Attraction between Like-Charged Macroions by Coulomb Depletion

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A novel mechanism for counterion-mediated attraction between like-charged spherical macroions is proposed, which originates from a depletion zone of counterions between nearly touching macroions that is induced by Coulomb interactions. Using computer simulations of the primitive model, we show that this depletion effect dominates over the electrostatic contribution in the case of strong Coulomb coupling when all the counterions form a quasi-two-dimensional layer on the spherical macroionic surface. Its range is given by the typical spacing of counterions on the macroion surface. [S0031-9007(98)06791-X]

Since the early days of colloid science there has been a continuing controversy over the possibility of attraction between two like-charged colloidal spheres ("macroions") [1]. Such an attraction would strongly affect the colloidal coagulation rate, which is of direct practical importance for the stability of paints, inks, etc. On the other hand, it is also of great fundamental interest to understand the effective interactions between mesoscopic colloids from a microscopic point of view.

While the bare Coulomb force between the macroions is, of course, always repulsive, the problem is made nontrivial by the presence of the microscopic counterions (ensuring global charge neutrality of the system), which screen the direct Coulomb repulsions. For weak Coulomb coupling or high dilution of the macroions, the linearized screening theory of Debye and Hückel [2] always leads to an effective repulsion between macroions, as described by the electrostatic part of the celebrated Derjaguin-Landau-Verwey-Overbeek (DLVO) pair potential [3]. By enhancing the colloidal charge Ze, the colloidal number density ρ, and the valency q of the counterions, or by reducing the dielectric constant ϵ of the solvent, the Coulomb coupling can become extremely large, such that the usual DLVO picture of counterion screening breaks down. The intriguing question is whether an effective attraction (or "overscreening" of counterions) is possible under such conditions.

Recent pioneering experiments have found an attraction between colloidal spheres in the presence of charged walls [4] but not in the bulk [5]. As far as theory is concerned, several mechanisms leading to macroionic attraction have been proposed, which are based upon either colloidal charge fluctuations [6], charge fluctuations of condensed counterions [7–9], or strong counterion correlations [10,11]. At this stage we remark that *a priori* the results should depend on the geometric shape of the macroions. This can be directly demonstrated by comparing the electric potential for a single counterion in

the field of one macroion: For a macroionic *plate* it scales linearly with the plate distance binding any counterion to the plate. This is completely inverted for a single macroionic *sphere,* since the three-dimensional Coulomb potential cannot bind a counterion at finite temperature. In the intermediate case of a *rodlike* macroion, it depends on the strength of the Coulomb coupling whether there is counterion condensation or not. This already gives a clue that the effective interaction between plates and rods might be qualitatively different from that between spheres.

In this Letter, we propose a new mechanism of counterion-mediated attraction between two spherical macroions. In contrast to the previous pictures, which explain attraction in terms of *electrostatic* interactions, we put forward the crucial role of the finite size of the macroions being an excluded volume for the counterions. This can result in a *depletion zone* of counterions between the macroions, which is induced by the combined effect of the macroionic excluded volume and the Coulomb interactions. Provided the Coulomb coupling is extremely large, an imbalanced pressure from the counterions acting onto the macroionic surfaces leads to an effective attraction between the macroions.

Let us make three remarks about the special nature of this mechanism: First, the attractive electrostatic forces discussed in previous theoretical approaches are still present but the *total force is dominated by the depletion effect*. Second, though the depletion picture is similar to that used to describe mixtures of large and small hard spheres such as colloids and polymers [12], it is not influenced by the microscopic core of the counterions. It is the Coulomb repulsion between the counterions as well as the Coulomb attraction between the macroions and counterions together with the excluded volume of the macroions which produces the depletion zone. Therefore we call this effect *Coulomb depletion*. Third, as for the previous mechanisms, the attraction occurs only for very large Coulomb couplings when the counterions

are practically forming a two-dimensional layer on the spherical macroionic surfaces. Its range is given by the typical distance of counterions on the macroion surface.

Our results are based on computer simulations of the primitive model of strongly asymmetric electrolytes frequently used for theoretical studies of the effective interactions. We study a pair of macroions, each of them carrying a bare charge Ze, which are confined in a cubic box of length L. The box length $L = (2/\rho)^{1/3}$ is fixed by a given macroion number density ρ. The two macroions are placed symmetrically along the body diagonal of the cube such that the center of the cube coincides with the center of mass of the two particles. Their positions are denoted by $\vec{R}_1$ and $\vec{R}_2$. Furthermore the box contains $N_c = 2Z/q$ counterions carrying an opposite charge $-qe$. The whole setup is shown in Fig. 1. Within the primitive model, the discrete structure of the solvent is neglected. Coulomb and excluded volume interactions result in the following pair potentials between macroions ("m") and counterions ("c"), with r denoting the interparticle distance:

$$V_{mm}(r) = \begin{cases} \infty, & \text{for } r \leq 2R, \\ Z^2 e^2/\epsilon r, & \text{for } r > 2R, \end{cases} \quad (1)$$

$$V_{mc}(r) = \begin{cases} \infty, & \text{for } r \leq R + R_c, \\ -Zqe^2/\epsilon r, & \text{for } r > R + R_c, \end{cases} \quad (2)$$

$$V_{cc}(r) = \begin{cases} \infty, & \text{for } r \leq 2R_c, \\ q^2 e^2/\epsilon r, & \text{for } r > 2R_c. \end{cases} \quad (3)$$

Here, R and R_c are the mesoscopic macroion and microscopic counterion radii, respectively. The counterion Coulomb energy on the macroion surface in units of the thermal energy $k_B T$ provides a natural macroion-
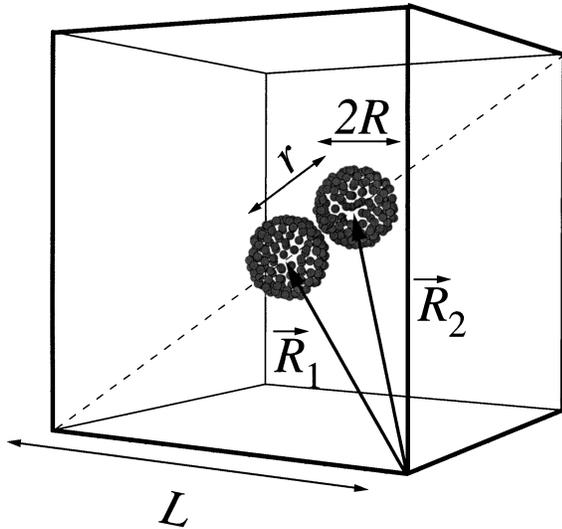

FIG. 1. Schematic view of the setup: Two nearly touching macroions at positions $\vec{R}_1$ and $\vec{R}_2$ are placed along the body diagonal of a cube with length L. The counterions condensed onto the macroionic surfaces are shown as small black spheres.

counterion coupling parameter $\Gamma_{mc} \equiv (Z/q)(\lambda_B/R)$, where $\lambda_B = q^2 e^2/\epsilon k_B T$ is the Bjerrum length.

Using statistical mechanics in the canonical ensemble, the total effective force $\vec{F}_i$ acting on macroion i ($i = 1, 2$) is the direct Coulomb repulsion plus the counterion average of the force from the macroion-counterion interaction (2). The latter is given by [13,14] $-\langle \sum_{j=1}^{N_c} \vec{\nabla}_{\vec{R}_i} V_{mc}(|\vec{R}_i - \vec{r}_j|) \rangle_c$. Here, $\{\vec{r}_j\}$ are the counterion positions and the canonical counterion average $\langle \cdots \rangle_c$ is defined via

$$\langle \cdots \rangle_c = \frac{1}{\mathcal{N}} \left[\Pi_{j=1}^{N_c} \int_V d^3 r_j \right] \cdots \exp\left[-\frac{V_c}{k_B T} \right] \quad (4)$$

with the total counterionic potential energy

$$V_c = \sum_{i=1}^{2} \sum_{k=1}^{N_c} V_{mc}(|\vec{R}_i - \vec{r}_k|) + \sum_{k,l=1; k<l}^{N_c} V_{cc}(|\vec{r}_k - \vec{r}_l|). \quad (5)$$

In (4), the prefactor $\frac{1}{\mathcal{N}}$ ensures proper normalization, $\langle 1 \rangle_c = 1$. Separating finally the Coulomb and the excluded volume part in $V_{mc}(r)$, the total force involves *three* terms, $\vec{F}_i = \vec{F}_i^{(1)} + \vec{F}_i^{(2)} + \vec{F}_i^{(3)}$, where $\vec{F}_i^{(1)} = -\vec{\nabla}_{\vec{R}_i} V_{mm}(|\vec{R}_2 - \vec{R}_1|)$ is the *direct Coulomb repulsion*. Furthermore, $\vec{F}_i^{(2)}$ is the *counterion-induced electrostatic force*

$$\vec{F}_i^{(2)} = \left\langle \sum_{j=1}^{N_c} \vec{\nabla}_{\vec{R}_i} \frac{Zqe^2}{\epsilon |\vec{R}_i - \vec{r}_j|} \right\rangle_c \quad (6)$$

and the *depletion* force $\vec{F}_i^{(3)}$ can be expressed as an integral over the surface S_i of the ith macroion

$$\vec{F}_i^{(3)} = k_B T \int_{S_i} d\vec{f} \, \rho_c(\vec{r}), \quad (7)$$

where $\vec{f}$ is a surface vector pointing towards the macroion center and $\rho_c(\vec{r}) = \sum_{j=1}^{N_c} \langle \delta(\vec{r} - \vec{r}_j) \rangle_c$ is the equilibrium counterion density field. The forces $\vec{F}_i^{(2)}$ and $\vec{F}_i^{(3)}$ have different physical origins. Any counterion screening effect is embodied in the electrostatic term $\vec{F}_i^{(2)}$, which, for strong Coulomb coupling, practically cancels the direct Coulomb repulsion $\vec{F}_i^{(1)}$. Moreover, $\vec{F}_i^{(1)} + \vec{F}_i^{(2)}$ contains any electrostatic fluctuations and correlations. The third term, $\vec{F}_i^{(3)}$, on the other hand, involves the counterion density on the macroionic surface and measures the imbalance of the counterionic pressure on the macroions. Clearly it is this term that describes the depletion effect.

We have calculated the canonical averages (6) and (7) using extensive Monte Carlo computer simulations. Since by symmetry, $\vec{F}_1 = -\vec{F}_2$, it is sufficient to study $\vec{F}_1$. We projected $\vec{F}_1$ onto the body diagonal defining $F = \vec{F}_1 \cdot (\vec{R}_1 - \vec{R}_2)/|\vec{R}_1 - \vec{R}_2|$. Hence a negative sign of F implies attraction, and a positive sign repulsion. For the macroion distances explored in the present study, the presence of the impenetrable walls does not affect the forces. This was carefully checked against a situation

TABLE I. Parameters for the runs A, B, and C.

Run	A	B	C
Z	280	32	320
q	1	2	2
ϵ	78	5	2
R (Å)	554	48.9	554
$\rho R^3 \times 10^4$	5.6	51	1.9
R_c (Å)	2.8	2.2	2.8
T [K]	293	298	293
Γ_{mc}	3.7	147	330
Γ_{cc}	0.06	9.7	6.9

with periodic boundary conditions, yielding identical results. Three different parameter combinations (runs A, B, and C) were investigated which are summarized in Table I. While the parameter set of run A corresponds to the typical case of aqueous charge-stabilized suspensions, the Coulomb coupling Γ_{mc} is very high for runs B and C where divalent counterions and an organic solvent with a small dielectric constant ϵ were chosen. The latter situations required very long production runs with typically more than 5×10^6 Monte Carlo moves per counterion to obtain small statistical errors. We expect the system to be fluidlike in every case.

For large Γ_{mc} and finite ρ, the counterions form practically a two-dimensional layer on the macroionic surfaces. As can be seen from a counterion snapshot for run C in Fig. 2, there are pronounced correlations and ordering effects within the two counterionic layers in the intervening space between the macroions. This is due to the mutual Coulomb repulsion of the counterions, which can be measured in terms of the coupling parameter $\Gamma_{cc} = \lambda_B/a$, where $a = \sqrt{q/Z}\sqrt{8\pi/\sqrt{3}}\,R$ is a typical counterion distance corresponding to the spacing of a triangular lattice.

Results for the total projected electrostatic force, $F^{(1)} + F^{(2)}$, and the projected depletion force $F^{(3)}$ are shown in Fig. 3. For moderate Coulomb couplings (run A), both forces are repulsive and $F^{(3)}$ is completely masked by the electrostatic force. This drastically changes for large Coulomb couplings (runs B and C), where the depletion force becomes attractive and dominates the total force. If Γ_{cc} is large as in run B, the electrostatic force $F^{(1)} + F^{(2)}$ becomes attractive for small distances, too, in agreement with recent findings [9,10]. We reemphasize, however, that the dominant part of the interaction is the depletion force being 1 order of magnitude larger than $F^{(1)} + F^{(2)}$. Since the depletion attraction is triggered by the mutual repulsions between counterions of nearby macroionic surfaces, it is expected to be short ranged with a range of the order of a. This is indeed confirmed for strong Coulomb couplings (runs B and C); see Fig. 3.

Finally, in Fig. 4, we show the counterionic density field $\rho_c(\vec{r})$ on the macroion surface. Because of rotational
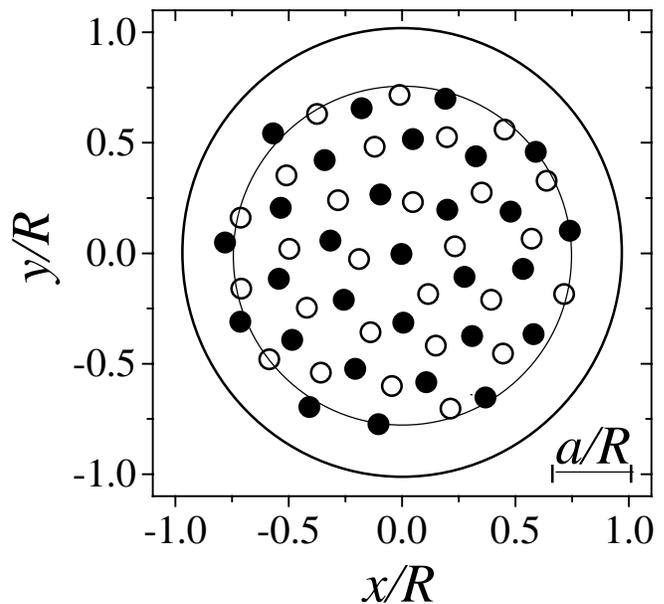

FIG. 2. Counterion snapshot for run C projected along the body diagonal. The outer circle is the macroion core. Positions are shown only for counterions between the macroions if their projection falls within the inner circle. The full (open) circles are for counterions from macroion 1 (2). The macroion distance is $r/R = 2.16$. The reduced counterion spacing a/R is also shown.

symmetry around the body diagonal of the cube, the density field depends only on the polar angle θ formed with the body diagonal. For moderate Coulomb couplings (run A), the counterions accumulate in the intervening space between the macroions resulting in a peak of
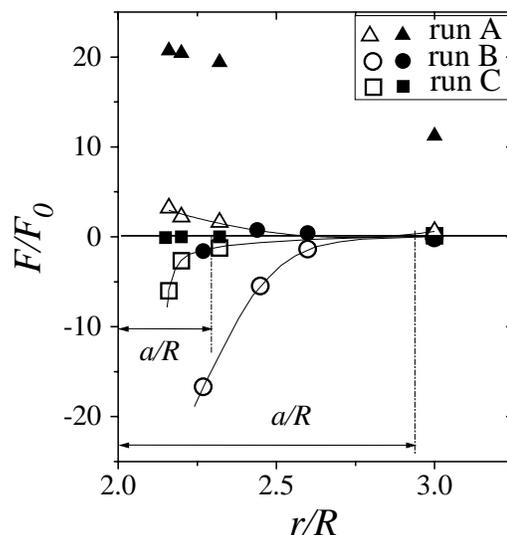

FIG. 3. Projected forces in units of $F_0 \equiv (Z^2 e^2/R^2) \times 10^{-4}$ versus macroion distance r/R. The full symbols are for $F^{(1)} + F^{(2)}$, the open symbols for $F^{(3)}$: Run A (triangles), run B (circles), and run C (squares). The statistical error is smaller than the symbol size. The lines are a guide to the eye. For runs B and C, the range a/R is also shown.
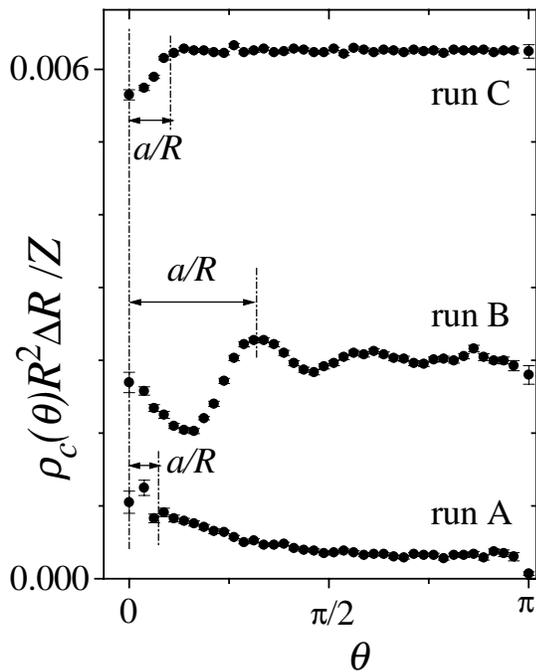
FIG. 4.   Reduced counterion density $\rho_c(\theta)$ versus polar angle θ for runs A, B, and C. In order to improve the statistics we averaged the density over a small spherical shell of thickness ΔR which was 0.025 (run A), 0.000 87 (run B), and 0.001 (run C).

$\rho_c(\theta)$ for small θ. This is in accordance with Poisson-Boltzmann theory [13]. For large Coulomb couplings, on the other hand, there is a depletion zone of counterions around $\theta = 0$ with a typical range of a/R which causes the attractive depletion force.

In conclusion, we have pointed out the importance of Coulomb-induced depletion forces, which dominate interactions between macroions for small distances and strong Coulomb coupling. The nature of the depletion force changes from repulsive to attractive if the Coulomb coupling is enhanced. Its sign results from a nontrivial interplay between Coulomb repulsion between nearby counterionic layers and Coulomb energy gain of counterions between the two macroions. We close with a couple of remarks: First, it would be interesting to verify an attractive depletion force experimentally for strongly deionized small colloidal spheres with polyvalent counterions using techniques as in Refs. [4,5]. One can discriminate uniquely between the depletion and the van der Waals attraction since only the former depends on the concentration of added salt. Second, due to the particular topology of two spheres (i.e., the existence of "inner" and "outer" regions), the depletion effect cannot be obtained from a Derjaguin approximation based on the forces between thin macroionic plates [15]. It would further be interesting to study colloidal phase separation

induced by the depletion attraction together with the counterionic contributions to the total free energy [16]. Last, in our primitive approach we assumed a constant macroion charge Z smeared out homogeneously over the spherical macroionic surface. We expect that the depletion attraction becomes even stronger for a discrete or fluctuating distribution of macroionic charges.

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