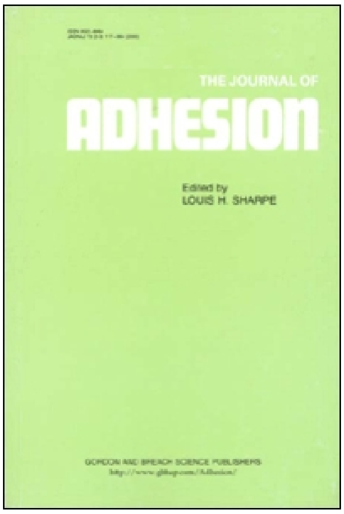

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

A consistent alternative to the dlvo theory

Jan J. Spitzer[a]
[a] IPM Emulsion Polymer Research, Charlotte, North Carolina, USA

To cite this Article Spitzer, Jan J.(2003) 'A consistent alternative to the dlvo theory', The Journal of Adhesion, 79: 10, 893 — 903
To link to this Article: DOI: 10.1080/714906147
URL: http://dx.doi.org/10.1080/714906147

The Journal of Adhesion, 79: 893–903, 2003

ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460390247707

A CONSISTENT ALTERNATIVE TO THE DLVO THEORY

Jan J. Spitzer
IPM Emulsion Polymer Research,
Charlotte, North Carolina, USA

An overview of a new theory of repulsions between charged surfaces is given. The theory is based on consistent Maxwellian electrostatics with linear distribution laws, which predict the existence of co-ion exclusion boundaries. The theory covers interactions from infinity to contact in terms of three electrostatic models: the low potential (LP) model, the co-ion exclusion (CX) model, and the high potential (HP) model. The new theory predicts short-range electrostatic forces that are much stronger than those derived from the nonlinear DLVO theory; no universal Van der Waals adhesion at short distances is predicted. For planar charged surfaces, these short-range electrostatic forces decay according to the inverse square of separation in accordance with experimental observations.

Keywords: Adhesion and disadhesion; Short-range repulsions; DLVO theory; Dissociative electrical double layer; Maxwellian electrostatics; Co-ion exclusion; Ionic atmosphere transitions

INTRODUCTION

The understanding of adhesion at charged surfaces in aqueous electrolyte solutions is of interest in many natural phenomena and in many technical applications. For example, anaerobic bacteria *adhere* to cellulosic fibers in termites' guts, thereby enabling the hydrolysis of cellulose; or colloidal clay platelets *disadhere* (swell) in wet soils, possibly causing structural damage to buildings. Many such seemingly unrelated phenomena are best understood in terms of *molecular forces* that act between charged and uncharged (macro) molecules that

Received 25 April 2003; in final form 27 June 2003.

One of a Collection of papers honoring Jacob Israelachvili, the recipient in February 2003 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

Address correspondence to J. J. Spitzer, IPM Emulsion Polymer Research, 6643 Lyndonville Drive, Charlotte, NC 28277, USA. E-mail: ipmlatexes@ctc.net

comprise adhesive/disadhesive systems [1, 2]. Excluding the consideration of covalent bonding across interfaces, the adhesive/disadhesive phenomena in ionic solutions are dependent on electrostatic and van der Waals forces, as invoked in the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [3].

One general prediction of the DLVO theory is that charged surfaces always adhere at close separations because of the attractive van der Waals forces (primary minimum). In other words, at close separations the electrostatic forces are not strong enough to prevent van der Waals adhesion. However, recent measurements of unexpectedly large repulsive forces between charged surfaces at close separations contradict this general prediction (montmorillonites, mica, phospholipids) [1, 2, 4–7]. Often only "infinite" repulsion is observed. In the absence of theoretical alternatives to the DLVO theory, these short-range forces have been assigned to "hydration" forces [1, 2, 4, 5, 7]; however, such "hydration" forces have not yet been theoretically explained.

The nonlinear Poisson-Boltzmann Equation (PBE), which is used in the DLVO theory to calculate electrostatic repulsions, has long been known to be inconsistent [8–10]. The Maxwellian requirement that the potential, ψ, of a volume element, dV, be proportional to the charge d$q = \rho$dV (Poisson equation) is violated when the exponential dependence between ρ (local charge density) and ψ is invoked according to the Boltzmann theorem. Indeed, the authors of the DLVO theory [3, pp. 22–55] warned against the use of the nonlinear PBE:

> This method of determining $n_{-}(x,y,z)$ and $n_{+}(x,y,z)$ from $\psi(x,y,z)$ is correct only for such small values of the electric potential $\psi(x,y,z)$ that it is permissible to develop the exponential form according to MacLaurin series and to break off after the linear term. For in that case there is a linear relation between ψ and ρ. For larger values of the electric potential the latter is no longer true, and the determination of the mean value of $n(x,y,z)$ from $\psi(x,y,z)$, as indicated is then, strictly speaking, not allowed.

It follows that the nonlinear PBE gives inaccurate theoretical results for the short-range (high potential), coulombic interactions, because it violates Maxwellian electrostatics. A Maxwellian model is, therefore, needed to provide a physically consistent alternative to the DLVO theory.

Recent developments [11–16] of the Dissociative Electrical Double Layer (DEDL) model, incorporating the Lubetkin-Middleton-Ottewill Law (LMO), address the electrostatic inconsistency of the nonlinear Poisson-Boltzmann equation, as epitomized by the Verwey and Overbeek comment cited above. This new model is based on the Maxwellian requirement of linearity between potential and charge distributions. The new model can predict unusually strong repulsions at close separations of charged surfaces; no universal adhesion minima that arise from van der Waals forces are predicted.

THEORETICAL OVERVIEW

There are two particular characteristics of the DEDL-LMO theory.

Firstly, the Debye-Hückel (DH) linear distribution laws are retained to guarantee Maxwellian consistency, including the consistency of calculating electrostatic free energies by different charging processes. The resulting difficulty of negative co-ion concentrations is solved elegantly by the introduction of the co-ion exclusion boundary, b. This boundary divides the ionic atmosphere into the DH type (far away at "infinite" separations), and the counter-ion-only atmosphere (between the surface charge and the DH atmosphere; see Figure 1). The hypothesized co-ion exclusion boundaries come about because the co-ions may not remain in regions where their average repulsive electrostatic energy (free energy) is higher than their average thermal energy. The model is shown schematically in Figure 1 for two interacting double layers, with relevant charge distributions described in the legend.

Secondly, the DH model is enhanced by the explicit incorporation of double layer association; experimental observations indicate that charge densities that are determined by colloidal methods are lower than those determined analytically. Therefore, some counter-ions form a "Stern layer," with the degree of association, α, defined by (Figure 1)

$$\alpha = -\frac{\sigma_a}{\sigma_0} = \frac{1}{1 + p\kappa}. \tag{1}$$

The dependence on ionic strength *via* the DH constant, κ, was determined from experimental data and termed the LMO law [12–14]. The empirical constant, p, determines the sensitivity of the association to ionic strength.

The DEDL-LMO model predicts two kinds of double layers that merge under a singular physicochemical condition. The co-ion exclusion (CX) double layer described in Figure 1 is applicable to high Stern potentials. When the primary surface charge density decreases, the co-ion exclusion boundary, b, moves toward the Stern layer until the singular condition $b = a$ is reached. The CX double layer then becomes a low potential (LP) double layer. This singular condition for planar geometry is derived as

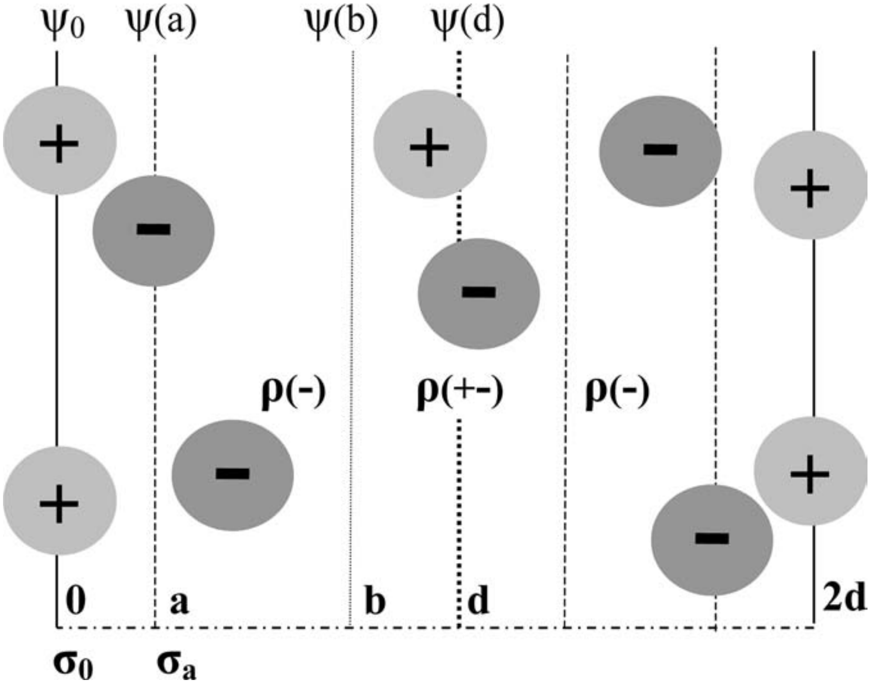

FIGURE 1 The basic structure of the co-ion exclusion (CX) double layer, which consists of the DH ionic atmosphere $\rho(+-)$ between b and d, and of counter-ion-only atmosphere $\rho(-)$ between a and b. At $x = 0$ there is analytical surface charge density, σ_0, and at $x = \mathrm{a}$ there is "Stern" surface charge density, σ_a. These charge distributions give rise to the corresponding Maxwellian potential distributions.

$$\psi^S(a) = \left[\frac{(1-\alpha)\sigma_0}{\varepsilon_0\varepsilon\kappa}\right]^S = \psi_t^+ = \frac{kT}{z_+e}, \tag{2}$$

where $\psi^S(a)$ is the Stern Potential, ${\psi_t}^+$ is thermal electrostatic potential of co-ions, σ_0 is analytical surface charge, $(1-\alpha)$ is the degree of dissociation of the Stern layer, $1/\kappa$ is the famous Debye length, ε_0 and ε are the permittivities of vacuum and of the solvent, respectively, z_+ is the valency of co-ions, e is electronic charge, and kT is the thermal energy. The LP double layers are defined by

$$\psi^{LP}(a) \le \left[\frac{(1-\alpha)\sigma_0}{\varepsilon_0\varepsilon\kappa}\right]^S = \psi_t^+ \tag{3}$$

and the CX double layers by

$$\psi^{CX}(a) \geq \left[\frac{(1-\alpha)\sigma_0}{\varepsilon_0 \varepsilon \kappa}\right]^S = \psi_t^+. \tag{4}$$

Equation (2) represents the *physicochemical continuity* between the LP double layers (they have only the DH ionic atmospheres), and the CX double layers of Figure 1, which have both the DH atmosphere and the counter-ion-only atmosphere.

The co-ion exclusion surface, b, is a free electrostatic boundary, the location of which is determined from the known potential (*cf.* Equation (2))

$$\psi(b) = \frac{kT}{z_+ e} = \psi_t^+ \tag{5}$$

and from the continuity of the electric field across the exclusion boundary, b, as shown in Equation (6):

$$\left(\frac{d\psi}{dx}\right)_{in} = \left(\frac{d\psi}{dx}\right)_{out}. \tag{6}$$

The differential equation for the "inner," counter-ion-only ionic atmosphere (*cf.* the region $a < x < b$ in the CX model, Figure 1), is derived as

$$\nabla^2 \psi = -\frac{\rho_-}{\varepsilon_0 \varepsilon} = \lambda^2 [\psi - \psi_t^-], \tag{7}$$

where λ is defined analogously to the well-known DH constant, κ, but without the co-ion concentration terms, and ψ_t^- is the thermal electrostatic potential of counter-ions, *cf.* Equation (2). The Debye constant, κ, is defined by

$$\frac{n_0 e^2}{\varepsilon_0 \varepsilon kT}(z_+^2 \nu_+ + z_-^2 \nu_-) = \kappa^2, \tag{8}$$

where n_0 is the bulk concentration of strong electrolyte composed of ν_+ moles of co-ions and ν_- moles of counter-ions. The constant λ in Equation (7) is defined as

$$\frac{n_0 e^2}{\varepsilon_0 \varepsilon kT}(z_-^2 \nu_-) = \lambda^2, \tag{9}$$

where the symbols are defined above and in Figure 1. Equations (1) through (9) define the electrostatically consistent (Maxwellian) basis of the DEDL-LMO theory for any geometry and magnitude of surface charges (or potentials).

To gain a more tangible understanding of the workings of the DEDL-LMO model, we now consider what happens when the double layers in Figure 1 are pushed together in a 1:1 electrolyte. The Stern potential, $\psi(a)$, is higher than 25.7 mV, and the midpoint potential, $\psi(d)$, is less than 25.7 mV. On approach, the potentials increase additively in a Maxwellian manner, and the co-ion exclusion boundary, b, at constant potential, Equation (5), moves toward the midpoint separation distance, d. The added electrolyte is being squeezed out from between the plates. When $b = d$, then $\psi(d) = \psi(b) = 25.7\,\mathrm{mV}$, and the CX double layer interaction changes into the High Potential (HP) interaction. This transition separation distance, d_{HP}, is given by

$$d_{HP} = a + \left(\frac{1}{\lambda}\right)\sinh^{-1}\left[\frac{(1-\alpha)\sigma_0}{\varepsilon_0\varepsilon\lambda(\psi_t^+ - \psi_t^-)}\right]. \tag{10}$$

At closer separations, the double layers interact in the HP mode of interaction, when all electrolyte has been expelled from between the plates. These and other transitions are described in detail in Spitzer [16].

One of the most important results to date is the prediction of a new limiting law in the limit of surface contact:

$$\lim_{d\to a} P^{HP}(d) = \left(\frac{p}{1+p\kappa}\right)^2 \frac{\sigma_0^2}{\varepsilon_0\varepsilon}\frac{1}{(d-a)^2}. \tag{11}$$

The limiting repulsive forces are predicted to decay according to the inverse square distance of separation. In the limit of low concentration ($\kappa \to 0$ in Equation (11)), the already diminished dependence on ionic strength drops out completely, giving

$$\lim_{\substack{\kappa\to 0\\ d\to a}} P^{HP}(d) = p^2\frac{\sigma_0^2}{\varepsilon_0\varepsilon}\frac{1}{(d-a)^2}, \tag{12}$$

where the empirical LMO constant, p, characterizes the dissociation of charged surfaces.

RESULTS AND DISCUSSION

The calculation in the HP mode of interactions for montmorillonite gels met with a quantitative success [11], allowing for a simple explanation of "hydration" forces. With similar success, the HP model was applied [12–14] to the extensive data on repulsions in homo-ionic montmorillonites [6], which allowed the empirical derivation of the LMO law (Equation (1)).

The HP model was recently applied to a new set of data for Li-montmorillonites [5] to re-check the validity of the contact limiting law, Equations (11) and (12). The experimental data taken from Figure 5 of Zhang *et al.* [5] are plotted in Figure. 2. The DEDL limiting repulsive laws are seen to be obeyed in the limit of close separations.

The DEDL-LMO model is composed of three electrostatic models, the LP, the CX, and the HP interaction regimes, which allow calculations of repulsive pressures over the total interaction space [16].

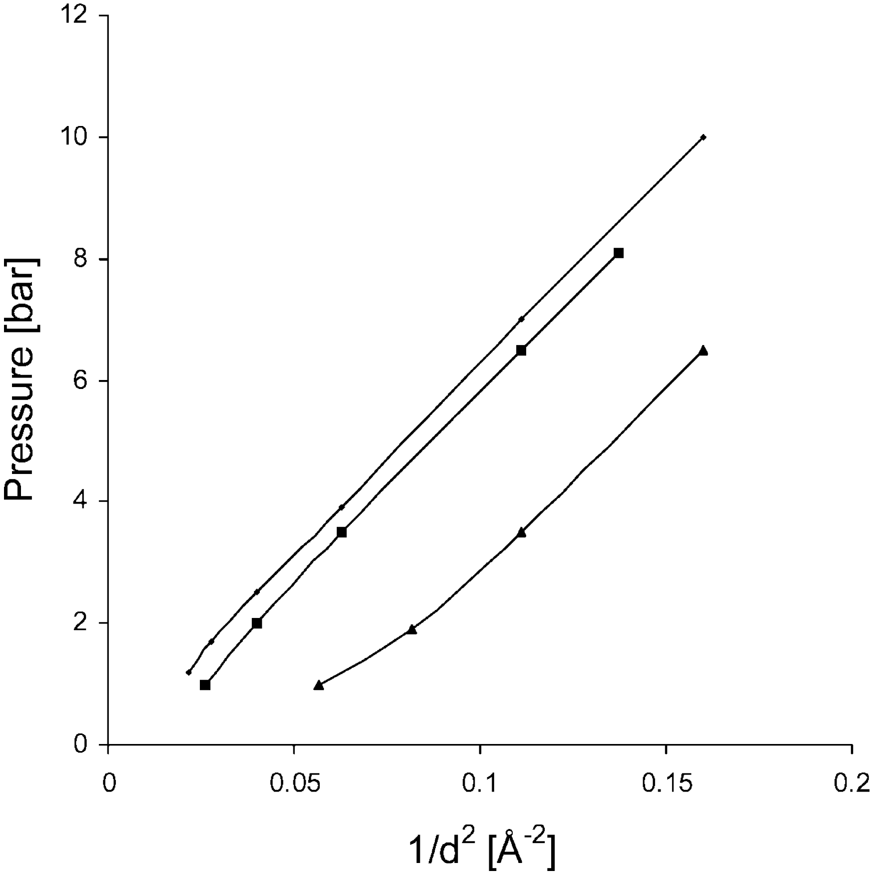

FIGURE 2 Experimental repulsive forces [5] replotted against separation distance. The top curves are two superposed sets of data at 10^{-4} and 10^{-3} molar, the bottom curve at 10^{-1} does not obey the limiting laws as the interaction takes place in the CX mode rather than the HP mode. Thus, between 0.01 and 0.10 molar electrolyte begins to seep between the plates.

In Figure 3 the repulsions are calculated for two flat double layers with charge density of 30 μC/cm^2 and the LMO parameter $p = 0.90$ Å (slightly dissociating double layer); these parameters may be suitable for a mica surface. The calculated data encompass both the exponential decaying forces at large separations, as well as the large repulsive forces in the short-range interaction regime. The overall calculated pressures are similar to the famous experiments with crossed mica cylinders obtained with the Surface Forces Apparatus (SFA) [1, 2] by Israelachvili and his school. The great advantage of these measurements is that forces can be measured over very large separation ranges. In comparison, the data for montmorillonite gels cover only a narrow separation range close to the surface contact. However, as in the case of the montmorillonite gels, very large repulsions were measured with crossed mica cylinders. The mica data are similar to the montmorillonite data, when recalculated into planar geometry [17], which again confirms the limiting law of repulsions given by Equations (11) and (12).

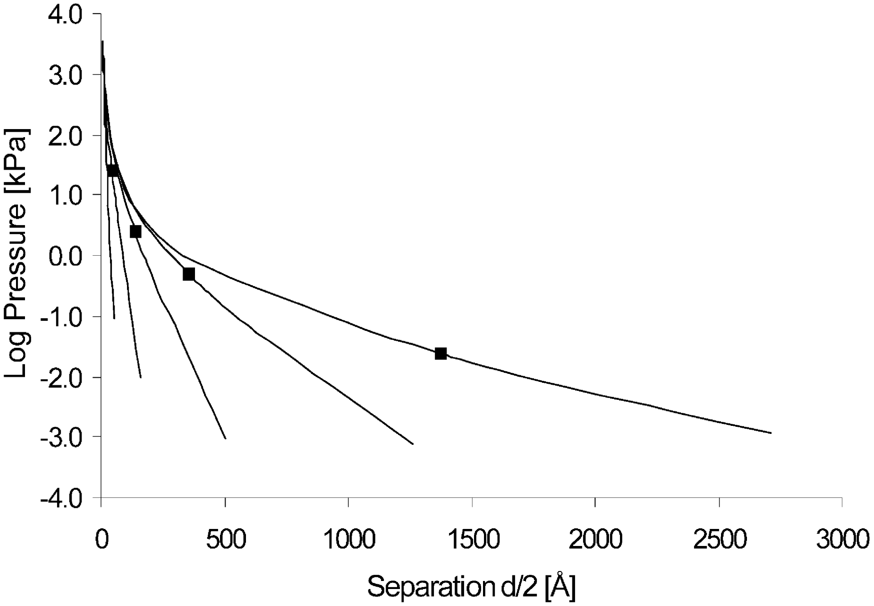

FIGURE 3 Repulsions for flat double layers from infinity to contact. The highlighted points indicate the CX/HP transition (Equation (10)), and the curves cover the ionic strength from 10^{-5} to 10^{-1} molar (1:1) electrolyte (right to left).

The DEDL-LMO model can predict enormous repulsive forces in the close interaction regime in the range of hundreds of megapascals (Table 1). The magnitude of these forces depends, *inter alia*, on the value of the LMO parameter p; the larger its value, the more easily the Stern layer dissociates. At any given ionic strength and separation distance, the degree of association, α, increases, as shown in Table 1, which indicates that the Stern layers assume increasingly hydrated character.

The van der Waals attractive pressure P(vdW) remains the same at the constant separation distance of 10.0 Å; it is calculated from

$$P(vdW) = \frac{A}{6\pi}\frac{1}{(2d)^3}, \tag{13}$$

where the Hamaker constant $A = 2.2 \times 10^{-20}$ J, and d is the midpoint separation distance. The electrostatic repulsions, *P(el)*, are calculated from the midpoint potential, $\psi(d)$.

We can see that the very large repulsive electrostatic pressures, *P(el)*, dominate the total pressure, $P(tot) = P(el) + P(vdW)$, at large values of the LMO parameter, p. These data are calculated for 0.20 molar 1:1 electrolyte (high ionic strength), which shows that stable, nonadhesive repulsions can exist at high ionic strengths at highly hydrated charged surfaces. The DLVO theory cannot explain such electrolyte stability because the nonlinear Poisson-Boltzmann equation underestimates the electrostatic repulsions. For the slightly dissociable double layer with $p = 0.20$ Å in Table 1 (poorly hydrated double layers) the electrostatic repulsion is smaller than the van der Waals attraction, resulting in an overall adhesive force.

TABLE 1 Pressures for a Double Layer with Increasingly "Hydrated" Character

P (Å)	α	P(el) (MPa)	P(vdW) (MPa)	P(tot) (MPa)	ψ(d) (mV)
0.20	0.986	0.32	−1.17	−0.85	31
0.25	0.965	1.18	−1.17	0.01	44
0.50	0.932	5.61	−1.17	4.44	110
1.00	0.872	21.80	−1.17	20.63	230
2.00	0.773	71.90	−1.17	70.73	430
4.00	0.630	195.00	−1.17	193.83	710

The data are calculated for ionic strength of 0.20 molar 1:1 electrolyte in water at 25°C, for two surfaces separated by 10.0 Å, with ionic size of 3.0 Å, and surface charge density 30 μC/cm^2.

CONCLUSIONS

The DEDL-LMO theory provides a self-consistent Maxwellian description of ionic distributions at charged surfaces, characterized by co-ion exclusion boundaries and consequent ionic transitions during interactions. These linear ionic distributions are brought about because co-ions cannot remain, on average, in regions where their repulsive electrostatic energy (free energy) is higher than their average thermal energy. The theory covers interactions from infinity to contact in terms of three contiguous and continuous electrostatic models of low potential (LP), co-ion exclusion (CX), and high potential (HP) interactions.

The most significant result is the prediction of large coulombic forces at high potentials and short separations compared with the nonlinear PBE of the DLVO theory. The larger coulombic forces follow a new limiting law at close separations, where electrostatic forces decay according to the inverse square of separation. This law is confirmed by the data on montmorillonite gels and is in qualitative agreement with Israelachvili's experiments on crossed mica cylinders. However, quantitative theoretical work on the crossed cylindrical geometry is necessary.

As pointed out by Verwey and Overbeek in their initial exposition of the DLVO theory, the nonlinear PBE represents an "unallowed" application of Poisson's equation. Its use in the DLVO theory at close separations (at high potentials) underestimates electrostatic repulsions, giving rise to incorrect prediction of universal van der Waals adhesion. The new DEDL theory utilizes strictly Maxwellian electrostatics, which allows the prediction of larger electrostatic forces than those predicted by the nonlinear PBE; universal van der Waals adhesion is unlikely at charged surfaces.

ACKNOWLEDGEMENTS

Prof. R. H. Ottewill, FRS, OBE, is thanked for continuing interest in this work. Stimulating correspondence and discussions with Prof. J. N. Israelachvili, FRS, are appreciated. An anonymous referee and the Editor in Chief are thanked for suggestions to improve the manuscript.

REFERENCES

[1] Israelachvili, J. N., *Intermolecular and Surface Forces* (Academic Press, London 1985).
[2] Israelachvili, J., and Wennerström, H., *Nature* **379**, 219–225 (1996).

[3] Verwey, E. J., and Overbeek, J. Th. G., *The Theory of Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948), pp. 22–25.

[4] Viani, B. E., Low, P. F., and Roth, C. B., *J. Colloid Interface Sci.* **96**, 229–244 (1983).

[5] Zhang, F., Low, P. F., and Roth, C. B., *J. Colloid Interface Sci.* **173**, 34–41 (1995).

[6] Lubetkin, S. D., Middleton, S. R., and Ottewill, R. H., *Phil. Trans. R. Soc. Lond.* **A311**, 353–365 (1984).

[7] Lis, L. J., McAllister, M., Fuller, N. Rand, R. P., and Parsegian, V. A., *Biophys. J.* **37**, 657–666 (1982).

[8] Onsager, L., *Chem. Rev.* **13**, 73–88 (1933).

[9] Robinson, R. A., and Stokes, R. H., *Electrolyte Solutions* (Butterworths, London, 1959), Chaps. 4 and 9.

[10] Hiemenz, P. C., *Principles of Colloid and Surface Chemistry* (Marcel Dekker, New York, 1977), Chap. 9.

[11] Spitzer, J. J., *Nature* **310**, 396–397 (1984).

[12] Spitzer, J. J., *Langmuir* **5**, 199–205 (1989).

[13] Spitzer, J. J., *Langmuir* **8**, 1659–1662 (1992).

[14] Spitzer, J. J., *Colloid & Polymer Science*, **270**, 1147–1158 (1992).

[15] Spitzer, J. J., *Langmuir*, **18**, 7906–7915 (2002).

[16] Spitzer, J. J., *Langmuir*, **19**, 7099–7111 (2003).

[17] Sposito, G., and Grasso, D., in *Interfacial Forces and Fields*, Hsu, J.-P. (Ed.) (Marcel Dekker, New York, 1999), Chap. 5./