

Particle-counterion clustering in highly charge-asymmetric complex fluids

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The formation of particle-counterion clusters through electrostatic interaction is studied in this work for a highly charge asymmetric colloidal suspension. The occurrence of such clustering is probed by the particle electrophoretic mobility, i.e., with the aid of a transport property. The results show that the effective charge manifesting under the presence of an external electric field is the renormalized charge predicted by an extension of the Debye-Hückel-Bjerrum theory to the fluid state of highly charged colloids.

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I. INTRODUCTION

Charged colloidal suspensions present an outstanding challenge to modern theories of statistical mechanics due to the charge asymmetry between a colloid and a counterion, that makes the use of traditional methods of liquid-state theory unfeasible. Recently, an extension of the Debye-Hückel-Bjerrum theory to the fluid state of a highly asymmetric charged colloid has been presented [1,2]. The full free energy of the colloidal suspension was calculated as the sum of electrostatic and entropic contributions, encountering that counterions condense onto particles forming clusters composed of a colloid and n counterions. A direct consequence of this particle-counterion clustering phenomena is the appearance of an effective particle charge (Z_{ef}), lower than the bare charge (Z), governing the colloidal features.

This theory does not consider correlations between condensed counterions, which are treated as pointlike. Ionic size effects and correlations should be taken into account if the fluid is composed of multivalent counterions or solvents with low dielectric constants [3]. For water and monovalent counterions these effects are insignificant and thus can be neglected [4].

Since the works of Oosawa [5] and Manning [6], the concept of counterion condensation and effective charge are widely accepted in the field of linear polyelectrolytes. In the case of colloidal suspensions formed by spherical charged particles, the notion of effective charge is employed for explaining equilibrium and dynamical properties [7], although the relation between this phenomenological parameter and the underlying physics is not always clear [8].

In this paper, effective charge arguments are employed in studies of transport properties; particularly, in the electrophoretic mobility (μ) of very highly charged spherical colloids. It will be shown that μ is controlled by a renormalized surface charge, predicted by Levin-Barbosa-Tamashiro (LBT) liquid state theory. As a result, a new colloidal entity consisting of a particle and a number of associated counterions should be considered for explaining the experimental behavior of μ . The paper is organized as follows. First, the method for determining effective charges from electrophoretic mobility measurements together with a description

of the liquid state theory predicting such quantities are presented. The next section describes the experimental system. Spherical gel particles will be employed because of their very highly charged surface, yielding charge asymmetries in the fluid as high as $10^5 - 10^6:1$. Results are presented and discussed afterwards. The influence of surface charge and salt concentration over the electrophoretic mobility will be presented and discussed in terms of charge renormalization based on particle-counterion clustering phenomena. Finally, some conclusions are given.

II. THEORY

A. Effective charge determination from electrophoretic mobility measurements

The velocity U of a charged colloidal particle moving in the presence of a weak electric field E is linearly related to the strength of the applied field by the electrophoretic mobility: $\vec{U} = \mu \vec{E}$. For spherical polyelectrolytes of radius b immersed in a uniform medium of dielectric constant $\epsilon_o \epsilon_r$, the electrophoretic mobility is written as [9]:

$$\begin{aligned} \mu = & \frac{2}{b} h(b) + \frac{b^2}{9} \int_b^\infty \left(1 - \frac{3r^2}{b^2} + \frac{2r^3}{b^3} \right) G(r) dr - \frac{2}{3\lambda^2} \\ & \times \int_0^b \left(\frac{r^3}{b^3} - \frac{\cosh(\lambda r) - \sinh(\lambda r)/\lambda r}{\cosh(\lambda b) - \sinh(\lambda b)/\lambda b} \frac{r}{b} \right) G(r) dr \\ & + \frac{2}{3\lambda^2} \left(1 - \frac{b\lambda}{3} \frac{\sinh(\lambda b)}{\cosh(\lambda b) - \sinh(\lambda b)/\lambda b} \right) \\ & \times \int_b^\infty \left(1 - \frac{r^3}{b^3} \right) G(r) dr, \end{aligned} \quad (1)$$

where $\lambda = (\gamma/\eta)^{1/2}$ is defined in terms of the friction coefficient γ and the continuum medium viscosity η , and

$$h(b) = \frac{3}{2\eta\lambda^2 b^2} \int_0^b \rho_{fix} r^2 dr \quad (2)$$

with ρ_{fix} being the fix charge density of the polymer network. The radial function $G(r)$ and the constant $h(b)$ con-

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tain the electrical parameters of the particle. For low potentials and homogeneously distributed charge, $G(r)$ is equal to [9]:

$$G(r) = -\frac{\epsilon_o \epsilon_r \kappa^2}{\eta} \frac{d}{dr} \psi^{(o)}. \quad (3)$$

In this expression, $\psi^{(o)}$ stands for the electric potential in the absence of external electric field and $\kappa = [e^2 / (\epsilon_o \epsilon_r kT) \sum_i z_i^2 n_i]^{0.5}$ is the inverse of the Debye length. In solving Eq. (1), the particle charge distribution is needed. For surface charged polyelectrolytes, $\psi^{(o)} = Ze / [4\pi\epsilon_o\epsilon_b(1 + \kappa b)]$ with Z the number of surface charges. Using this equilibrium potential, the electrophoretic mobility becomes [10]:

$$\mu = \frac{\sigma_s}{\eta\lambda^2} \left[\frac{3}{b} + \frac{2}{b} \left(1 - \frac{\lambda b}{3} \frac{\sinh(\lambda b)}{\cosh(\lambda b) - \sinh(\lambda b)/\lambda b} \right) + \frac{2b\lambda^2}{3(1 + \kappa b)} \right]. \quad (4)$$

In the limit $\lambda \rightarrow \infty$, Eq. (4) tends to the hard-sphere behavior, as expected. Far from this limit, Eq. (4) accounts also for the particle permeability to the solvent. For deswollen polyelectrolytes, the contribution arising from those terms is negligible and the particle behaves as a hard sphere. It is also worth emphasizing that the described model is valid only for low potentials, allowing the use of the linearized Poisson-Boltzmann equation. The linear dependence of the electrophoretic mobility with the surface charge density [$\sigma_s = eZ(4\pi b^2)^{-1}$], results from this linearization.

Equation (4) can be employed for describing the electrophoresis of highly surface charged particles if Z is substituted by an effective charge $Z_{\text{ef}} < Z$ [11]. By allowing for particle-counterion cluster formation, the validity of the linearized Poisson-Boltzmann equation is extended into the nonlinear regime [12].

B. Liquid-state theory of charged colloids

Consider a system consisting of N particles inside a volume V . The particles are idealized as hard spheres of radius b , each carrying Z ionized groups of charge e , uniformly spaced on the surface. Consequently, a total of ZN counterions must be present in order to preserve the overall electro-neutrality of the system. The solvent is described as a uniform medium of constant permittivity.

The fluid state of the system will be composed of bare particles of density ρ_o , free counterions of density ρ_f , and clusters consisting of a particle and n associated counterions ($0 < n \leq Z$). On the other hand, ρ_n represents the density of clusters with n counterions. It is assumed that one condensed counterion neutralizes one of the particle charges, in such a way that the effective charge density of a n cluster is $\sigma_n = eZ_{\text{ef}} / (4\pi b^2)$.

The contributions to the Helmholtz free-energy density, $f = -F/V$, arise from electrostatic interactions and entropic terms [1]. The particle-counterion contribution is obtained in

the framework of Debye-Hückel [13], applied to a n cluster of effective charge σ_n inside the ionic atmosphere. The resultant free-energy density is obtained through a Debye charging process, yielding [1,2]:

$$\beta f^{pc} = -\frac{\lambda_b}{2b(1 + \kappa b)} \sum_{n=0}^Z (Z-n)^2 \rho_n, \quad (5)$$

where $\beta^{-1} = kT$ and $\lambda_b = e^2 \beta / (4\pi\epsilon_o\epsilon_r)$ is the Bjerrum length.

The particle-particle contribution to the free energy is obtained in the frame of the van der Waals theory, giving rise to [1,2]:

$$\beta f^{pp} = -\frac{1 + 2\kappa b}{(1 + \kappa b)^2} \frac{\rho_f}{2}, \quad (6)$$

where the long-ranged interaction between two clusters is screened by the cloud of free counterions, producing an effective short-ranged potential of a Derjaguin-Landau-Verwey-Overbeek form.

The electrostatic free energy due to the interactions between free counterions is estimated to be equal to that of a one-component plasma [2,14]. In particular and although the counterions are assumed to be point particles, the electrostatic repulsion between two equally charged counterions will keep them from approaching each other closer than a distance d . This can be calculated using the one-component plasma theory to be $d = [(1 + 3\kappa\lambda_b)^{1/3} - 1] / \kappa$ [1,15]. The result for this free-energy contribution is [2,14]:

$$\beta f^{cc} = -\rho_f F(\rho_f), \quad (7)$$

where

$$F(\rho_f) = \frac{1}{4} \left[1 + \frac{2\pi}{3^{3/2}} + \ln \left(\frac{\omega^2 + \omega + 1}{3} \right) - \omega^2 - \frac{2}{3^{1/2}} \tan^{-1} \left(\frac{2\omega + 1}{3^{1/2}} \right) \right], \quad (8)$$

$$\omega(\rho_f) = \{1 + 3[4\pi\lambda_b^3 \rho_f]^{1/2}\}^{1/3}. \quad (9)$$

In the bulk, this contribution is negligible.

The final contribution to the free energy is due to entropic motion of counterions and particles being expressed as a sum of ideal-gas terms:

$$\beta f^{\text{entr}} = \sum_s \left[\rho_s - \rho_s \ln \left(\frac{\phi_s}{\zeta_s} \right) \right] \quad (10)$$

with s accounting for bare particles, free counterions, and clusters particle counterion. $\phi_n = \frac{4}{3}\pi\rho_n b^3$ and $\phi_f = \frac{4}{3}\pi\rho_f d^3$ are the volume fractions occupied by each specie. ζ_s are the internal partition functions for an isolated specie s . Since bare particles and unassociated counterions do not have an internal structure, their internal partition functions are simply given by $\zeta_o = \zeta_f = 1$. However, for a n cluster the internal partition function is $\zeta_n = Z! / [(Z-n)! n!] \exp[(Zn - n^2/2)\lambda_b/b]$ [1].

TABLE I. Bare surface charges (Z) and particle size ($2b$) at three solution pH 's.

pH	$Z(e^-)$	$2b$ (nm)
10.1 ± 0.1	$(2.27 \pm 0.02) \times 10^5$	231 ± 6
6.8 ± 0.1	$(1.24 \pm 0.02) \times 10^6$	227 ± 5
5.8 ± 0.1	$(1.52 \pm 0.02) \times 10^6$	234 ± 6

Combining all these contributions, the total free energy of the colloidal suspension is obtained, $f = f^{\text{entr}} + f^{pc} + f^{cc} + f^{pp}$. Minimization of f against n leads to the relation between bare and effective charges. Polydispersity in clusters is not relevant, as reported in Ref. [1]. As a consequence, the cluster distribution can be replaced by one characteristic particle-counterion cluster.

III. EXPERIMENT

Deswollen gel particles based on poly-(2-vinylpyridine) crosslinked with divinylbenzene (0.25%) [16] were employed as experimental system. The use of such a system allows very high charge asymmetries to be introduced in the fluid [17]. Deswollen particle states guarantee that the particles behave, hydrodynamically, as hard spheres and consequently $\mu \rightarrow \mu_{\text{hard sphere}}$ in expression (4).

Dynamic light scattering was employed for obtaining the mean particle hydrodynamic diameter: $2b = (230 \pm 6)$ nm. Particle charge was determined by titration [17]. The weak character of the chemical surface groups permits particle charge control through changes in the medium pH . Surface charges covering one order of magnitude were obtained by modifying the pH between 10.1 and 5.8, keeping the particles in the deswollen state (see Table I).

Electrophoretic mobilities were obtained by Doppler light scattering using a Zetamaster-S (Malvern Instruments), working with a 632.8 nm He-Ne laser. All measurements were carried out in dilute regime ($\rho = 5 \times 10^9 \text{ cm}^{-3}$), in order to avoid undesirable interactions between particles and multiple scattering. The medium pH was fixed by the addition of HCl or NaOH while the background electrolyte was modified by using NaCl. The temperature was set to 25 °C in all experiments.

IV. RESULTS AND DISCUSSION

The electrophoretic mobility of a colloid is an interesting transport property depending on the charge asymmetry of the fluid. Theoretical predictions for this variable disagree with experimental results, even though the theories are applied in their validity regions. This situation is shown in Fig. 1 by plotting the electrophoretic mobility against the particle surface charge. As expected, μ increases with Z , but not in a linear fashion as theoretically predicted (dashed line). In addition, theoretical electrophoretic mobilities are much higher than experimental ones, indicating that not all the surface charge reverts on the particle motion.

This result suggests that an effective charge, lower than the bare one, should be introduced in the physical picture, to

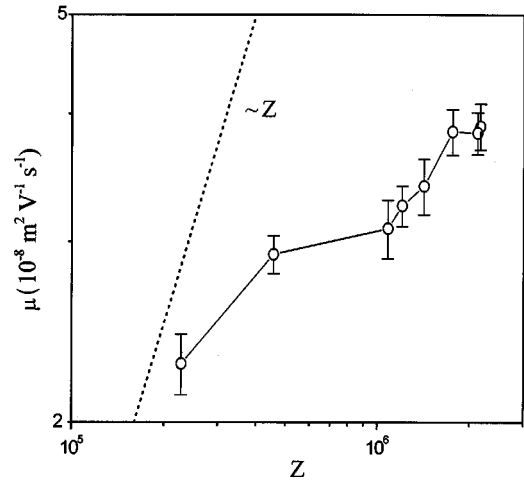


FIG. 1. Electrophoretic mobility as a function of bare charge ($[NaCl] = 1$ mM). The linear dependence $\mu - Z$ is shown for reference.

account for the discrepancies. In this paper, we claim that this charge renormalization could be caused by the strong electrostatic interaction between the colloidal particles and the counterions, leading to the formation of particle-counterion clusters, with a renormalized surface charge $Z_{\text{ef}} = Z - n$. This effect would be specially relevant when high charge asymmetries are present in the complex fluid.

Levin-Barbosa-Tamashiro liquid-state theory has been applied in this paper to renormalize the particle charge (Fig. 2), obtaining a very good agreement between the experimental results and theoretical predictions for the electrophoretic mobility. Now, μ depends linearly on the renormalized charge Z_{ef} , with physical meaning on particle-counterion clustering phenomena. Additionally, the equilibrium classical picture of a colloid surrounded by its diffuse double layer is recovered, if the particle is replaced by a cluster formed by the particle itself and n counterions. This conclusion is only applicable to

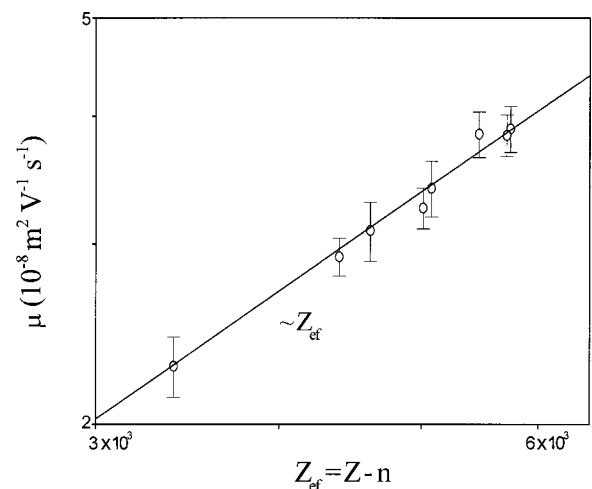


FIG. 2. Electrophoretic mobility versus the effective charge predicted by LBT liquid-state theory. The solid line is the theoretical prediction [expression (4)].

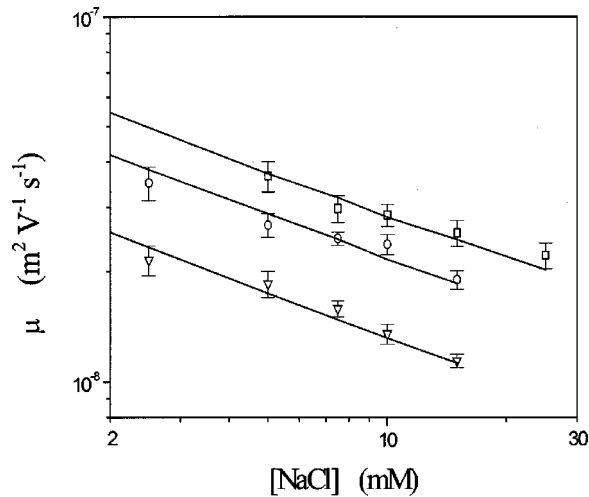


FIG. 3. Electrophoretic mobility as a function of salt concentration. ∇ ; $Z=2.27 \times 10^5$, \circ ; $Z=1.24 \times 10^6$, and \square ; $Z=1.52 \times 10^6$. The lines are theoretical fits leaving the fraction of condensed counterions as free parameter.

aqueous suspensions with monovalent counterions. Whenever electrostatic interactions between condensed counterions are significant, as is the case for low dielectric solvents and multivalent counterions, the theory needs to be extended in order to account for these correlations. In the experimental situation considered here, these effects are negligible and the agreement is thus worthy of mention.

In order to further validate this scenario, electrophoretic mobilities were measured as a function of salt concentration, for three surface charge values. The results are shown in Fig. 3. As can be seen, μ decreases with salt concentration as a consequence of electric double layer compression. If surface bare charges are considered, theoretical predictions agree qualitatively with experimental results, but overestimate the measured values. From fitting the experimental results with Eq. (4) (Fig. 3), the fraction of bare charge that contributes to μ can be obtained (Table II). The resultant fraction of condensed counterions agree reasonably well with LBT predic-

TABLE II. Experimental $(1 - Z_{\text{ef}}/Z)$ and predicted (n/Z) fraction of condensed counterions.

Z	$1 - Z_{\text{ef}}/Z$	n/Z
$(2.27 \pm 0.02) \times 10^5$	0.976 ± 0.008	0.99280
$(1.24 \pm 0.02) \times 10^6$	0.995 ± 0.008	0.99858
$(1.52 \pm 0.02) \times 10^6$	0.995 ± 0.008	0.99884

tions, remarking the necessity of including the particle-counterion clustering that occurs as a result of the intense electrostatic interactions between the particle and the counterions. Moreover, this agreement confirms that $Z_{\text{ef}} = Z - n$ is salt independent, at least in the range where ionic size effects or correlations are negligible.

As a consequence, effective charges obtained from transport properties, such as the electrophoretic mobility, are based on a particle-counterion phenomenon that renormalizes the charge that manifests on the colloidal features. On considering this entity as the colloidal particle, predicted electrophoretic mobilities agree with experimentally measured ones.

V. CONCLUSIONS

The electrophoresis of highly charged, spherical particles in a primitive electrolyte reflects the occurrence of a charge renormalization, which is consequence of the strong electrostatic interaction between the colloid and the counterions. The resultant particle-counterion cluster presents an effective charge $Z_{\text{ef}} = Z - n$, which is predicted by an extension of the Debye-Hückel-Bjerrum theory to the fluid state of highly charged colloids. These effective charges should be taken into account for a proper description of the electrophoresis of highly charged colloids and presumably when studying other transport properties of any charged system.

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