

Importance of Charge Regulation in Attractive Double-Layer Forces between Dissimilar Surfaces

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Direct force measurements between oppositely charged latex particles in aqueous electrolyte solutions were carried out with a multiparticle colloidal probe technique based on atomic force microscopy. Force profiles between two dissimilarly charged surfaces can be only described when charge regulation effects are taken into account, while constant charge or constant potential boundary conditions are inappropriate. Surface potentials and regulation parameters are determined from force data obtained in symmetric systems with the Poisson-Boltzmann theory and constant regulation approximation. The resulting quantities are used to predict the force profiles in asymmetric systems, and good agreement between theory and experiment is found. These findings show that charge regulation is important to quantify double-layer forces in asymmetric systems.

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Surface forces are essential in industrial processes, material engineering, and biology [1–8]. In industrial processes, such as papermaking or food processing, these forces control the stability of particle suspensions and their rheology [1–3]. Surface forces are equally important in the context of new materials, especially in self-assembly [1,4] or surface patterning [5]. In biological systems, such forces are further responsible for interactions involving proteins, nucleic acids, or membranes [6–8]. Surface forces are commonly described by the classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [1]. This approach superposes van der Waals and double-layer forces, whereby the latter are commonly treated within the mean-field Debye-Hückel (DH) or Poisson-Boltzmann (PB) approaches. Additional non-DLVO interaction mechanisms have been identified, such as ion-ion correlation forces [8–10] or specific interactions induced by polymers [1,11,12]. Nevertheless, DLVO theory remains the cornerstone of our picture of surface forces in a wide variety of systems.

Direct force measurements between surfaces across an electrolyte solution became possible only recently. The surface forces apparatus was the first reliable technique to probe surface forces and was crucial to assess the validity of the DLVO theory [1]. This method still remains unsurpassed in its distance resolution in the sub-nm range, and is best suited to study repulsive forces between mica surfaces. Attractive forces between dissimilar surfaces could be measured with this apparatus only recently with a dedicated video system [13].

The colloidal probe technique based on the atomic force microscope (AFM) represents an alternative technique for direct force measurements [14,15]. The standard setup measures the interaction force between a colloidal particle attached to the cantilever and a planar substrate with a resolution of a few tenths of pN. While this technique does

not directly yield the absolute surface separation, this quantity can be reliably estimated for solid substrates from the constant compliance region. Because of the inherent asymmetry between the probe and the surface, dissimilar systems are relatively easily studied, and several reports of attractive double-layer forces between oppositely charged substrates are available [9,16–19]. These reports involve different types of oxides [9,16,17], whose charge has been eventually modified by adsorbed polyelectrolytes [17] or multivalent ions [9]. Attractive double-layer forces were equally observed in systems involving a metal electrode, whose potential was controlled with a potentiostat [18,19]. The striking aspect in these studies is that the strength of the attractions varies widely, especially at closer separations. The purpose of the present Letter is to demonstrate that charge regulation is likely to be responsible for such variations, and that proper description of double-layer forces in dissimilar systems requires the consideration of regulation effects.

The classical description of the electrical double-layer relies on the DH equation for the electrostatic potential [1]

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi, \quad (1)$$

where κ^{-1} is the Debye length given by $\kappa^2 = 2e^2c/\epsilon\epsilon_0kT$ where e is the elementary charge, c the concentration symmetric monovalent electrolyte, $\epsilon\epsilon_0$ the dielectric permittivity of water, and kT the thermal energy. While the DH equation is only valid for small potentials, higher potential can be treated within the PB equation [1]

$$\frac{d^2\psi}{dx^2} = \frac{\kappa^2kT}{e} \sinh\left(\frac{e\psi}{kT}\right). \quad (2)$$

Here we solve Eq. (2) for two plates numerically with a deferred correction technique with the constant regulation

(CR) approximation. This approximation implies the following boundary condition [20,21]:

$$\pm\kappa^{-1}\frac{d\psi}{dx}\Big|_{x=x_{\pm}} = \frac{2kT}{e}\sinh\left(\frac{e\psi_{\pm}}{2kT}\right) - \frac{p_{\pm}[\psi(x_{\pm}) - \psi_{\pm}]}{(1-p_{\pm})}\operatorname{sech}\left(\frac{e\psi_{\pm}}{2kT}\right), \quad (3)$$

where x_{\pm} are the positions of the right (+) and left (−) plane, while ψ_{\pm} and p_{\pm} refer to the surface potentials and to the regulation parameters of the respective plane. The constant charge (CC) boundary conditions are recovered for $p_{\pm} \rightarrow 1$, while constant potential (CP) boundary conditions imply $p_{\pm} = 0$. Since $-\infty < p_{\pm} \leq 1$, the CP boundary condition is not a lower bound to the force [21], but remains a useful reference for highly regulating surfaces. The charge regulation process is normally determined by ionization processes and ion adsorption to the surfaces, but here these details are unimportant. While realistic models of surface charging lead to regulation parameters p_{\pm} varying with the separation distance, assuming this parameter to be constant often provides an excellent description of the force profile down to contact [20]. Within this CR approximation, each surface can be characterized by two parameters, namely, the surface potential and the regulation parameter. Once the potential profile is known, the interaction force follows from the swelling pressure [1]

$$\Pi = 2kTc[\cosh(e\psi/kT) - 1] + \frac{\varepsilon\varepsilon_0}{2}(d\psi/dx)^2, \quad (4)$$

and its integration leads to the interaction energy

$$W = \int_h^{\infty} \Pi(h')dh', \quad (5)$$

where $h = x_+ - x_-$ is the separation distance between the surfaces. The force F between two bodies can be accurately estimated with the Derjaguin approximation

$$F = 2\pi R_{\text{eff}}W \quad (6)$$

where R_{eff} is the effective curvature radius.

A novel multiparticle colloidal probe technique is used to measure forces between two individual colloidal particles [12]. This method is implemented with a closed-loop AFM (MFP-3D, Asylum) mounted on an inverted optical microscope. This approach has two major advantages over the standard colloidal probe technique. First, the internal surface area in the colloidal suspension exceeds a few m^2 , and therefore the measurements are less sensitive to impurities. Second, degassing these suspensions in vacuum for 2 h prior to the experiment eliminates nanobubbles that may otherwise adhere to the surface of the latex particles [22,23]. To study interactions between different types of particles, the fluid cell was separated with a vertical Teflon wall. Particles suspended in an electrolyte KCl solution of adjusted pH with HCl are left to sediment on

the glass substrate functionalized with mixture of 3-(ethoxydimethylsilyl) propylamine and hexamethyldisilazane. In one part of the cell, sulfate latex particles of $1.55 \mu\text{m}$ radius with a conductometric charge of -67 mC/m^2 were used, and in the other part amidine latex particles of radius of $1.65 \mu\text{m}$ and a conductometric charge of $+350 \text{ mC/m}^2$. After about 4 hours, particles not attached to the substrate were removed by flushing with degassed electrolyte solution, and the wall was lifted. A tipless cantilever similarly functionalized with 3-(ethoxydimethylsilyl)propylamine was used to pick up one particle from one side of the cell and to measure the interaction of this particle with another particle from the same or different sides of the cell. Both particles were centered laterally with the optical microscope through interference fringes with a precision of about $0.2 \mu\text{m}$. In this fashion, forces between two amidine particles (++) , between two sulfate particles (−−), and between amidine and sulfate particles (+−) could be measured. The spring constants of the cantilevers were near 0.3 N/m as measured with standard techniques [12], providing a good compromise between force resolution and the avoidance of jump-in instabilities. Zero separation was determined from the constant compliance region to about 0.2 nm . The forces were normalized to the effective radius $R_{\text{eff}} = (R_1R_2)/(R_1 + R_2)$ where R_1 and R_2 are the radii of the interacting particles measured by optical microscopy with a precision of about $0.2 \mu\text{m}$.

Relevant surface properties were determined by direct force measurements between the respective particles in the symmetric systems. At pH 4.0, the highly charged particles are strongly repulsive (Fig. 1). The forces can be quantitatively interpreted by fitting the solution of the PB equation with CR boundary condition [20]. The ionic strengths obtained from the fitted decay lengths agree with the expected values within 15%. The resulting surface potentials are given in Table I, whereby the sign was assigned based on the surface composition of the particles. These potentials are in reasonable agreement with surface potentials obtained with the standard electrokinetic model from electrophoretic data. The resulting surface charge densities are much smaller in magnitude than the ones measured by conductivity, indicating the importance of surface ionization processes [3,24] and renormalization of charge by ion condensation [8]. The forces are consistent with regulation parameters $p_+ \simeq 0.41$ for the amidine latex and $p_- \simeq 0.33$ for the sulfate latex, which are independent of solution conditions. At pH 5.6, the amidine particles are neutral within an experimental error of about $\pm 3 \text{ mV}$, and they interact through an attractive van der Waals force [Fig. 1(b), right inset] [1]

$$F = -\frac{R_{\text{eff}}H}{6h^2}. \quad (7)$$

The best fit leads to a Hamaker constant $H = 4.5 \times 10^{-21} \text{ J}$, which is about half of the value expected

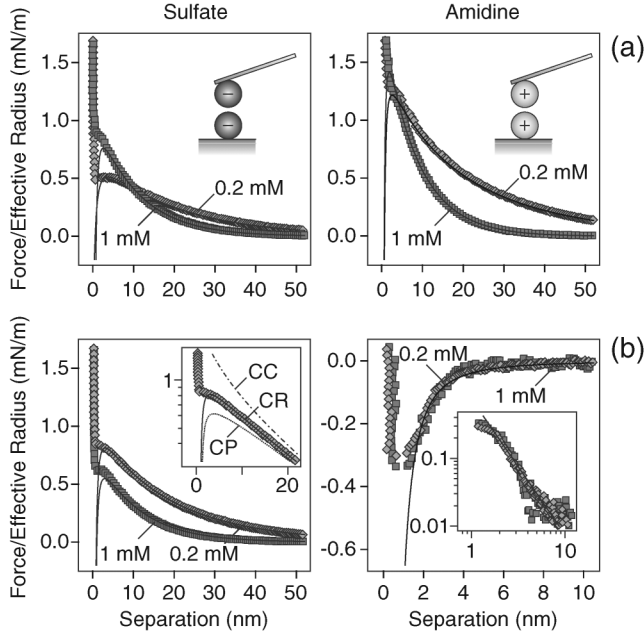


FIG. 1. Force profiles measured with the AFM in symmetric systems involving two individual particles. Sulfate latex (left column) and amidine latex (right column) for different ionic strengths at (a) pH 4.0 and (b) pH 5.6. Solid lines are best fits with PB theory with charge regulation and including the van der Waals force. The left inset in (b) compares the fit to the CR boundary conditions and the conditions of CC and CP. The amidine particles at pH 5.6 are neutral and interact by van der Waals forces. The right inset in (b) shows the expected scaling behavior.

for polystyrene [25]. This deviation is likely due to surface roughness, which is in the range of 0.4–1.3 nm as found from topographic AFM images. The force was independent of solution conditions, and is consistently added to the double-layer forces obtained from PB theory. While the amidine particles are strongly positively charged at pH 4.0, their charge decreases rapidly with increasing pH , and they become neutral at pH 5.6. This behavior can be rationalized by the presence of additional ionizable groups.

The effect of charge regulation on the double-layer forces in the asymmetric systems is shown in Fig. 2. The experimental data are compared with PB model calculation based on the CR approximation whereby the surface potentials and the regulation parameters are taken from the force measurements in the symmetric systems (Table I). Given the fact that predictions in asymmetric systems contain no adjustable parameters, the agreement between experiment and theory is very good.

This comparison reveals that proper description of the charge regulation is important to reliably predict double-layer forces in asymmetric systems. The predictions with CC and CP boundary conditions disagree with the experiment massively, and only predictions involving the charge regulation do capture the experimental data well. At pH

TABLE I. Surface potentials of the particles used.

Ionic strength (mM)	pH	Sulfate latex ψ_- (mV)	Amidine latex ψ_+ (mV)
0.2	4.0	-45.4	+69.9
1.0	4.0	-40.6	+48.6
0.2	5.6	-54.1	0
1.0	5.6	-35.0	0

4.0, two highly but oppositely charged surfaces [Fig. 2(a)] show attractive forces for all three boundary conditions. However, at separations of a few nm the magnitude of the forces predicted with CC and CP boundary conditions differs by 2 orders of magnitude. To obtain reliable force estimates, charge regulation effects must be taken into account, whereby the presently used CR approximation is sufficiently accurate. The discrepancies at shorter separations for 1.0 mM are probably related to its failure. At pH 5.6, the effect of charge regulation is even more dramatic, since one of the surfaces is neutral [Fig. 2(b)]. In this case, CC suggests repulsive forces, while CP attractive ones. With the determined regulation parameters, we predict an attractive force in full agreement with experiment. In this asymmetric system, one could not even foresee the correct

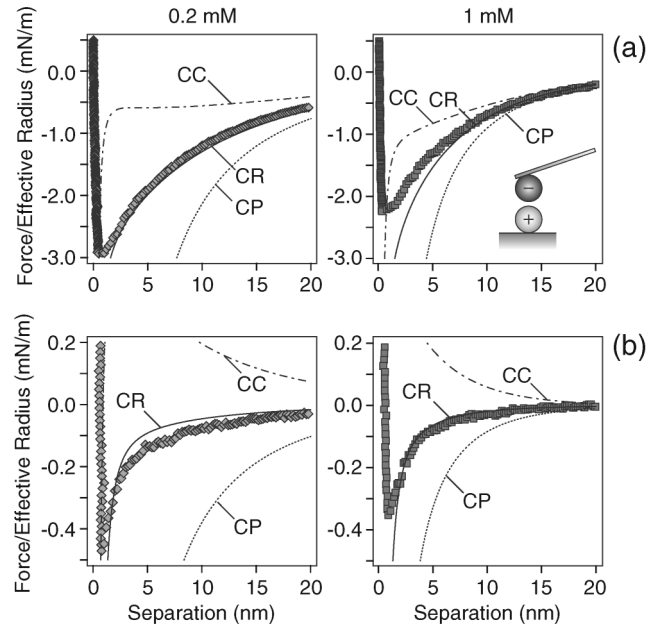


FIG. 2. Force profiles measured with the AFM in asymmetric systems between two individual dissimilar sulfate and amidine latex particles. Ionic strength of 0.2 mM (left column) and 1.0 mM (right column) at (a) pH 4.0 and (b) pH 5.6. The solid lines are predictions of the PB model with CR approximation. All parameters were obtained from force measurements in symmetric systems. The importance of charge regulation is evident from the large differences between CC and CP boundary conditions.

sign of the force without knowledge of the regulation behavior.

These strong charge regulation effects can be rationalized by inspecting the explicitly known DH interaction energy for large distances [26]

$$\frac{W}{\epsilon\epsilon_0\kappa} = 2\psi_+\psi_-e^{-\kappa h} + [(2p_+ - 1)\psi_-^2 + (2p_- - 1)\psi_+^2]e^{-2\kappa h} + O(e^{-3\kappa h}). \quad (8)$$

The first term reflects the fact that oppositely charged surfaces attract at large distances. The next term may be repulsive or attractive, and its sign is determined by the regulation of the surface with the potential of lower magnitude. The second term may override the first one, especially at distances comparable to the Debye length or when the potential of one of the surfaces is small. While the first term is independent of the regulation properties, regulation effects are indeed extremely important for the second term, particularly, when one of the surfaces is (close to) neutral. This strong dependence of the forces in asymmetric systems on regulation effects is in substantial contrast to symmetric systems, where such effects manifest themselves more weakly. In symmetric systems, the first term in Eq. (8) dominates, while the second term represents a correction only, as illustrated by the modest difference between CC and CP boundary conditions [Fig. 1(b), left inset].

The present direct force measurements between dissimilar charged colloidal latex particles clearly demonstrate the relevance of charge regulation. These effects become important for large differences between the magnitudes of the respective surface potentials. When one of the surfaces is close to neutral, these effects even determine the sign of the double-layer force. In the present analysis, all relevant parameters are obtained from force measurements in symmetric systems, and the experimentally observed forces in asymmetric systems can be predicted without adjustable parameters. The CR approximation is sufficiently accurate to capture the main features. Therefore, properties of a charged surface at a given solution composition can be characterized with two parameters, namely, the surface potential and the regulation parameter. While the relation between surface potential and surface properties is well documented [1,3,24], little is known on how the regulation parameter depends on the surface chemistry and the solution composition. However, the knowledge of this parameter is essential to reliably predict double-layer forces in asymmetric systems, especially when one surface is weakly charged. Such charge regulation effects are relevant in surface patterning [5], lubrication [7], or systems containing multivalent ions [8,10]. Additionally, charge regulation will be important between interacting surfaces

with laterally inhomogeneous charge distributions, which occur for mineral particles [24], proteins [27], biological membranes [6], and surfaces with adsorbed polyelectrolytes [12] or surfactants [28,29].

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