Freezing Transition for Colloids with Adjustable Charge: A Test of Charge Renormalization

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By exploiting the peculiar adsorption properties of fluorinated surfactants, which allows one to trim the number of ionizable groups on the surface of latex particles, we have determined for the first time the phase diagram of aqueous colloidal suspensions as a function of the bare particle charge. Comparison of the experimental freezing line with numerical simulations of a Yukawa system yields an effective charge in close agreement with the prediction of charge-renormalization models. Conductivity data suggest that effective-charge arguments may also be helpful in studies of transport properties.

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Aqueous suspensions of charged colloids represent a valuable model of the fluid structure due to the extreme flexibility of the interparticle interactions, which can be continuously varied between the hard-sphere and the one-component plasma limits [1]. The common procedure of changing the suspension ionic strength by adding salt indeed allows one to tune the range of the potential. Further information concerning the system thermodynamics and phase equilibria would be gained, however, if the strength of the interaction, at fixed range, were controlled by trimming the particle charge. In the present Letter we show that this result can indeed be achieved by exploiting the controlled adsorption of an ionizable species on the particle surface, and we present for the first time a full phase diagram of a colloidal suspension as a function of a controllable bare particle charge. A further motivation to study suspensions of particles with adjustable charge is the following. The observed properties of charged colloids can very often be modeled by using a simple Yukawa form for the interaction potential, as derived from the linearized Poisson-Boltzmann equation. A major drawback is that one has to assume for the particle charge an *ad hoc* value usually much smaller than the "bare" charge measured by titration methods. Alexander *et al.* [2] and, independently, Belloni [3] have proposed a physical reason for the occurrence of an effective charge value, suggesting that most of the dissociated counterions recondense within a thin layer around the particle until the electric potential near its surface is lowered to a value of a few $k_{\mathrm{B}}T$. The most attractive feature of this charge-renormalization mechanism is its ability to predict a value for a physically meaningful charge which does not depend on the peculiar particle-surface chemistry. More recently, Kjellander and Mitchell [4] have given a rigorous foundation to the charge-renormalization approach.

So far, tests of charge renormalization have been limited to systems with fixed bare particle charge, by dertermining the effective charge as a function of the particle concentration and of the ionic strength from structure factor [5,6] or shear modulus [7,8] data. The only exception is a study of mixed ionic-nonionic surfactant solutions [9]; for this system the possibility of controlling the fractional amount of charged groups within a micelle allowed a demonstration that the effective particle charge required to fit the suspension structure factor saturates to a value in quantitative agreement with the predictions of charge renormalization.

We have determined the effective charge as a function of the number of ionizable groups on the particle surface by matching the experimental charge-dependent freezing line separating the fluid from the colloidal-crystal phase to the phase diagram predicted for a Yukawa system [10,11]. The results strongly support the prediction of charge-renormalization models. Moreover, a simplified analysis of conductivity data suggests that effective-charge arguments may also be helpful for studies of transport properties.

We have studied suspensions of colloidal spheres of radius $R = 45$ nm and low degree of polydispersity ($\leq 5\%$) made of FEP, a polytetrafluoroethylene copolymer (Ausimont S.p.A., Milano, Italy) produced by microemulsion polymerization in the presence of the anionic surfactant sodium perfluorooctanoate (PFO). The charge of the particles, as they come out from the polymerization process, is largely determined by physisorbed PFO, while the chemically anchored terminal FEP groups contribute to the charge only to a lesser extent [12]. Surface adsorption of ionizable surfactants is a common feature in emulsion polymerization of latex particles. The peculiar solution properties of fluorinated surfactants make a difference, however. While in the case of, say, polystyrene latexes the adsorbed charge can easily be dialyzed out, PFO is weakly soluble in water and adsorbs quite strongly on FEP both as a salt and even more so in the acidic form (perfluorooctanoic acid, PFOA) obtained by flushing the suspension through ionic-exchange resins. This

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can be shown by monitoring the conductivity of a suspension as a function of exposure time to resins. An initial sharp drop of the conductivity, which takes place on a time scale of tens of minutes, corresponding to complete removal of carbonate and other spurious ions, is followed by a very slow decrease related to desorption of surfactant molecules. Decreasing the conductivity by a factor of 2 requires a few days of intense treatment by exchange resins. Surfactant desorption is conversely negligible if the sample is not exposed to resins. The "bare" charge of FEP particles can then be adjusted by careful trimming of PFOA desorption.

By exploiting this fact, we have studied suspensions at fixed number density of particles $\rho = 6.3 \times 10^{19}$ m^{-3} treated by an ion-exchange procedure in closed-circuit flow [13] for different periods up to one week. The number of ionizable groups N of the different samples, whose conductivity was a monotonically decreasing function of the exposure time to resins, has been measured by conductometric titration with NaOH. This allowed us to relate the suspension conductivity before titration to the bare particle charge according to the experimental calibration curve in Fig. 1. The lowest value attained by N sets an upper bound for the value of the chemically bound charge due to the terminal groups of the polymer chains, confirming that the main contribution to the particle charge comes from physisorbed surfactant.

Each suspension was then de-ionized once again after titration until the initial conductivity was recovered. Under this condition suspensions with $N \gtrsim 500$ were in a bcc colloidal-crystal phase. Resins were then excluded from the flow circuit, and the salt concentration c_s was increased by adding NaCl in small amounts until crystal melting was visually observed. Figure 2 shows the experimental charge-dependent fluid/crystal coexistence intervals estimated by observing the simultaneous occurrence of Bragg spots from the crystallites and of diffuse light scattered by the fluid.

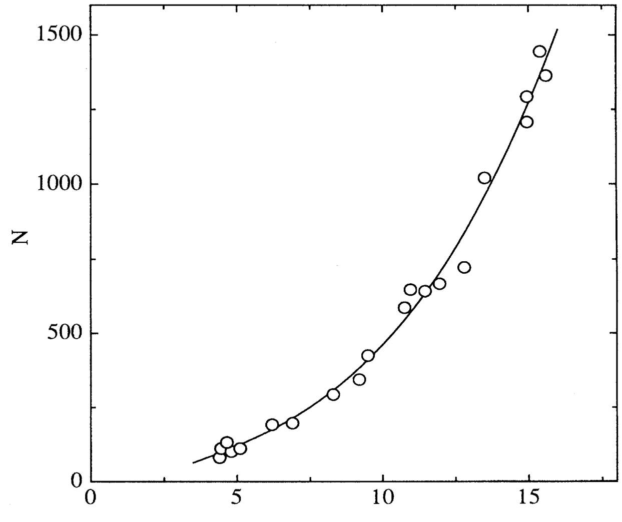

FIG. 1. Titrated particle charge as a function of the initial sample conductivity for FEP suspensions flushed for different periods through resins. Full line is a polynomial fit to the data.

Figure 2 shows the experimental (c_s, N) diagram at fixed ρ. We notice that on increasing c_s the freezing line bends considerably upward and becomes almost vertical, while the coexistence interval slightly broadens. This asymptotic independence of the freezing line from the salt concentration qualitatively means that the disordering effect of a larger ionic strength can be less and less counteracted by increasing the particle bare charge. In other words, the strength of the electrostatic interaction cannot be increased beyond a given limit, which is a first indication of the predicted saturation of the effective charge.

In order to provide a quantitative test, we compared our data to the numerical simulation by Robbins *et al.* [10], later modified by Meyer and Frenkel [11], of the phase diagram for a system interacting via a Yukawa potential $V(r) = U \exp(-\kappa r)/r$, where $U = (Z^2 e^2)/(4\pi\varepsilon\varepsilon_0)(e^{2\kappa R})/(1 + \kappa R)^2$, $\kappa = e[(Z\rho + \rho_s)/k_B T]^{1/2}$ is the screening parameter, Ze is the particle charge, and ρ_s the salt number density. Reference [11] allows evaluation of the melting line in terms of the dimensionless parameters $\lambda = \kappa \rho^{1/3}$ and $\tilde{T} = \lambda \exp[\lambda] k_B T/U$, which are determined by the parti-

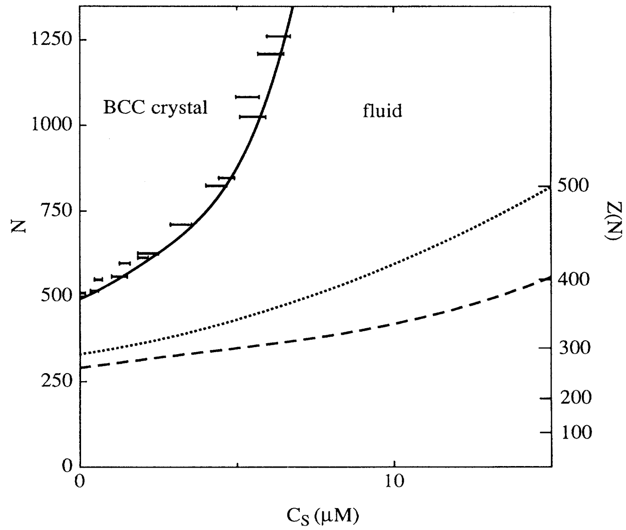

FIG. 2. Phase diagram of FEP colloidal suspensions with variable particle charge. C_s is the concentration of added NaCl. Bars are the experimental fluid-crystal coexistence intervals. Curves are the polynomial interpolations to the numerically predicted freezing lines using the particle bare charge N (dashed), the number of effectively ionized group at constant dissociation equilibrium $Z(N)$ (dotted), and the renormalized charge Z_{eff} (full).

cle charge and by the salt concentration. Figure 2 shows that the melting line calculated using $Z = N$ for the particle charge is completely at odds with the experimental data points.

A first explanation of this discrepancy could be simply related to surface chemistry. The high concentration of H^+ ions near the particle surface indeed measurably reduces the local pH compared to the bulk value, limiting the dissociation of PFOA, which has a $pK \approx 4$. The number of *actually ionized* groups $Z(N)$ will then be considerably smaller than the number of possible *ionizable* groups N measured by titration. Thanks to a program kindly given to us by L. Belloni, we have numerically solved the Poisson-Boltzmann equation within the framework of constant dissociation equilibrium (rather than under the condition of constant charge) using $pK = 4$ for PFOA to get $Z(N)$, which can be compared to N by looking at the right y axis in Fig. 2. However, when $Z(N)$ is used to calculate the phase diagram, it yields a nearly horizontal freezing line positioned at much too low N (see Fig. 2). Thus chemical considerations alone are insufficient to reproduce the experimental results.

We then followed the procedure suggested in [2] by assuming as a bare particle charge the dissociated charge $Z(N)$ and numerically solving the Poisson-Boltzmann equation in a spherical Wigner-Seitz cell. The effective parameters of the linearized Yukawa approximation are then determined by asymptotic matching to the far field limit of the full Poisson-Bolzmann solution. This scheme yields the effective charge Z_{eff} and the effective screening length $\kappa_{\mathrm{eff}} = [4\pi\lambda_B(2\rho_s + Z_{\mathrm{eff}}\rho)]^{1/2}$ which are used to calculate the phase diagram. The full line in Fig. 2 shows that the agreement is excellent.

The above result is better appreciated if we choose to plot the charge number Z giving the best fit to the experimental melting line versus the number of titrated groups. Figure 3 shows that Z is almost constant despite N changing by more than a factor of 2. While the dashed curve for $Z(N)$ indicates that partial dissociation accounts for the saturation effect only to some extent, the full line, giving the renormalized charge Z_{eff} calculated according to Ref. [2], is in close agreement with the data. We also notice that the experimental saturation value $Z_{\mathrm{eff}} \approx 400$ does not differ too much from a simple qualitative criterion proposed by Belloni [14] for the value of the renormalized charge $Z_{\mathrm{eff}} \approx (4R/\lambda_B)(1 + \kappa_{\mathrm{eff}}R)$, where $\lambda_B = e^2/4\pi\varepsilon k_B T$ is the Bjerrum length ($\lambda_B \approx 0.71$ nm in water). Indeed, for $\rho_s \approx 3.61 \times 10^{21}$, corresponding to $C_s = 8\ \mu M$, which from Fig. 2 is approximately the ionic strength where the melting line becomes κ-independent, we get $Z_{\mathrm{eff}} \approx 450$ and $\kappa_{\mathrm{eff}}{}^{-1} \approx 56$ nm.

Figure 3 also allows one to discuss the conductivity results of Fig. 1. The effectively transported charge Z_{tr} has been evaluated from the sample conductivity by assuming independent migrations of the counterions, which seems to be reasonably consistent with the existent data on similar systems [15]. Moreover, the results of Ref. [15] suggest that for strongly overlapping double layers relaxation effects become negligible. Writing then $\sigma = \rho Z_{\mathrm{tr}} e(\mu_P + \mu_{H^+})$, where $\mu_{H^+} \approx 3.6 \times 10^{-7}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$ is the proton electrophoretic mobility, we evaluated the particle mobility μ_P within Henry's approximation [16]. In analogy with static charge-renormalization arguments, we assumed for the ζ potential a Debye-Hückel form, using Z_{tr} as the value for the particle charge: $\zeta = Z_{\mathrm{tr}} e/[4\pi\varepsilon R(1 + \kappa R)]$. The open dots in Fig. 3 show that the calculated values for Z_{tr} are almost coincident with those for Z_{eff}, suggesting that the renormalized charge may also be a useful concept for describing transport properties. Although the approximations made in evaluating μ_P may be questioned, more refined expressions for the macroion mobility will not sensibly alter the trend and numerical range for Z_{tr}. Indeed, if a suspension is fully ion-exchanged and no salt is added, the colloidal particles, having typical electrophoretic mobility of order $5 \times 10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$, contribute less then 20% to the suspension conductivity due to the dominant proton mobility.

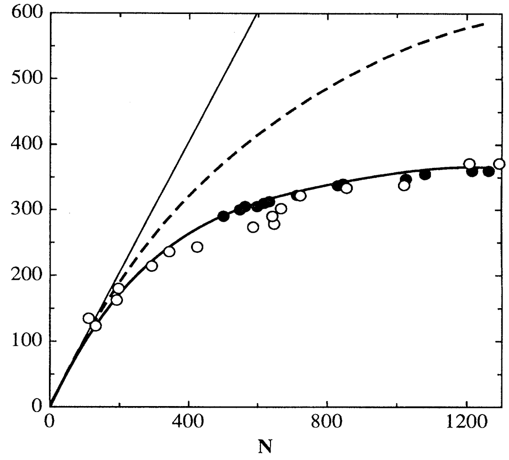

FIG. 3. Values for the particle charge derived from a fit to the freezing line (full dots) and from conductivity data (open dots). Lines are the particle charges at constant dissociation equilibrium without renormalization [$Z(N)$, dashed] and from the Poisson-Boltzmann cell model (Z_{eff}, full).

We notice that a saturating transported charge leads to a saturation value for the particle electrophoretic mobility. This effect, though interpreted in terms of an enhanced friction factor, has been clearly seen in recent measurements on suspensions of particles of different size and number of ionizable groups [17].

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