Electrostatic Attraction and Phase Separation in Solutions of Like-Charged Colloidal Particles

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Model systems of charged spherical macroions with either monovalent, divalent, or trivalent counterions interacting solely through hard-core and Coulomb forces have been investigated by Monte Carlo simulations. Although the direct macroion-macroion interaction is purely repulsive, we find for sufficiently strong electrostatic coupling an effective attraction that separates the solution into two fluid phases. The attraction is short ranged and arises from correlations among counterions localized near different macroions. This mechanism for attraction differs from that attraction inferred to operate in solutions of charged latex particles presently challenging the classical DLVO theory.

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The physicochemical properties of solutions of charged colloids in a wide variety biological and technologically important systems are dominated by electrostatic forces. Although the electrostatic interactions in such systems have been extensively studied over the past 50 years, they remain a central problem in colloidal science [1,2]. A large body of experimental evidence confirms the intuitive expectation that purely repulsive forces operate between like-charged colloidal particles [3]. However, in recent years it has been experimentally inferred that attractive forces may exist between like-charged objects in the colloidal domain, e.g., from the reduced swelling of lyotropic liquid lamellar phases when monovalent counterions are replaced by divalent ones [4,5] as well as from the observed phase separation [6,7] and the deduced interaction potentials [8,9] in concentrated suspensions of charged latex particles. At present, these and related phenomena are being intensively studied by various experimental techniques.

On the theoretical side, Derjaguin, Landau, Verwey, and Overbeek proposed a theory [10,11], now known as the DLVO theory, which predicts a purely repulsive electrostatic force between like-charged colloidal particles. However, in the mid-1980s, this cornerstone of colloid science was challenged by the demonstration that like-charged planar surfaces attract each other at sufficiently strong electrostatic coupling [12,13]. Related attractions have been proposed also for other geometries. But despite considerable theoretical and computational effort [14–23], the existence of attractive electrostatic forces between like-charged and spherical colloidal particles in bulk solution have long remained controversial. However, recent simulation studies of primitive asymmetric electrolytes have shown the existence of short-range attractive electrostatic forces between like-charged colloidal particles [24–26]. Here, we demonstrate that such attractive forces can lead to a coexistence of two fluid phases of different electrolyte density. Furthermore, we argue that such an attractive force is not operating in the charged latex solutions [6,7].

Consider a model system representing aqueous solutions of ionic surfactant micelles in the absence of added salt. The model contains two types of spherical charged particles: (i) macroions of diameter $\sigma_{\mathrm{MM}} = 40$ Å and charge $Z_{\mathrm{M}} = -60$, representing the micelles, and (ii) small ions of diameter $\sigma_{\mathrm{II}} = 4$ Å and charge $Z_{\mathrm{I}} = +1, +2$, or $+3$, representing the counterions. The solvent enters the model only by its relative dielectric permittivity ε_r. The interaction between the particles is pairwise additive, and for pair ij, where i and j denote either macroion or counterion, it is given by

$$U_{ij}(r) = \begin{cases} \infty, & r < \sigma_{ij} \\ \frac{Z_i Z_j e^2}{4\pi\varepsilon_0\varepsilon_r}\,\frac{1}{r}, & r \geq \sigma_{ij}\,, \end{cases} \tag{1}$$

where e is the elementary charge, ε_0 is the permittivity of vacuum, r is the center-to-center separation between the particles, and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$. All particles were enclosed in a cubic box, and periodic boundary conditions were applied.

The model was solved by Monte Carlo (MC) simulations using the canonical ensemble. The long-range Coulomb interactions were handled by the Ewald summation technique [27–29]. The notorious problem of very limited mobility of the macroions, due to the strong accumulation of counterions near the macroions [14], was overcome by an efficient cluster move technique [30,31].

Simulations with three different counterion valencies were performed at temperature $T = 298$ K, relative dielectric permittivity $\varepsilon_r = 78.4$, and macroion number density $\rho_{\mathrm{M}} = 0.5 \times 10^{-6}$ Å^{-3}, corresponding to a macroion volume fraction $\phi_{\mathrm{M}} = 0.0168$. The main results were obtained from systems containing $N_{\mathrm{M}} = 80$ macroions and a sufficient number of counterions, $N_{\mathrm{I}} = |Z_{\mathrm{M}}/Z_{\mathrm{I}}|N_{\mathrm{M}}$, to ensure overall electroneutrality. Simulations with different system sizes were performed to exclude system size effects. Unless otherwise stated, the particles were initially placed randomly in the box, and the simulations involved at least 50 000 attempted MC moves per particle after equilibration.

Figure 1 shows two-dimensional projections of typical system configurations at the end of the simulations. With monovalent counterions [Fig. 1(a)], the macroions

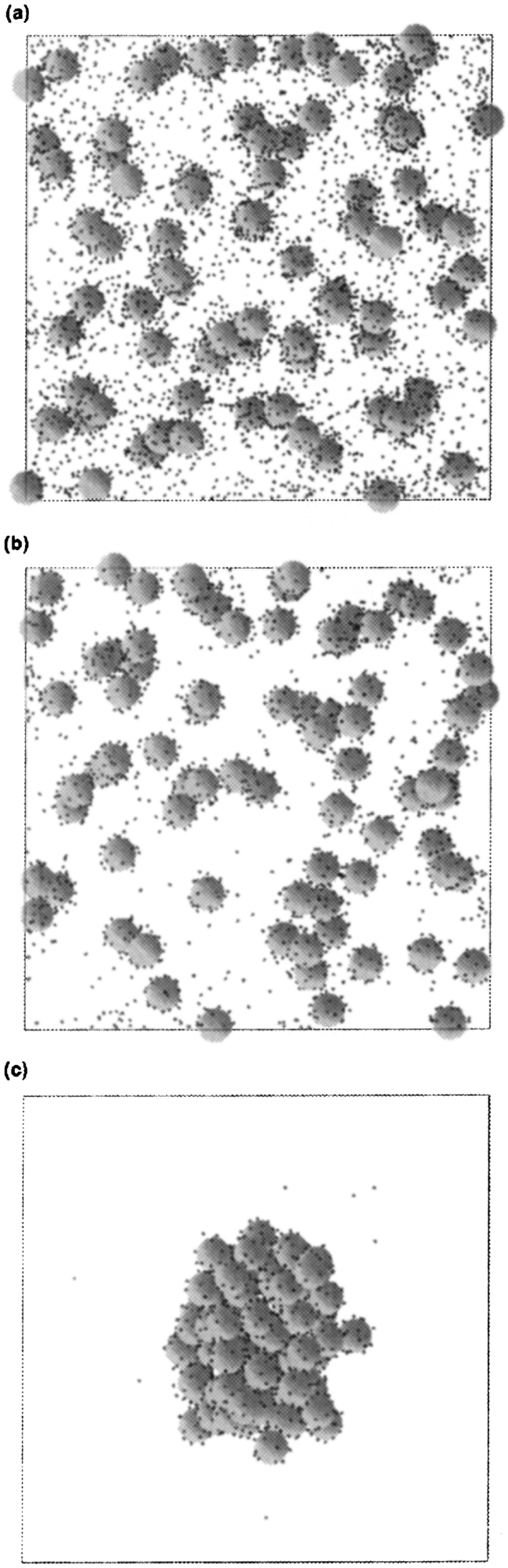

FIG. 1. Typical configurations of charged colloidal solutions. The simulated system contains 80 macroions, each carrying 60 elementary charges (large spheres), and corresponding number of (a) monovalent, (b) divalent, or (c) trivalent counterions (dots). The side of the box is 430 Å and particles are drawn to scale. Periodic boundary conditions are applied in all three directions to avoid surface artifacts.

are well separated (in three dimensions) and a considerable fraction of the counterions are accumulated near the surfaces of the macroions, although many counterions are distributed throughout the intervening solution. In the case of divalent counterions [Fig. 1(b)], we observe a tendency of macroion paring and a stronger counterion accumulation near the macroions. Finally, with trivalent counterions [Fig. 1(c)], the macroions form a large aggregate (with occasionally one or two macroions separated) and nearly all counterions are associated with macroions. For mono- and divalent counterions, the equilibrium is achieved after 10 000 MC moves per particle, whereas for trivalent counterions approximately 500 000 MC moves are required. Simulations were also performed where the macroions initially formed a compact primitive cubic lattice structure. In the case of mono- and divalent counterions, the macroions are completely dissociated after 5000 MC moves, whereas, in the case of trivalent counterions, the aggregate remains but is melted after 200 000 MC moves.

The promotion of a macroion aggregation with increasing the counterion valency has further been documented by investigating the macroion-macroion structure factor $S_{\mathrm{MM}}(k)$ at different system sizes at constant number density. Figure 2 shows that $S_{\mathrm{MM}}(k)$ for monovalent and divalent counterions is independent of the system size. In contrast to this observation, for trivalent counterions equilibrium $S_{\mathrm{MM}}(k \rightarrow 0)$ grows fairly linearly with the number of macroions, indicating a large-scale instability of the system. In fact, the structure factors are similar to the form factor of a homogeneous sphere [32] consistent with the configuration shown in Fig. 1(c). We also note that the aggregates are fluidlike, since higher order maxima are very weak. Hence, our results obtained with trivalent counterions using different start configurations and different system sizes unambiguously demonstrate a large-scale aggregation of macroions, and we conclude that for a macroscopic system the equilibrium state would be two coexisting fluid phases of different number density of the asymmetric electrolyte.

The structure of the colloidal solution has further been quantified by means of the radial distribution function (rdf) $g_{ij}(r)$, measuring the relative density of particles of type j at distance r from a particle of type i. Figure 3 displays the macroion-macroion rdf's for each of the three simulated systems. In the case of monovalent counterions, $g_{\mathrm{MM}}(r)$ confirms the conventional view that macroions are well separated and form a fluid with only short-range order (solid curve). A positive density correlation is seen at $r \approx \rho_{\mathrm{M}}^{-1/3}$ indicating a purely repulsive interaction between the macroions within this distance. Moreover, the closest macroion-macroion separation, approximately 70 Å, greatly exceeds the contact separation of 40 Å. The replacement of the monovalent ions with divalent ones leads to a qualitative change in $g_{\mathrm{MM}}(r)$. Figure 3 (dashed curve) shows that (i) the characteristic maximum at $r \approx \rho_{\mathrm{M}}^{-1/3}$ has completely vanished, (ii) $g_{\mathrm{MM}}(r) < 1$ at

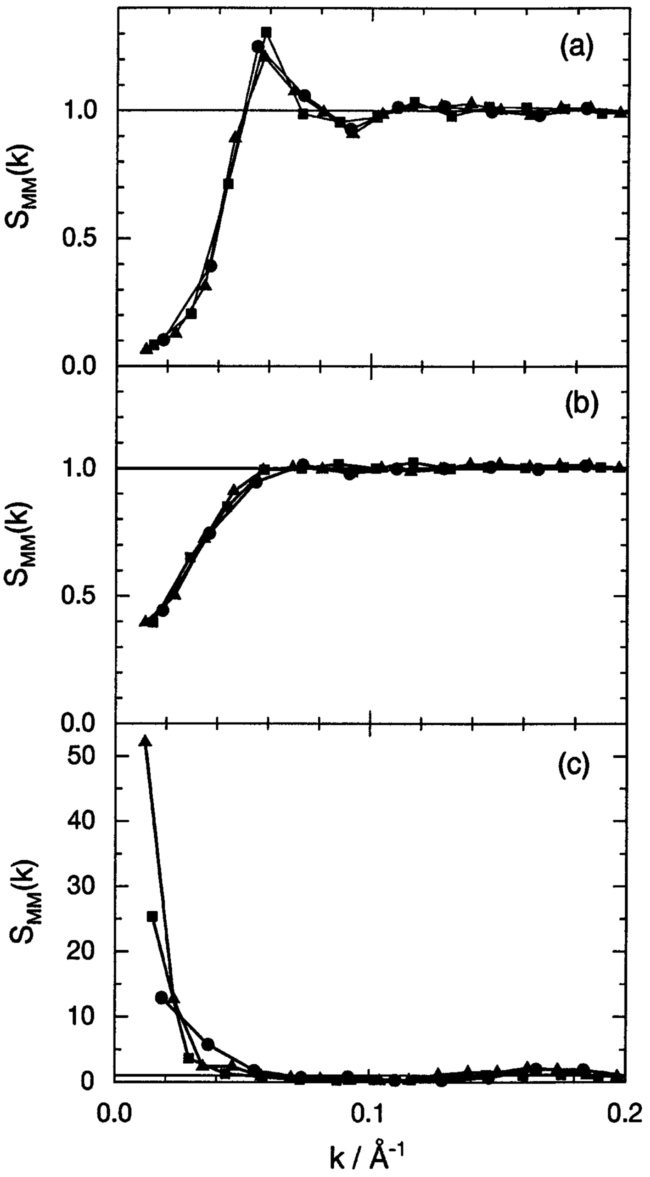

FIG. 2. Macroion-macroion structure factors $S_{MM}(k)$ for (a) monovalent, (b) divalent, or (c) trivalent counterions with $N_M = 20$ (circle), 40 (square), and 80 (triangle) macroions at constant number density. The horizontal line at $S_{MM} = 1$ corresponds to systems of uncorrelated macroions.

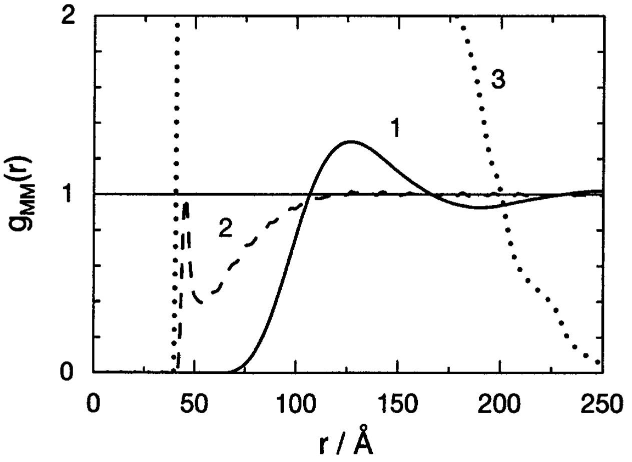

FIG. 3. Macroion-macroion radial distribution functions $g_{MM}(r)$ at indicated counterion valency ($Z_I = 1$, 2, or 3). For $Z_I = 3$, g_{MM} has a global maximum at $r \approx 1.1\sigma_{MM}$ and a secondary maximum at $r \approx 1.5\sigma_{MM}$ (truncated). The horizontal line at $g_{MM} = 1$ corresponds to systems of uncorrelated macroions.

all separations $r < 100$ Å, and (iii) a sharp local maximum appears at $r \approx 1.1\sigma_{MM}$. From (i) and (ii), we conclude that the long-range repulsive force is strongly reduced in magnitude, and from (iii) that an attractive force component is operating at short separations. Finally, Fig. 3 (dotted curve) shows that, with trivalent counterions, $g_{MM}(r)$ displays a very strong peak at $r \approx 1.1\sigma_{MM}$ and a secondary peak at $r \approx 1.5 - 2\sigma_{MM}$ consistent with the aggregation seen in Fig. 1(c). Hence, we have by necessity an attractive force of electrostatic origin acting among the macroions, which is sufficiently strong to induce a phase separation (a system of uncharged hard spheres do not exhibit such a coexistence of two fluids of different density).

Thus, the presented results unambiguously demonstrate that a solution of like-charged colloidal particles plus counterions interacting solely through hard-core repulsive forces and long-range Coulomb forces (the so-called primitive model) displays conditions where two phases of different electrolyte density are in equilibrium. At low electrostatic coupling (monovalent counterions), a single phase appears which is characterized by repulsive forces among the macroions. At high electrostatic coupling (trivalent counterions), two coexisting phases are present owing to effectively attractive forces among the macroions. For the intermediate system (divalent counterions), we have still a one-phase system, but it is close to the two-phase boundary. The attraction arises from spatial correlations of counterions associated with different macroions [33], and the effect of these correlations become more important as the counterion valency is increased. With increasing counterion charge, the electrostatic double layer becomes thinner and this reduces the range of the double layer repulsion. At a sufficiently high counterion charge, the attractive correlation force dominates at short separations.

Recently, Rouzina and Bloomfield have examined the attraction between like-charge planar surfaces arising from counterion correlations [34]. They considered the reduced parameter $\Gamma = Z_I^2 l_b / a_Z$, where $l_b = (e^2/4\pi\varepsilon_0\varepsilon_r kT)$ is the Bjerrum length and $a_Z = [Z_I/(\sigma/e)]^{1/2}$ is the average distance between two neighboring counterions at the charged surface characterized by the surface charge density σ. Rouzina and Bloomfield concluded that (i) an attraction appears when $\Gamma > \Gamma^* \approx 2$ and (ii) the attraction is short ranged, important only at $h \lesssim a_Z$, where h is the distance between the charged surfaces. In our systems, we have $\Gamma = 0.7$, 2.0, and 3.7 for monovalent, divalent, and trivalent counterions, respectively. Evidently, our results are consistent with the predictions of Rouzina and Bloomfield, since (i) the phase separation appears between $\Gamma = 2.0$ and 3.7 and (ii) the attraction is short range $[(h \approx 4\ \text{Å}) < (a_Z = 16\ \text{Å})]$.

Finally, our results are consistent with experimental data for solutions of charged surfactant micelles—a coexistence of two fluid micellar solutions with either mono- or divalent counterions has never been observed. Moreover, we would like to stress that our findings should not be directly compared with solutions of charged latex particles, owing to the size and charge differences. Nevertheless, since (i) our results support the predictions by Rouzina and Bloomfield, (ii) $\Gamma \ll 1$ for typical charged latex systems with monovalent counterions in aqueous solutions ($\Gamma = 2$ corresponds to one elementary charge per 13 Å^2), and (iii) the experimentally observed attraction appears at length scales of μm, we conclude that the recently reported attraction in aqueous solutions of latex systems [6,7] cannot be rationalized by the mechanisms controlling the aggregation observed in this work.

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