

SURFACE FORCES — THE LAST 30 Å

Barry W. Ninham

Department of Applied Mathematics, Institute of Advanced Studies, Research School of Physical Sciences, The Australian National University, Canberra, A.C.T. 2600, Australia

Abstract — Phenomena which depend on surface forces have been interpreted for the most part in terms of continuum theories (van der Waals, double-layer forces). These make the approximation that a liquid separating two interacting surfaces behaves as if it has bulk liquid properties. Where this is clearly wrong, theory has been decorated to admit additional parameters. These derive from postulated effects encompassed by undefined terms like hydration shells and Stern layers. Recent measurements and theories show that these assumptions can be much too drastic. Below typically 30-50 Å separation, precisely the region of most interest for many problems of colloid science and biology, continuum theories often break down, and are now seen to represent only the long-range tail of the actual forces operating. A complex variety of surface-induced (structural, hydration, solvation) forces have been studied. The current situation calls for a revision of extant ideas on colloidal particle interactions.

INTRODUCTION

Some very important progress has been made in our understanding of surface forces over the past few years. And to make sense of some of the complicated phenomena which have been revealed, it may be useful to begin by focussing on concepts. The classical problems of surface forces in colloid science on which most of our intuition is based begins with the idea of a bulk electrolyte separating two solid planar surfaces. We then consider that there are two distinctly different opposing forces, van der Waals (usually attractive), and double-layer forces (usually repulsive). A plot of potential of interaction against distance yields the familiar picture with a barrier to flocculation, primary and secondary minima (1) (cf. Fig. 1). Calculations of these forces involves two diametrically opposed notions.

For van der Waals forces, we assume that a liquid adjoining a solid surface (or in solution chemistry adjoining a solute molecule) is uniform with bulk liquid properties up to the "interface" (Fig. 2). For a single surface, or for two single immiscible liquids, this idea was well established by Gibbs. He gave a precise formal definition of an interface in terms of adsorption excesses, which can be related to distribution functions of statistical mechanics. Then in estimating van der Waals forces by Lifshitz theory, the free energy change with distance as two surfaces come together is treated as a perturbation, i.e. the adsorption excesses (which measure surface-induced liquid structure) are unperturbed to lowest order.

For double-layer forces, water is again treated as a continuum with prescribed dielectric properties. The ions of the electrolyte now play the role of an intervening "liquid", but one whose density profile is not constant. An ionic concentration gradient is set up by the charged surface, and it is the overlap of these diffuse profiles which gives rise to the (osmotic) repulsive force.

The simplification behind the first kind of calculation leads to what will have to be called a "primitive" model. It assumes bulk liquid up to an "interface", which could be "hydrated", or the boundary of the Stern layer, but in any event is sharp. The second kind of calculation provides an example of a *structural* force arising from a "civilised" model of the interfacial region. It is a much more sophisticated concept. Here (in general) the surface induces liquid structure reflected in the decay in density profile, polarisation, hydrogen bond arrangements, concentration, whatever, to bulk liquid values. A neighbouring surface perturbs that profile to give a force which reflects changes in liquid structure. In both cases the force measures change in free energy with distance between the surfaces, but the nature and origin of the force is very different.

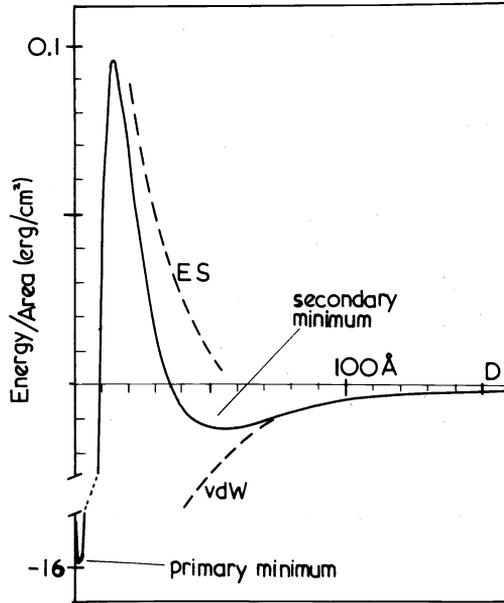


Fig. 1. Conventional picture (1,8) of the interaction potential between two planar lyophilic colloidal particles: --- attractive van der Waals and repulsive electrostatic double-layer interactions, and ——— total potential.

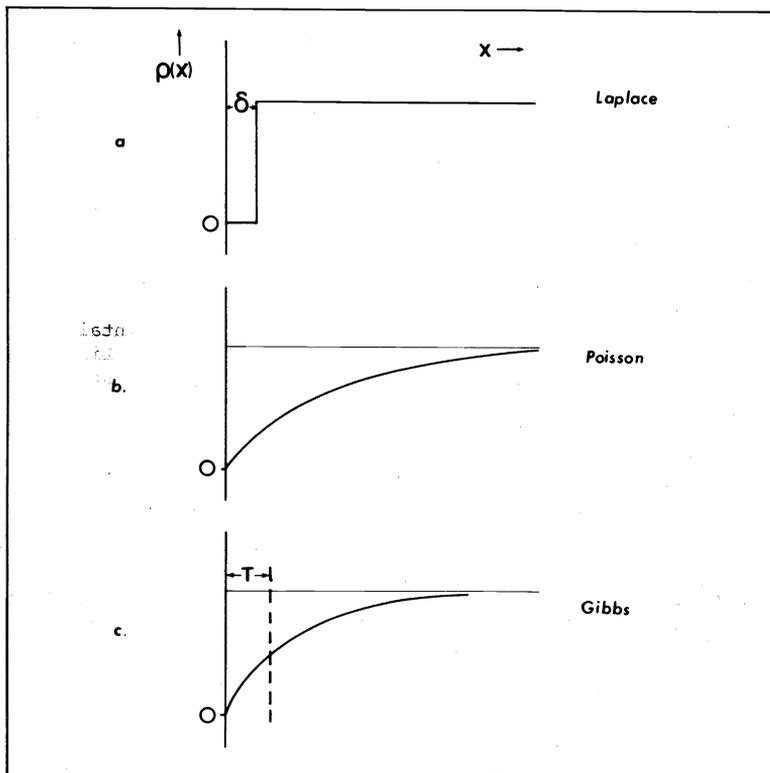


Fig. 2. Schematic representation of density profile of a simple liquid near a solid surface according to (a) Laplace, (b) Poisson and (c) Gibbs. Gibbs' dividing surface replaces the actual density profile by an effective uniform profile. For a single surface Poisson's objection can be swept aside, but for two surfaces, interactions can depend strongly on the overlapping profiles.

A further idea is contained in the extension of electrical double-layer theory to include surface charge regulation (2). Where the surface has dissociable groups, specific cation binding and therefore surface charge changes self-consistently due to another surface. Now there is not only a force due to surface-induced liquid structure, but the force depends too on liquid-induced surface structure.

These three notions, the primitive model, the civilised model (surface or solute-induced liquid structure), and liquid-induced surface structure are the key to what follows. They are hardly new. The primitive model might be attributed to Laplace (3), who in his still extant theory of capillary action assumed that the density profile of a liquid could be treated up to an infinitesimal distance from an interface. The civilised model can be attributed to Poisson (4) who, appropriately, precisely 150 years ago took issue with Young and Laplace. The theory of Poisson (which allowed for rapid variation in density) gave results practically identical to that of Laplace. The dispute occasioned a controversy resolved by Challis in his lucid 1834 review (5) on capillary attraction. Challis explained how the near identity of the two apparently different theories would emerge if liquids were nearly incompressible. Poisson's objections to Laplace were dismissed until the problem was revived by Clerk Maxwell in 1875 (6). Maxwell was the first to calculate structural forces in thin films, and arrived at 3 Å for the decay length of surface forces in water - in rough agreement with measurements exactly 100 years later. The idea of forces due to liquid structure surfaced again with a paper of Marčelja (7). Newton was of the opinion that in capillary action "chemical combinations were owing", speculated no further, and of course was correct.

Experiments of Israelachvili and collaborators over the past few years have confirmed the classical theories of van der Waals and electrostatic forces at *large distances* (8). This is to be expected. Liquid structure reflects the granularity of matter, unimportant far from a surface, or a solute molecule, and water can be treated as a continuum at low enough salt concentration where Debye-Hückel theory holds. But the open question is how large is a *large distance*? For simple liquids it turns out to be 10 or 20 molecular diameters, depending on the surface, and the liquid (9,10). For water it is somewhere around and less than 50 Å, and is dramatically influenced by the nature of the surface (11). The new results and theoretical developments involve an extension and quantification of older crude ideas about "hydration", and site binding which in fact predate the DLVO theory. Hydration forces can sometimes dominate interactions below 30 Å, depending on the surface, can be repulsive or attractive, and depend critically on pH and counterion concentration. Like the double-layer forces with which they are inextricably tangled, they are accessible and comprehensible only within the civilised model, applied to liquids *both* at surfaces and near solute molecules.

In what follows I shall attempt to review some of the new results and ideas, as seen from the particular perspective of a continuing program of work carried out over the past few years by theoretical and experimental colleagues with whose work I am most familiar.

BREAKDOWN OF CONTINUUM THEORIES

To see how the older theories have been modified, suppose that we maintain the fiction that in water a decomposition into several kinds of force is allowed (1). Lifshitz theory of van der Waals forces did more than finally put numbers to Hamaker's constant. Subject to validity of the primitive model [a point stressed by de Boer and Hamaker (12)] the Lifshitz theory showed that van der Waals forces between surfaces are very much more complicated and subtle than the familiar form $E = -A/12\pi\ell^2$ based on two-body summation of dispersion forces. The theory relies on macroscopic dielectric data and includes: many-body forces not accessible through earlier theories, temperature-dependent entropically driven forces which can dominate interactions in biological and other low Hamaker constant systems; retardation which damps out ultraviolet contributions (London dispersion forces) beyond 40-50 Å, infrared contributions reflecting dipole-induced dipole correlations due to intramolecular vibrations; spatial dispersion which can give rise to very long-range highly non-additive forces between long molecules, and effects of different geometries. The strong temperature-dependent (intrinsically many-body) forces (13) which dominate low Hamaker constant systems exhibited qualitatively those features expected of the hydrophobic interaction (14,15). These forces were further screened by addition of salt (12), an effect which shows immediately that van der Waals and electrostatic forces are intimately coupled. In summary, the Hamaker constant is not constant, and van der Waals forces are an extremely complicated function of surface separation, material properties and geometry. These things are known, but limitations of the theory imposed by the primitive model assumptions were overlooked, and deserve repetition.

(a) Below distances of around 30 Å, the forces cannot generally be calculated to an accuracy of much more than a factor of 2 because the required dielectric data in the far ultraviolet is generally not available. Extrapolation to atomic separations to compute surface energies of simple liquids is not permissible and provides misleading confidence in the range of validity of the theory.

(b) Surface forces are intrinsically *many-body* forces inaccessible except qualitatively via methods of liquid state physics based on two-body molecular potentials. This is so even when bulk liquid properties are well described by such potentials, e.g. one can deduce rigorously from the theory (if retardation is ignored) that at large distances the potential of mean force between two solute molecules (2) immersed in a simple liquid (1) of density ρ_1 , all molecules of which interact via dispersion forces only, has the form (16)

$$W_{22}(r) = \frac{3\hbar}{\pi r^6} \int \frac{d\xi}{\epsilon_1} [\alpha_2 + \rho_1 \alpha_1] h_{21}(r') d^3 r', \quad (1)$$

where $\alpha_{1,2} = \alpha_{1,2}(i\xi)$ are molecular polarisabilities, h_{21} measures the adsorption excess of solvent (1) about a solute molecule (2), and $\epsilon_1 \approx 1 + 4\pi\rho_1\alpha_1$ is the dielectric constant of the solvent. The corresponding result deduced from statistical mechanics using a two-body force description misses the factor ϵ_1^2 . This reflects the absence of many-body forces, and their omission usually produces an error of at least 3 in even the simplest liquid. At small distances the Lifshitz theory clearly breaks down because it is restricted to a weak overlap approximation. Adsorption excesses are then obviously intrinsically three-body effects. With temperature-dependent forces in water even the qualitative form of interactions is not remotely accessible by two-body force summation.

Despite these limitations, we can obtain some idea of when the primitive model breaks down as follows: Imagine (cf. Fig. 3) two half-spaces (2) separated by a liquid (1). The actual density profile can be replaced by a step function uniform up to the Gibbs dividing surface of width τ , where the region τ is a vacuum. The system is clearly a triple film whose energy of interaction is (9,16)

$$\begin{aligned} E(X) &\approx -\frac{1}{12\pi} \left[\frac{A_{22}}{X^2} - \frac{2A_{21}}{(X-\tau)^2} + \frac{A_{11}}{(X-2\tau)^2} \right] \\ &\approx -\frac{1}{12\pi} \left[\frac{A_{22} - 2A_{21} + A_{11}}{X^2} - \frac{4\tau(A_{21} - A_{11} + \dots)}{X^3} \right]. \end{aligned} \quad (2)$$

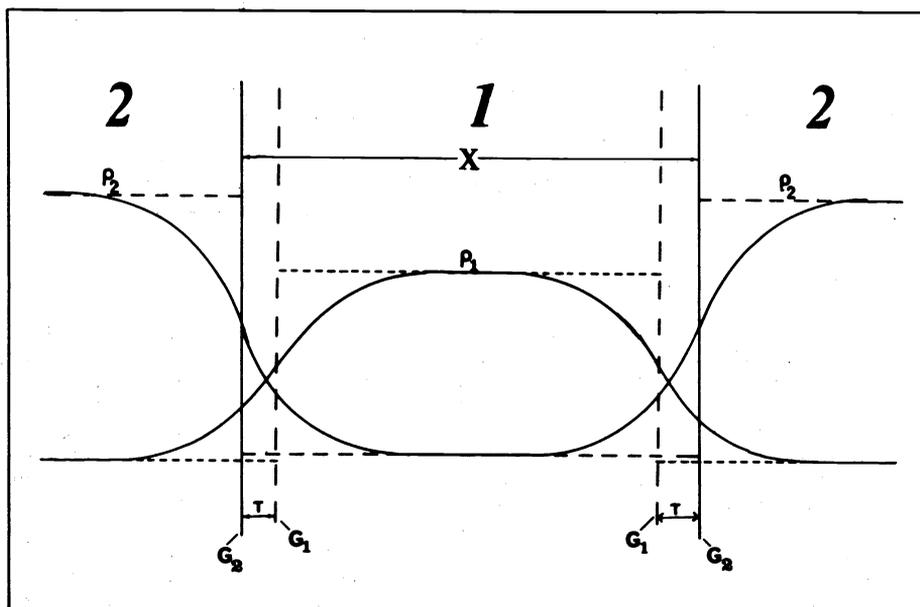


Fig. 3. Model system comprising: a thin film of liquid (1) separating an immiscible liquid (2). The Gibbs dividing surfaces for each liquid are separated by a distance τ .

The argument can be made precise using statistical mechanics (16), and τ is related to adsorption excesses. The formula is only qualitatively correct because of the restriction to two-body forces, but τ can be estimated to be at least of the order of a molecular diameter. The first term in eqn (2) is the continuum result. The second tells us how rapidly that (asymptotic) result breaks down and goes over to a new force law at small distances. Substitution of typical Hamaker constants shows that the second term is as large as the first - and continuum theory then invalid, at distances between 10-20 molecular diameters.

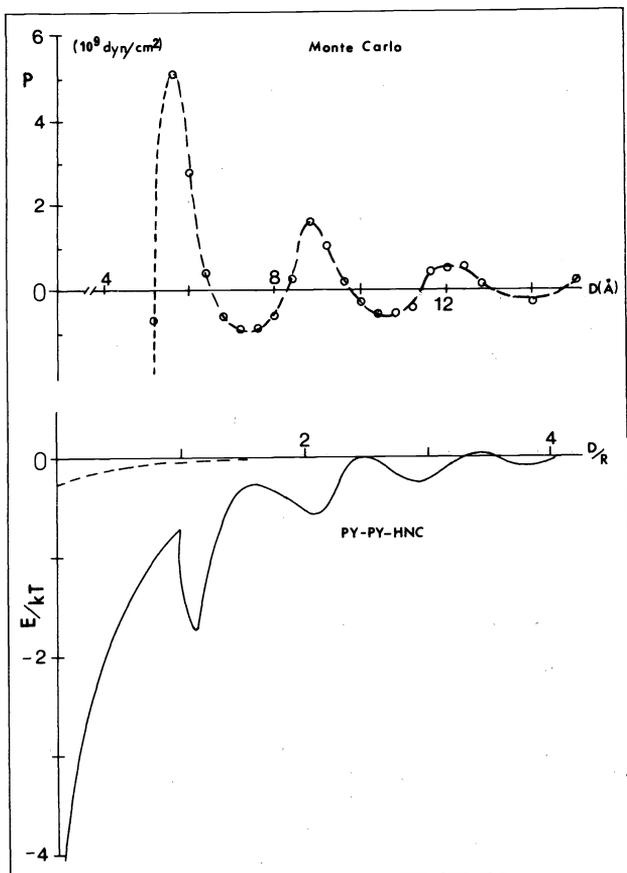


Fig. 4. Monte Carlo calculations (17) of the force and theoretical estimates (18) of the energy per unit area between hard walls separated by a Lennard-Jones liquid. Beyond about 6-10 molecular diameters ($\sim 50 \text{ \AA}$) the continuum results take over. The lower broken line shows van der Waals energy calculated by continuum theory.

Integral equation methods of liquid state physics - admittedly crude - or Monte Carlo simulation of Lennard-Jones or hard sphere fluids give out the results indicated (Fig. 4), i.e. a breakdown in continuum theory below 30-50 Å.

These predictions were confirmed in the remarkable experiments of Horn and Israelachvili (10) who measured forces (distance resolution $\sim 1 \text{ \AA}$) between molecularly smooth mica in a "simple" liquid (cf. Fig. 5). The liquid octamethyltetracyclosiloxane, a silicone oil which has nearly spherical molecules ($\approx 10 \text{ \AA}$ diameter) interacts only via hard core repulsive and attractive dispersion forces. Together with their further experiments on liquid crystals and on cyclohexane, they do show that primitive model approximations to van der Waals forces break down at distances less than 10 or more molecular diameters.

HYDRATION FORCES

Next in a logical development are the corresponding forces which exist in water - free from the complications of surface charge and electrolyte. The oscillations in surface forces discussed above reflect the organisation imposed on the liquid by a surface due to the hard core repulsion of the molecular potential, and possibly by the hard wall nature of the mica surfaces. Water has a much more open structure than a simple liquid, and one might expect surface-induced order to reflect the predominance of different molecular properties like polarisation, or hydrogen bond rearrangements in determining distribution functions. The first measurements of structured forces in water were the continuing series of experiments of Rand, Parsegian and co-workers (19) who worked with (zwitterionic) lecithin multilayers, and later those of Israelachvili and Adams (8) with mica. If van der Waals forces - calculated via continuum theory - are subtracted out from the measured curves, what remains in the former experiments is a strong repulsive interaction, below 30 Å separation which fitted to an exponential, had decay length of 2 Å. The forces are monotonic! An attempt to explain the results was due to Marčelja and Radić (7), who ascribed the phenomenon to strong surface-

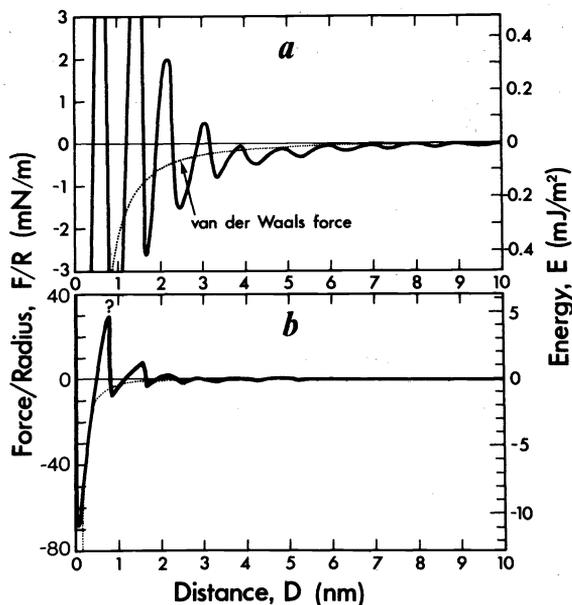


Fig. 5. Experimental measurements (10) of force and energy per unit area between molecularly smooth mica plates separated by the liquid octamethylcyclotetrasiloxane, which is essentially a hard sphere of diameter 9-10 Å. Measured oscillations extend to and merge into usual continuum van der Waals force (dotted curve) only after about eleven diameters. (b) the net force plotted on a reduced scale.

induced dipolar orientation. A mean field theory argument gave out a good description provided the decay length was assumed given. The theory had obvious and admitted deficiencies, but represented an important advance, capturing for the first time the idea of surface-induced structural forces. The same theoretical ideas later saw good service in elucidating similar problems which abound in hydrophobic and hydrophilic solutions (14,15). The important observation is that solute-solute interactions cannot be described in terms of primitive models. There are difficulties with interpretation of the multilayer experiments because it is hard to disentangle the supposed surface force (due to water removal on compression) from a consequent induced lateral compression of the multilayer head-group and hydrocarbon moieties. The forces operating between multilayer surfaces are nonetheless real, repulsive, and several orders of magnitude larger than any continuum electrostatic forces.

A complementary set of experiments due to Pashley and Israelachvili (20) with surfactant bilayers adsorbed on mica again shows strong hydration forces, roughly exponential, with decay length around 3-8 Å, depending on cation type. The strength of the force however is somewhat less than those observed by Rand and Parsegian, an observation which presumably reflects the fixed nature of head-groups in the mica experiment or the anionic nature of the counterions. The origin of the forces here is presumably different. In another experiment the bilayers are replaced by monolayers, thereby altering the nature of the interacting surfaces from hydrophilic to hydrophobic. The structural force either disappears, or is replaced by an attractive structural force of quite different form.

With "bare" mica surfaces, predominantly hydrophobic, interacting across water, any structural forces are either absent, or comparable with van der Waals forces as computed by continuum theory. The sole detailed theoretical attempt to model these phenomena so far is the work of Gruen, Marčelja and Pailthorpe (21), who carried out a molecular dynamics simulation (Fig. 6) of the charged mica-water-mica system to study the induced polarisation profile. The decay of the surface-induced polarisation and the associated repulsive forces between two like surfaces have been calculated in detail for the ice structure. It is a source of satisfaction that this result confirms the mean field theoretic ideas, which augurs well for future theoretical understanding.

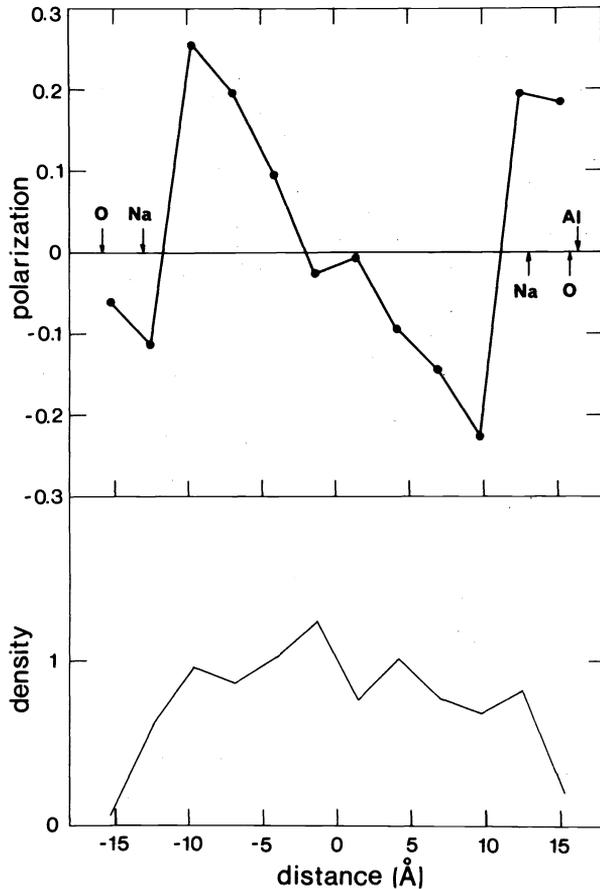


Fig. 6. Molecular dynamics calculation (21) of polarisation and density profiles for ST2 water between mica surfaces. The polarisation is displayed as a fraction of the polarisation value for fully oriented water dipoles at bulk water density, while density is measured relative to bulk density. The bin size, i.e. the distance between successive data points, is 2.76 Å which approximately corresponds to the distance between successive molecular layers. Since the system is small and not yet fully equilibrated there is substantial scatter in the data.

PROBLEMS OF THE DOUBLE LAYER

This problem of liquid structure is endemic, and too much contemplation on the matter induces autism. For the logic pursued so far could lead to the conclusion that those familiar but undefined concepts like Stern layers, zeta potential, outer and inner Helmholtz planes, capacitance of the inner layer, dielectric constant profile, discreteness of charge effects, ionic hydration, now appear to be a means of constructing a Ptolemaic system by addition of more and more fitted, but unpredictable parameters. There is most urgent need for first principle definitions of these concepts - if they exist - from statistical mechanics. Otherwise theory degenerates into a curve fitting exercise, and loses predictive capacity. Fortunately some progress has been made, especially due to the work of Chan and his co-authors (22).

What is emerging is that extant theories of the double layer are right for particular systems - those in fact most studied. But too generous extrapolation outside certain circumscribed limits is simply wrong.

The problem of the double layer has several facets. Nearly all work has focussed on the primitive model in which water is treated as a continuum of given dielectric constant. The charged ions whose interactions are mediated by the dielectric constant then form a new "solvent". The forces resulting from overlap of surface-induced double layers are par excellence an example of structural forces. Gouy-Chapman (or non-linear Poisson-Boltzmann equation) clearly represents a limiting law perhaps valid, if at all, at low surface charge and low ionic concentrations. When the theory fails, we have become accustomed to

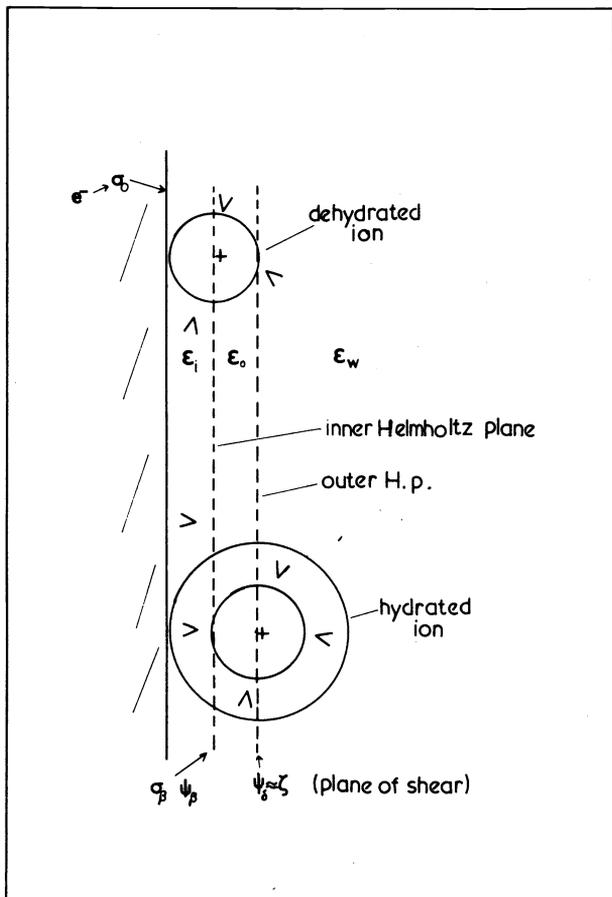


Fig. 7. Illustrating concepts of the classical double layer, i.e. as developed for the mercury electrode. Surface charge is σ_0 at potential ψ_0 . ϵ_i , ϵ_0 and ϵ_w denote dielectric constants of inner, outer Stern layers, and bulk water. IHP, OHP are inner and outer Helmholtz planes with charge and potentials σ_β , ψ_β ; σ_δ , ψ_δ respectively. ψ_δ is assumed equal to measured zeta potential ζ .

decorations which invoke water structure injected through the back door by e.g. assignment of an effective ionic (hydration) radius, and assignment of an (arbitrary) low dielectric constant to the first (arbitrarily chosen) one or two surface layers of water. To question such dogma is almost heresy, yet reality demands it. The theoretical situation is summarised in Table 1 and Fig. 7.

TABLE 1. Problems of the double layer

(1) Primitive model (point ions, water as continuum).

(a) Non-linear Poisson-Boltzmann equation is a mean-field theory without formal systematic justification.

(b) Boundary conditions usually constant charge σ_0 or potential ψ_0 (extended to include surface charge regulation by surface ion binding, verified by Healy (2) and Pashley (11)).

(c) Image interactions ignored. Poisson-Boltzmann equation alone gives no change in surface tension for air-water interface due to dissolved electrolyte (Onsager-Samaras limiting law).

(d) Surface charge smeared out. Unreasonable at very low σ .

(e) Asymptotic behaviour of forces $\propto e^{-\kappa r}$, κ^{-1} = Debye length. Incorrect for unsymmetric electrolytes at higher concentrations.

(f) At zero σ , van der Waals temperature dependent forces (12) (screened) and double layer forces inseparable. At non-zero σ , no theory exists or affects separation into two forces.

(2) Primitive model (finite sized ions).

(g) Finite size takes account of too high surface counterion concentrations at high σ (Stern potential).

(h) Plane of shear and of ζ potential arbitrary.

(i) Discreteness of charge effect: corrects electrostatic interactions (surface and bulk activity coefficients) for assumed finite size.

(j) Observed ζ -potential vs. PDI concentration fitted by (i) provided arbitrary small ϵ assigned to arbitrarily thin surface layer of water.

(k) Meaning of "hydration" shell (finite size of ion) unclear and unjustified.

The problems outlined in table 1 are not nearly exhaustive, and cannot be reviewed in detail. It is perhaps not as bad as it seems, since in defense of these earlier theories, it must be said that a number of features alluded to above do emerge, within the framework of the primitive model from more refined statistical mechanical theories currently in vogue. Let us focus on a few points only.

MEANING OF IONIC "HYDRATION" - EXPERIMENTAL EVIDENCE

The question is this. How valid is the concept of ion size? Consider an aqueous electrolyte solution. We wish to test the primitive model, i.e. a bare ion is presumed to take up bound water of hydration. Ignore ion "pairs". Beyond an effective hydration radius water behaves as bulk water. Carry out the statistical mechanics of such a system, and calculate mean molal activity coefficients which depend only on concentration, and a single parameter a , the distance of closest approach of anion and cation. The measured values can be converted from the Lewis-Randall to the MacMillan-Mayer ensemble, and the a values which fit the data are as follows (23):

TABLE 2. a values for selected salts in Å (± 0.1 Å)

LiCl	3.9	(3 M)									
NaCl	3.3	(3 M)	NaBr	3.5	(2 M)	NaNO ₃	2.7	(2 M)			
KCl	3.05	(5 M)	KBr	3.2	(3 M)	KI	3.2	(4 M)	KNO ₃	1.7	(1.7 M)
CsCl	2.75	(4 M)									
MgCl ₂	4.4	(1.4 M)									
CaCl ₂	4.25	(1.6 M)									
BaCl ₂	3.9	(1.2 M)									

Bare Ion Radii (Å)

Li	0.68	Na	0.98	K	1.33	Cs	1.67
Mg	0.65	Ca	0.94	Ba	1.29		
Cl	1.81	Br	1.96	I	2.19		

Figures in parentheses denote molality beyond which theory and experiment deviate by more than 5%. "Effective" hard core radii do depend on concentration, but weakly. The values so obtained do make sense. Thus the radii of hydrated cations satisfy (24) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$; $\text{Mg}^{++} > \text{Ca}^{++} > \text{Ba}^{++}$. The halide ions are unhydrated and the radii are additive. But note that for CsCl the value is absurd since the sum of the bare ion radii is $1.67 + 1.81 = 3.48 \gg 2.75$ Å. And when we come to nitrates, sulphates and non-halide ions, the required radii are completely absurd. The problem would disappear if we were to construct a self-consistent theory which takes account of water structure induced by the ions. There is an extra attractive force due to the discrete nature of water.

The evidence is clear. For simple 1-1 alkali halides — those systems (selectively) most studied in colloid science, the primitive model is not too bad at low concentrations ($< 1 \text{ M}$). But it breaks down badly for more complex ions. It is not surprising then that there could be a breakdown of double layer theories for those cases where the hydrated ion model of ions is inadmissible.

THE CIVILISED MODEL

First steps to extend the primitive model to include explicitly model solvents have been made (22,25,26), and results although in main limited to linear theories, are of much interest. For some light has now been thrown on (a) the concept of ionic hydration, (b) breakdown of continuum solvent approximation, (c) meaning of the Stern layer and the myth of local dielectric constant, (d) adsorption of ions at electrodes. The ions have charge ze , radius a_1 . The model solvent (density ρ) is made up of hard sphere molecules (radius a_2) in which are embedded fixed dipole moments μ . The solvent is *not* water, and hydrogen bonding can only be taken into account by inclusion of quadrupole interactions and polarisability. Results known so far are listed below.

Known results in the civilised model:

(1) $\epsilon = \epsilon(\rho, \mu, T, a_2)$ derived from statistical mechanics.

(2) Debye-Hückel theory has been established rigorously for this model system.

(3) Born energy, defined as the free energy change of removing an ion from vacuum into a dipolar solvent at infinite dilution of ions

$$F_{\text{BORN}} = - \frac{(ze)^2}{2(a_1 + a_s)} (1 - 1/\epsilon), \quad a_s \leq a_2, \quad \text{solvent radius.} \quad (3)$$

In linear theories a_s is a complicated functional of solvent properties only, and is independent of valence z . In a more refined theory we can expect a_s to depend on z and a_1 . The ion appears to have an effective radius $(a_1 + a_s)$: If the solvent behaves as a continuum of dielectric constant ϵ , we expect the ion to have an effective radius $(a_1 + a_2)$, because the sphere of radius $(a_1 + a_2)$ is the excluded co-volume between ion and solvent. Since the solvent molecules are not behaving as a continuum dielectric, this model predicts $a_s < a_2$. This point can be illustrated by a study of

(4) Polarisation density = dipole moment/volume. In macroscopic theory

$$P_{\text{mac}} = \frac{(\epsilon - 1)}{4\pi} E(r) = \frac{(\epsilon - 1)}{4\pi} \frac{(ze)^2}{\epsilon r^2} \quad (4)$$

is the polarisation density around an ion. Evaluation of $P(r)$ from linear (mean spherical approximation) statistical mechanics calculations gives the result shown in Fig. 8.

$P(r)$ is a measure of the way in which dipolar solvent molecules align to screen or depolarise the field due to the ion. The oscillation in $P(r)$ about the macroscopic value is due mainly to the finite size of solvent. The concept of "local" dielectric constant $\epsilon(r)$ (position-dependent) is not useful, as $\epsilon(r)$ would take on negative values. Note that present theory does not allow for dielectric saturation, a non-linear effect. It is not clear if the oscillations will be so important in water.

(5) Potential of average force (free energy change in bringing two ions together from infinite separation). Results are as indicated in Fig. 9. Deviation from continuum result for $r \leq 8a_2$ indicates effect of structuring of dipolar solvent about the ions. Results so far are limited to weak overlap approximation.

(6) Double layer in the civilised model. Electrolyte defined as ions plus dipoles. Exclude electronic polarisabilities, higher multipoles, and image effects at the wall. Results restricted to linear theories.

Two quantities of interest are σ_0 vs. ψ_0 and potential at plane of closest approach ψ_β . In these approximations

$$\psi_0 = \frac{4\pi\sigma_0}{\epsilon} \left(\frac{1}{\kappa} + a_1 + a_2 \frac{(\epsilon - 1)}{\lambda} \right) \quad (5)$$

$$= \frac{\sigma_0}{C_{\text{dl}}} + \frac{\sigma_0}{C_{\text{ion}}} + \frac{\sigma_0}{C_{\text{solv}}}, \quad (6)$$

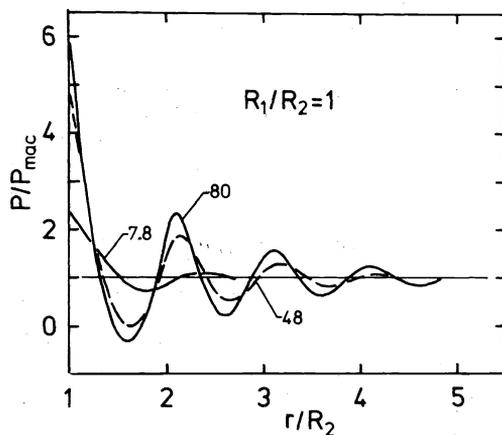


Fig. 8. The normalised polarisation density (22) $P(r)/P_{\text{mac}}$ about an ion in a hard sphere dipolar solvent as a function of the distance from the centre of the ion. Curves are labelled with the dielectric constants of the dipolar solvent.

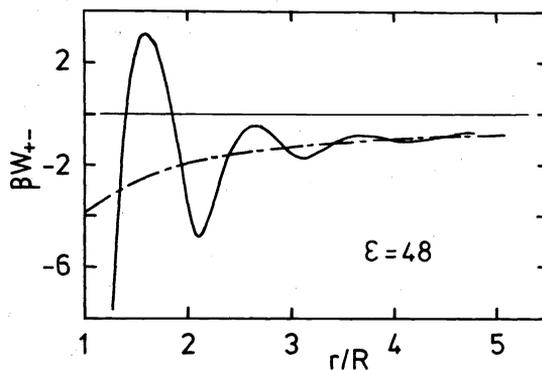


Fig. 9. The potential of mean force between two univalent ions of opposite signs and having the same size as the dipoles (—). The function $-\beta e^2/\epsilon r$ is shown (---). The dielectric constant of the dipolar solvent is 48. Monte Carlo results are similar.

where λ is defined by $\lambda^2(1+\lambda)^4 = 16\epsilon$, $\kappa^2 = 4\pi\beta e/\epsilon \sum \rho_i z_i^2$ and $\kappa a_1, \kappa a_2 \ll 1$, i.e. low concentration. The terms in eqn (6) can be interpreted as a potential drop across 3 capacitances in series: C_{dl} the usual double-layer capacitance, C_{ion} a capacitance due to ion size, and C_{solv} , the more interesting contribution from the solvent. For $\epsilon \approx 80$, $\lambda \approx 3$, and this last term has the appearance of a Stern layer with $\epsilon_{\text{eff}} \approx 3$. In the special case $a_1 = a_2 = a$ molecules are excluded in a layer of width a from the wall. That layer should have dielectric constant $\epsilon = 1$. However the thermodynamic result eqn (6) says that this region

appears to have $\epsilon \approx 3$. Hence the depolarisation ability of a dipolar solvent is *more* efficient than a *uniform* ϵ of bulk value 80 up to a distance a from the wall.

Another model of the electrical double-layer that has been considered is one in which the surface charge is developed by the specific, non-coulombic adsorption of potential determining ions on to a neutral surface (22). For this case the linear relationship between the adsorbed surface charge density, σ_β and the potential at the plane of adsorbed charges, ψ_β is given by

$$\psi_\beta = \frac{4\pi\sigma_0}{\epsilon} \left(\frac{1}{\kappa} + a_2 \frac{(\epsilon - 1)}{\lambda\tau} \right) \quad (7)$$

$$= \frac{\sigma_0}{C_d} + \frac{\sigma_0}{C_{\text{solv}}}, \quad (8)$$

where τ is defined by $\tau = 1 + \lambda(a_2/a_1)$. On comparing with the corresponding result for a uniform surface charge, we note the absence of an ionic contribution to the total capacity. Furthermore for $\epsilon \sim 80$, the effective Stern layer dielectric constant is $\epsilon_{\text{eff}} \sim 10$ instead of 3 as in the case of a uniform surface. The larger value of ϵ_{eff} is consistent with the experimental observation that a lower inner layer capacity is used to fit potential vs. charge data for mercury (uniform surface charge) than for oxide surfaces (adsorbed surface charge).

The results in eqns (7) and (8) can be understood in terms of the differences in the polarisation response of the dipolar solvent to a uniform surface charge or to a layer of discrete adsorbed charges (22). While the final results between the surface charge and surface potential for this ion-dipole model electrolyte can be interpreted in terms of an effective Stern layer, the detailed structure of the double layer, for example the potential and polarisation profile close to the charged surface can be very different from that predicted by the linear Gouy-Chapman theory.

This can be understood if we examine the polarisation density (22,25).

EXPERIMENTAL EVIDENCE ON DOUBLE LAYER FORCES

That large distance behaviour of double-layer forces is given correctly by Gouy-Chapman theory was first established by Mysels and Lyklema (27) working on soap films. The much later work of Israelachvili and Adams (8), and of Pashley (11) verified that the non-linear Poisson-Boltzmann equation (with charge regulation (2)) describes electrostatic forces down to distances of about 30 Å at salt concentrations in 1-1 electrolytes $< 10^{-3}$ M. The interpretation *assumes* that van der Waals forces which ultimately cause the interacting molecularly smooth mica surfaces to jump into contact are correctly given by continuum theory. There is every reason to believe this is an incorrect assumption and the calculations are necessarily uncertain but for reasons not fully understood it does seem that DLVO theory effectively "works" down to contact on mica as an excellent approximation. 2-1 electrolytes await systematic exploration.

The story is dramatically different as salt concentration increases (11). Over some sharp range, cations exchange with adsorbed H^+ ions, induce surface water structure which in turn produces large repulsive solvation (hydration, structural) forces. The phenomenon does *not* occur in acid solutions, and is not yet understood theoretically except at a sensible phenomenological level. The same story obtains for coalescence of air bubbles (28), amphoteric latex spheres (29) at high salt and for mercury drops (30) and vesicles (31), indicating that cooperative specific cation adsorption and consequent structural effects are ubiquitous. The phenomenon is clearly of much importance in biological questions (19). The first attempts to model these structural forces are due to Marčelja *et al.* and appear to confirm that the earlier mean field theory is substantially correct.

DISCUSSION

The central thesis addressed in this paper is that surface forces at small distances are dominated by surface-induced liquid structure, and go over to continuum theories only beyond about 10-20 molecular diameters. The actual distance beyond which continuum theory is valid depends on the surfaces, and the solvent. The "new" forces which take over in the last 30-50 Å are extremely subtle and complicated. It is precisely this distance regime which is all important in questions involving biological membranes and problems to do with surfactants and microemulsions (32-35). The next generation of theories one can hope will be able to tell us why and in what manner, e.g. Mg and Ca, behave differently at surfaces, and to do so will have to abandon attempts to retain the primitive model - whether in surface science or in solutions. It turns out that the solvent cannot be ignored, and there now stands revealed

a whole hierarchy of new forces. Further progress, especially with all important association colloids (32,33) will depend on theoretical and experimental work on head-group interactions. This ultimately takes us back to the old problem of solutions and a tractable theory of simple liquids, and water.

REFERENCES

1. E.J. Verwey and J.Th.G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, New York (1948).
2. B.W. Ninham and V.A. Parsegian, *J. Theor. Biol.* 31, 405 (1971).
T.W. Healy and L.R. White, *Adv. Coll. Interface Sci.* 9, 303 (1978).
T.W. Healy, D.Y.C. Chan and L.R. White, *Pure & Appl. Chem.* 52, 1207 (1980).
3. Marquis de Laplace, *Mechanique Celeste*, Suppl. to Vol. 10, Paris (1806).
4. M. Poisson, *Nouvelle Théorie de l'Action Capillaire*, Paris (1831).
5. J. Challis, *Report on the Present State of the Analytical Theory of Hydrostatics and Hydrodynamics*, British Association Reports III (1833) 131; IV (1834) 253.
6. J. Clerk Maxwell, *Capillary Action*, *Encyclopaedia Britannica*, 9th ed. (1875), pp.56-71, updated by Lord Rayleigh, 11th ed. (1911).
7. S. Marčelja and N. Radić, *Chem. Phys. Letts.* 42, 129 (1976).
S. Marčelja, *Croatica Chemica Acta* 49, 347 (1977).
8. J.N. Israelachvili and G.E. Adams, *Nature* 262, 774 (1976); *J.C.S. Far. Trans. II* 75, 975 (1978).
9. D.J. Mitchell, B.W. Ninham and B.A. Pailthorpe, *J. Coll. Interface Sci.* 64, 194 (1978).
10. R.G. Horn and J.N. Israelachvili, *Chem. Phys. Letts.* 71, 192 (1980).
11. R.M. Pashley, *J. Coll. Interface Sci.* (2 papers, in press, 1981).
12. J. Mahanty and B.W. Ninham, *Dispersion Forces*, Academic Press, London, New York (1976), and references contained therein.
13. V.A. Parsegian and B.W. Ninham, *Biophys. J.* 10, 664 (1970).
14. D.Y.C. Chan, D.J. Mitchell, B.W. Ninham and B.A. Pailthorpe, *Water, A Comprehensive Treatise* (ed. F. Franks), Plenum, New York (1976).
15. D.Y.C. Chan, D.J. Mitchell, B.W. Ninham and B.A. Pailthorpe, *J.C.S. Far. Trans. II* 74, 2050 (1978).
16. D.J. Mitchell, B.W. Ninham and B.A. Pailthorpe, *J.C.S. Far. Trans. II* 74, 1098 (1978).
17. J.E. Lane and T.W. Spurling, *Chem. Phys. Letts.* 67, 107 (1979).
See also D.E. Sullivan, D. Levesque and J.J. Weiss, *J. Chem. Phys.* 72, 1170 (1980).
18. D.Y.C. Chan, D.J. Mitchell, B.W. Ninham and B.A. Pailthorpe, *J.C.S. Far. Trans. II* 76, 776 (1980).
19. D.M. LeNeveu, R.P. Rand and V.A. Parsegian, *Nature* 259, 609 (1976).
D.M. LeNeveu, V.A. Parsegian and D. Gingell, *Biophys. J.* 18, 209 (1977).
V.A. Parsegian, N. Fuller and R.P. Rand, *Proc. Natl. Acad. Sci. (U.S.A.)* 76, 2750 (1979).
20. R.M. Pashley and J.N. Israelachvili, *Colloids & Surfaces* 2, 169 (1981).
21. D.W.R. Gruen, S. Marčelja and B.A. Pailthorpe, submitted to *Chem. Phys. Letts.*
22. D.Y.C. Chan, D.J. Mitchell and B.W. Ninham, *J. Chem. Phys.* 70, 2946 (1979).
D.Y.C. Chan, D.J. Mitchell, B.W. Ninham and B.A. Pailthorpe, *J. Chem. Phys.* 69, 691 (1980).
S.L. Carnie and D.Y.C. Chan, *J. Chem. Phys.* 73, 2949 (1980); 74, 1293 (1981).
D.Y.C. Chan, D.J. Mitchell and B.W. Ninham, *J. Chem. Phys.* 72, 5159 (1980).
S.L. Carnie, D.Y.C. Chan, D.J. Mitchell and B.W. Ninham, *J. Chem. Phys.* 74, 1472 (1981).
23. D.J. Mitchell and B.W. Ninham, unpublished results.
24. R.A. Robinson and R.H. Stokes, *Electrolyte Solutions*, Butterworths, London, 2nd ed. (1959).
25. D.Y.C. Chan, *Proceedings of the IUTAM-IUPAC Symposium on Interaction of Particles in Colloidal Suspensions* (Canberra, 1981) (to be published in *Adv. Coll. Interface Sci.*).
26. S.A. Adelman and J.M. Deutch, *J. Chem. Phys.* 60, 3935 (1974).
G.N. Patey and J.P. Valleau, *J. Chem. Phys.* 63, 2334 (1975).
J.S. Høye and G. Stell, *J. Chem. Phys.* 68, 4145 (1978).
27. J. Lyklema and K.J. Mysels, *J. Amer. Chem. Soc.* 87, 2539 (1965).
28. R.L. Lessard and S.I. Ziemanski, *Ind. Eng. Chem. Fundam.* 10, 260 (1971).
29. T.W. Healy, A. Homola, R.O. James and R.J. Hunter, *Farad. Disc.* 65 (1978) 156.
30. S. Usui and T. Yamasaki, *J. Phys. Chem.* 71, 3195 (1967); *J. Coll. Interface Sci.* 29, 629 (1969).
31. A.M. Gottlieb, P.T. Inglefield and Y. Lange, *Biochim. Biophys. Acta* 307, 444 (1973).
32. J.N. Israelachvili, D.J. Mitchell and B.W. Ninham, *J.C.S. Far. Trans. II* 72, 1525 (1976).
33. D.J. Mitchell and B.W. Ninham, *J.C.S. Far. Trans. II* 77, 601 (1981).
34. E. Ruckenstein and R. Nagarajan, *J. Coll. Interface Sci.* 79, 2622 (1975).
35. J.T. Duniec, J.N. Israelachvili, B.W. Ninham, R.M. Pashley and S.W. Thorne, *FEBS Letts.* (submitted).