# *Ab initio* Description of Counterion Screening in Colloidal Suspensions

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(Received 16 September 1991)

A classical version of the Car-Parinello method is proposed, combining density-functional theory for the counterions and molecular dynamics for the macroions, to simulate charged colloidal suspensions. The classic Derjaguin-Landau-Verwey-Overbeek (linear screening) theory is shown to fail for large macroion packing fractions.

PACS numbers: 82.70.Dd, 61.20.Gy

Charge-stabilized colloidal suspensions are very asymmetric ionic systems made up of highly charged macroions of radius $R \approx 10-10^3$ nm, and oppositely charged microscopic counterions, dissolved in water or some other polar solvent. The macroion charge $Ze$ is due to surface dissociation and amounts typically to a few hundred elementary charges. The ionicity of the suspension may be enhanced by adding salt, thus allowing the electrostatic (Debye) screening length $\lambda_D$ to be tuned. In the "primitive model" picture of electrolytes, the molecular solvent is replaced by a continuum of dielectric constant $\epsilon$. The microscopic co-ions and counterions form electric double layers near the macroion surfaces, of width comparable to $\lambda_D$; these double layers provide a short-range repulsion between macroions, ensuring the stability of the suspension.

In the traditional statistical description of charge-stabilized suspensions, the adiabatic approximation is invoked to eliminate the co-ion and counterion degrees of freedom and construct a screened, effective pair potential between macroions. If the interaction between the electric double layers associated with two neighboring macroions is treated within linearized Poisson-Boltzmann theory, a simple Debye-like effective pair potential $\sim\exp(-r/\lambda_D)/\epsilon r$ results, which is the electrostatic part of the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) potential [1]. The DLVO approach has been frequently questioned, both on theoretical [2] and experimental [3] grounds. Besides the restrictions to linear screening, the theory neglects, by construction, double-layer fluctuations and simultaneous interactions of more than two double layers, which, contrary to the bare Coulomb interactions, are not pairwise additive, and would result in effective triplet and higher-order forces between macroions. In fact, the DLVO potential has frequently been used with an *adjustable* macroion charge to interpret experimental data for the static structure factor $S(k)$.

The deficiencies of DLVO theory can, in principle, be circumvented by an *ab initio* statistical approach, where macroions and counterions are treated on an equal footing within a model incorporating, besides the usual excluded-volume constraints, only bare Coulomb interactions. Such a model may then be examined via Monte Carlo or molecular dynamics (MD) computer simulations [4], or within the framework of nonlinear integral equations for the pair structure [5], but such first-principles calculations become rapidly untractable for large size and charge asymmetries, typical of colloidal suspensions.

In this Letter we propose an alternative *ab initio* approach, combining density-functional theory (DFT) and MD simulations, directly inspired by the Car-Parinello method for ion-electron systems [6,7]. The subsequent discussion will be restricted to salt-free suspensions, containing only spherical macroions, of radius $R$, and counterions. While the degrees of freedom of the former will be treated explicitly, the counterion component will be described, for each macroion configuration and within the adiabatic approximation, by the instantaneous inhomogeneous one-particle density $\rho_c(\mathbf{r})$. The free energy of the counterions is a functional of $\rho_c(\mathbf{r})$, and depends parametrically on the macroion configuration $\{\mathbf{R}_j\}$ ($1 \le j \le N_m$). It is conveniently separated into ideal, external, Coulombic, and correlation parts

$$\mathcal{F} = \mathcal{F}_{\text{id}} + \mathcal{F}_{\text{ext}} + \mathcal{F}_{cc} + \mathcal{F}_{\text{corr}}, \tag{1}$$

$$\mathcal{F}_{\text{id}} = k_B T \int d\mathbf{r}\, \rho_c(\mathbf{r}) \{\ln[\Lambda_c^3 \rho_c(\mathbf{r})] - 1\}, \tag{2a}$$

$$\mathcal{F}_{\text{ext}} = \int d\mathbf{r}\, \rho_c(\mathbf{r}) V_{\text{ext}}(\mathbf{r}, \{\mathbf{R}_j\}) = \sum_{j=1}^{N_m} \int d\mathbf{r}\, \rho_c(\mathbf{r}) v_{mc}(|\mathbf{r} - \mathbf{R}_j|), \tag{2b}$$

$$\mathcal{F}_{cc} = \frac{e^2}{2\epsilon} \int\int d\mathbf{r}\, d\mathbf{r}' \frac{\rho_c(\mathbf{r})\rho_c(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{2c}$$

where $\Lambda_c$ is the de Broglie thermal wavelength of the counterions, which are assumed to be monovalent, and $v_{mc}(r)$ denotes the macroion-counterion pair potential, which is Coulombic ($-Ze^2/\epsilon r$) for $r > R$. $\mathcal{F}_{\text{corr}}$ accounts for the counterion correlations; since the counterions Coulomb repel each other, it is a reasonable approximation to neglect their size, so that they form an inhomogeneous one-component plasma (OCP) of point charges. For $\mathcal{F}_{\text{corr}}$ we finally adopt the local-density approximation [8]:

$$\mathcal{F}_{\text{corr}} = \int d\mathbf{r}\, f_{\text{OCP}}^{\text{ex}}(T, \rho_c(\mathbf{r})), \tag{2d}$$

where $f_{\text{OCP}}^{\text{ex}}$ denotes the excess free energy per unit volume of the homogeneous OCP at temperature $T$ and number density $\rho_c=\rho_c(\mathbf{r})$; $f_{\rm OCP}^{\rm ex}/k_BT\rho_c$ is well known as a function of the dimensionless Coulomb coupling constant $\Gamma_c=e^2/\epsilon a_c k_B T$, where $a_c=(3/4\pi\rho_c)^{1/3}$ [9].

The one-particle density may then be calculated by minimizing the approximate free-energy functional $\mathcal{F}([\rho_c(\mathbf{r})];\{\mathbf{R}_j\})$, defined by Eqs. (1) and (2a)-(2d), with respect to $\rho_c(\mathbf{r})$, subject to the global charge-neutrality constraint,

$$\int_V d\mathbf{r}\,\rho_c(\mathbf{r})=N_c=ZN_m\,. \tag{3}$$

Once $\rho_c(\mathbf{r})$ has been determined for a given macroion configuration, the counterion-induced force acting on the $j$th macroion follows from the Hellmann-Feynman theorem,

$$\begin{aligned}\mathbf{F}_j&=-\nabla_{\mathbf{R}_j}\mathcal{F}([\rho_c(\mathbf{r})];\{\mathbf{R}_j\})\\&=-\int d\mathbf{r}\,\rho_c(\mathbf{r})\nabla_{\mathbf{R}_j}v_{mc}(|\mathbf{r}-\mathbf{R}_j|)\,.\end{aligned}\tag{4}$$

In the case of a weak inhomogeneity and small macroion density, one is justified in neglecting $\mathcal{F}_{\rm corr}$ and expanding $\mathcal{F}_{\rm id}$ to second order in $\rho_c(\mathbf{r})-\bar\rho_c$, where $\bar\rho_c=N_c/V$ is the mean density of the counterions. Then, the above variational problem may be solved exactly. The resulting $\rho_c(\mathbf{r})$ is then a superposition of Debye orbitals centered on the $\mathbf{R}_j$, and the standard DLVO pair potential between macroions is recovered, provided the constraint is imposed that $\rho_c(\mathbf{r})$ vanishes whenever $|\mathbf{r}-\mathbf{R}_j|<R$. More generally, a quadratic free-energy functional always leads to strictly pairwise additive interactions, and higher-order terms in the functional Taylor expansion yield more-than-two-body effective interactions between macroions.

The variational problem cannot, however, be solved analytically with the full free-energy functional (1), and one must resort to numerical simulation. Following the ideas of Car and Parinello [6], the counterion density $\rho_c(\mathbf{r})$, or, more precisely, its Fourier components $\rho_{\mathbf{k}c}$, are regarded as dynamical variables coupled to the macroion degrees of freedom; classical equations of motion are derived from the Lagrangian

$$\begin{aligned}\mathcal{L}=&\tfrac{1}{2}M\sum_{j=1}^{N_m}\dot{\mathbf{R}}_j^2+\tfrac{1}{2}m_f\sum_{\mathbf{k}}|\dot\rho_{\mathbf{k}c}|^2\\&-\sum_{i<j}v_{mm}(|\mathbf{R}_i-\mathbf{R}_j|)-\mathcal{F}([\rho_c(\mathbf{r})];\{\mathbf{R}_j\})\,,\end{aligned}\tag{5}$$

where $M$ is the physical macroion mass, $v_{mm}$ is the direct macroion-macroion pair potential (which is purely Coulombic for $|\mathbf{R}_i-\mathbf{R}_j|>2R$), overdots denote time derivatives, while $m_f$ is a fictitious mass associated with the dynamical variables $\rho_{\mathbf{k}c}$. If, in appropriate units, $m_f$ is chosen $\ll M$, the resulting one-particle density is expected to stay close to the true adiabatic solution along the phase-space trajectory mapped out by MD simulations of the equations of motion for the $\mathbf{R}_j$ and $\rho_{\mathbf{k}c}$ derived from the Lagrangian (5).

A technical difficulty arises from the fact that $\rho_c(\mathbf{r})$ is a rapidly varying function in the vicinity of the macroion surfaces; as a result of the combination of excluded-volume effects for $|\mathbf{r}-\mathbf{R}_j|<R$ and strong Coulomb attraction for $|\mathbf{r}-\mathbf{R}_j|>R$, the counterions pile up in the electric double layers, where $\rho_c(\mathbf{r})$ rises sharply above the mean counterion density $\bar\rho_c$. Hence a very large number of Fourier components (with wave vectors $\mathbf{k}$ compatible with the periodic boundary conditions imposed on the basic simulations cell) is required to yield a reasonably accurate representation of $\rho_c(\mathbf{r})$. The present situation is even worse than the quantum-mechanical ion-electron case [6] because of the high macroion charge. In the latter case a pseudopotential is constructed to avoid the rapid oscillations of the true valence-electron wave function inside the ion core, such that the resulting pseudo wave function agrees with the true wave function outside the core region, but remains smooth inside, while conserving the norm. We have followed a similar idea in the present, purely classical context, to suppress the discontinuous behavior of the local density $\rho_c(\mathbf{r})$ at the macroion surfaces. Our procedure involves two closely related steps. First the conterions are allowed to penetrate the macroions by suppressing the macroion-counterion repulsion for $r<R$ and replacing it by a smooth extrapolation of the Coulomb attraction. In practice we replaced the true macroion-counterion pair potential by the "pseudopotential" $v'_{mc}(r)=-(Ze^2/\epsilon r)erf(r/R_c)$, where $R_c\simeq R/2$. The extra (unphysical) counterion charge inside the macroion core is compensated by increasing the macroion charge from $Ze$ to $(Z+Z^*)e$, so that the total macroion charge (renormalized surface charge plus counterion charge of opposite sign inside the core) remains, on average, equal to the physical charge $Ze$; the average counterion density $\bar\rho_c$ is increased accordingly. It is important to stress that $Z^*$ is *not* an adjustable parameter, but is uniquely determined as explained below. The permeability of the macroions leads to spurious fluctuations of the counterion charge density inside the cores. These fluctuations are stabilized by simultaneously assigning a severe free-energy handicap to the excess counterion charge; this is achieved by modifying the free-energy functional for counterion densities exceeding a cutoff value $\rho_c^{\rm cut}$ so as to stiffen $\rho_c(\mathbf{r})$ inside the cores. In practice, we added an arbitrary positive free-energy contribution to $f_{\rm OCP}^{\rm ex}$ in the correlation term (2d), which increases rapidly for counterion densities $\rho_c>\rho_c^{\rm cut}$.

The whole pseudopotential procedure sketched above should result in a counterion density $\rho_c(\mathbf{r})$ which is smooth inside the macroion cores, but coincides with the physical counterion density outside the cores. The auxiliary parameters $Z^*$ and $\rho_c^{\rm cut}$ were determined self-consistently, for given values of the temperature $T$ and macroion density $\rho_m=N_m/V$, by explicit solutions of the variational problem for a highly simplified geometry, involving a single macroion in its spherical Wigner-Seitz cell [10]. For this geometry, $\rho_c(\mathbf{r})$ was calculated for the two situations where the macroion core is penetrable and impenetrable by the counterions. $\rho_c^{\rm cut}$ was chosen equal to the value of $\rho_c(\mathbf{r})$ at the surface of the impenetrable macroion, while $Z^*$ was varied until the total charge of the penetrable macroion matched the physical charge $Ze$ of the impenetrable macroion, thus ensuring strict equality of the two counterion densities outside the core, in view of the spherical geometry and Gauss' theorem. Since the local environment of a macroion in a concentrated suspension has approximately spherical symmetry, it is reasonable to assume that the previousely determined values of $\rho_c^{\rm cut}$ and $Z^*$ are transferable to the many-particle configurations generated during the simulations. This transferability was explicitly checked during the MD runs by monitoring the total counterion charge inside the macroions; the latter was always found to differ by less than 1% from the assumed $Z^*$ value. Moreover the root-mean-square dipole moment of the charge distribution inside the penetrable macroions was found to be systematically only a very small fraction (less than 1%) of the characteristic dipole $Z^*eR$.

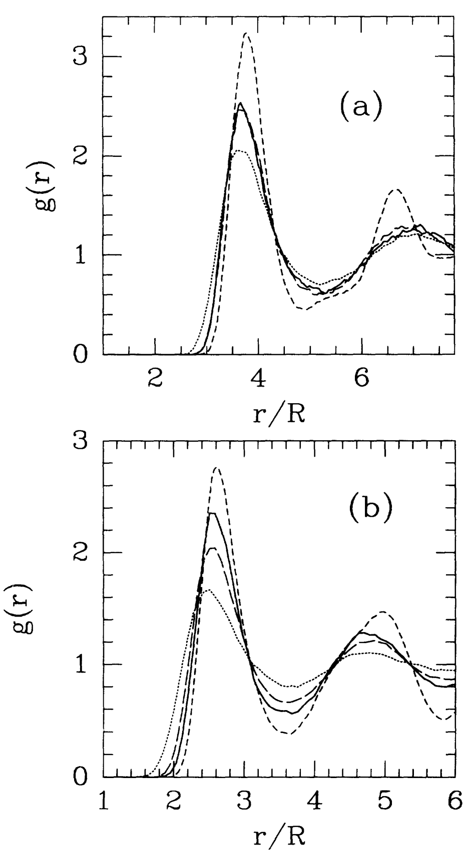


FIG. 1. Macroion-macroion pair correlation function $g(r)$ vs reduced distance $r/R$ for (a) run 1 and (b) 2 (solid lines). The other curves are based on Debye-like pair potentials, calculated from DLVO theory (long-dashed curve), mean-spherical-approximation-like theory [2] (short-dashed curve), and the Poisson-Boltzmann cell theory of Ref. [10] (dotted curve).

The whole procedure was implemented in two extensive MD runs and the results compared to those based on the pairwise additive, effective DLVO potential between macroions. Room temperature ($T=300$ K) was imposed by a Nosé thermostat [11] for the macroions, $\epsilon$ was taken to be equal to 78 (water), while $R=53$ nm. $\rho_c(\mathbf{r})$ was defined on a $64^3$-point grid and statistical averages taken over $10^4$ time steps of length $\Delta t=0.0015\tau_0$, $\tau_0=(MR^2/k_BT)^{1/2}$. In run 1, $Z=200$, $N_m=31$, and the macroion packing fraction $\eta=4\pi\rho_m R^3/3=0.1$, the resulting $Z^*=66.6$, while $\rho_c^{\rm cut}R^3=11.6$. In run 2, $Z=100$, $N_m=53$, and $\eta=0.3$ ($Z^*=67.3$, $\rho_c^{\rm cut}R^3=12.5$). In both cases counterion screening is expected to be relatively weak, since $\lambda_D$ turns out to be comparable to $R$.

The macroion-macroion pair distribution function $g(r)$ from run 1 is compared in Fig. 1(a) to the corresponding results based on the DLVO potential, and on two modifications of this effective pair potential [2,10]. In this case DLVO theory is seen to provide a reasonable effective interaction between macroions, whereas the $g(r)$'s calculated from the two modified theories strongly overestimate or underestimate the macroion structure. At the higher packing fraction (run 2), however, significant differences arise between the pair distribution functions calculated from DLVO and *ab initio* theories, as illustrated in Fig. 1(b), while the two modified effective pair potentials are found to fail completely. Strong discrepancies between *ab initio* and DLVO-type theories are also apparent in the macroion bond-angle distribution function $g_3(\theta,r)$ shown in Fig. 2 for the same state point and for all macroion spacings $r \leq 3.2R$. This function provides a measure of triplet correlations in the suspension.

In summary, we have proposed an *ab initio* procedure for the simulation of charge-stabilized colloidal suspensions, which properly includes nonlinear screening and

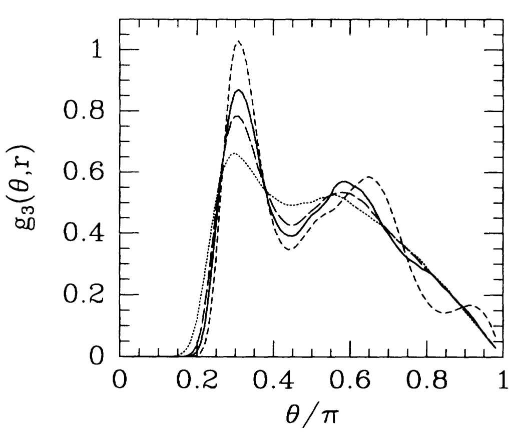


FIG. 2. Bond-angle distribution function $g_c(\theta,r)$ of particle triplets that have two interparticle distances smaller than $r=3.2R$ vs reduced bond angle $\theta/\pi$. The thermodynamic state and the symbols are as in Fig. 1(b).

many-body interactions between macroions induced by the counterions. The traditional DLVO theory is found to fail for large macroion packing fractions. The present method may be extended to treat the strong screening regime in the presence of a high concentration of added salt, a situation which is expected to enhance the discrepancies between *ab initio* and DLVO results. Whereas MD was used in the present work, which was restricted to static equilibrium properties, the *ab initio* method may also be combined with Brownian dynamics [12] to investigate macroion diffusion and other time-dependent properties. Work along these lines is in progress.

The authors are very grateful to Dahlia Remler whose clearly written Car-Parinello program formed the basis for the developments described here, and to Alberto Meroni for valuable assistance in the computations. H.L. acknowledges financial support by Deutsche Forschungsgemeinschaft. Part of this work was done while P.A.M. was on the Louis Néel Chair sponsored by the Société Lyonnaise de Banque. Laboratoire de Physique de l'Ecole Normale Supérieure de Lyon is Unité de Recherche Associée No. 1325 of the Centre National de la Recherche Scientifique.

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