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Surface forces: Changing concepts and complexity with dissolved gas, bubbles, salt and heat

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ABSTRACT

A number of missing factors influence surface forces strongly; so much so that the classical theory is often irrelevant to the real world. Among these factors, dissolved atmospheric gas or other sparsely soluble solutes play a central role in long range hydrophobic forces. Bubble–bubble interactions exhibit unexplained non-Hofmeister ion specificity. Inhomogeneity in temperature between bubbles and solvent can be used to catalyse high temperature reactions at low temperatures.

Further, the additivity of electrostatic and dispersion forces assumed in DLVO theory is inadmissible. It also neglects ion specificity (Hofmeister effects) due to dispersion forces acting on ions.

An account is given of these complexities that are missing from classical theories of surface forces. It is shown how these phenomena can be exploited for a range of novel technologies.

1. The classical picture of molecular and surface forces: limitations and insights

The van der Waals interaction potential between two atoms behaves as $V(r) \sim r^{-6}$, where r is the distance between the centre of the atoms. This was known to Newton. The potential of interaction between two planar surfaces at separation L follows by pairwise addition. It varies as L^{-2}. Newton tried to measure this force, but gave up, with the comment (Art. 31 of the Principia) "surface combinations were owing".

Unlike gravity, surface forces decay rapidly over very short distances and depend critically on material properties. And, as for contamination, it will always be with us.

For the opposing electrical double layer forces between two charged surfaces in a continuum electrolyte, the repulsive forces decay exponentially with distance; asymptotically, $V(L) \sim \exp.(-\kappa L)$ with κ^{-1} the electrolyte Debye length. The pre-factor depends on assumed boundary conditions, constant potential or constant charge. These conditions were relaxed with the extension to allow charge regulation [1•]. This was a conceptual advance. The degree of ionisation of surface charges – and therefore surfaces forces – recognises, and changes in its response to the proximity of, and signalling from, another body.

These few lines, with a few decorations, underlie the DLVO theory of colloid particle interactions. The theory was a core belief to physical and electrochemists. It still is. It ranks with the book of Genesis as a credible account of creation, and is less useful.

The theory has severe limitations, acknowledged by both Deryaguin and Overbeek: because a liquid between interacting bodies is assumed to have bulk properties up to a molecular distance from an idealised surface. Further, apart from the contamination issue, most surfaces are not molecularly smooth or chemically homogeneous and in addition solvent molecules may interact directly with the surface, for example via hydrophilic or hydrophobic effects in the case of water. Specific ion effects are also ignored. Lastly, the theory has further, amplified problems at high electrolyte concentrations, where only very short range surface forces are expected and these other factors can dominate.

The DLVO ansatz supposes van der Waals and electrostatic forces are additive. They are not [2•,3].

2. First steps beyond DLVO theory

2.1. Complexities with double layer forces

The standard Debye length for symmetric electrolytes is not valid for asymmetric electrolytes. It has a much more complex form. Direct force measurements for 12:1, 8:1 electrolytes (cytochrome C) and insulin 5:1 and 3:1 give precise agreement with theory [4,5].

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2.2. Oscillatory forces

At small distances, of the order of several molecular sizes, the electrostatic forces are dominated by oscillations. These are sometimes called depletion forces. They act to stabilise emulsions and other systems where e.g. proteins or micelles form part of a fluid that separates two interacting objects [6].

This "molecular granularity" shows up in any liquid, from van der Waals hard core fluids [7,8•,9] to colloidal suspensions of micelles [6]. The oscillations decay with separation and merge into the continuum theories after about 6 oscillations.

2.3. Hydration: surface induced liquid structure

The assumption that a liquid adjoining a surface has bulk properties up to contact (a molecular distance) can break down for reasons other than molecular granularity. The profiles of surface induced liquid order (e.g., dipole or hydrogen bond ordering) can overlap to give rise to either repulsive or attractive hydration forces. These dominate at small separation distances. For surfaces rough at a molecular level, e.g. phospholipid head groups of a bilayer, the oscillations are smoothed out and decay with an exponential form with a range of the order of a molecular diameter (0.3 nm). They dominate van der Waals interactions up to say 3 nm separations. Correlated fluctuations in constituent surface dipoles of head groups can give rise to other forces They can appear in force measurements as a hidden contribution that changes effective hydration decay length. Thus, the smaller ethanolamine dipolar head group has a larger such contribution than does the bulkier phosphotidyl choline group. The apparent hydration range is smaller for the former [10].

Hydration forces were first calculated, correctly, by J Clerk Maxwell in a magnificent paper in 1876 and forgotten [11]. They were rediscovered exactly 100 years later by Marcelja [12•].

3. Complexity in van der Waals forces

3.1. Lifshitz theory: emerging concepts of recognition

D'Arcy Thompson , in *Growth and Form* CUP (1918), had reported the views of the early founders of the cell theory of biology and of the early physiologists of the 19th century, that progress in their new sciences would wait on, and depended on advances in molecular forces.

That plea had been articulated most eloquently in 1894 by the Russian physicist P.N. Lebedev, discoverer of light radiation pressure as follows

" …..of special interest and difficulty is the process which takes place in a physical body when many molecules interact simultaneously , the oscillations of the latter being interdependent owing to their proximity. If the solution of this problem ever becomes possible we shall be able to calculate in advance the values of the intermolecuar forces due to molecular inter-radiation, deduce the laws of their temperature dependence, solve the fundamental problem of molecular physics whether all the so-called 'molecular forces' are confined to the already known mechanical interaction of light radiation, to electromagnetic forces, or whether forces of hitherto unknown origin are involved. ….". It is especially fitting that his speculations and grand vision on forces should have been confirmed by the Russians in the dramatic simultaneous advance in theory by Lifshitz in 1955, and in experiments by Abrikossova and Deryaguin in 1956. Deryaguin was Lebedev's son-in-law and Lebedev was a friend of J. Clerk Maxwell.

The vision was implemented by his step-son Deryaguin through Lifshitz. It was extended by Dzyaloshinski, Lifshitz and Pitaevski who developed a complete theory of interactions between planar dielectric bodies separated by a liquid. The liquid was assumed to have bulk properties (i.e., hydration was ignored).

Given that assumption, the theory invoked the full apparatus of quantum field theory to give what seemed to be a complete solution of the problem. It included temperature dependence of interactions, all many body interactions, so called retardation and contributions from all electromagnetic frequencies. Its genius lay in recognising that the measured dielectric susceptibilities of interacting materials as a function of frequency included implicitly all many body interactions [13•].

A difficulty was that no one had any idea of how to use the theory, a problem solved by Ninham and Parsegian [14]. The theory underwent all sorts of further extensions to different shapes, layered, magnetic and conducting materials and electrolytes [15].

The key insight from our point of view is this: the potential is a sum of contributions from all electromagnetic frequencies. Some can be positive, some repulsive depending on the interacting materials. Each frequency component F(ω) is damped exponentially (for planar media)

$$F(\omega, L) \sim \left[-A(\omega)/L^2\right] \exp\{-2\,\omega L/c\,\varepsilon(i\omega)\}$$

where ω is the frequency, L distance of separation, c the velocity of light, and ε(iω) the dielectric susceptibility of the intervening medium at frequency ω in the imaginary axis. The pre-factor is complicated.

The conceptual picture that emerges is this: two objects sense and recognise temperature dependent zero frequencies first. As they come closer infrared frequencies kick in (~20–50 nm), followed by optical frequencies (~4 nm) far ultraviolet (1 nm) until atomic contact or hydration where chemistry takes over.

In other words, two objects feel each other's specific vibrations, and respond appropriately. Sometimes that specificity can be very strong and the forces very long ranged.

(An extreme example is that of parallel thin cylinders. If non-conducting, the interaction potential is $V(r) \sim r^{-4}$. If conducting, e.g. DNA molecules, the interaction goes as $1/\{[r^3/2]\ln r\}$. This force is strictly non additive and essentially infinitely long ranged. For two dimensions, and for conducting planes, the potential (Casimir force) is by comparison short ranged [16].)

With electrolytes the situation become more complicated in that the temperature dependent contributions are modified to decay with another factor, depending on the Debye length, exp.($-2\kappa L$) [15].

3.2. Semi classical and quantum field theory: a digression

The in-principle notion of recognition, dependent on material properties and physico- chemical environment, was agreeable. But the claims for generality, even granted the bulk medium approximation, went too far. The theory turned out to include a hidden sleight of hand. (Technically, at a certain point in the development, a nonlinear coupling constant integration in a Dyson integral equation for the dielectric susceptibility was approximated by a linear integration). The mystique of quantum field theory was exposed. The whole theory collapsed to a semi-classical theory. That is; it was nothing more than Maxwell's equations for the electromagnetic field with boundary conditions plus the Planck hypothesis for quantisation of light [17•].

This equivalence of QFT with semi-classical theory allowed much more difficult extensions of theory to be tackled. Much of the literature in physics on molecular interactions is derived at zero temperature, e.g., the Casimir Polder and Casimir interactions for "retarded" van der Waals interactions. "Retardation" refers to a weakening of the interactions attributed to the finite velocity of light. It turns out that this is quite wrong! [18].

Similarly the literature treatment of resonance or retarded Forster interactions involving excited state-ground state interactions on