Strong Attraction between Charged Spheres due to Metastable Ionized States

René Messina, Christian Holm, and Kurt Kremer

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128, Mainz, Germany

(January 7, 2022)

Abstract

We report a mechanism which can lead to long range attractions between like-charged spherical macroions, stemming from the existence of metastable ionized states. We show that the ground state of a single highly charged colloid plus a few excess counterions is overcharged. For the case of two highly charged macroions in their neutralizing divalent counterion solution we demonstrate that, in the regime of strong Coulomb coupling, the counterion clouds are very likely to be unevenly distributed, leading to one overcharged and one undercharged macroion. This long-living metastable configuration in turn leads to a long range Coulomb attraction.

PACS numbers: 81.72Dd, 61.20Ja
One of the great challenges in the theory of charged colloidal suspensions is the understanding of effective attractions between like-charged macroions that have recently been observed experimentally in confined systems [1, 2], and for which no clear theoretical explanation is available. The usually employed mean field DLVO theory [3, 4] foresees purely repulsive electrostatic forces between like-charged macroions. However, with divalent counterions present, simulations (using a pair of macroions) find short range attraction for high macroion volume fraction in aqueous systems [5] or at extremely low dielectric constant a Coulomb depletion force [6]. Recent simulations of similar systems in aqueous solutions also find attractive forces [7-9]. However all simulations have in common, that the observed attraction occurs only for very small distances away from the colloid surface (order of counterion size).

In this letter we investigate highly charged macroions in bulk and present two important new results. The first concerns the ground state of an isolated macroion surrounded by excess counterions where it is found that the first few overcharging counterions lower considerably the energy. As a second finding we demonstrate that for two highly charged macroions separated by intermediate distances thermal fluctuations are sufficient to distribute the counterions unevenly, leading to one overcharged and one undercharged macroion. This results in a long range effective Coulomb attraction between the macroions.

Consider one or two spherical macroions of radius $r_m$ and bare charge $Q = -Z_m e$ (where $e$ is the elementary charge and $Z_m > 0$ within the framework of the primitive model [10] surrounded by an implicit solvent of relative dielectric permittivity $\epsilon_r$. The small counterions with diameter $\sigma$ and charge $+Z_c e$ are confined in a cubic box of length $L$, and the macroion(s) are held fixed. The colloid volume fraction $f_m$ is defined as $N_m 4 \pi r_m^3 / 3 L^3$ (where $N_m$ is the number of macroions). In the case of an isolated macroion, it is located at the center of the box, whereas in the case of a macroion pair, they are placed symmetrically along the axis passing by the two centers of opposite faces.

The (MD) method employed in the present work is similar to the one used by Kremer and
To simulate a constant temperature ensemble, the ions are coupled to a heat bath and their motion is governed by the Langevin equation:

\[ m \frac{d^2 \vec{r}_i}{dt^2} = -\nabla V_{\text{tot}}(\vec{r}_i) - m \Gamma \frac{d \vec{r}_i}{dt} + \vec{f}_i(t), \]

where \( m \) (chosen as unity) is the mass of the counterions, \( i \) is the \( i^{th} \) counterion, \( V_{\text{tot}} \) is the total potential force made up of a Coulomb term and an excluded volume term, which are both pairwise additive, \( \Gamma \) is the friction coefficient, and \( \vec{f}_i \) a random force. These two last quantities are linked by the dissipation-fluctuation theorem:

\[ \langle \vec{f}_i(t) \cdot \vec{f}_j(t') \rangle = 6m \Gamma k_B T \delta_{ij} \delta(t - t'). \]

For the ground state simulations the random force was set to zero.

Excluded volume interactions are introduced via a pure short range repulsive Lennard-Jones (LJ) potential given by

\[ V_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r - r_0} \right)^{12} - \left( \frac{\sigma}{r - r_0} \right)^{6} \right] + \epsilon, \text{ for } r - r_0 < r_{\text{cut}}, \]

and 0 otherwise, where \( r_0 = 0 \) for the counterion-counterion interaction, \( r_0 = 7\sigma \) for the macroion-counterion interaction, \( r_{\text{cut}} (= 2^{1/6}\sigma) \) is the cutoff radius. This leads to \( r_m = 7.5\sigma \), whereas the closest center-center distance of the small ions to the macroion is therefore \( a = 8\sigma \). The Coulomb potential between a \( Z_i \) and a \( Z_j \) valent ion at distance \( r \), where \( i \) and \( j \) denote either macroion or counterion, is given by

\[ V_{\text{coul}}(r) = k_B T_0 l_B \frac{Z_i Z_j}{r}, \]

with the Bjerrum length \( l_B = e^2 / 4\pi \epsilon_0 \epsilon_r k_B T_0 \), where \( \epsilon_0 \) is the vacuum permittivity. To link this to experimental units and room temperature we denote \( \epsilon = k_B T_0 \) (\( T_0 = 298 \text{ K} \)) and fix \( \sigma = 3.57 \text{ Å} \). We neglect hydrodynamical interactions and hydration effects. Being interested in strong Coulomb coupling we choose, for the rest of this paper, \( \epsilon_r = 16 \), corresponding to \( l_B = 10\sigma \).

To study the possibility of overcharging a single macroion, we recall the Gillespie rule also known as the valence-shell electron-pair repulsion (VSEPR) theory. From this one knows that the ground state structure of two, three and four electrons disposed on a hard sphere corresponds to simple geometrical situations, namely a line (two electrons diametrically opposed), a triangle, and a tetrahedron, respectively. A straightforward calculation shows that, for a central charge of \( +2e \), the maximally obtainable overcharging is \(-2e\) (i.e. 2 electrons), being independent of macroion radius. The excess electrons gain more energy by assuming a topological favorable configuration than by escaping to infinity, the simple
reason of overcharge. We resort to simulations to elucidate this behavior for one colloid with a high central charge.

To quantify this phenomenon, we have considered three macroionic charge $Z_m$: 50, 90 and 180 corresponding to a surface charge density of one elementary charge per 180, 100 and 50 Å², respectively, and fixed $Z_c = 2$ for the rest of this letter. Then we add successively overcharging counterions (OC). The electrostatic energy as a function of the number of OC is displayed Fig. 1. We note that the maximal (critical) acceptance of OC (4, 6 and 8) increases with the macroionic charge (50, 90 and 180 respectively). Furthermore for a given number of OC, the gain in energy is always increasing with $Z_m$. Also, for a given macroionic charge, the gain in energy between two successive overcharged states is decreasing with the number of OC. Note that at $T = 0$, the value $\epsilon_r$ acts only as a prefactor. It means that the ground state structure is solely dictated by topological rules (i.e., the counterions arrangement around the sphere).

The resulting curve can be very simply explained by assuming that the energy $\epsilon$ per ion on the surface of a neutralized macroion depends linearly on the inverse distance between them, hence is proportional to $\sqrt{N}$ for fixed area, where $N$ is the number of counterions on the surface. The energy gain $\Delta E_1 = (N + 1)\epsilon(N + 1) - N\epsilon(N)$ of the first OC is a pure surface correlation term. For the next OC one needs to take into account the Coulomb repulsion $l_BZ_c^2/a$, leading to lowest order in $1/N$ for the energy gain of the $n^{th}$ OC:

$$\Delta E_n = n\epsilon(N)\left[\frac{3}{2} + \frac{3n}{8N}\right] + l_BZ_c^2(k_BT_0)\frac{(n-1)n}{2a}.$$  (2)

Determining $\epsilon(N)$ from the measured value for $\Delta E_1$, we obtain a curve that matches the simulation data almost perfectly, compare Fig.1.

An energy per ion, which scales like $\sqrt{N}$, has been found for an ionic Wigner crystal (WC) on a planar surface where each ion interacts with an oppositely charged background charge which is smeared out over its Wigner-Seitz cell. This energy per ion is given by $\epsilon(c)/k_BT_0 = -\alpha c^{1/2}l_BZ_c^2$, with $\alpha = 1.96$, and $c$ is the two-dimensional concentration of the crystallized counterions of valence $Z_c$. This Ansatz has been tried recently to explain...
strong ionic correlations observed in various soft matter systems. In our simulation we find for \( \Delta E_1/(k_B T_0) \) -18.0, -24.4, and -35.3 for \( Z_m = 50, 90, \) and 180, respectively, whereas the Wigner crystal scenario predicts -21.0, -28.0, and -39.5, which is off by a decreasing rate of 17 – 12%. This might be due to the assumption of a homogeneous background charge, and the assumption of a planar geometry, neither of which are fully fulfilled, however the error gets smaller for higher values of \( Z_m \).

Using the Wigner crystal ionic energy and eq. (2), the maximally obtainable number \( n_{\text{max}}^* \) of OC counterions is readily found to be

\[
n_{\text{max}}^* = \frac{1}{2} + \frac{9\alpha^2}{32\pi} + \frac{3\alpha}{4\sqrt{\pi}} \sqrt{N} + \left[ \frac{3\alpha}{16\sqrt{\pi}} + \frac{27\alpha^3}{256\pi^{3/2}} \right] \frac{1}{\sqrt{N}} + \mathcal{O}(1/N).
\]

This value depends only on the number of counterions \( N \). It originates from the topological arrangement of the ions around a central charge, and is independent of Bjerrum length or radius of the macroion. For large \( Q \) it reduces to the form \( Q_{\text{max}}^*/e \approx \frac{3\alpha}{4\sqrt{\pi}} \star \sqrt{Z_mZ_c} \) which was derived in Ref. [15] in a more elaborate fashion.

To obtain the interaction potential profile, we added one counterion coming from infinity towards a macroion of bare charge \( Z_m = 180 \) and computed the global electrostatic energy of the system, see Fig. 2. The first OC starts to gain correlational energy at distance \( r \approx 12\sigma \) from the center of the colloid, which is about \( 4\sigma \) from the surface. This fits only roughly with the distance \( Z_c^2l_B/4 \) predicted from WC theory [14,15], and is more of the order \( c^{-1/2} \).

With adding more excess counterions the Coulomb barrier increases, and for the ninth OC it exceeds the gain in correlational energy, when being on the macroion surface. Thus the configuration becomes metastable. The curve for the first OC can be nicely fitted with an exponential fit of the form \( E_1(r)/k_B T_0 = -35.3 \exp \left[ -7.1(r - a)/a \right] \). For the \( n^{\text{th}} \) OC simply the appropriate Coulomb monopole contribution \( 4l_B(n - 1)/r \) needs to be added, see Fig. 2. This exponential dependence is not predicted by the WC theory, where a \( 1/r \) dependence should be seen due to the interaction of the removed ion with its correlation hole.

Next, we consider two spherical like charged macroions at a colloidal volume fraction \( f_m = 7 \cdot 10^{-3} \) at room temperature \( T_0 \), at fixed center-center separation \( R \), in presence of their
divalent counterions (ensuring global charge neutrality). Initially the counterions are randomly generated. Figure 3 shows two macroions surrounded by their quasi-two-dimensional counterions layer. The striking peculiarity in this configuration is that it corresponds to an overcharged and an undercharged sphere. There is one counterion more on the left sphere and one less on the right sphere compared to the bare colloid charge. Such a configuration is referred as ionized state. In a total of 10 typical runs, we observe this phenomenon 5 times. We have also carefully checked against a situation with periodic boundary conditions, yielding identical results. However it is clear that such a state is in “pseudo-equilibrium” because it is not the lowest energy state.

To estimate the energy barrier, electrostatic energy profiles at zero temperature were computed, where we move one counterion from the overcharged macroion to the undercharged, restoring the neutral state (see Fig. 4). We have checked that the path leading to the lowest barrier of such a process corresponds to the line joining the two macroions centers. One clearly observes a barrier, which increases linearly with the charge $Z_m$. The ground state corresponds as expected to the neutral state. The overcharged state is only slightly higher in energy, the difference being approximately the monopole contribution $E/k_B T_0 = l_B (4/8 - 4/12) \approx 1.67$. The physical origin of this barrier can be understood from the single macroion case where we showed that a counterion gains high correlational energy near the surface. This gain is roughly equal for both macroion surfaces and decreases rapidly with increasing distance from the surfaces, leading to the energy barrier with its maximum near the midpoint. For the single macroion case we showed that the correlational energy gain scales with $\sqrt{Z_m}$, whereas here we observe a linear behavior of the barrier height with $Z_m$. We attribute this effect to additional ionic correlations since both macroions are close enough for their surface ions to interact strongly. For large separations we find again that the barrier height increases with $\sqrt{Z_m}$, as expected. This $Z_m$ dependence of the barrier also shows that at room temperature such ionized states only can occur for large $Z_m$. In our case only for $Z_m = 180$, the ionized state was stable for all accessible computation times. Unfortunately, it is not possible to get a satisfactory accuracy of the energy jumps at non-
zero temperatures. Nevertheless, since we are interested in the strong Coulomb coupling regime, which is energy dominated, the zero temperature analysis is sufficient to capture the essential physics.

Results concerning the effective forces at zero temperature between the two macroions are now investigated which expression is given by

$$F_{eff}(R) = F_{mm}(R) + F_{LJ} + F_{mc},$$

where $F_{mm}(R)$ is the direct Coulomb force between macroions, $F_{LJ}$ is the excluded volume force between a given macroion and its surrounding counterions and $F_{mc}$ is the Coulomb force between a given macroion and all the counterions. Because of symmetry, we focus on one macroion. To understand the extra-attraction effect of these ionized-like states, we consider three cases: (i) $F_{ion} = F_{eff}$ in the ionized state (ii) $F_{neut} = F_{eff}$ in the neutral case (iii) $F_{mono} = F_{eff}$ simply from the effective monopole contribution. Our results are displayed in Fig. 5 for $Z_m = 180$, where the ionized state was also observed at room temperature. The non-compensated case leads to a very important extra attraction. This becomes drastic for the charge asymmetry of ±2 counterions at short separation $R/a \approx 2.5$, a situation which was also observed in our simulation at room temperature [16]. In contrast to previous studies [3, 4], these attractions are long range. For a sufficiently large macroion separation (from 3.5) the effective force approaches in good approximation the monopole contribution.

In summary, we have shown that a sufficiently charged colloid can in principle be highly overcharged due to correlation effects of the counterions, and that this effect is quantitatively well described by a Wigner crystal, i.e. eqs. (3) and (4). In the strong Coulomb coupling regime, this energy gain can be of the order of many $k_B T_0$.

Furthermore, due to this energetically favorable overcharged state it was found that for two like-charged macroions, an initially randomly placed counterion cloud of their neutralizing divalent counterions may not be equally distributed after relaxation, leading to two macroions of opposite net charges. The resulting configuration is metastable, however separated by an energy barrier of several $k_B T_0$ when the bare charge is sufficiently large. Such
configuration possess a natural strong long range attraction.

We acknowledge useful discussions with H. Lwen and M. Deserno. This work is supported by Laboratoires Européens Associés (LEA) and a computer time grant hkf06 from NIC Jülich.
REFERENCES

[1] G. M. Kepler and S. Fraden, Phys. Rev. Lett. 73, 356 (1994).

[2] J. C. Crocker and D. G. Grier, Phys. Rev. Lett. 73, 352 (1994); 77, 1897 (1996); A.E Larsen and D. G. Grier, Nature (London) 385, 230 (1997).

[3] B. V. Derjaguin and L. D. Landau, Acta Physicochim. (USSR) 14, 633 (1941).

[4] E. J. Verwey and J. T. G. Overbeek, Theory of the stability of Lyophobic Colloids (Elsevier, Amsterdam, 1948).

[5] N. Grønbech-Jensen, K. M. Beardmore, and P. Pincus, Physica 261A, 74 (1998).

[6] E. Allahyarov, I. D’Amico, and H. Lwen, Phys. Rev. Lett. 81, 1334 (1998).

[7] E. Allahyarov, I. D’Amico, and H. Lwen, Phys. Rev. E. 60, 3199 (1999).

[8] J. Z. Wu, D. Bratko, H. W. Blanch, and J. M. Prausnitz, J. Chem. Phys. 111, 7084 (1999).

[9] P. Linse and V. Lobaskin, Phys. Rev. Lett. 83, 4208 (1999).

[10] T. L. Hill, Statistical Mechanics (Addison-Wesley, Reading, Mass., 1960).

[11] K. Kremer and G. Grest, J. Chem. Phys. 92, 5057 (1990).

[12] A theory that predicts molecular geometries using the notion that valence electron pairs occupy sites around a central atom in such a way as to minimize electron-pair repulsion. See for example D. W. Oxtoby, H. P. Gillis and N. H. Nachtrieb, Principles of Modern Chemistry (Saunders College Publishing, 1999), Chap. 3, p. 80.

[13] L. Bonsall and A.A. Maradudin, Phys. Rev. B15, 1959 (1977).

[14] I. Rouzina and V.A. Bloomfield, J. Phys. Chem. 100, 9977 (1996); B.I. Shklovskii, Phys. Rev. Lett. 82 3268 (1999); V.I. Perel and B.I. Shklovskii, Physica A 274, 446 (1999).

[15] B.I. Shklovskii, Phys. Rev. E 60, 5802 (1999).
[16] R. Messina, (unpublished).

List of Figures

FIG. 1: Electrostatic energy (in units of $k_B T_0$) for zero temperature configurations of a single charged macroion of radius $r_m = 7.5\sigma$ as a function of the number of overcharging counterions for three different bare charges $Q$ (in units of $e$). The neutral case was chosen as the potential energy origin, and the curves were produced using the theory of eq.(2), compare text.

FIG. 2: Electrostatic energy (in units of $k_B T_0$) of a divalent counterion as function of distance from the center of a macroion with radius $r_m = 7.5\sigma$ and charge $Q = -180$ (in units of $e$). The energy is normalized to zero at distance infinity. Data and fits are shown for the first, the second, the eighth and ninth overcharging (OC) counterion.

FIG. 3 Snapshot of a “pseudo-equilibrium” configuration at room temperature $T_0$ where the counterion-layers do not exactly compensate the macroions charge. Here the deficiency charge is $\pm 1$ counterion (or $\pm 2e$ as indicated above the macroions) and $R/a = 3.6$.

FIG. 4 Total electrostatic energy (in units of $k_B T_0$) of the system, for zero temperature configurations, of two macroions at a center-center separation of $R/a = 2.4$ as a function of one displaced counterion distance from the left macroion for three typical values $Q$ (in units of $e$). The exact neutral state was chosen as the potential energy origin. The lines are a guide to the eye. The insert indicates the path (dotted line) of the moved counterion. The ending arrows of the arc indicate the start position (left sphere) and final position (right sphere) of the moved counterion.

FIG. 5 Reduced effective force between the two spherical macroions at zero temperature for $Z_m = 180$ as a function of distance from the center. The different forces are explained in the text. The lines are a guide to the eye.
FIG. 1
Messina et al.
Physical Review Letters
FIG. 2
Messina et al.
Physical Review Letters
FIG. 3
Messina et al.
Physical Review Letters
FIG. 5
Messina et al.
Physical Review Letters