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Absence of many-body effects in interactions between charged colloidal particles

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The effects of confining walls and many-body forces on charge-stabilized colloidal suspension are calculated using *ab initio* density functional theory. A Derjaguin-Landau-Verweg-Overbeek pair-potential interaction describes the results quantitatively, with small adjustments to the parameters. We find no evidence for three-body effects or any attraction between colloidal particles with like charges. [S1063-651X(99)50402-9]

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Colloidal suspensions have been extensively employed as model systems for the study of condensed matter and its phase behavior [1]. The energy, length, and time scales associated with colloidal suspensions allow for experimental probing of otherwise inaccessible regimes and have led to new physics, e.g., recent experiments on crystallization kinetics have resulted in a new understanding of nucleation and growth [2] and the low shear modulus of colloidal suspensions has been used for shear-induced ordering and melting studies [3]. Also, many of the properties of these systems can be studied with a systematic variation of the characteristics of the suspensions, such as the sizes and charges of the particles, packing fractions, and the chemical makeup of the solvent. The main handicap in using colloids as model condensed matter systems is the multicomponent nature of the suspensions and the complicated delicate balance between different types of interactions between the components. Ideally, one would like a system characterized by a simple effective pairwise interaction potential.

For charge-stabilized colloidal suspensions, the most commonly used effective pair potential is due to Derjaguin, Landau, Verweg, and Overbeek (DLVO) [4]. The DLVO potential consists of a van der Waals attraction and a screened Coulomb repulsion. The van der Waals contribution to the potential is relatively short ranged and generally negligible in stable suspensions. The non-negligible purely repulsive screened Coulomb part of the potential can be derived from linearized mean-field Poisson-Boltzmann equations, and should, strictly speaking, hold in the low surface charge, low salt, low counterion density, and low packing fraction regime, although the functional form of the DLVO potential with a renormalized charge has been argued to remain valid beyond these situations [5]. DLVO theory has been shown to be consistent with some experimental observations [6–8], but there are yet other experimental facts [9–12] that even the renormalized DLVO theory fails to explain. The main experimental challenges to the theory are numerous indications of a surprising long-range attraction between colloidal particles. The observation of stable sizeable voids and amorphous clustering in colloidal dispersions [12], evidence for liquid-vapor condensation [9] and the existence of long-lived metastable crystallites [10] suggests the presence of a long-range attractive component in the interaction potential. So do measurements of particles' trajectories near a wall [11,7].

A common feature of the experiments where long-range attraction was observed is the confinement of colloidal particles near a (charged) wall or near other colloidal particles. In contrast, in experiments in which forces between two separated colloidal particles far from walls and other particles were measured, no attraction was found [6,13]. In this Rapid Communication, we study the influence of confinement on the effective pair potential between charged colloidal particles. We also address the question of possible many-body effects.

Our model system consists of spherical, charged colloidal particles, often referred to as macroions, small counterions, and a solvent. We do not include salts in this analysis. As in any standard primitive model approach, we do not include the degrees of freedom of a solvent explicitly, but rather treat the solvent as a continuum with a dielectric constant ϵ. The degrees of freedom of the macroions are treated explicitly, while the counterions are described by a density distribution $\rho(\vec{r})$.

Within the adiabatic approximation for the counterions, the effective Hamiltonian for our system can be expressed as

$$\mathcal{H}=\sum_{I}\frac{M_I}{2}\dot{\vec{R}}_I^2+\sum_{I,J<I}U(R_{IJ})+\mathcal{F}. \tag{1}$$

M_I and $\vec{R}_I$ are the masses and coordinates of the macroions. U is the macroion-macroion (Coulomb) interaction potential energy; $R_{IJ}=|\vec{R}_I-\vec{R}_J|$. The free energy of the counterions has the following form in the local density functional theory [14,15]:

$$\mathcal{F}=\int d^3\vec{r}\rho(\vec{r})\left[\phi_{ext}+\frac{1}{2\epsilon}\phi_{int}+\phi_{id}(\rho)+\phi_{corr}(\rho)\right]. \tag{2}$$

The first term in the expression for $\mathcal{F}$, ϕ_{ext}, consists of macroion-counterion and counterion-wall interaction potentials. The second term in $\mathcal{F}$ is the internal (Coulomb) interaction between counterions: $\phi_{int}(\vec{r})=\int d^3\vec{r}'[\rho(\vec{r}')/|\vec{r}-\vec{r}'|]$. The third and forth are ideal gas and correlation contributions to the free energy. The ideal gas term is ϕ_{id}

$=k_BT\{\log[\Lambda_B^3\rho(\vec{r})]-1\}$, where Λ_B is the de Broglie thermal wavelength, k_B is the Boltzmann constant and T is the temperature. The correlation energy can be written in terms of Ψ_{OCP}—the excess free energy per unit volume of a one-component plasma [16]. Given $\mathcal{F}$, the total force acting on a macroion becomes

$$F_I=-\nabla_{\vec{R}_I}\mathcal{F}(\rho(\vec{r}),\phi_{ext})-\nabla_{\vec{R}_I}\sum_J U(R_{IJ}). \tag{3}$$

The equilibrium counterion density $\rho(\vec{r})$ can be obtained from a functional minimization: $\delta\mathcal{F}/\delta\rho=\mu$, where μ is the Lagrange multiplier, determined by the density constraint $\int d^3\vec{r}\rho(\vec{r})=NZ$. Z is the charge of a macroion and N is their number.

An efficient scheme for solving a functional minimization of this type was developed by Car and Parrinello [17] in the context of quantum-mechanical electronic properties calculations, and also used by Löwen, Madden, and Hansen [15] for colloidal suspensions. Expressing the counterion density in terms of a ‘‘wave function’’ $\psi(\vec{r})$ as in a quantum mechanical approach $\rho(\vec{r})=|\psi(\vec{r})|^2$, one can consider the Fourier components of $\psi(\vec{r})$, $\psi_{\vec{k}}$ to be dynamical variables in a Lagrangian:

$$\mathcal{L}=\sum_{\vec{k}}\frac{m_{\vec{k}}}{2}|\dot{\psi}_{\vec{k}}|^2+\sum_I\frac{M_I}{2}\dot{\vec{R}}_I^2-\mathcal{F}-\sum_{I,J<I}U(R_{IJ}). \tag{4}$$

$m_{\vec{k}}$ are fictitious masses determining the time scale of the dynamics of counterion density and M_I are the masses of the macroions. This Lagrangian generates dynamics for macroions and for the counterion density. One can also use this Lagrangian to minimize $\mathcal{F}$ for a fixed macroion configuration by performing dynamical simulated annealing on $\psi_{\vec{k}}$.

For spherical, charged, and hard-core macroions, and hard walls, the counterion density will exhibit a large variation near the hard-core boundary. Because the counterion density is evaluated on a finite grid in actual numerical calculations, a large number of Fourier components in the Fourier expansion of the counterion density is required to express a rapid variation, making the free energy minimization very costly. We use pseudopotentials that allow the hard core of the macroions and walls to be penetrated, thus eliminating the rapid change in density. A good choice for a pseudopotential is a function that is smooth both in real and in Fourier space, such as a Gaussian. In practice, our pseudopotential for macroion-counterion interaction was chosen similar to that of Löwen, Madden, and Hansen [15]: $-Z/(\epsilon r)\mathrm{erf}(r/R_c)$, where R_c is of the order of a half of a macroion radius. The stiffening mechanism for pseudopotentials [15] was also used.

We first simulated two macroions, separated in the z direction, in a periodic cubic box of length 1 μm at the temperature $T=300$ K in water, $\epsilon=78$. The radius of a macroion was chosen to be $a=53$ nm. We performed calculations with charges $Z=200e^-$, $400e^-$, and $600e^-$, corresponding to surface charges of 0.006, 0.011, and 0.017e^-/nm^2, respectively. (e^- stands for the elementary charge.) The counterion density was evaluated on a 96^3 grid. The forces and interaction potentials between macroions were measured as a function of their separation. The DLVO pair potential between two macroions, separated by a distance R_{IJ}, is given by

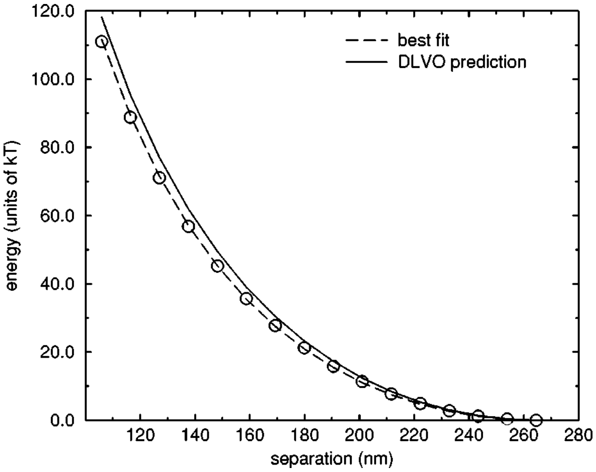

FIG. 1. Total interaction potential energy of a macroion in a periodic system with two macroions and free counterions in the primary simulation cell. The DLVO prediction (solid line) is compared to the numerical local density approximation data (open circles) and the best fit of a DLVO-type potential is also plotted (dashed line). The potentials are shifted to be zero at a maximum macroion separation.

$$U_{DLVO}(R_{IJ})=\frac{Z^{*2}e^2}{\epsilon}\frac{\exp(-\kappa R_{IJ})}{R_{IJ}}, \tag{5}$$

where the inverse Debye screening length, κ, is given by $\kappa^2=4\pi\rho e^2/k_BT\epsilon$ and the effective charge is $Z^*=Z\exp(\kappa a)/(1+\kappa a)$. Due to periodic boundary conditions, we included the interactions between macroions in the primary cell and their periodic images in image cells in the total macroion potential. Assuming additivity of two-body forces and potentials (the validity of this assumption for our system will be proven later), the predictions for the total potential energy of a macroion according to DLVO theory for our parameters in an infinite periodic system for the charge $Z=200e^-$ is plotted in Fig. 1. Our minimization results are indicated on the same plot as well as the total potential resulting from an *optimal* fitted pair potential of the DLVO form that reproduces our data. The numerical values for κ and Z^* for best fits for all charges are given in Table I. Our data are consistent with the expectation that as the charge of a macroion increases, moving us further away from a linear regime, deviations from the DLVO prediction become more pronounced.

Next we confined macroions between two parallel walls in the x direction while maintaining periodic boundary conditions in the y and z directions. The walls were chosen to be short-range repulsive for counterions but not influencing the macroions in the interior—a pseudopotentialtype approximation of hard, uncharged walls. Specifically, the wall-counterion interaction potential was prescribed to be of the form $u_w\exp[-(|\vec{r}-\vec{R}_w|/\sigma_w)^2]$; u_w and σ_w determine the strength and extent of the wall-counterion interaction, whereas $|\vec{r}-\vec{R}_w|$ measures the distance from a wall. An illustration of a two-dimensional counterion density profile in this geometry is shown in Fig. 2. The macroions were placed

TABLE I. The parameters corresponding to the optimal effective pair interaction potential between macroions in different geometries and for different charges. R_x measures the macroion distance from a wall, and u_w and σ_w are wall-counterion potential parameters. κa and Z^* are obtained from the fit. The DLVO prediction for a periodic system are $Z=200$, $Z^*=206$, and $\kappa a=0.26$; $Z=400$, $Z^*=422$, and $\kappa a=0.37$; and $Z=600$, $Z^*=648$, and $\kappa a=0.45$.

	R_x (nm)	u_w (k_BT)	σ_w (nm)	κa	Z^* (e^-)	Z (e^-)
1				0.37	213	201
2	265	100.0	50.0	0.45	220	203
3	185	100.0	50.0	0.44	216	200
4	106	100.0	50.0	0.31	207	199
5	265	300.0	50.0	0.46	221	203
6	185	300.0	50.0	0.44	216	200
7	106	300.0	50.0	0.28	206	199
8				0.67	475	406
9	265	100.0	50.0	0.77	499	409
10	265	300.0	50.0	0.79	505	410
11				0.94	782	595
12	265	100.0	50.0	1.03	820	595

at different x locations—different distances from a wall—and the forces and interaction potentials between them were measured as before. The data were fit to the DLVO pair potential for the periodic system as described above and the fitting parameters, κ and Z^*, are given in Table I. The repulsive walls expel counterions, excluding them from a certain fraction of the volume. The density of counterions in the nonexcluded region increases, decreasing the Debye screening length. One also notices the increase of the Debye screening length as the macroions are moved closer to the walls. This is consistent with the observation that near the walls the counterion density is reduced due to the influence of the finite tail of the wall-counterion interaction potential. All of these effects are expectedly more apparent for more repulsive walls and higher macroion charges.

Finally, we turn to a check of the validity of the assumption of additivity of the forces, and for a possible signature of a three-body component in the effective interparticle potential. Maintaining our previous pseudopotential parameters by increasing the system size appropriately, we studied the following geometries for $Z=200e^-$ in a unit cell with periodic boundary conditions. First, we positioned the three macroions in configurations of equilateral triangles of different sizes and calculated the force on one of the macroions as a function of the edge of the triangle. In Fig. 3, we plot our data for the force in these configurations as a function of the distance and compare it to the force obtained from an additive pair potential. We use the optimal parameters from Table I for the comparison. Secondly, we also placed the three macroions in an asymmetric triangular configuration where two macroions were close to each other (separation of 106 nm) and a third macroion was at a distance of 250 nm from either of the two. We measure a force of 10.0

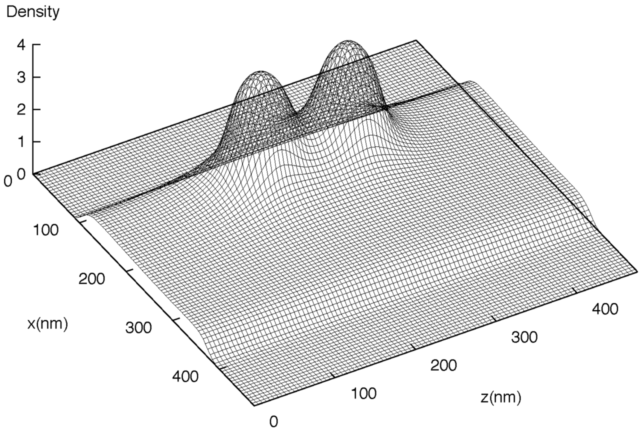

FIG. 2. Example of a two-dimensional projection of the counterion density in the primary simulation cell. The two macroions in the cell are located at ($x=185$ nm, $z=201$ nm) and ($x=185$ nm, $z=328$ nm), while the system is confined between two walls parallel to the y-z plane, centered at $x=0$ nm and $x=530$ nm in the x direction.

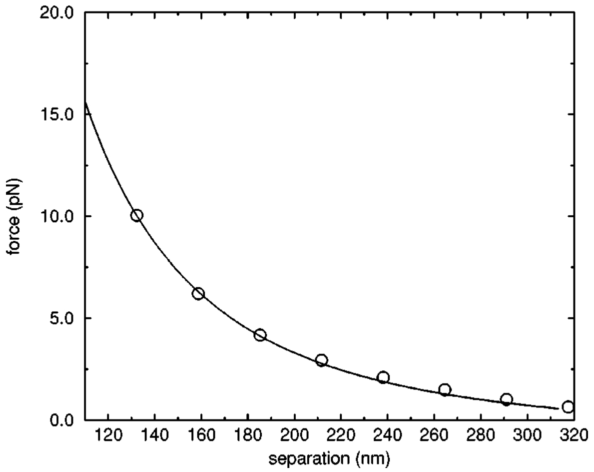

FIG. 3. Test of the additivity of the effective macroion potential. Three macroions were placed in equilateral triangular configurations and the force on a macroion as a function of the distance between two macroions was measured. Open circles are our data, whereas the solid line indicates the force from an additive DLVO-type potential with the parameters $Z^*=212.5e^-$, $\kappa a=0.374$.

$\times 10^{-12} N \pm 0.5 \times 10^{-12} N$ on either one of the first macroions while pairwise additive forces predict $9.8 \times 10^{-12} N \pm 0.5 \times 10^{-12} N$ for the value. Thus, we detect no three-body component in the effective forces.

In conclusion, we have measured the forces and found effective interaction potentials between charged colloidal particles suspended in a liquid and surrounded by free counterions in bulk and near a ‘‘soft’’ wall using an *ab initio* density functional theory approach. A DLVO pair-potential interaction describes the results quantitatively, with small adjustments to the parameters. We also checked for possible three-body effects in the presence of a third macroion. No evidence for a detectable three-body component was found. Our results suggest that long-range attraction cannot be induced by counterion confinement (i.e., pure exclusion from a region) alone [18]. In the future, it would be desirable to incorporate charged walls to be able to pinpoint the effects of electrostatic interactions when compared to the purely geometric effects studied here.

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