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Nonlinear effects in the stability of highly charged colloidal suspensions

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We investigate the nonlinear effects related to the formation of particle-counterion clusters in highly charged asymmetric colloidal suspensions. The ocurrence of such clustering is experimentally probed by studying the stability of the colloidal system. The results demonstrate that a renormalized charge is needed in order to explain the observed critical coagulation concentrations. This renormalization is predicted by an extension of the Debye-Hückel-Bjerrum liquid state theory [A. Diehl, M. C. Barbosa, and Y. Levin, Europhys. Lett. **53**, 86 (2001)]. Therefore, counterion *condensation* seems to become apparent in particle aggregation processes through control of the repulsive barrier that keeps the system stable. As a consequence of the agreement, new insights into the microscopic state of highly charged complex fluids follow.

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The stability of charged colloidal suspensions plays a relevant role in a wide variety of industrial and biological applications [1]. Although the electrostatic interactions in such systems have been extensively studied over the past decades, they still remain a central problem in colloid science [2,3]. A particularly interesting question concerns itself with the occurrence of liquid-gas phase separations for like-charged colloidal particles at very low salt concentrations. As pointed out by Diehl, Barbosa, and Levin [4], while in the context of the linearized density-functional theory it was found that phase separation could occur for pairwise repulsive interactions [5], recent simulations showed no evidence of phase transition in suspensions with monovalent counterions [6]. This apparent discrepancy between simulation results and the density-functional theory have been carefully analyzed recently by these authors. Within their theory, the strong electrostatic interaction between the colloids and the counterions leads to particle-counterion clustering. As a result of this nonlinear effect, the colloid can be regarded far from its surface as if it carried an effective, partially neutralized charge $Z_{\mathrm{ef}}=Z-n$, with Z and n being the surface bare charges and number of *condensed* counterions, respectively. This counterion *condensation* effect stabilizes charged colloidal suspensions against phase separation, in agreement with the above-mentioned simulations.

In this paper, we focus in a higher salt concentration regime and investigate, experimentally, whether this charge renormalization controls the stability of highly charged colloidal suspensions against aggregation. It is well known that many equilibrium and dynamical colloidal features are controlled by charge values much lower than particle bare charges [7]. The highly charge-asymmetry introduced in the fluid or the high particle volume fractions seem to be the causes leading to effective charge arguments. However, the physical interpretation of such effective charges is not so straightforward [8] and thus, the microscopic state of a complex fluid is, in many cases, not well understood. This lack of knowledge unables predictions on properties and processes that depend on the particle charge. We will employ effective charge arguments in the studies of colloidal stability of very highly charged spherical colloids, demonstrating that the colloidal stability is controlled by a renormalized surface charge. This renormalization is predicted by an extension of the Debye-Hückel-Bjerrum liquid state theory [4,9]. In addition, it will be stated that a new colloidal entity consisting of the colloidal particle and a given number of *condensed* counterions should be now considered for a proper description of the colloidal features.

Let us consider two spheres of radius a each carrying a surface charge Ze, whose centers are separated by a distance r. The interparticle interaction is obtained from the long-accepted theory due to Derjaguin, Landau, Verwey, and Overbeek (DLVO) [10,11], consisting of the superimposition of repulsive and attractive interactions. The Coulombic term is derived from the nonlinear Poisson-Boltzmann equation, describing the electric potential in a solution of pointlike, simple ions. The electric potential outside a charged sphere is usually obtained by linearizing the otherwise intractible Poisson-Boltzmann equation. The repulsive electrostatic interaction is then obtained by using the Derjaguin method [12], invoking the linear superposition approximation to yield:

$$\frac{V_r}{kT}=Z^2\left(\frac{e^{\kappa a}}{1+\kappa a}\right)^2\lambda_b\frac{e^{-\kappa r}}{a}, \tag{1}$$

where $\lambda_b=e^2/(4\pi\epsilon_0\epsilon kT)$ is the Bjerrum length for the solvent, whose dielectric constant at temperature T is $\epsilon_0\epsilon$. λ_b is the characteristic lengthscale at which the electrostatic interaction between a pair of monovalent ions has magnitude kT. The Debye-Hückel screening length κ^{-1} is given by $\kappa^2=4\pi\lambda_b c$ and sets the distance over which electric fields are screened by a total concentration of monovalent ions c.

On the other hand, the DLVO theory includes terms accounting for the van der Waals interactions between particles:

$$\frac{V_a}{kT}=-\frac{A}{6}\left[\frac{2a^2}{r(4a+r)}+\frac{2a^2}{(2a+r)^2}+\ln\left(\frac{r(2a+r)}{(2a+r)^2}\right)\right], \tag{2}$$

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TABLE I. Experimental bare surface charges determined by titration (Z), particle size ($2a$), and critical coagulation concentration (CCC) at three solution pH's.

pH	Z	$2a$ (nm)	CCC (mM)
10.1 ± 0.1	$(2.27\pm0.02)\times10^{5}$	231 ± 6	~10
6.8 ± 0.1	$(1.24\pm0.02)\times10^{6}$	227 ± 5	~20
5.8 ± 0.1	$(1.52\pm0.02)\times10^{6}$	234 ± 6	~30

where A is the Hamaker constant of the colloid material.

Superimposition of these two interaction potentials leads to an attractive, deep minimum at very short interparticle distances, a repulsive barrier at intermediate separations, and a very weak attractive potential tail at large r. Upon increasing the salt concentration the repulsive electrostatic barrier is lowered and eventually eliminated, giving rise to particle aggregation. The concentration at which this occurs corresponds to the critical coagulation concentration (CCC). Several methods developed over the past five years to measure electrostatic interactions between colloidal spheres with sub-kT resolution, reveal that the DLVO theory quantitatively describes the interactions between isolated, unconfined pairs of spheres [3].

However, the applicability of Eq. (1) is restricted to low potentials, since linearization of the Poisson-Boltzmann equation is assumed in its derivation. Within the Debye-Hückel-Bjerrum liquid state theory, the nonlinearities omitted in the process of linearization can be reintroduced into the theory through the allowance of particle-counterion association [9]. As a consequence, we expect that the fluid will be composed of free unassociated particles, free counterions, and clusters consisting of a colloid and $0<n<Z$ associated counterions. Assuming that each *condensed* counterion neutralizes one of the particle charges, the effective charge carried by every particle-counterion cluster would then be $Z_{\mathrm{ef}}=Z-n$. This charge would be the one governing the repulsive interaction between particles, responsible for the colloidal stability of the system. Upon substitution of Z in Eq. (1) by Z_{ef}, the consistency of the DLVO theory is recovered and application to highly charged colloids is straightforward [13].

Determination of the number of *condensed* counterions follows from the knowledge of the total free energy of the fluid f. The free energy can be expressed as a sum of electrostatic and entropic (f_{en}) contributions. The first one is just a superimposition of the free energies arising from particle-counterion (f_{pc}), particle-particle (f_{pp}), and counterion-counterion (f_{cc}) interactions. Minimization of the total free energy $f=f_{\mathrm{en}}+f_{\mathrm{pc}}+f_{\mathrm{pp}}+f_{\mathrm{cc}}$ under the constraints of a fixed number of particles and counterions leads to the fraction of condensed counterions, n/Z [9]. Polydispersity in clusters is not relevant as proved in Ref. [9], hence the fluid essentially will consist of one characteristic particle-counterion cluster.

In order to see if the theoretical n/Z values justify the experimentally observed colloidal stability, deswollen spherical gel particles based on poly-(2-vinylpyridine) crosslinked with divinylbenzene (0.25%) were employed as experimental systems. The use of such colloids allows very high charge asymmetries to be introduced in the fluid [14], thus constituting an ideal system for testing the validity of the theory. Dynamic light scattering was employed for obtaining the mean particle hydrodynamic diameter: $2a=(230\pm6)$ nm. Particle charge was determined by titration [14]. 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). In this situation, the particle Hamaker constant is equal to 2.5×10^{-21} J, as taken from Ref. [15].

All measurements were performed with a modified Malvern Instruments 4700 System (UK), working with a 632.8 nm wavelength He-Ne laser. The suspension destabilization was induced by addition of NaCl, identifying the critical coagulation concentration, at a given surface charge, with the salt concentration at which the particle size increased, indicating that aggregation had taken place. The experiments were done under very dilute conditions ($\phi\sim10^{-5}$) in order to assure that only encounters between two particles were relevant in the initial stages of aggregation. The temperature was set to 25 °C in all cases and the pH was fixed by addition of NaOH or HCl.

The results for the critical coagulation concentration are shown in Table I. The CCC raises as Z increases, as expected. However, in view of the high surface charge values, higher CCC could have been anticipated. In fact, the computed values using expressions (1) and (2) with the bare charge are much higher than the experimentally measured ones. This discrepancy between experimental and expected CCC demands a close look to the microscopic state of the fluid. It seems that an effective charge, lower than the bare one, should be introduced in the physical picture to account for those discrepancies. This fact has been known for a long time. Nevertheless, the physical interpretation of such charges still remains rather unclear. The renormalization approach [7(a), 7(c)] consists in matching the nonlinear and linearized Poisson-Boltzmann equation at the edge of a spherical cell that surrounds every colloidal particle. The presence of other particles induces a strong accumulation of counterions in the vicinity of a particle, thus causing the electrostatic potential to decay faster than it would for an isolated particle. This effect is a plausible cause of charge renormalization in concentrated dispersions. However, it fails when very dilute colloidal suspensions are considered, since in this case the colloids can be regarded as isolated particles. We claim that this charge renormalization could be caused by the strong electrostatic interaction between the colloidal particles and the counterions, that may lead to the formation of particle-counterion clusters with a consequent renormalized surface charge $Z_{\mathrm{ef}}=Z-n$. This effect would be

TABLE II. Experimental and predicted fraction of *condensed* counterions (n/Z) for three surface, bare charges. In addition, n/Z values determined from electrophoretic measurements are also presented. The errors in *experimental* n/Z have been reduced as much as permitted by the experimental methods.

Z	Experimental n/Z	Theoretical n/Z	n/Z^{a}
$(2.27\pm0.02)\times10^{5}$	0.9943 ± 0.024	0.992 80	0.976 ± 0.08
$(1.24\pm0.02)\times10^{6}$	0.9982 ± 0.024	0.998 58	0.995 ± 0.08
$(1.52\pm0.02)\times10^{6}$	0.9985 ± 0.024	0.998 84	0.995 ± 0.08

[a] Reference [16].

specially relevant when high charge asymmetries are present in the complex fluid, as is the case for the experimental system considered here.

The experimental fraction of *condensed* counterions is obtained by using the fact that at the CCC, the repulsive barrier responsible for the colloid stability of the system dissapears. By setting the total DLVO interaction potential, $V(r)=V_r+V_a$, and its first derivative equal to zero, the position of the barrier as well as Z_{ef} can be obtained, thus allowing determination of n/Z. The experimental CCC fixes the value of κ. The results, shown in Table II, agree well with the predictions of a very recent extension to the Debye-Hückel-Bjerrum liquid state theory [4,9]. This agreement suggests that the complex fluid will be composed of clusters formed by one particle and n counterions, the amount of the latter being given by the value of n/Z. Far from its surface, these clusters can be considered as new colloidal particles, each one carrying a surface charge equal to $Z-n$. This renormalized surface charge controls the repulsive interaction between particles, thus determining the colloidal stability of the system. This scenario is further supported by recent experiments [16]. Fractions of *condensed* counterions were obtained in that work by comparing measured and theoretical electrophoretic mobilities. In that case, an electric field was applied to the colloidal suspension and the particle velocity was measured. The results for n/Z are presented in Table II for comparison. The agreement is worth mentioning and generalizes the occurrance of counterion *condensation* to different physical situations.

Summarizing, we have presented results concerning the colloidal stability of highly charged spherical particles in a primitive electrolyte, encountering that the fraction of bare charge needed to account for the experimental CCC is reasonably well predicted by an extension of the Debye-Hückel-Bjerrum theory to the fluid state of highly charged colloids. These same values for n/Z were obtained in electrophoresis, further supporting the theory. As a consequence, the proper description of a highly charged dispersion implies consideration of charge renormalization effects, which arise as a consequence of the strong electrostatic interaction between the colloid and the counterions. We thus conclude that the nonlinear effects associated with the presence of double layers around particles, strongly modify the behavior of the colloidal system in the strong-coupling limit, and hence should be taken into account for a proper prediction of its behavior.

The validity of these conclusions is restricted to aqueous and highly charged suspensions with monovalent counterions. Whenever electrostatic interations between *condensed* counterions are significant, the theory needs to be extended in order to account for these correlations. For solvents with low dielectric constants, multivalent counterions or small colloids (sizes comparable to λ_b) these effects become important and the Poisson-Boltzmann approach breaks down. In the limit $\lambda_b/a\rightarrow0$, the Poisson-Boltzmann equation is recovered. In the experimental situation considered here, this is the case and the encountered agreement is worth mentioning.

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