Specific Ion Effects: Why DLVO Theory Fails for Biology and Colloid Systems

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The classical Derjaguin-Landau-Verwey-Overbeek theory that underpins colloid and surface science is shown to be flawed, especially at biological salt concentrations. This is in part because the dispersion forces acting on the ions are ignored. When these are included properly very different results are obtained. These results have substantial implications for biological and for ordinary colloid systems at moderate salt concentrations.

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The forces between charged objects in an aqueous electrolyte solution is a central preoccupation of colloid science. Whether the application is to membrane biology or protein interactions, soil science, electrochemistry, polymers, or mesostructured fluids, a knowledge of the forces is crucial. The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of interparticle interactions [1,2] treats colloid stability in terms of a balance of attractive van der Waals forces and repulsive electrical double-layer forces. While there have been many improvements (e.g., Lifschitz theory of attractive forces [3,4], ion fluctuation forces [4,5], charge regulation in the double layer [6]), the theory has remained unchallenged for half a century. There is a huge amount of literature devoted to force measurements, either direct via the surface force apparatus technique of Israelachvili and colleagues [7,8], or by atomic force microscopy, or osmotic measurements pioneered by Parsegian [9,10]. But, except for a few cases [9,11,12], agreement with theory is illusory in the sense that the measurements can be accounted for only by invoking fitting parameters to accommodate surface potential or charge. There is a high degree of ion pair and buffer specificity [9]. Forces can vary in magnitude by a factor of 50 or more by simply changing the counterion from, e.g., bromide to acetate [11]. The same problem is mirrored in the simple experiment of bubble bubble interactions [13], or in explaining the interfacial tension of an electrolyte-air interface [14]. This shows up in biological and biochemical applications particularly where so-called Hofmeister effects are ubiquitous [15,16], as indeed they are for polyelectrolytes, and mesostructured fluids.

The current situation is clearly unsatisfactory for a number of reasons. Even with five adjustable parameters, theory often disagrees with experiment at short ranges less than, for instance, 100 Å [17]. It does not properly take into account specific ion effects [8,9,11,], which are ubiquitous in biochemistry and colloid science. Above $0.1M$, the regime of biological interest, theory loses all pretence of predictability [15]. These problems can be resolved by including dispersion forces acting on the dissolved ions at the same level as electrostatic forces [18]. Interactions between charged particles, strongly dependent on specific ion effects, can differ substantially from the DLVO results.

Even given a fitting parameter such as effective charge or potential, at short length scales experiments often show substantial deviations from DLVO theory. These deviations are usually accounted for by invoking a zoo of so-called "extra-DLVO" forces [7,8]. These may be hydration forces, hydrophobic, oscillatory, membrane fluctuations, or water structure forces. But, any assessment of the important short range forces is impossible if they are obtained by subtracting a wrong form for the long range forces from an experimental force curve.

The problem lies in [18] the inconsistency built into the DLVO theory which separates forces between particles into double-layer and van der Waals forces. The electrostatic forces are handled by a nonlinear Poisson-Boltzmann description or decorations thereof. The van der Waals forces are treated in a linear (Lifschitz) theory. In the biological regime (oil-water, high salt), the dominant part of the interaction is precisely equivalent to an extension to two interfaces of the Onsager-Samaras theory for the change in interfacial tension at an air-water interface due to dissolved salt [18]. This limiting law is incorrect except possibly at extremely low concentrations. So, also, the DLVO ansatz, the separation of forces, is equally invalid. Both the electrostatic and the dispersion forces have to be handled at the same level. Only then will it be possible to estimate the short range forces. Importantly, we can actually calculate the dispersion forces and, hence, their effect on the forces between the particles. We now show that when ionic dispersion forces are included consistently the modified theory that emerges gives quantitatively different results that can accommodate specific ion effects. While the macroscopic-continuum model is probably not accurate enough, it is essential to maintain its use here to focus on the main point. The DLVO theory has appeared to work reasonably well for low salt concentrations ($<5 \times 10^{-2}M$), where electrostatics dominates. At biological concentrations, however, electrostatics is strongly screened. There, and in other systems with high concentrations, the dispersion forces on the ions can be expected to dominate electrostatic forces.

The dispersion potential, in a macroscopic-continuum model, between an ion at a distance x from an air-water interface can be well approximated by [4,18]

$$U_{\text{dispersion}}(x) \approx B/x^3, B \approx (n_w^2 - n_{\text{air}}^2)\alpha^*(0)\hbar\omega_i/8\,, \tag{1}$$

where n_w (n_{air}) is the refractive index of water (air), $\hbar\omega$ is an electron affinity for the ion, and $\alpha^*(0)$ is the static excess polarizability of the ion in water. The static excess polarizability is the change in polarizability of an ion compared to an equivalent volume of water and can be deduced from partial molar volumes of the bulk solutions and refractive index data. The electron affinities are unknown, but must be between an infrared and an UV frequency. In Gaussian units α^* has dimensions of volume, and a lower bound would be, for instance, $\alpha^* = 1\ \text{Å}^3 = 10^{-24}\ \text{cm}^3$. α^* can in fact be much larger, e.g., for an unhydrated anion of radius 2 Å, $\alpha^* \sim 30\ \text{Å}^3$. α^* can be negative due to electrostriction. For CH_3COO^-, having approximately the same electron density as water, we expect very little excess polarizability; for Br^- we expect large excess polarizability. We can thus estimate the dispersion energy. With the parameters taken to be $\omega_i = 10^{15}$-rad/s, $\alpha^* = 2\ \text{Å}^3$, and $n_w = 1.33$, one find that a typical value is $B = 2 \times 10^{-50}\ \text{J m}^3$. In Ref. [14] we used the dispersion coefficients ($B_\pm$) as fitting parameters. We showed that one can accommodate surface tension changes for a large group of salts, i.e., combinations of cations and anions, if dispersion constants of this order of magnitude were used. Inclusion of the dispersion potentials of the counterions has a very important influence on ion density, charge density, self-consistent potential, and on the double-layer force. There can be very large effects on the force when two charged surfaces come close together.

We begin by showing how to calculate the contribution of the ions at concentration c to the free energy of interaction of two parallel plates separated by a distance $2L$. This is found using the Gibbs adsorption equation. In this expression the free energy (F) is found from the internal energy (E) using a coupling constant integration that slowly turns on the interaction [2]:

$$F(c, 2L) = \int_0^c \frac{dc_0}{c_0} E(c_0, 2L)\,, \tag{2}$$

$$E(c_0, 2L) = -k_B T[\Gamma_+(c_0, 2L) + \Gamma_-(c_0, 2L)]\,, \tag{3}$$

$$\Gamma_\pm = c_0 \int_0^{2L} dx\{\exp(-\beta[\pm e\phi + U_\pm(x)]) - 1\}\,. \tag{4}$$

The free energy is directly related to the separation dependence of the adsorption excess $\Gamma_\pm$. Here, ϕ is the electrostatic potential felt by the ions. This is the only term involved in the basic DLVO theory which totally neglects the possibility of other potentials acting on the ions, here given by $U_\pm(x)$. Here, we take the interaction potential to consist of contributions from both image and dispersion potentials. We approximate the image and the dispersion potentials in the presence of two interfaces as

$$U_{\text{dispersion}}(x, 2L) \approx \left[\frac{B_\pm}{x^3} + \frac{B_\pm}{(2L - x)^3}\right], \tag{5}$$

and

$$U_{\text{image}}(\kappa, x, 2L) \approx \frac{e^2(S_1 + S_2)}{16\pi\epsilon_w\epsilon_0}\,, \tag{6}$$

where

$$S_1 = -\ln[1 - \Delta^2 \exp(-4\kappa L)]/L\,, \tag{7}$$

$$S_2 = \Delta^{-1} \sum_{p=1}^{\infty} \left[\frac{e^{-2\kappa[2L(p-1)+x]}}{2L(p - 1) + x} + \frac{e^{-2\kappa(2Lp-x)}}{2Lp - x}\right]. \tag{8}$$

Here, $\Delta \equiv (\epsilon_w - \epsilon_{\text{air}})/(\epsilon_w + \epsilon_{\text{air}}) \approx 1$, with ϵ_{air} and ϵ_w being the dielectric constants of air and water. The inverse Debye length is $\kappa_D = \sqrt{(2\beta e^2 c_0)/(\epsilon_0\epsilon_w)}$, where $\beta = 1/k_B T$, k_B is the Boltzmann constant, and T is the temperature. For $T = 300$ K this becomes $\kappa_D = 0.325([c])^{1/2}\ \text{Å}^{-1}$, where $[c]$ is the molarity of the salt solution. Numerically, we include only the first 200 of the infinite number of images for the image (dispersion) potential. We assume a cutoff radius of 2 Å for the ions to ensure that the potential does not diverge at either interface. The potential does not diverge on the interface in a complete theory [4].

To obtain the self-consistent electrostatic potential (ϕ) we need to solve the nonlinear Poisson-Boltzmann equation:

$$d\phi^2/dx^2 = -e(c_+ - c_-)/(\epsilon_w\epsilon_0)\,, \tag{9}$$

where the ion concentrations are given by

$$c_\pm = c_0\{\exp(-\beta[\pm e\phi + U_\pm(x)])\}\,. \tag{10}$$

There are many possible boundary conditions. Here for the purpose of demonstration and comparison we use the fixed potential boundary conditions: $\phi_0 = \text{const}$ and $d\phi/dx|_{x=L} = 0$. We solve the Poisson-Boltzmann equation numerically using the method of relaxation. Once the self-consistent potential is known, the integrations are performed numerically to obtain the free energy. To obtain the interaction free energy, we subtract off the free energy at infinite separation. This quantity can be related to the measured force (f) between crossed cylinders (of radii R) using the Deryaguin approximation [19]:

$$f/R \approx 2\pi[F(2L) - F(\infty)]\,. \tag{11}$$

The fact that one cannot separate double-layer and dispersion forces causes some difficulty when comparing the various theories, since the image effect would usually need to be included in the double-layer force, but in fact in a full calculation it contributes to the dispersion force. We thus calculated three different kinds of double-layer forces here. These are differentiated by exactly what goes into the microscopic potential U acting on the ions. They are (i) DLVO, i.e., $U = 0$; (ii) DLVO + images, $U = U_{\text{image}}$; (iii) DLVO + images + dispersion $U =$

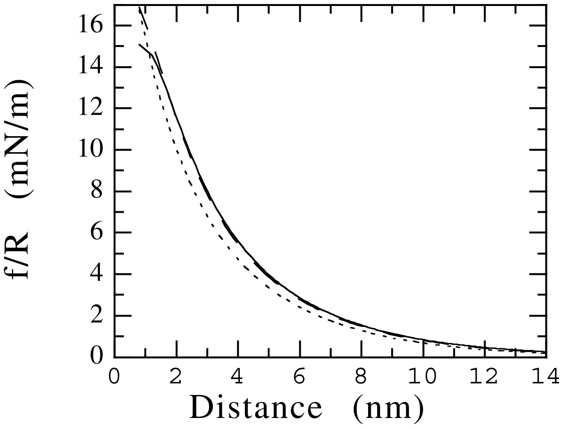

FIG. 1. Calculated force, using the Deryaguin approximation, between charged interfaces (100 mV) across a $0.01M$ salt solution. Three different cases are considered: $U = 0$ (dotted line), $U = U_{\text{image}}$ (dashed line), and finally $U = U_{\text{image}} + U_{\text{dispersion}}$ (solid line).

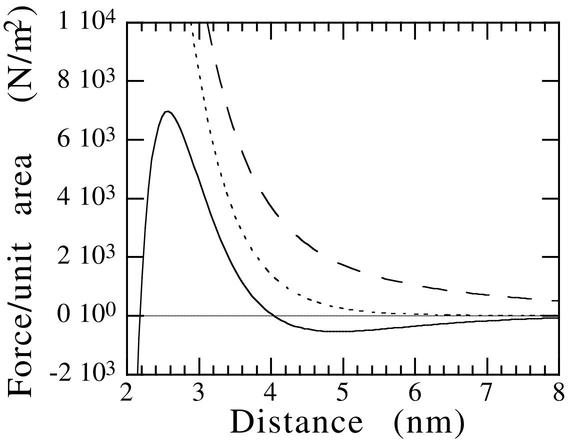

FIG. 3. Calculated force per unit area ($f = -\partial F/\partial d$) between charged interfaces (10 mV) across a $0.3M$ salt solution. Three different cases are considered: $U = 0$ (dotted line), $U = U_{\text{image}}$ (dashed line), and finally $U = U_{\text{image}} + U_{\text{dispersion}}$ (solid line).

$U_{\text{image}} + U_{\text{dispersion}}$. The image potential gives rise to one term that cancels out one part of the ordinary dispersion interaction (the zero frequency term) and replaces it with a term that decays exponentially at large separations [18]. The most interesting comparison is therefore between the latter two cases. As examples, we use values of the dispersion potentials which previously have been shown to give good results for the surface tension of ionic solutions [14] ($B_- = 31 \times 10^{-50}$ J m^3 and $B_+ = -1 \times 10^{-50}$ J m^3).

We begin with a case where the DLVO theory works well, $0.01M$ solution with a plate potential of 100 mV (Fig. 1). Here, we can see that the modifications caused by the ionic dispersion potentials are small. However, when we increase the concentration to that of the biological regime ($0.1M$, 10 mV) (Fig. 2), we find very substantial modification of the double-layer force. This is particularly true for distances less than 30 Å, where the force actually has the opposite sign. At even higher concentrations ($0.3M$, 10 mV), the results are even more dramatic. When ionic dispersion potentials are included, the force can become attractive at both small and large separations with a repulsive barrier at intermediate separations (Fig. 3). This is similar to the secondary minimum found in ordinary DLVO theory. However, one should note that the ordinary electrostatic DLVO force, which this should be compared with, is always repulsive and always decreases monotonically. The most important conclusion here is that ordinary DLVO theory is simply wrong in the biological context. Of course, the ionic dispersion forces affect the force between the plates because they modify the concentration profile, and an example is shown in Fig. 4. We note that there

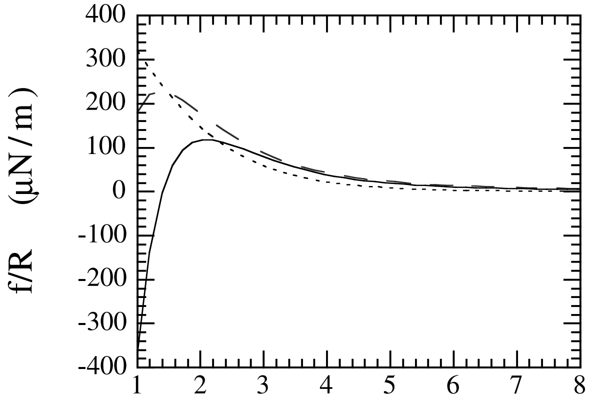

FIG. 2. Calculated force, using the Deryaguin approximation, between charged interfaces (10 mV) across a $0.1M$ salt solution. Three different cases are considered: $U = 0$ (dotted line), $U = U_{\text{image}}$ (dashed line), and finally $U = U_{\text{image}} + U_{\text{dispersion}}$ (solid line).

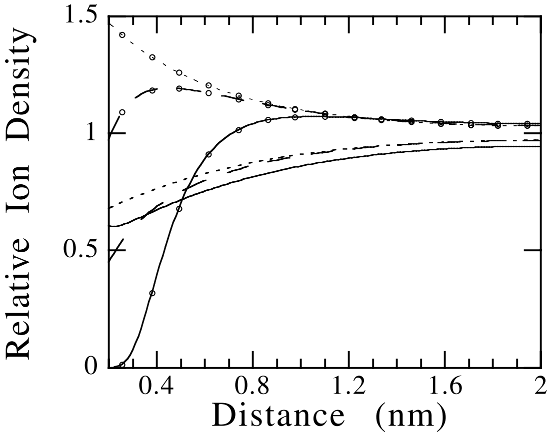

FIG. 4. Relative ion concentration profile for an $0.3M$ salt solution between positively charged interfaces ($\phi_0 = 10$ mV). The counterion (anion) distribution has been marked with open circles to distinguish between anions and cations. Three cases are considered: $U = 0$ (dotted line), $U = U_{\text{image}}$ (dashed line), and finally $U = U_{\text{image}} + U_{\text{dispersion}}$ (solid line).

can be very large effects on the counterion distribution. In the ordinary DLVO theory counterions accumulate close to the surface. At high salt concentrations, when dispersion potentials are accounted for, there may instead be a total depletion very close to the interface. Depending on several factors, dispersion potentials may give rise to either accumulation or depletion of ions close to an interface. How important the effects of dispersion potentials are depends, for instance, on the salt concentration, the magnitude and sign of the dispersion potentials, and on the magnitude and sign of the surface potential (surface charge). We have consequently considered an air-salt solution-air system. The extension to the interaction between, e.g., oil or mica surfaces is straightforward. The dispersion potentials towards the interfaces may change both in magnitude and sign, depending on the optical properties of the interacting surfaces, the salt solution, and the ions (consistent with the known fact that KI adsorbs negatively at an air-water interface and positively at a dodecane-water interface [20]). This gives rise to reduced or enhanced double-layer forces. As we have demonstrated the double-layer force may even become attractive. Similar results have been found using the constant surface charge boundary condition.

The main conclusion of this Letter is that, while the traditional DLVO theory works well for low concentrations of order $0.01M$, it is often very wrong for the biological regime, or for any system where the concentration is of order $0.1M$ or higher. This has very important implications for a whole range of colloidal problems, and also obviously for anyone interested in modeling biological systems. This Letter shows the undoubted importance of ionic dispersion forces. However, in order to solve the full problem we need to produce an analytic theory which takes into account all the forces. The purpose of this simplification is to highlight the effects of including dispersion potentials. Detailed comparison with experiments can be done only if different ions sizes are accounted for. It will also be important to consider dissolved gas [21] and the way dispersion forces are handled in the surface region.

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