

Double Layers and Interparticle Forces in Colloid Science and Biology: Analytic Results for the Effect of Ionic Dispersion Forces

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We study analytically two of the central problems of colloid science: the structure of the double layer surrounding a charged particle and the forces between two such particles. Traditionally, these have been understood using a combination of electrostatic forces acting on the ions and the entropy of the same ions. Here we derive explicit formulas showing how the often dominant dispersion forces between ions and the surfaces can dramatically change the structure of the double layer and the forces.

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The subject of colloid science, which deals with the forces between particles suspended in liquids, should underpin a whole host of important subjects, from physical chemistry to molecular biology, and a whole range of commercially important areas, such as paints and minerals processing. However, despite a vast and an impressive experimental effort, the theories of colloid science are largely incapable of predicting the observed behavior of any given colloidal system. The centerpiece of theoretical colloid science has for over 50 years been the Deryaguin-Landau-Verwey-Overbeek (DLVO) theory [1–3], which ascribes long-range forces between interfaces to the competing effects of van der Waals attraction and electrostatic double layer repulsion. This theory elegantly captured the essential physics of the problem for low ionic concentrations and had some success in matching experimental results within its intended range of validity: ionic concentrations between 10^{-3} and $\sim 5 \times 10^{-2}$ M. However, at higher concentrations—including, crucially, concentrations of biological interest—electrostatic effects become heavily screened, and the DLVO theory fails. It has been demonstrated [4] that the *dispersion potential* between the ions and the interfaces actually dominates over electrostatics in such situations. This decays only as a power law and is almost unaffected by screening. This is because it arises from quantum fluctuations in the background electromagnetic field, and these fluctuations are too rapid for the ions to move significantly in response. Dispersion forces can also account for specific ion (i.e., Hofmeister) effects, which are completely neglected in standard DLVO theory. A series of recent papers [5–7] has demonstrated using numerical calculations how dispersion forces can drastically modify the structure of the ionic double layer and hence the forces between particles due to the overlap of their double layers (one half of the DLVO theory). In this Letter we attack the same problems *analytically*, deriving explicit expressions for the contribution of ionic dispersion forces to (i) the potential (and hence double layer concentration profile) near a single surface and (ii) the potential and

pressure between two surfaces. The effects of ionic dispersion forces on the other part of the DLVO theory, the van der Waals interaction between two surfaces, are not addressed in this Letter but have been studied elsewhere (see [8] and references therein).

The first problem we treat here is that of a single charged planar interface between a solid and a 1:1 electrolyte. The local concentration of ions of species i , $c_i(x)$, can be found by equating the chemical potential of those ions at x with that of the bulk and is given by the Boltzmann equation, $c_i(x) = c_0 \exp[-\beta(e\phi(x) + U_i(x))]$. Here x is the distance of the ion from the interface, e is the elementary charge, ϕ is the electrostatic potential at the ion's position, $kT \equiv \beta^{-1}$ is the thermal energy, c_0 is the bulk concentration, and U_i is an arbitrary external potential. The electrostatic potential experienced by a given ion is simply due to the sum of its interactions with all the other charges in the system. For a given distribution of charge, the potential at any point can be found by solving Poisson's equation $\epsilon(d^2\phi/dx^2) = -\sum_i z_i e c_i$, where ϵ is the dielectric constant of the electrolyte. By combining this with Boltzmann's equation, we obtain the Poisson-Boltzmann (PB) equation, which can in principle be solved to find the average electrostatic potential profile and ionic concentration profiles. Note that this is a mean-field theory, and as such fluctuations in the ionic concentration profiles are neglected, as are effects due to their finite size.

In the standard approach to modeling this sort of system, U_i in Boltzmann's equation is taken to be zero—only the electrostatic interaction is included. We extend the standard approach by setting U to be the dispersion interaction U_{disp} between the ions and the interface, which can be approximated as $U_{\text{disp}}(x) = B/x^3$ (neglecting retardation effects), where B is a coefficient that depends on the excess polarizability of the particular ion in question [9]. In Ref. [7] a typical value for this coefficient is estimated to be $B \sim 2 \times 10^{-50} \text{ Jm}^3$, although for a very highly polarizable ion it might be more than 20 times this value. It is important to stress that

the value of the dispersion coefficient is in general different for every ionic species; thus specific ion effects can be at least partly explained within the framework of this model.

Our equations can be simplified by adopting the dimensionless variables $V \equiv e\phi/kT$ and $X \equiv \kappa x$, where $\kappa = \sqrt{(2\beta e^2 c_0)/\epsilon}$ is the inverse Debye length of the system. The Poisson-Boltzmann equation is then

$$\frac{d^2 V}{dX^2} = \frac{1}{2}(e^{V-\beta U_-} - e^{-V-\beta U_+}), \quad (1)$$

where the subscripts + and - denote the cations and the anions, respectively.

For nonzero U , Eq. (1) is difficult to solve. However, this problem can be dealt with by assuming $V \ll 1$ and $\beta U \ll 1$, which gives us the linearized form of the Poisson-Boltzmann equation:

$$\frac{d^2 V}{dX^2} = V + \beta(U_+ - U_-). \quad (2)$$

If the potential at the plate is fixed at $V = V_0$ and $U_{\pm} = 0$, this has the well-known solution $V = V_0 e^{-X}$ —the Debye-Hückel solution [10,11]. We wish to find a solution for $U = U_{\text{disp}}$. We note first that U_{disp} diverges at $x = 0$. This could be fixed by using a more sophisticated version of the potential, which takes into account the finite size of the ions [9], but it is much simpler to fix the potential at a distance of one ionic radius from the interface rather than at the interface itself. This cutoff distance, x_c , is for simplicity taken to be the same for all ionic species. It is assumed that there is zero charge density between $X = 0$ and $X = X_c$. To summarize, our boundary conditions are $V(X_c) = V_0$ and $V(\infty) \rightarrow 0$.

The exact solution to Eq. (2) with $U = U_{\text{disp}}$ can be found to be

$$V(X) = A e^{-X} + H(X), \quad (3)$$

where

$$H(X) = \frac{\beta \kappa^3 (B_+ - B_-)}{4} \times \left[\frac{1}{X} + \sinh(X) \text{Chi}(X) - \cosh(X) \text{Shi}(X) \right]. \quad (4)$$

Here $\text{Shi}(X) = \int_0^X (\sinh t)/t dt$, $\text{Chi}(X) = \gamma + \ln X + \int_0^X (\cosh t - 1)/t dt$ (γ is Euler's constant), and $A = (V_0 - H(X_c)) e^{X_c}$.

The first term in Eq. (3) decays exponentially with distance from the plate—classic Debye-Hückel (DH) behavior. The second half of the solution, however, deviates from the usual DH behavior and is due entirely to the presence of dispersion forces. Far from the interface, this dispersion-dependent part of the solution has the asymptotic expansion

$$H(X) \simeq -\frac{\beta \kappa^3 (B_+ - B_-)}{2} \left(\frac{1}{X^3} + \frac{12}{X^5} + \frac{360}{X^7} + \dots \right). \quad (5)$$

This clearly decreases more slowly than the DH-like term with increasing X . In fact, at large enough distances from the interface, this part of the solution will dominate and the exponential term will become negligible. To put this another way, when dispersion forces between the ions and the interface are taken into account, the potential far from a flat interface *no longer decays exponentially*. Note that this far-from-the-plate solution makes no reference to the conditions at the plate; thus it should be valid even when V_0 and B_{\pm} are large, provided we are sufficiently far from the plate.

It is also of interest to examine the ion densities far from the plate, which to lowest order are identical: $c_{\pm} = c_0(1 - \beta \bar{B} x^{-3})$, where $\bar{B} \equiv \frac{1}{2}(B_+ + B_-)$ is the average dispersion constant. Thus each ion behaves as if it feels the average force associated with both species. This unusual result occurs because of the electrostatic force between the ions. Even though the electrostatic effects of the surface are negligible, the ions are strongly coupled to each other via local electrostatic effects. The charge density $\rho = e(c_+ - c_-)$ behaves in an unusual way. To lowest order, it is $\rho = 6(\epsilon \Delta B / e x^5)$, where $\Delta B \equiv B_+ - B_-$. Thus ρ is independent of concentration and grows in inverse proportion to the electric charge.

We now examine the case of two plates separated by a distance d (or, in dimensionless units, $D \equiv \kappa d$). We simply superimpose the general one-interface solution for each plate and impose the boundary conditions on the potential $V(X_c) = V(D - X_c) = V_0$ and $\frac{dV}{dX}|_{(D/2)} = 0$. The resulting potential is

$$V(X) = A_2 [e^{-X} + e^{-(D-X)}] + H(X) + H(D - X), \quad (6)$$

where this time the coefficient of the exponential term is

$$A_2 = \frac{V_0 - H(X_c) - H(D - X_c)}{e^{-X_c} + e^{-(D-X_c)}}. \quad (7)$$

This solution comes into play when we calculate the pressure between the two interfaces below. Note that the following derivation of the pressure closely follows that in Ref. [12].

The pressure between the plates is given by $P_{\text{in}} = -\frac{\delta F}{\delta d}$, where F is the free energy of the system and d is the separation of the interfaces (or plates). The free energy can be split into two contributions: $F = F_{\text{PB}} + F_{\text{disp}}$. The first contribution, F_{PB} , corresponds to the energy of the standard PB model, with no dispersion potential added; this includes the electrostatic energy and the entropic energy of the system [13]. The second, F_{disp} , accounts for the dispersion energy of the ions. (Note that we are not including the van der Waals interaction between the plates.) We have

$$F_{\text{PB}} = \frac{\epsilon}{2} \int_{x_c}^{d-x_c} \left(\frac{d\phi}{dx} \right)^2 dx + kT \int_{x_c}^{d-x_c} \sum_i c_i \left(\ln \frac{c_i}{c_0} - 1 \right) dx, \quad (8)$$

$$F_{\text{disp}} = \int_{x_c}^{d-x_c} \sum_i c_i U_i dx. \quad (9)$$

In order to calculate $\delta F/\delta d$, we imagine inserting a small slice of width δd at $x = d/2$ midway between the plates, thereby increasing the plate separation from d to $d + \delta d$. We then consider the corresponding change in the free energy. The change in the PB part of the free energy, δF_{PB} , follows exactly from ordinary PB theory and is calculated in [12]. The change in the dispersion part of the free energy, δF_{disp} , is found to be

$$\begin{aligned} \delta F_{\text{disp}} = & \delta x \left(\sum_i c_i U_i \right)_{d/2} + \int_{x_c}^{d-x_c} dx \sum_i \delta c_i U_i \\ & + 2\delta x \int_{x_c}^{d/2} dx \sum_i c_i \frac{dU_i}{dd}. \end{aligned} \quad (10)$$

The next step is to substitute the Boltzmann equation, in the form $\ln(c_i/c_0) + \beta(z_i e \phi + U_i) = 0$, into the expression for $\delta F \equiv \delta F_{\text{PB}} + \delta F_{\text{disp}}$, which causes many of the terms to cancel out. We further note that $\frac{d\phi}{dx}|_{d/2} = 0$ by symmetry. Dividing through by $-\delta d$ then gives us P_{in} . The total pressure is $P = P_{\text{in}} - P_{\text{out}}$, where $P_{\text{out}} = kT \sum_i c_0$ is the pressure outside the plates; so the final result is

$$P = kT \sum_i [c_i(d/2) - c_{0i}] - 2 \sum_i \int_{x_c}^{d/2} c_i \frac{dU_i}{dd} dx. \quad (11)$$

This is a general expression—so far we have made no assumptions beyond those inherent in the mean-field approximation.

If $U = 0$, the second term in Eq. (11) is zero, and the first term is exactly the same as the expression for the electrostatic pressure between two plates in the DLVO theory [3]. However, with the interaction U turned on, the pressure is modified in two distinct ways: indirectly via the effect of dispersion forces on the ionic concentration profile, which changes the value of the first term; and directly through the second term, which is only nonzero if dispersion forces are included. This term can be thought of as being due to the ions “pulling” on the plates via the dispersion interaction.

We now calculate the pressure explicitly as a function of plate separation by using our solution to the linearized PB equation, Eq. (6). We investigate each term separately. For the first term, we use the Boltzmann equation to express c at the midplane in terms of V and U , and we expand the exponential in a Taylor series keeping only the lowest-order terms in βU_{\pm} and V . On substituting Eq. (6) for V , and assuming a large plate separation so that Eq. (5) is valid, we obtain

$$P_1 \approx 4kTc_0 A_2^2 e^{-\kappa d} - \frac{16c_0(B_+ + B_-)}{d^3}. \quad (12)$$

This represents the pressure due to the overlap of the ionic

double layers. It is valid when $\beta U_{\pm} \ll 1$ and $V \ll 1$ at the midplane, which holds even if they are large at the plates, provided the plate separation is sufficiently large. In the case $B_{\pm} = 0$ (i.e., no dispersion forces), the second term in Eq. (12) vanishes, and we are simply left with the standard DLVO expression for electrostatic pressure, which drops exponentially with plate separation. When $B_{\pm} \neq 0$, however, the second term comes into play. It decays as d^{-3} —much more slowly than the exponential decay of the first term. Thus for a large enough plate separation, the second term will actually dominate over the first. Interestingly, the same power law was found for the pressure due to charge correlation effects between charges adsorbed on flat surfaces [14–16], even though the physical mechanism behind the pressure in Eq. (12) is entirely different. It is important to note that at very large separations the dispersion interaction will become retarded, and Eq. (12) will no longer be valid; however, this should only become an issue for plate separations greater than 10 nm [3].

After similarly evaluating the second term in Eq. (11), again keeping only the lowest-order terms in βU_{\pm} and V , we find $P_2 \approx [14c_0(B_+ + B_-)/d^3]$. This term, which represents the pressure due directly to the dispersion interaction between the ions and the plates, should in fact already be accounted for in the total van der Waals energy of the system through the influence of the ions on the dielectric properties of the medium. We will not discuss this term further, except to point out that it is smaller in magnitude and has the opposite sign to the second term in Eq. (12).

The fact that the second term in Eq. (12) will always dominate over the first at large enough plate separations has three important consequences. The first is that when dispersion forces are present, the double layer pressure between two plates at intermediate separations (between

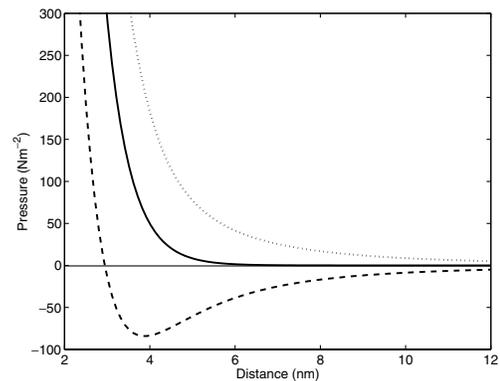


FIG. 1. Double layer pressure between charged interfaces ($\phi = 2.6$ mV) across a 0.3 M salt solution, calculated using Eq. (12). Three different cases are considered: $B_- = -0.3 \times 10^{-50} \text{ Jm}^3$ (dotted line), $B_- = 0$ (solid line), and $B_- = +0.3 \times 10^{-50} \text{ Jm}^3$ (dashed line). $B_+ = 0$ in all three cases. The cutoff distance is $x_c = 2 \text{ \AA}$.

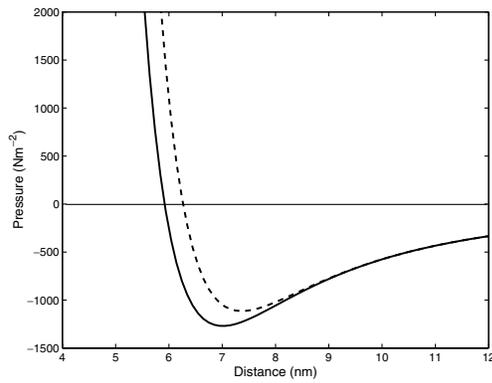


FIG. 2. Double layer pressure between charged interfaces ($\phi = 130$ mV) across a 0.3 M salt solution. The dispersion constants are $B_- = 20 \times 10^{-50}$ Jm³ and $B_+ = 0$ for both curves. The dashed curve is calculated using the approximate analytical expression Eq. (12), and the solid curve is the corresponding exact numerical solution. The cutoff distance is $x_c = 2\text{\AA}$.

a Debye length and the distance at which retardation becomes important) does *not* decay exponentially, but rather as a power law. Second, the magnitude of the pressure at large separations is determined by the strength of the dispersion forces alone; it is (to a good approximation) independent of the potential at the interfaces. Last, if the sum ($B_+ + B_-$) is positive, the second term in Eq. (12) is negative, and thus the pressure as a whole will become *attractive* at large enough plate separation. This contrasts strongly with the standard double layer pressure in the DLVO theory, which is always repulsive.

The effects of dispersion forces on the double layer pressure are illustrated in Fig. 1. Equation (12) is plotted as a function of plate separation for three different values of B_- (for simplicity, B_+ is assumed to be zero). For all curves $V_0 = 0.1$ (which at room temperature corresponds to a plate potential of $\phi_0 = 2.6$ mV) and $c_0 = 0.3$ M. The V_0 and B_- values were chosen to ensure that the linearity condition holds. The most important thing to note here is that when B_- is positive the pressure changes from positive (repulsive) to negative (attractive) beyond a certain plate separation—in this case, at $d \approx 3$ nm. At lower ionic concentrations, the effect of changing B_- is much reduced, since the first term in Eq. (12) dominates to a much larger plate separation.

At these low B and V_0 values, the pressure profiles given by Eq. (12) are identical to the corresponding exact numerical solutions for the pressure, except at very small d . Figure 2 shows that the agreement is still quite good when B and V_0 are large, and the match improves as d increases. This is consistent with our expectation that

Eq. (12) should hold even when V_0 and B are large, for sufficiently large plate separations.

In this Letter, we have given explicit expressions for the double layer structure and the force between planar surfaces including the effect of ionic dispersion forces. In particular, we have shown that at intermediate distances the double layer pressure takes the form of a power law, in strong contrast to the behavior predicted by the standard DLVO theory. The theory presented here highlights a crucial and previously neglected aspect of interparticle interactions. It is by no means complete; most importantly, it must be coupled with a calculation of the total van der Waals energy of the system which takes into account the presence of the ions and their nonuniform distribution between the plates. Many other effects, including image forces, finite-size effects, and water structure, must also be taken into account before we can claim a theory with true predictive power.

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