On progress in forces since the DLVO theory

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Abstract

The simplicity, consistency and an understanding of the limitations of the original DLVO theory has been lost. Where the theory apparently fails, new words to describe 'non-DLVO' forces have been invented. 'Extra-DLVO' forces, words like hydration, structural, oscillatory, hydrophobic, depletion, fluctuation, protrusion forces infest the literature. Some are real enough but some have the status of phlogiston. All predictability has disappeared in a confused proliferation of parameters. The original theory does not account for specific ion effects embraced by the term Hofmeister series. Nor did it pretend to. There is a fundamental inconsistency even at the continuum level in treating double layers via a non linear theory, and van der Waals-Casimir-Lifschitz forces by a linear theory. Further no theories have considered the effects of dissolved gas which are extremely important. An account will be given of the present situation in colloidal interactions, and how to resolve it. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

For colloid science the theory of DLVO stands at the same level of importance as does Darwin's theory of the origin of species in Biology. Planck, the founder of quantum mechanics once said that 'A new scientific truth does not triumph by convincing its opponents and making them see light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it'. Paradoxically though, the new theory then takes on the status of the previous dogma, and questioning takes on the status of heresy. Modern neo-Darwinists go to extravagant lengths to reconcile what they attribute to Darwin with what they now believe. The reconciliation is as obscure as the debate between Athanasius and Arius on the nature of Christ. Darwin was in fact a Lamarkian.

Much the same has happened to DLVO. That is natural and does not lessen the impact of DLVO. In trying to assess where we now stand, it seems sensible first to ask what we understand by the theory, and not to attribute to its authors more than they intended. The seminal contribution [1] was the book 'THEORY OF THE STABILITY OF LYOPHOBIC COLLOIDS — The Interaction of Sol Particles Having an Electrical Double Layer' by E.J.W. Verwey and J.Th.G. Overbeek with the collaboration of K. Van Ness, Elsevier (1948).[1] The title says it all, and if that is not enough, the first chapter clearly circumscribes, in so far as a distinction between lyophobic and lyophilic colloids can be made, what the limitations of the theory are. The book was written by Overbeek under the direction or protection of Verwey during the war when the Netherlands was occupied, and both were supposed to be working for the German war effort in the Philips Corporation. The content of the book was amply discussed between both authors in addition to their

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[1]Since the original theory of DLVO appeared 50 years ago, the number of papers related to the subject have proliferated without bound. That alone is sufficient testimony to the importance and enduring nature of DLVO. It is impossible to cite except selectively and within an available knowledge base of an author. However, it can be hoped that however, and obviously biassed the choice of literature is, the selection below will provide at least an entry point into a complex and vast field of modern science.

regular Phillips work and prepared and written mostly during the evening hours. The book which has never been reprinted would have appeared much earlier had not the war intervened. Fortunately Theo Overbeek is still with us and still contributing strongly. It would be presumptuous to say more, except to say that his many contributions and influence have been legion, grow in stature with time, and that he is distinguished further as possibly the most generous and gentlemanly scientist of the century.

The other half of the story appeared in a paper by Deryaguin and Landau in Russian in 1941 which can be found in the collected works (in English) of either. The present author arranged the publication of a selection of Deryaguin's papers [2,3] (Progress in Surface Science, 3 volumes) and wrote his life history and obituary for those volumes. Deryaguin's influence on Russian science was immense, his copy book being blotted by the famous polywater saga. It is of interest that the polywater story, long since thought dead and buried, is now about to reappear with a vengeance, and is real. The DL paper was written following an acrimonious debate between Sam Levine (still active at Manchester) and Deryaguin in 1939. Sam had almost got the DLVO theory first, but treated the double layer interaction wrongly. The error is still repeated at intervals of every few years by authors who claim DLVO got it wrong. The DL paper is succinct and clear, as is characteristic of all Landau's work. However, it is a physicist's contribution, authoritatively dismissing all the subtleties of chemistry. It is a remarkable paper too as the polemic and ungenerous paragraphs dismissing Levine's work have been matched in vitriol only in recent times by arguments in the modern literature, best ignored, on the vexed question of 'hydration'.

At around the same time (1938) Langmuir, who also worked on the double layer had published a different theory of colloid stability [4].[2] It was based on a competition between repulsive forces between hard plates (electrical double layer and steric forces) and entropy associated with of the supernatant, essentially two phase equilibrium. Langmuir kept some of his clay suspensions for 30 years to check on stability, not so long as Faraday, whose gold sols still sit unchanged after more than a century. The same ideas were developed later by Onsager [4] to explain observations on tobacco mosaic virus, and later still for latex suspensions.

These two apparently contradictory theories have now been reconciled via modern statistical mechanics.

There were two kinds of forces, electrostatic double layer and van der Waals attractive, that acted between solid particles. The combination together with the Smoluchowski theory of coagulation on the one hand, and the statistical mechanics of two phase equilibrium on the other, were enough to give a good account of phenomena, at least and it is important to say so, for those systems for which the theory was devised. The main focus was on the subtleties of the long range double layer forces, with the attractive forces, calculated by summation of the new

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[2] For earlier work see [4]. A vast amount of work has been done since in this area which is one of the few success stories in extending DLVO.

quantum mechanical London dispersion forces, remaining somewhat uncertain. The Debye length which measures the range of the double layer varies from approximately 100 Å (10−3 M). 30 Å (10−2 M) to 10 Å (10−1 M) for a 1−1 electrolyte. For applications in cell biology where the Debye length is < 8 Å, or in micellar chemistry at high salt, or ionic microemulsions or polyelectrolytes where the screening length is often of the same order as hydrated ion sizes, the theory will obviously break down. Indeed Deryaguin taught his students that DLVO only worked between approximately 10−3 and 5.10−2 M.

2. Ockham's razor and assumptions

At the present time there are a plethora of new forces emerging, so called non-DLVO forces, which go variously under the names hydration, long range hydrophobic, protrusion, Helfrich, depletion, ion fluctuation, Sugami forces, silica gel, polymer bridging, specific ion effects, and there is much confusion. This paper focusses on the present state of understanding of interparticle forces.

If we wish to understand the status of the DLVO theory, it may be useful to go back and explore concepts and assumptions that underlie it. The theory of thin liquid films [5−7][3] was developed by J. Clerk Maxwell in a seminal article that appeared in the 9th edition of the Encyclopedia Britannica in 1876. There he also reviewed the history of capillary action. Newton had deduced that molecular forces should have an inverse 6th power attraction and, following earlier attempts, tried to measure the forces between plates. He gave up and in Art. 31 of the Principia explains why he quit — surface contaminations were owing. A familiar story. Thomas Young deduced the range of atomic forces from the strength of materials, in his 1805 paper, worked out the theory of contact angles and wetting, on the assumption that a solid surface was smooth up to an infinitesimal distance from the surface. He went to great pains to explain his theories in simple language, avoiding mathematics as far as possible. This theory was stolen without attribution by Laplace who forgot about contact angles and put his mathematical theory of capillary forces into the supplement of volume 6 of his Celeste Mechanique. When the omission was pointed out, the great man corrected it again, without attribution, a matter that caused outrage to Young's biographer, George Peacock.

In his thesis, Poisson developed a different theory published in 1831. He insisted that a liquid near an interface must have a non-uniform profile (of e.g. density, orientation) induced by interactions of the liquid molecules with the interface. A raging argument ensued which was reviewed by the Rev Challis of Trinity College Cambridge in two papers that he gave to the 1836 meeting of the British Association for Advancement of Science. Challis outlined the present state of theory in what we now call colloid science, both molecular forces, and the hydrodynamics of suspensions, and it is not without interest that the term Mathe-

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[3]Contains references to most of this history and work referred to.

matical Physics seems first to have been coined by him for what we now call colloid and surface science. He also was the first to suggest the measurement of forces between surfaces using the new interferometry which came into sight due to Fresnel's work on diffraction.

Unfortunately, as documented by Maxwell, Poisson made a mistake of a factor of two in his calculations. The Young–Laplace assumption won out on the grounds of Ockham's razor, and Poisson's honour restored by Maxwell in his 1876 article. Maxwell invoked what we might now call a Landau Hamiltonian, mean field theory, and scaled particle theory to develop a theory of stability of thin films that depended on hydration forces. He deduced the range of these exponential forces correctly from the bulk properties of liquids. They were short ranged, with a decay length of a molecular diameter. While Maxwell's article was updated by Lord Rayleigh in the 11th edition it was forgotten, as was Poisson, and the revival of a such a theory had to wait exactly 100 years when it was rediscovered independently by Marcelja.

The important point insisted on by Poisson was the existence of a short ranged surface-induced profile of order at a liquid interface due to interactions of the liquid molecules with the surface. Then in Maxwell's theory, the overlap in profiles of these for two surfaces gave rise to a repulsive interaction. These days we would call this a hydration force.

For a single surface Gibbs put the whole business of surface thermodynamics on a sound thermodynamic basis at about the same time as Maxwell. The Gibb's dividing surface, and his adsorption equation resolved the dispute between Poisson and Young–Laplace, in principle, but only for a single interface. (For two surfaces the position of the Gibbs dividing surfaces changes with distance of separation, reflecting the change in profile.)

Earlier than DLVO, and from the beginning Deryaguin [2,3] had insisted on the existence of structural component of disjoining pressure, a 'non DLVO force'. However, the ranges he claimed in various situations seemed much too large to have any credibility. For the double layer interaction with charged interfaces in the DLVO theory, surface-induced order is explicit in the profile of electrolyte, and it is the overlap in profiles that gives rise to the double layer force.

3. Assumptions of DLVO

Consider for argument interactions between only planar surfaces. Then the assumptions are:

1. The surfaces are molecularly smooth and solid. They are inert except in so far as they provide a source of counterions that leave behind charged surfaces.
2. An intervening solvent (water) for an electrolyte has bulk liquid properties up to the interface.
3. Electrical double layer and van der Waals forces are treated independently and assumed additive.

4. The boundary conditions for the double layer are constant charge or constant potential. (A decoration due to the earlier Stern layer theory — which brings in several extra unknown and undefined parameters: position of inner and outer Helmholtz planes, inner and outer dielectric constants has sometimes to be allowed in extensions of the theory. This would give six fitting parameters. With a mixed electrolyte there would be more, which decorations, though necessary at high surface charge or potential, are clearly absurd, as the fitting parameters are undefined anyway. And besides in constructing such elaborate extensions, the sizes of the ions bear no relation to those deduced from bulk electrolyte solutions. No allowance is taken for the entropy of such layers. To impute such extensions to DLVO is insulting, as all predictability is lost, and whatever theory remains is lost in a continuum of parameter space.)

5. The double layer interaction potential is computed using the non-linear Poisson Boltzmann equation for point ions. Discreteness of charge effects are taken into account by a smeared out surface charge approximation. This can be shown to be a good approximation at very low, and very high electrolyte concentrations, but poses difficulties at intermediate ranges (typically 10^{-3} to 10^{-1} M.)

6. The opposing attractive van der Waals forces between the plates is calculated on the assumption that an intervening liquid has a uniform density and orientation profile. It is obtained by pairwise summation of London dispersion forces. The electromagnetic quantum mechanical correlations that lead to these forces are in the ultraviolet so that low Hamaker constant systems (oil in water, e.g.) are not included. At large distances, large means here roughly greater than 100 Å, Casimir had shown that the London potential proportional to the inverse 6th power of distance between two atoms took on a different form proportional to the inverse 7th power. The corresponding attractive potentials between plates are then inverse 2nd power and inverse 3rd power of separation, respectively.

7. Contact angles are ignored.

8. Repeptisation posed some difficulty.

Notice especially that there is at least one fundamental contradiction here. The van der Waals force calculations (see [1]) due to Hamaker under the direction of de Boer which were used in DLVO are made on the assumption that the liquid has bulk properties up to the interfaces. Any overlap of surface-induced order be it 'hydration', density or molecular orientation is not included. By so doing, the Young–Laplace as opposed to the Poisson assumption, we have implicitly said that interfacial free energies can be taken as infinite, as they are unperturbed by interactions. This is a serious approximation, the limitations of which are discussed very clearly by Hamaker.

(One can get over this by putting in cutoff for the van der Waals force of the order of a molecular distance. Then the van der Waals energy of interaction/unit area on 'contact' should be twice the interfacial energy. These energies, proportional to a Hamaker constant divided by cut-off distance squared, depend on the 4th power of the cut-off distance. This is because the Hamaker constant depends on the square of the effective polarisabilities. However, even that flexibility cannot be

accommodated for water, for which three-quarters of the measured surface tension at the air water interface is due to non-dispersive (temperature-dependent) interactions. This kind of difficulty is not a part of DLVO theory which deals with long range forces only. Yet such nonsense infests the literature and leads to the silliness of van der Waals 'contact planes' which together with 'extensions' embodied in item 4 above would give a minimum of eight hidden or fitting parameters).

The genius of DLVO lies not in complicated models that add more and more parameters, but in its extraction of the essential physics of the problem of lyophobic colloid stability.

4. Progress in forces

Since the appearance of DLVO theory there has been much progress in liquid state physics. Once an arcane art and backwater of modern science, colloid science has moved to center stage, and taken on more sophisticated clothes. Some of the products of these new fashion houses are bizarre.

4.1. Electrostatic forces

The double layer forces were first measured by Mysels and Lyklema [8] using soap films, and the decay length established to be the Debye length. If we keep for the moment assumptions 1–3, the first theoretical step forward (item 4) was the relaxation of the condition of constant charge or potential through charge regulation, due to the author and Parsegian [9]. One difficulty of the original theory was removed. Site binding models proliferated, apparently with some success. Direct measurements of Pashley and Israelachvili in Canberra with molecularly smooth mica surfaces in aqueous electrolytes revealed an ion-specific and pH-dependent short ranged repulsive 'secondary hydration' force. This new force was attributed to a competition between hydronium ion and counterion for surface sites. It dominated the double layer force, and the decay length appeared to be approximately 3 Å for 1–1 electrolytes, 10 Å for 2–1, and 20 Å for 3–1 solutions. The 'theory' invoked several parameters, the area per charged surface site, and separate binding constants for competing cations and hydronium, and was unable to explain the behaviour of caesium and quaternary ammonium salts. However, it did seem to be important. The specificity of these apparent secondary hydration forces could be exploited in compaction of ceramics, for example. In fact the theory was much too simple minded and wrong even given its assumptions. One reason is because it ignores the entropy of the competing adsorbed cations. 'Secondary hydration forces' can be exploited as a phenomenological tool. However, the origin of these ion-specific effects and of repeptisation phenomena, as we shall see below, cannot be accommodated by electrostatic and site binding models alone. A further difficulty arose much later when it was realised that the Debye length in asymmetric bulk electrolyte solutions, even at very low concentrations when a point ion model is permissible, is incorrect. The predicted double layer decay length for such

systems was confirmed by direct measurement [10,11]. The analytic result for the Debye length has important implications for the real world of industry and biology. Trace amounts of multivalent ions with surfactants, or mixtures presented by biology that contain trace amounts of highly charged proteins or RNA with salt, can appear not to satisfy conventional theory.

Quantitative prediction of interactions in the double layer beyond the Poisson Boltzmann approximation can only be described by extensions that include the hypernetted chain and sometimes bridge diagrams of statistical mechanics. These extensions take account of short range interactions in the electrolyte between ions, and ions and the surfaces. The double layer problem is vastly more messy than the bulk electrolyte one. Such a program has come into sight by the work of Marcelja and Kjellander,[4] now extended to include water molecular potentials. However, the computational difficulties are still immense for mixed electrolytes. With simulation work the necessity to impose a finite size to the simulation box usually means that an incorrect Debye length is used.

Worse still, most of the modern calculations are based on the assumption that the primitive model of electrolytes is valid. It is most certainly not. A comparison of bulk activity coefficients predicted and those measured show that while the assumptions are consistent for 1–1 alkali halide solutions in that the deduced hard core radii are additive, the model fails badly for say nitrates, sulphates, caesium, acetate and many other ions [12]. The implications are obvious: If a measurement of surface forces agrees with theory and requires a fitting parameter involving the size of ions, that parameter had better be consistent with bulk values. If the force measurement gives the same result for NaCl as for $NaNO_3$ we had better be suspicious rather than accepting.

4.2. Molecular size and the continuum approximation

The double layer force is an exemplar par excellence of the Poisson idea. For here we assume first that water is a continuum background of bulk dielectric properties only. Then the 'liquid' between the interacting surfaces is a dilute classical ionic plasma, which can be decorated to allow finite size of the ions (the primitive model). The charged surface induces a profile of density in the co-ions and counter-ions. The force which arises between two surfaces occurs due to the overlap of these profiles. What is not known here is the surface potential set by specific ion adsorption, and this remains a fitting parameter, assumed to be independently measurable from say a zeta potential measurement.

By contrast, recall again that the opposing van der Waals force was calculated with the assumption that an intervening liquid between two surfaces had bulk density down to 'contact'. No profile of density, any surface-induced liquid struc-ture was allowed. (And indeed no liquid-induced surface structure or dissolution as

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[4]The literature in this field of extended double layer theory is immense. See work associated with S. Marcelja, R. Kjellander, D.J. Mitchell, B. Jonsson, H. Wennerstrom to enter the field.

occurs for silica as allowed.) As Poisson had argued, this is in principle absurd. As already remarked [5−7], for a single surface, one can define thermodynamically a Gibbs dividing surface which sets the zero of distance. However, for two surfaces, the interaction arises due to overlap of the profiles, as was shown explicitly by Everett and Radke [13]. The Young−Laplace assumption is implicitly equivalent to the statement that interfacial tensions are infinite and unperturbed by interactions. Yet interactions are defined thermodynamically as the change of interfacial tension of the system as the particles approach. For the double layer problem, the theory is consistent with the Gibbs adsorption isotherm, that is, it is thermodynamically consistent. However, for the other half of the story involving van der Waals interactions it is not. This apparent philosophical nicety, which indeed worried Hamaker and de Boer, was swept under the carpet. It could be set to one side. After all, the notion of a molecularly smooth surface might be considered extravagant madness by an anthropomorphic huddle of water molecules at the surface even of mica. And that might be considered more important. The DLVO theory dealt with long range interactions with the balance of forces that determined stability typically of the order of the Debye length, i.e. far from the surfaces.

But the question remained: How far does surface-induced liquid structure extend? Theoretical exploration of this question via statistical mechanics showed that the answer turned out to be surprisingly large, especially for low Hamaker constant systems like oil and water [14]. It was unlike the pair distribution function for bulk liquids, wherein correlations disappeared after one or two molecular diameters. For the colloid problem, oscillatory forces between smooth surfaces extended for up to approximately eight molecular diameters before merging back into the continuum approximation. This astonishing prediction was confirmed when the author persuaded his colleagues Horn and Israelachvili to measure van der Waals forces between mica in liquid octamethyltetracyclosiloxane (see Refs. in [5−7]). This is a large molecule, roughly 7 Å × 9 Å, designed by Hildebrand for diffusion work. The interactions are purely hard core plus van der Waals. Theory was confirmed, and reconfirmed for hard sphere — van der Waals — permanent dipole liquids like propylene carbonate. So the granularity of liquids shows up to very large distances. If surface roughness exceeds molecular size, or at the mobile surface of the liquid−liquid, phospholipid water interface, these oscillations are smoothed, as in the Maxwell or Marcelja mean field theories. The oscillatory forces are *not* surface-induced liquid structure in the sense of Deryaguin or Poisson, but arise due to (statistical) geometric packing constraints forced on the liquid molecules due to the presence of the surfaces. However, they can be important in lubrication and microviscosity. These oscillatory forces show up in and stabilise colloids in systems with large molecules like polymer solutions, micellar and emulsion systems and are then sometimes called 'depletion forces' [15−17].[5]

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[5]A vast industry now exists on 'depletion forces'. See [15−17] for direct measurements
[6][18] has a fairly complete account of developments and extensions of Lifschitz theory (see in particular [19−23]).

4.3. Lifschitz theory [18−23][6]

In 1958 (item 6 above) there appeared the Lifschitz theory of molecular interactions in vacuo, quickly followed by a complete theory that included an intervening medium due to Dzyaloshinski, Lifschitz and Pitaevski in 1961. Up until then, even allowing the continuum assumption for an intervening medium, vacuum or not, no one had much of an idea of how to go beyond the simple idea of adding pairwise London forces between molecules or even how to take account of an intervening liquid. (Retardation was dealt with by adding up Casimir Polder forces.) Multilayered structures like soap films presented a big problem. The idea of Lifschitz was to exploit the fact that a measurement of dielectric susceptibility of a medium as a function of frequency implicitly subsumed all many body forces. So a theory that used these experimentally available dielectric response functions should represent a complete solution of the many body problem. Lifschitz theory recovered all the earlier results trivially, but gave one peculiar result: At very large distances the interaction went back from a retarded form as predicted by Casimir, to a more slowly decaying non-retarded inverse distance squared behaviour and proportional to temperature. And indeed this form was measured by Abrikossova and Deryaguin in a famous experiment. The later theory of DLP which included effects due to an intervening medium invoked the full apparatus of quantum field theory in a tour de force that appeared indeed to represent a full solution of the whole problem. Recall that for this part of the interaction problem we are still dealing only with uncharged surfaces. The theory and the experiments were completely ignored in the West, partly due to cold war tensions, partly due to personalities, and partly due to sheer incomprehension of a mathematically obstruse theory. Besides, while general statements could be extracted about conditions for wetting and the nature of forces, no one had the slightest idea of how to actually use the theory to calculate numbers.

(The stability of a film of liquid on a substrate, tantamount to deciding if a particular liquid wets or does not wet a surface is predictable via the theory. However, only close to the saturated vapour pressure. How close depends on molecular size and strength of interaction of the liquid molecule with the substrate. In practice the Lifschitz isotherm log $(P/P(saturated)) \propto A/1−3$ holds only when $P/P(sat)$ is approximately or > 0.99. At other pressures the BET, multilayer, and Langmuir isotherms that require statistical mechanical modelling take over [24][7].)

The theory of DLP was a great step forward in that it appeared to circumvent the whole intractable problem of many body forces through its use of measured bulk dielectric response functions. However, it must be stressed again that it is a perturbation theory. That is, it depends on the assumption that an intervening liquid between interacting surfaces has bulk liquid properties up to a molecular

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[7]See [18] chapter 6 [19−24]. The concept of dispersion self energy developed by these authors plays the same role for dispersion energies as does the Born self energy of an ion and is of the same order of magnitude. It is the key to theories of solubility, surface free energies, and ion specificity. It has been ignored completely.

distance from the surfaces. This is thermodynamically inconsistent, being equivalent to the statement that surface energies (or alternatively, the positions of the Gibbs dividing surfaces) are changed infinitesimally with distance of separation. This limits the theory to 'large' distances (Young–Laplace vs. Poisson again) where 'large' is undefined.

The complete QED solution announced, and this seems to be not generally understood, in fact is not correct — even accepting its assumption that an intervening liquid between our interacting surfaces can be replaced by a uniform bulk medium. For at a certain point in the development of the theory, an integration over the coupling constant in Dyson's equation of quantum electrodynamics is replaced by a linear approximation. It is equivalent mathematically to the weak overlap approximation for the double layer problem.

The consequence is that an apparently formidable armoury of tools is equivalent to using a sledgehammer to crack the proverbial peanut. The complicated formulae can be derived almost trivially by solving Maxwell's equations with appropriate boundary conditions and assigning the semi-classical free energy of an oscillator to each allowed mode. The problem solved was one of applied mathematics, difficult technically for different geometries, but not, as it appeared as profoundly difficult as it seemed.

The next step was how to use these complicated formulae, a problem solved by Parsegian and the author. What emerged was that the van der Waals forces required for colloid science were indeed substantially correct for high Hamaker constant systems at distances less than approximately 50–100 Å. Beyond such distances, which correspond in DLVO if we balance forces, to electrolyte concentrations greater than approximately 10^{-2} molar, retardation was seen to be much more subtle than previously (Biology usually works at 10^{-1} molar).

But the DLVO theory was badly wrong for low Hamaker constant systems like oil or phospholipids in water and it must be said that DLVO did not claim competence here. Here an estimate of Hamaker constants derived from pairwise summation of London forces failed. The complete dielectric response functions had to be used, and these subsumed non-additive many body forces due to temperature-dependent dipole–dipole, dipole-induced dipole forces besides the London forces. And retardation showed up very complex behaviours. Contributions from different frequencies decayed exponentially, locked in at different distances, depending on geometry and nature of interacting materials, so that one had the beginnings of an inkling of specificity. Macromolecules as it were 'felt' their vibes, the microwave fluctuations first, later the infrared, the visible next, and finally, on contact the ultraviolet, i.e. chemistry took over at close separations. The theory and its predictions were much more accurate for condensed media than for interactions involving a vacuum for technical reasons that we need not go into.

The theory was confirmed for thin films of liquid helium, spreading of oil on water, and earlier by Tabor and Winterton, and Israelachvili and Tabor with molecularly smooth mica across air. These were the first to see the transition from non-retarded to retarded forces. (Not precisely, if the theory were indeed correct, it should be valid at least in the case of interactions across a vacuum. No amount of

adjusting unknown dielectric parameters could reconcile measurement and theory until it was realised that the experimentalists had made a systematic error of a factor of two in the radius of their mica cylinders.)

Forces between phospholipid bilayers in water that balanced short range hydration forces against van der Waals attraction deduced from osmotic stress measurements appeared to come out right, although for some time the results appeared to be in conflict with those from direct measurement of surface forces. This disagreement occasioned much acrimony. That problem was resolved when it was realised that the surface force measurements done with adsorbed bilayers on mica were a different animal to force measurements of multilayer bilayers in water. For the first, at large distances the force is dominated by interactions between mica across water. At small distances it is dominated by forces between the lipid bilayers. The system is a triple film, and when the theoretical analysis is done correctly, both experiments give the same answer consistent with Lifschitz theory.

There were many extensions of the theory to different geometries which revealed even more subtleties. With added salt new fluctuation forces due to ion–ion correlations emerged, which decayed as $\exp(-2Kl)$. These were confirmed by direct measurement. With cylindrical geometries like model polyelectrolytes, these forces had quite different, and very long ranged forms, even being strictly non-additive for conducting polymers or reverse microemulsion systems [25,26].[8]

There was reason for satisfaction and congratulation with the progress made. The satisfaction was premature. Careful reflection revealed that the triumph of direct force measurements was flawed. In fact with charged molecularly smooth surfaces, those which concerned DLVO, or those on which one could deposit or adsorb surfactant bilayers, the surface charge required to fit the data was indeed a fitting parameter. Ion specificity, missing from the original theory, was still unexplained.

4.4. 'Hydrophobic' interactions [27][9]

And then came the flood. Two or three floods. The most disturbing event was the measurement of new very long range 'hydrophobic' forces ten to one hundred times larger than any conceivable van der Waals–Lifschitz forces. The first direct measurements were between mica on which CTAB was adsorbed from solution near the point of zero charge. The forces could be fitted to an exponential with decay length of 1 nm. The new 'hydrophobic' forces proliferated with different 'hydrophobic' surfaces formed by Langmuir Blodgett deposition, adsorption, single and double chained surfactants, and solid surfaces hydrophobised by polymer

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[8]See [18] chapter 7 for ion fluctuation forces, [19–23], also [25] and for measurements that confirm the existence of such very long range forces [26].

[9]The number of papers on 'hydrophobic' interactions is immense. Most are nonsense, a situation which arises due to neglect of surface thermodynamics. The effects are real however. All measurements can be interpreted in terms of capillary condensation or subcritical fluctuations in one form or another. See [27], this issue and subsequent papers of these authors and collaborators.

adsorption, silalinisation, or solids proper. A bewildering prolixity of surface forces emerged with a range that increased with time to a record exponential decay length of 300 nm. The phenomena, which were real, rivalled polywater as a mystery. For some systems spontaneous cavitation occurred prior to contact. However, adhesion energies were exactly what one would have expected for oil-like interfaces in contact.

Much of that mystery is resolved. Most are due in one form or another to capillary condensation, and emerge from a proper consideration of Gibbs surface thermodynamics, as discussed in a succeeding article in this issue. For solid hydrophobic surfaces, hydrophobic in the sense that contact angle for a drop of water on the substrate is finite, but $< 90°$, subcritical density fluctuations give rise to depleted densities between surfaces which are responsible for the large forces.

At the other extreme, for anionic surfaces hydrophobed by labile cationic surfactant adsorption, a different mechanism, still capillary condensation, obtains.

Wetting studies on isolated surfaces of silica or mica show that the finite contact angle occurs because the surfactant migrates across the three phase line, and that at the adjoining solid water interface the density of coverage is approximately one surfactant molecule per 700 $Å^2$ for silica, 100 $Å^2$ for mica. The wet surfaces that interact are hardly then 'hydrophobic' in any sense because the maximum area per surfactant molecule is only approximately 50 $Å^2$. The mechanism of interaction between two such surfaces immersed in water–surfactant solutions near the point of zero charge is now very different. It arises because charge regulation, a highly non-linear delicately posed process, induces additional adsorption with decreasing surface separation. The short ranged hydrophobic attraction between the hydrophobic tails of adsorbed surfactants then drives a two dimensional van der Waals gas-like condensation which provides the source of the free energy of interaction. In principle, all the phenomena observed are consistent with capillary condensation, i.e. thermodynamics, in one form or another. If the gross source of the driving free energy is clear, what still remains mysterious and yet to be understood, is the range and variability in range of these forces. And thereby hangs an emerging tale to which we return later. They are mediated by and take on long range due to dissolved gas and other solutes

4.5. Helfrich forces [28][10]

Yet another class of forces came into prominence at the same time. Here we

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[10] We do not attempt to enter the vast and popular literature that derived from the ideas of Helfrich on undulation forces. See [28]. There is a big problem in unravelling undulation forces from DLVO and hydration forces to pin down bending moduli. This is apart from the difficulty of 'bootstrapping' harmonic theories — where the forces are by definition weak — to allow anharmonic fluctuations. The problem arises because in interpreting say SAXS or SANS experiments on mesostructured fluids it is usual to postulate additivity of DLVO forces (and hydration forces) and the fluctuation forces to arrive at bending moduli. However, the forces are not additive and the choice of surface charge to characterise double layer forces is both highly ion specific and arbitrary,as is the choice of 'Hamaker' constant.

come back to an extension of Langmuir and Onsager's ideas. If, and still confining ourselves for simplicity to planar interfaces, we admit that multilayer structures like liposomes or oil swollen lamellar phases or microemulsions can be stabilised at very large distances of separation there is a problem. The idea of Helfrich was that fluctuations in the now flexible surfaces can produce steric interactions that accomplish the job. They are irrelevant for the stabilisation of phospholipid liposomes. The theory of these fluctuations rests on a harmonic approximation, a perturbation theory, that assumes additivity of van der Waals, double layer, and the fluctuation forces and these were bootstrapped up to provide the dominant mechanism of long ranged repulsion. That is a serious difficulty, inconsistent as usual. The theory also ignores the original ideas of Langmuir, that concern the role of entropy in two phase equilibrium, and the phase behaviour of surfactants. For in deducing bending and compressibility moduli of surfactant and microemulsion mesophases from neutron and small angle scattering data to fit the Helfrich theory, one assumes some kind of double layer interaction and van der Waals Hamaker constant. The fluctuation forces and these are *not* additive. Worse, and more confusing, the double layer forces assumed and subtracted out from the analysis of the scattering data make no sense at all in the presence of salt. This annoyance perturbs no one.

5. A plethora of forces

There are even more 'non-DLVO' forces that have been invoked in all kinds of situations, to the point that the simplicity of the original theory has been utterly obscured. So where are we? Most of the decorations we have discussed can now be fitted into a larger picture. For example depletion and oscillatory forces make sense if treated on a sound statistical mechanical footing, and hydrophobic forces make sense if treated from a proper thermodynamic basis. Failure of DLVO in particular situations that involve mixed or trace amounts of highly charged ions or polyelectrolytes or micelles in biology make sense.

The business of 'hydration' deserves further comment. Like the term 'hydro-phobic' the concept is not defined, a matter of some convenience. Thus for bulk electrolytes measurements of hydrated ion sizes give a different answer depending on the experiment and theory used. The same is true in colloid science. The complex pattern of events observed with the silica–water interface is illustrative [29,30].[11] It is a non-equilibrium entity. Surface gelation occurs — to a greater or lesser degree — depending on the manner of preparation and history. The gel undergoes gradual evolution under water. The interaction pattern that arises when two surfaces are in contact and the gel layers overlap is a result of a complicated interplay of influences comprising high viscosity, elasticity and plasticity of these reactive layers that can show up also in capillary phase separation effects.

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[11] Polywater (and cement) exists and is ubiquitous with oxides.

Once this is recognised much of the confusion in the literature and disputes on interpretation fall into place. The philosophic challenges posed to theories of colloid science by this situation is another story. Thus, e.g. a fit of an experimental force measurement to a theory that supposes a sharp interface might invoke contributions from a double layer, with whatever decorations, and an attractive van der Waals force. Deviations between theory and experiment are then assigned to 'hydration forces'. However, clearly with a diffuse interface the van der Waals component is immeasurably small. Further the apparent double layer itself is modulated and drastically changed by the existence and extent of the charged silicic acid polymeric coatings of the real diffuse interface; and of associated steric forces. So the deduced 'hydration force' — which can vary from one with range of a few Å or less to μ, attractive or repulsive — is an artefact of incorrect application of theory to experimental measurements that can vary from situation to situation.

'Hydration' forces have been the subject of much debate, with a school of thought adamantly maintaining that hydration does not exist. This is nonsense. Were it so, one would have to abandon the primitive model of electrolytes completely, and ask further, if it were true why it is that surfactant and phospholipid self assembly depends on water or other hydrogen bonded solvents. And if there were no hydration effects in interactions the cloud points in polyoxyethylene surfactant phase diagrams would not exist, and one would dismiss also all NMR experiments.

6. The Hofmeister series [31]

But if we can dismiss most decorations as curve fitting, there is one serious problem among others that remains. This is the question of ion binding to surfaces and ion specificity, for proteins, solids, surfactant micelles and microemulsions.

This problem of ion binding, as revealed by salting out of proteins has been with us since 1888. It occurs over and over again, is most dramatic for anions and has been conveniently forgotten. Essentially what we have done is construct a theory that 'works' for sodium and potassium chloride with a few model colloids between 10^{-3} to 10^{-1} molar. However, the theory breaks down completely for other salts. This is not good and such a theory can claim little universality. In colloid science proper, for 1–1 salts and well defined systems flocculation rates and floc packing depend on cation in the same Hofmeister series. The usual attempts to accommodate this phenomenon by invoking different ion 'sizes' to different cations, and hence different Stern layer potentials does not work at all. The most careful direct measurements of double layer forces between mica in $LiNO_3$ due to Shubin and Kekicheff a few years ago show that however one adjusts four or five parameters within the classical extensions of DLVO theory — that would admit outer and inner Helmholtz planes and associated inner and outer dielectric constants to these

layers — the measurements make sense only if one assumes a hydrated Li radius of 5 Å. This is plainly absurd. 'Binding' to micelles or polyelectrolytes, phase inversion of microemulsions with change of counterion, ion specificity of bubble–bubble interactions, positive adsorption of salts like KCl to the oil–water interface — the air–water interface is completely different to the oil–water interface — and much else reviewed elsewhere all point to something being amiss, and indeed it is. The problem, at the simplest level, can not be swept away. It turns out that the extended Lifschitz theory that includes salt effects is precisely equivalent to an extension of the Onsager Samaris limiting law theory for the change in interfacial tension at an oil or air–water interface due to dissolved salt. This theory is a linear theory that invokes artificial cut-offs and even so 'works' only up to 10−4 molar. It is badly in error as Onsager himself remarked. So the Lifshitz theory is also just as crude.

What has gone wrong? It is just this: Ions experience not just an electrostatic interaction with an interface that leads to the double layer potential. They also experience a short ranged dispersion interaction that can lead to either positive or negative adsorption. Which situation obtains depends on the interface and the ions. Essentially the statement is that it is in general impossible to separate double layer and dispersion forces. Once that is recognised it becomes clear that many curious phenomena begin to fall into place. The emerging new theories take on a better predictive capacity. The Debye Huckel theory itself or its extensions also suffers the same limitations. The notion of pH becomes defined.

These problems, of forces, are non-trivial and in fact profound. The Lifshitz theory for dilute media can be used to show that even the long accepted Casimir Polder force between two atoms is correct only at zero temperature. At any finite temperature it is quite wrong, a matter which connects to our understanding of the vacuum. For condensed media, it turns out that even the Casimir force between ideal metal plates in a vacuum is at the same level of approximation as the Onsager limiting law. As is the Lifschitz theory [32,33].

6.1. Effects of dissolved gas

Another area of much importance so far completely neglected in all theories of colloid science and indeed of physical chemistry itself, poses even deeper challenges. Water at normal pressure and temperature contains dissolved gas at approximately 5.10−3 molar. In oil it is 10 times higher. At a hydrophobic interface the accumulated gas is significant. Effects due to dissolved gas are explicit in optical cavitation [34] and sonar cavitation experiments — on removal of dissolved gas the effects, which also depend on salt type and concentration, disappear. There is emerging biological data, and inferences from experiments with radio frequency fields that gas is responsible for free radical production, and that these free radicals can be long lived. However absurd such claims may appear, the effects are real. The truth is that we know nothing of water and its interactions with gas, salts and electromagnetic fields beyond the predictions of linear continuum theories which we know are too crude.

6.2. A summation

The improvement of a theory of Debye or of Onsager normally takes approximately 50 years. So too for the theory of DLVO. Except that here it may be longer. The fundamental physics and chemistry, within the boundaries and limitations recognised by its authors, did stand the test of time. Colloid science forgot its foundations laid by Gibbs, Maxwell, Young, Poisson and others. The DLVO theory did not. Like Darwin's theory, it has had to put up with the enthusiasm of converts who imputed to it claims that it did not assert. Without it, we would have had no platform from which to build a deeper understanding in the future.

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