Colloidal charge reversal: dependence on the ionic size and the electrolyte concentration

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Extensive Monte Carlo simulations and scaling arguments are used to study the colloidal charge reversal. The critical colloidal surface charge density \( \sigma_c \) at which the reversal first appears is found to depend strongly on the ionic size. We find that \( \sigma_c \) has an inflection point as a function of the electrolyte concentration. The width of the plateau region in the vicinity of the inflection point depends on the temperature and the ionic radius \( a \). In agreement with the theoretical predictions it is found that the critical colloidal charge above which the electrophoretic mobility becomes reversed diverges as \( Z_c \sim 1/a^2 \) in the limit \( a \to 0 \).

I. INTRODUCTION

A common way to stabilize colloidal suspensions against flocculation and precipitation is by synthesizing particles with acidic groups on their surface. When placed in water, these groups dissociate and colloids acquire a net negative charge. In aqueous suspension containing only monovalent electrolyte, the long range Coulomb repulsion prevents the colloids from approaching one another to distances for which the short range van der Waals interaction can lead to an irreversible sticking and precipitation. However, when beside the 1:1 electrolyte, suspensions contain some multivalent counterions, a number of curious and very counterintuitive effects can take place [1]. For example, it has been observed that in such suspensions two like-charged colloidal particles can attract one another [2, 3, 4, 5, 6, 7, 8, 9, 10]. This attraction is not a result of the van der Waals interaction, but rather a consequence of strong positional correlations between the multivalent counterions surrounding the colloidal particles [11, 12, 13, 14, 15, 16]. The mechanism of this attraction has been studied extensively, yet a fully predictive theory of this phenomenon still remains elusive.

Another curious effect observed in dilute colloidal suspensions containing multivalent counterions is the reversal of the electrophoretic mobility [1, 17, 18, 19, 20, 21]. The positional correlations induced by the long range van der Waals interaction, but rather a consequence of strong positional correlations between the multivalent counterions surrounding the colloidal particles [11, 12, 13, 14, 15, 16]. The mechanism of this attraction has been studied extensively, yet a fully predictive theory of this phenomenon still remains elusive.

The critical colloidal surface charge density \( \sigma_c \) at which the reversal first appears is found to depend strongly on the ionic size. We find that \( \sigma_c \) has an inflection point as a function of the electrolyte concentration. The width of the plateau region in the vicinity of the inflection point depends on the temperature and the ionic radius \( a \). In agreement with the theoretical predictions it is found that the critical colloidal charge above which the electrophoretic mobility becomes reversed diverges as \( Z_c \sim 1/a^2 \) in the limit \( a \to 0 \).

II. THE MODEL AND SIMULATIONS

The electrophoretic mobility, in general, is a complicated non-linear function of the electrokinetic \( \zeta \) potential [36, 37]. For small \( \zeta \) and large ionic strengths, however, the relationship between the two is linear and is given by the Smoluchowski equation [36, 38]. A change in the sign of the \( \zeta \) potential will, therefore, lead to the reversal of the electrophoretic mobility, which we will also associate with the overcharging (or the charge-reversal) of the colloidal particles. In principle, the overcharging (charge-reversal) and the reversal of the electrophoretic mobility are two distinct concepts — one is static and the other dynamical. In practice, however, the definition of charge reversal carries some ambiguity. The general trends, such as the behavior of the effective charge and of the electrophoretic mobility as a function of, say, the ionic size or electrolyte concentration are very similar in two cases [39]. We will, therefore, use the two concepts interchangeably. For a fixed electrolyte concentration, the value of the colloidal charge at which the \( \zeta \)-potential vanishes will be designated as the critical colloidal charge. Our goal is to find the dependence of this charge on the ionic size and the electrolyte concentration.

We consider a dilute aqueous mixture of colloidal parti-
cles inside a z : 1 electrolyte. The spherical colloidal particles have radius \( R \) surface charge \(-Zq\), where \( q \) is the elementary charge. For each colloidal particle there are \( Z \) monovalent counterions. All the ions are modeled as hard spheres of radius \( a \) with the charge \(+zq\) (electrolyte counterion), \(-q\) (electrolyte coion) or \(+q\) (colloidal counterion) at their centers. The solvent is treated as a continuum of dielectric constant \( \varepsilon \). The relative strength of the electrostatic interactions, as compared to the thermal energy, is measured by the ratio of the ionic radius to the Bjerrum length, \( \lambda_B = q^2 / 4\pi\varepsilon k_BT \).

As was argued in Ref. \[39\], the value of the \( \zeta \) potential may be associated with the electrostatic potential at the effective shear plane removed from the colloidal surface by one ionic diameter \[40\]. Since the maximum of the electrostatic potential also occurs at approximately the same position, the precise location of the shear plane does not influence strongly the value of the \( \zeta \)-potential. In this respect, our approach is quite similar to the one adopted by Bjerrum for simple electrolytes \[41\, 42\]. The static potential at the effective shear plane can then be calculated using the canonical Monte Carlo (MC) simulations \[39\]. Recent simulations show the basic correctness of this picture for normal wetting surfaces \[37\, 39\]. Working with \( \zeta \)-potential is also advantageous as compared to defining the effective charge in terms of condensed counterions located within a sheath surrounding the colloidal surface. Such definition carries a large degree of arbitrariness, since the condensed counterions will in turn drive a co-associations of coions. The effective charge will then be strongly sensitive to the precise value of the sheath width. This is not the case for \( \zeta \)-potential, which under the same conditions develops a maximum near the colloidal surface, so that \( \zeta \) is the location of the effective shear plane removed from the colloidal particle, \( \equiv \phi(R_s) \), where \( R_s = R + 2a \).

### III. SCALING ANALYSIS

The model presented in the previous section is quite complex, with a number of distinct length scales. To organize and interpret the data of the Monte Carlo simulations we shall, therefore, appeal to the dimensional and scaling analysis. There are five basic length scales: \( R, L, a, \lambda_B, \) and \( C^{-1/3} \). Since we are interested in very dilute suspensions, \( L \to \infty \). Although this limit can not be achieved in the simulations, our box size was always taken to be sufficiently large so that critical colloidal charge \(-Z_c q\) did not have any explicit dependence on \( L \). We are, therefore, left with four relevant length scale, so that for a fixed \( z : 1 \) electrolyte, \( Z_c \) is a function of only three dimensionless ratios

\[
Z_c = f\left(\frac{a}{R}, \frac{a}{\lambda_B}, \lambda_B C^{1/3}\right),
\]

where \( f(x, y, z) \) is a scaling function. Furthermore, we note that when the Debye length \( \xi_D = 1/\sqrt{4\pi\lambda_B(z^2 + z)}C \), is sufficiently short, \( R/\xi_D \gg 1 \) — which is almost always the case near the isoelectric point — the curvature effects will be screened, and the critical colloidal charge must be proportional to the colloidal surface area. This means that

\[
Z_c = \frac{4\pi R^2}{a^2} g\left(\frac{a}{\lambda_B}, \lambda_B C^{1/3}\right).
\]

We conclude that for sufficiently large salt concentrations, the reversal of the electrophoretic mobility will take place when the modulus of the colloidal surface charge density, \( \sigma \equiv Zq/4\pi R^2 \), is larger than the critical value \( \sigma_c \), which depends on the Bjerrum length, ionic radius, and the concentration of electrolyte through the scaling function \( g(x, y) \).

\[
\sigma_c = \frac{q}{a^2} g\left(\frac{a}{\lambda_B}, \lambda_B C^{1/3}\right).
\]

The similarity transformation, Eq. \( 5 \), is particularly useful when one wants to obtain the critical surface charge density for suspensions with large concentrations of electrolyte.
In these cases, the direct MC simulations become extremely slow, due to large number of microions which must be used to simulate a dilute colloidal suspension in the $L \to \infty$ limit. However, Eq. (5) tells us that this critical surface charge density can also be obtained by simulating a much smaller system at a slightly lower temperature and with a somewhat larger number of microions. For example, suppose that we want to find the critical surface charge density for a suspension containing 3:1 electrolyte at concentration $C = 1$ M, with ions of radius 2 Å. Instead of doing the direct simulation of this system, we can simulate a “similar” system with say half the number of microions, $C = 0.5$ M, at a slightly lower temperature, $\Lambda_B = 7.2 \times 2^{1/3} = 9.07$ Å and with ions of radius 2 × $2^{1/3} = 2.5$ Å. From Eq. (5), the critical charge of the original system (at concentration $C = 1$ M) will be $2^{2/3}$ times the critical charge of the “similar” system. The latter simulations, however, are much easier to perform since the number of microions involved is much smaller.

In Refs. [43] and [44] it was argued that the critical surface charge density is determined by the work that must be performed to transfer a multivalent counterion from the bulk electrolyte to the colloidal surface. In particular, it was found that $\sigma_c \sim (\Delta \mu)^2$, where $\Delta \mu$ is the change in the ionic solvation free energy between the bulk and the colloidal surface [44]. In the limit of vanishing $a$, $\Delta \mu$ diverges as $1/a$. This divergence is a consequence of Bjerrum pairing of oppositely charged ions in the bulk electrolyte [11, 41, 45]. The critical surface charge density, therefore, diverges as $\sigma_c \sim 1/a^2$. Thus, the scaling function with $x = 0$, $g(0, y)$, should be constant for all values of $y$. For small, but finite values of $x$, we expect to see a deviation from this behavior in two limits: when the entropic effects begin to dominate the electrostatics $C^{1/3} \Lambda_B < 0.5$, and when the hard-core repulsion begins to dominate everything, $C^{1/3} a > 0.2$.

IV. RESULTS AND DISCUSSION

In Fig. 1 we show the $\zeta$-potential as a function of the colloidal charge density for a suspension containing 3:1 electrolyte at a molar concentration of $C = 0.1$ M. The radius of the colloidal particle was fixed at $R = 30$ Å, while its charge $Z$ was varied. Most of the simulations were performed with the boxes of side length $L = 120$ Å, which is large enough to produce very small colloidal volume fractions, thus, minimizing the influence of the periodicity on the ionic distribution. However, for low salt concentrations we increased the box length to $L = 150$ Å and 210 Å, in order to increase the number of particles and to obtain a better statistics of ion distribution around the colloid.

For weakly charged colloidal particles the increase (in modulus) of the surface charge density was accompanied by a uniform decline of the $\zeta$ potential ($\zeta$ accompanied the colloidal charge and became more negative). However, when the colloidal charge became sufficiently large, counterion condensation became important and $\zeta$ increased as a function of the bare colloidal charge, becoming positive for sufficiently strongly charged colloids, see Fig. 1. To accurately determine the critical colloidal charge density $\sigma_c$ at which $\zeta = 0$, we used a linear interpolation of the simulation data, as shown in the inset of Fig. 1.

![FIG. 1: Zeta potential as a function of the colloidal surface charge density. The molar concentration of 3:1 electrolyte is $C = 0.1$ M, the radius of the microions is $a = 3$ Å, and the Bjerrum length is 7.2 Å. The inset shows the region where the $\zeta$ potential becomes reversed, $\zeta = 0$, with a very good linear fit (solid line) to the simulation data (circles), from which the precise value of $\sigma_c$ is determined.](image1)

We next studied the dependence of the critical surface charge density on the concentration of electrolyte. In Fig. 2, $\sigma_c$ is plotted as a function of $C$ for two different electrolytes: $a = 2$ Å, $\lambda_B = 7.2$ Å; and $a = 3$ Å, $\lambda_B = 10.8$ Å. Although clearly distinct, the two systems are “similar”, since the ratio $\lambda_B/a$ is the same in both cases. Therefore, if $\sigma_c a^2/\bar q$ is plotted as a function of $\lambda_B C^{1/3}$ (or as a function of $C\lambda_B^2$),
we plot the entropic effects dominate over the electrostatics. In Fig. 3 ionic size, or when the concentration becomes so small that separation between the microions becomes compatible to the radius \( a/\lambda \). Nevertheless, as was discussed in the previous section, if similarity transformation, a data collapse is not expected. The data for the two systems should collapse onto a single curve. This is precisely what is found, see the inset of Fig. 2.

If the electrolyte systems are not connected by the similarity transformation, a data collapse is not expected. We expect, however, the deviation from this constancy to take place when the product \( xy \) becomes sufficiently large — the separation between the microions becomes compatible to the ionic size, or when the concentration becomes so small that the entropic effects dominate over the electrostatics. In Fig. 3 we plot \( \sigma_c a^2/q \) as a function \( C\lambda_B^3 \), for various electrolytes of different \( \lambda_B \). The figure clearly shows the inflection point of \( \sigma_c \) as a function of the electrolyte concentration. Furthermore, in the limit of vanishing \( a/\lambda_B \), the inflection point turns into plateau which extends up to the concentrations for which \( C^{1/3}u \approx 0.2 \), consistent with the discussion presented earlier. In the limit of vanishing ionic size, the plateau region extends indefinitely.

**V. CONCLUSIONS**

Using extensive Monte Carlo simulations we have studied the dependence of the minimal colloidal charge at which the reversal of the electrophoretic mobility first takes place, on the concentration of 3:1 electrolyte and on the ionic size. The critical surface charge density \( \sigma_c \) was found to exhibit an inflection point as a function of the electrolyte concentration. In the limit of small \( a/\lambda_B \), the inflection point becomes a flat plateau, extending from the lower concentration \( C_l \) to the upper concentration \( C_u \). The value of the lower bound is delimited by the distances at which the entropic effects begin to dominate over the electrostatics, \( C_l^{1/3}\lambda_B \approx 0.5 \), while the value of the upper bound is determined by the distances at which the hard-core repulsion begins to dominate over everything \( C_u^{1/3}a \approx 0.2 \). In the interval \([C_l, C_u]\) the surface charge density is found to be \( \sigma_c \approx 0.013q/a^2 \), independent of the electrolyte concentration. The plateau disappears, turns into a simple inflection point with vanishing second derivative, when \( \lambda_B/a < 2.5 \). The same behavior was found to occur for electrolytes of other valences. For example, in Fig. 4 we plot the critical surface charge density as a function the electrolyte concentration for 2:1 electrolyte. Once again the inflection point and the formation of the plateau are evident. However, in this case, to compensate for the weaker electrostatic interactions between the coions and the counterions, the value of \( \lambda_B \) must be significantly lower for the plateau to appear clearly. What is surprising, however, is that the scaled surface charge density \( \sigma_c a^2/q \) appears not to depend on the valence of the electrolyte — or depend only very weakly — in the plateau region. In the case of 2:1 electrolyte we find that \( \sigma_c a^2/q \approx 0.015 \) as compared to the 0.013 for the 3:1 electrolyte. It will be interesting to see if this curious behavior persists for other values of \( z \). At the moment, there is no theory which can quantitatively account for these curious findings. We hope that the present study will provide a simulational benchmark against which the future theoretical predictions can be tested.

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