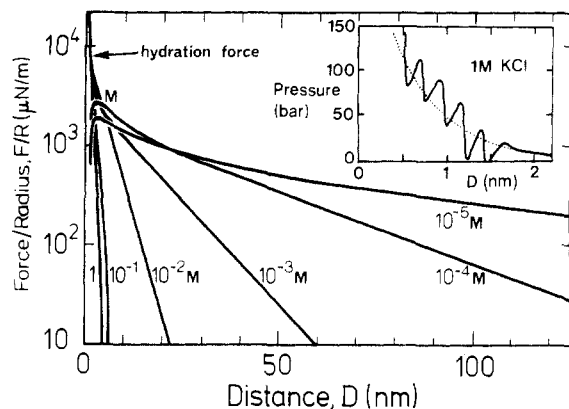
Figure 5. Typical repulsive DLVO and hydration forces between mica surfaces in monovalent electrolyte solutions (such as KCl or NaCl). In dilute solutions the interaction is pure DLVO, characterized by a near-exponential repulsive "double-layer" force and a shorter range attractive van der Waals force which ultimately wins out at short separations resulting in the force maxima (M). However, at higher electrolyte concentrations, as more cations adsorb (bind) onto the surfaces bringing with them their water of hydration, there appears an increasing (non-DLVO) hydration force characterized by short-range oscillations (of periodicity 0.22–0.26 nm) superimposed on a longer-ranged monotonically repulsive tail. The inset shows the hydration force measured below 2 nm in 1 M KCl solution in more detail, plotted in units of pressure. Data are from ref 4, 12, and 38.

force (Figure 6). Between "hydrophilic" surfaces this monotonic force is repulsive, its strength and range depending on the hydration or hydrophilicity of the surface or surface groups. This pure hydration force should be distinguished from the monotonically repulsive undulation force, though—as already mentioned—there is no doubt that hydration effects play a role in these latter forces as well.

In experiments between mica surfaces in various electrolyte solutions at increasing concentrations[38-40] (when the cations adsorb onto the negatively charged surfaces), it is found that the strength and range of the monotonic hydration forces increase with the adsorption and degree of hydration of the adsorbing cations, as might be expected. Thus at saturation adsorption (in high electrolyte concentrations) the weakest forces were found with Cs^+ as the adsorbing ion, the strongest with La^{3+}. Pashley[40] found the following "lyotropic series" for the strength of these forces: $La^{3+} > Mg^{2+} > Ca^{2+} > Li^+ \sim Na^+ > K^+ > Cs^+$, which follows the hydration of these ions. These repulsive hydration forces are also exponentially decaying with distance, the decay length increasing with the hydration of the cation but is also dependent on the amount adsorbed; typical values have ranged from 5 to 15 Å, which are significantly larger (and of longer range) than the decay lengths so far measured for hydration-undulation forces, which range from 1.5 to 3.5 Å.

The importance of purely repulsive hydration forces in determining various colloidal properties, clay swelling, capillary effects, and other interfacial phenomena has been discussed in ref 4, 6, and 41–43.
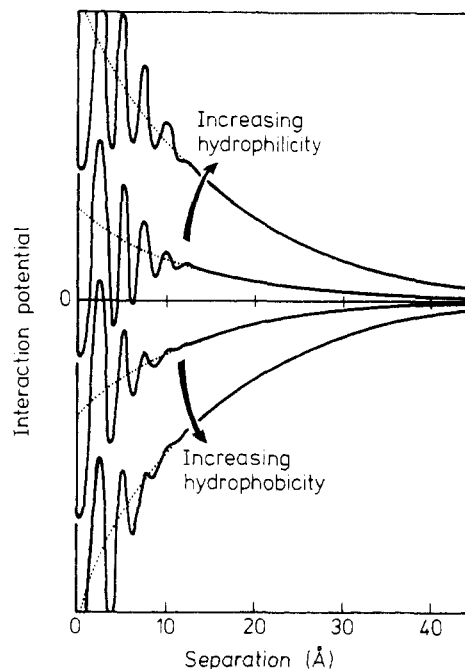
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Figure 6. Schematic hydration force between surfaces of varying degrees of hydrophilicity and hydrophobicity. The solvation (hydration) forces in water differ from those in other liquids in possessing a monotonic as well as an oscillatory component which, depending on the orientation of the water molecules at the surfaces (see Figure 7), can "swing up or down" carrying the oscillatory component with it. For hydrophilic surfaces the monotonic component is repulsive while for hydrophobic surfaces it is attractive, and for strongly solvated surfaces the monotonic component can dominate over the DLVO forces (i.e. the van der Waals attractive and electrostatic double-layer repulsive forces, which are not included here). So far in experiments between molecularly smooth surfaces such as mica there appears to be no evidence that similar monotonic solvation forces exist in nonaqueous liquids—even highly dipolar liquids.[4,7] In such liquids the oscillations simply decay with distance with the maxima and minima, respectively, above and below the base line of zero force or extrapolated double-layer force. Reprinted with permission from ref 47. Copyright 1987 Wiley.

Between two "hydrophobic" surfaces, i.e., surfaces that are inert to water in the sense that they are unable to interact with (or bind) water either by electrostatic means or via hydrogen bonds, there is now an additional long-range monotonically *attractive* force.[44-46] Its origin is as yet unclear but it may be simply a negative form of the monotonically repulsive hydration force between hydrophilic surfaces (Figure 7). The strengths of the attractive hydrophobic force laws so far studied have been found to correlate, i.e. increase, with the "hydrophobicity" of surfaces, as conventionally defined, for example, by the contact angle of water on these surfaces, or their interfacial tension with water. For a recent review of hydrophobicity and hydrophobic interactions see ref 47.

The hydrophobic interaction has been found to be far stronger than the van der Waals attraction between surfaces (out to distances of at least 10 nm), and for D

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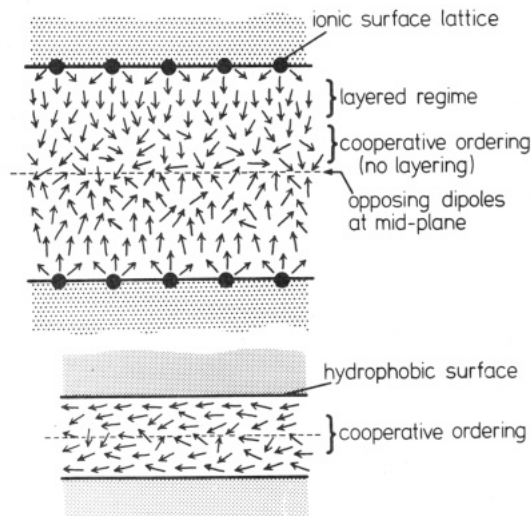
Figure 7. Top: Proposed antiparallel orientations (alignment) of water molecules at two opposing hydrophilic surfaces leading to (1) a diffuse layering close to each surface (oscillatory hydration force regime) and (2) a monotonic hydration force regime at larger separations which is repulsive because the molecules are antiparallel to each other as they abut at the mid-plane. Bottom: Parallel cooperative alignment of water molecules between two inert or hydrophobic surfaces leading to an attractive hydration (hydrophobic) force. Reprinted with permission from ref 4. Copyright 1985 Royal Swedish Academy of Sciences.

< 10 nm the interaction between two planar surfaces is well described by the relation[44-47]

$$E = E_0 e^{-D/D_0} \text{ mJ/m}^2 \qquad (2)$$

where the E_0 can take values up to 100 mJ/m^2. Thus the force law has an exponential (rather than a power law) distance dependence with a characteristic decay length of about 1 nm. This makes it rather long ranged, and it is perhaps for this reason that it has not been easy to carry out Monte Carlo or molecular dynamics simulations (computer "experiments") on the hydrophobic interaction, since—unlike the case with the relatively short-range oscillatory solvation forces—these much longer ranged forces would require thousands of water molecules for a successful simulation. Intuitively, however, one would expect that as two hydrophobic surfaces approach each other in water, the region between them becomes progressively more depleted of water, i.e. the liquid density of the water in the region between the surfaces falls—an effect that will result in an attractive force between them.

Recently, additional long-range attractive forces (again stronger than any possible van der Waals attraction) have also been measured between highly charged surfaces in the presence of *divalent* counterions, for example, between negatively charged surfactant and lipid bilayers in CaCl$_2$ solutions[34,48] (where Ca^{2+} is the counterion). Here, however, it is more likely that the extra attraction (which pulls the surfaces into strong adhesive contact) is not due to any hydrophobic

effect, but arises from ion-correlation effects, a sort of enhanced van der Waals-type attraction between the mobile ions and counterions on the two interacting surfaces. This effect was first predicted theoretically from computer simulations to test the validity of the Poisson–Boltzmann equation for 1:1 and 2:1 electrolytes.[49,50] Such attractive electrostatic (or ion-correlation) forces may be extremely important in overcoming the hydration and fluctuation repulsions between amphiphilic surfaces, thereby promoting the adhesion and fusion of micelles, bilayers, vesicles, microemulsion droplets, soap films, and biological membranes (which are known to involve divalent counterions such as Ca^{2+} and Mg^{2+}).

Concluding Remarks

There are four major forces that occur between surfaces in pure liquids: (i) van der Waals forces, (ii) electrostatic (double layer) forces, (iii) steric and fluctuation forces (due to protruding surface groups such as polymers or long head-groups, or arising from the undulations of thermally mobile fluid interfaces), and (iv) solvation (structural or hydration) forces, which are related to the structuring of liquids at and between two surfaces. Direct experimental measurements of these forces indicate that the van der Waals and double-layer forces, which together make up the DLVO theory, are well described by the Lifshitz theory (for the former) and the Poisson–Boltzmann equation (for the latter, except for surfaces of high charge density in the presence of divalent counterions).

More research is needed for clarifying the short-range oscillatory solvation forces in liquids, and especially in aqueous systems where long-range monotonically repulsive or attractive solvation forces also occur. In real systems where surfaces are neither molecularly smooth nor rigid, additional forces arise such as smeared out solvation forces or repulsive fluctuation forces. These may be thought of as merely perturbing the intrinsic interaction potential, but their effects can be quite dramatic, for example, in changing an oscillatory force into a smoothly varying monotonic interaction or in reducing the adhesion of two surfaces or particles by 1 or 2 orders of magnitude.

The subtleties that can occur in the last few angstroms as two surfaces, particles, or solute molecules approach each other in a medium can be quite remarkable—sometimes the forces are well described by continuum or "mean-field" theories, such as the DLVO theory, but more often they are not. The elucidation of these interactions both at the fundamental level and when applied to specific systems will no doubt remain a challenge to experimentalists and theoreticians for years to come.

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