Density dependent interactions and structure of charged colloidal dispersions in the weak screening regime

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We determine the structure of charge-stabilized colloidal suspensions at low ionic strength over an extended range of particle volume fractions using a combination of light and small angle neutron scattering experiments. The variation of the structure factor with concentration is analyzed within a one-component model of a colloidal suspension. We show that the observed structural behavior corresponds to a non-monotonic density dependence of the colloid effective charge and the mean interparticle interaction energy. Our findings are corroborated by similar observations from primitive model computer simulations of salt-free colloidal suspensions.

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Deionized colloidal dispersions have recently attracted much experimental [1, 2, 3] and theoretical attention [4, 5, 6, 7] because of their unique role as simple model systems in the field of surface charge regulation. In addition to experimental challenges posed by these systems, such as the need of control over the ionic strength of the medium, a number of intriguing observations have been made that challenge classical theories of electrostatic screening and electrokinetics (e.g., see [1, 8] and references therein). Some of the conceptual difficulties in the understanding of these systems stem from the counterion dominance in the ionic cloud of the colloid, which makes the screening ability of the medium dependent on the colloidal concentration. At the same time, the counterion condensation, which is controlled by the balance of the counterion chemical potential between the bulk suspension and the condensed layer, would depend on the concentration through the state-dependent screening parameters [4, 10, 11]. Therefore, modeling these systems within the usual one-component description can only be achieved using effective density-dependent interaction parameters, charge and screening length [12]. The dependence of the colloid effective charge on the volume fraction [4, 5, 12] or background ionic strength [13] has been predicted in a few mean-field models and is expected to be non-monotonic. However, this non-monotonic behavior has never been validated experimentally.

In this Letter, we present a study of the density dependence of the colloidal structure and interactions at low ionic strength. Experiments have been carried out over a wider range of concentrations than in any previous work. We analyze the particle structure factor obtained from light and neutron scattering at different particle volume fractions and demonstrate that (i) the variation of colloidal structure in deionized suspensions can be interpreted in terms of a one-component model (OCM) that considers Yukawa-like pair interactions between colloids with state-dependent parameters and, (ii) the non-monotonic concentration dependence of the interaction energy, as characterized by the colloid effective charge, is a general feature of deionized colloidal dispersions. Primitive model (PM) numerical simulations of salt-free suspensions corroborate our observations.

Stock suspensions of negatively charged particles (sulfonate polystyrene latex) were purchased from Interfacial Dynamics Corporation (Portland, USA) and master dispersions were prepared following the protocol described in Ref. [15, 16]. The samples were prepared by diluting the master suspensions directly into quartz cells with water/ethanol mixtures; filtered several times (pore size 0.2 µm) to remove dust particles. These mixtures were chosen in order to avoid crystallization by modifying the solvent dielectric constant [17], thereby providing a well controlled model system of charged dispersions with volume fractions as high as ~ 16%. Accurate values of particle radii and polydispersities, as obtained from DLS and SANS experiments, are given in Table I.

The effective interparticle interaction can be quantified through the analysis of the suspension static structure. This requires probing length scales comparable to the size of the particles. Usually such information can be obtained from static and dynamic light scatter-
ing (SLS/DLS) in the single scattering regime \[18\]. In
dense suspensions, however, these techniques cannot be
applied in most cases due to multiple scattering of light.
An elegant way to overcome this limitation is the use of
modern scattering techniques such as 3D dynamic light
scattering (3D-DLS) \[19\] or small angle neutron scattering
(SANS). While 3D-DLS provides valuable information
at small and intermediate values of the scattering
vector \( q \), access to large \( q \)-vectors from SANS allows to
normalize the static structure factor \( S(q) \) and, in that
way, unambiguously determine the suspension structure.
A detailed description of the light scattering (LS)
experiments is given in Ref. \[15\].

Multiple scattering of neutrons in our SANS experiments
has been suppressed by partially contrast matching
the particles using \( \text{H}_2\text{O} / \text{ethanol} - \text{D}_2\text{O} / \text{deuterated}
\text{ethanol} \) mixtures. The samples were kept in stoppered
quartz cells (Hellma, Germany) with a path length of 2\( \text{mm} \)
and containing a mixed-bed of ion-exchanger resins;
deionization was typically completed within 2
weeks. The measurements were performed with a mean
neutron wavelength of 1.27\( \text{nm} \) and at a detector dis-
tance of 20.3\( \text{m} \), which corresponds to a \( q \)-range of 0.01-
0.1\( \text{nm}^{-1} \). For details on the initial data treatment and
data analysis see Ref. \[20\] and references therein. The
SANS scattering intensity can be expressed as \( I(q) = A P(q)S(q)S_{\text{SANS}} \), where \( P(q)S_{\text{SANS}} \) is the
normalized effective particle form factor, \( S(q)S_{\text{SANS}} \) is the
effective interparticle structure factor and \( A \) is an amplitude,
which is proportional to the particle number density, \( n \),
and to the square of the neutron scattering length con-
trast between the particles and background fluid \[21\].
The effective SANS static structure factor can be deter-
dined from \( S(q)S_{\text{SANS}} = (A_0/A) [I(q)/I_0(q)] \), where
\( I_0(q) = A_0 P(q)S_{\text{SANS}} \) is the intensity scattered by a sus-
pension of non-interacting particles with amplitude \( A_0 \).

On the theory side, the static structure factor of colloidal
dispersions can be calculated by solving the Ornstein-Zernike
(OZ) equation together with the Rogers-Young (RY)
closure relation \[22\] for particles interacting with an effective
pair potential \( u_{\text{eff}}(r) \) of the Yukawa form

\[
\beta u_{\text{eff}}(r) = Z_{\text{eff}}^2 \lambda_B \left[ \frac{\exp(\kappa_{\text{eff}} a)}{1 + \kappa_{\text{eff}} a} \right]^2 \frac{\exp(-\kappa_{\text{eff}} r)}{r},
\]

with an effective charge \( Z_{\text{eff}} \), colloid radius \( a \), ther-
mal energy \( \beta^{-1} = k_B T \), screening parameter \( \kappa_{\text{eff}}^2 =
4\pi \lambda_B (Z_{\text{eff}} n + n_s) \) and concentration of salt ions
\( n_s = 2 \times 10^{10} N_A c_s \), where \( c_s \) is the molar con-
centration \[12\].

This procedure has been successfully used for calculating
the structure in the strong screening regime at \( \kappa_{\text{eff}} a \gg 1 \)
\[22\] but it becomes less accurate in systems with thick
double layers as the interparticle potential deviates from
the Yukawa shape \[22\]. Despite this deficiency, an appro-
priate choice of \( Z_{\text{eff}} \) still allows one to predict the struc-
ture factor of strongly interacting systems over a wide
range of conditions as long as the pair interaction energy
at the mean interparticle distance is correctly reproduced
\[24\]. Nevertheless, an agreement of the OCM structure
and the mean interaction energy with the original ones
does not guarantee that other thermodynamic proper-
ties, such as the osmotic pressure, can be predicted using
the effective parameters. The difficulty with the pressure
originates from the loss of the ionic degrees of freedom in
the coarse-grained description. Various solutions to this
issue have been suggested recently. In one, the missing
pressure contributions have been recovered via inclusion
of the boundary terms \[28\]. Alternatively, one can use
a modified OZ-RY approach to get the effective parameters
in the fit procedure \[3\]. The latter replaces the OCM
(Yukawa fluid) pressure by the osmotic pressure known
\textit{a priori} from primitive model simulations or mean-field
models (e.g. jellium) in calculating the isothermal compres-
sibility. We use this route to extract the effective
charges and effective potentials from the structure data
measured in experiment and simulations.

Fig. 1 displays the normalized scattering intensity for
two of the samples S3 in Table I a) \( \varphi = 2.5\% \) and b) \( \varphi = 7.6\% \). In a), the squares are from 3D-DLS and
circles from SANS measurements, thus illustrating the
complementarity of both experimental techniques. The
experimental error is estimated from the intensity statis-
tics in a series of measurements. For both SANS and LS,

![FIG. 1: (color online) Normalized scattering intensities of samples a) \( \varphi = 0.025 \) and, b) \( \varphi = 0.076 \). The squares are from 3D-DLS and the circles from SANS. The dashed line is the calculated \( S(q) \) and the continuous line its SANS experimental convolution, \( S(q)S_{\text{SANS}} \). Insets: scattering intensities for a) a diluted screened suspension and, b) \( \varphi = 0.076 \).](image-url)
the experimental data are in good agreement with theoretical calculations (lines) based on integral equations theory using the polydisperse RY closure relation \[22\] as described in Ref. \[5\]. The background salt concentration, \(c_s = 2 \times 10^{-7}\) M, was determined by measuring the conductivity of our deionized solvent mixtures as in Ref. \[23\]. Thus, the free parameters in our fitting procedure are the volume fraction \(\varphi\) and the effective charge \(Z_{\text{eff}}\). The dashed lines represent the calculated \(S(q)\) and the continuous lines correspond to the result after its experimental convolution, \(S(q)_{\text{SANS}}\), with the appropriate resolution function \[26\]. The structure factor exhibits a pronounced maximum, whose position \(q_{\text{max}}\) varies with the particle volume fraction as \(n^{-1/3}\) \[16\]. Additionally, in the Insets we also show the SANS scattering intensities for: a) a dilute, \(\varphi \approx 0.005\), screened (\(c_s \approx 0.005\) M of KCl) suspension and, b) the sample \(\varphi = 7.6\%\). Here, the lines are experimentally convoluted fits with polydisperse form, \(I_0(q) \propto P(q)_{\text{SANS}}\), and structure factor, \(I(q) \propto P(q)_{\text{SANS}}S(q)_{\text{SANS}}\).

In Fig. 2(a) we present the \(\varphi\)-dependence of the height of the main peak of the structure factor, \(S(q_{\text{max}})\), as obtained from the LS and SANS analysis. At low volume fractions, the peak height is about 2 and varies weakly with concentration until \(\varphi \approx 0.002\), then it decreases in the range \(0.002 < \varphi < 0.01\) to finally grow again for \(\varphi > 0.01\). We note that for \(\varphi > 0.06\), the values of \(S(q_{\text{max}}) > 3.0\) indicate a glassy state \[27\]. While the increase of \(S(q_{\text{max}})\) with concentration can be readily explained by shortening the distance between neighboring colloids and rising average interparticle repulsion, the decrease at \(\varphi \approx 0.01\) is a more complex feature. This depression can be attributed to the maximum of ionic condensation or a minimum of the effective macroion charge as discussed below. To test whether this behavior is specific to the experimental systems considered here, in the Inset of Fig. 2(b) we show results of PM simulations (solid symbols) of a salt-free charged colloidal suspension with charge asymmetry 200:1. The simulations were performed for systems with \(\lambda_B/a = 0.2\) using the same cluster Monte Carlo simulation protocol and settings as in Ref. \[28\] with 80 colloidal particles. The \(S(q_{\text{max}})\) from simulations shows a similar trend to the experiments although the main features are less pronounced. Nevertheless, one can show that this characteristic trend of the structure factor corresponds to a quite peculiar behavior of the pair interaction potential. Fig. 2(b) depicts the interaction energy between nearest neighbor colloids, \(\beta u_{\text{eff}}(r_m)\), as extracted from fits to the structure data of systems S1-S3. \(\beta u_{\text{eff}}(r_m)\) follows the trend observed for \(S(q_{\text{max}})\) with more pronounced features: a maximum at \(\varphi \approx 0.001\), a minimum at \(\varphi \approx 0.01\), and an increase at higher volume fractions. The same holds for the PM results; solid circles in the Inset of Fig. 2(b).

Furthermore, we were able to self-consistently prove our primitive model results by using their associated effective charges and screening lengths in OCM-NPT simulations (open squares in the Inset of Fig. 2(b)). Here, we used \(N = 1000\) colloidal particles and the osmotic pressure as obtained from the PM simulations.

The interactions between colloids are conveniently characterized by their effective charge. To compare the results between different systems we use the dimensionless ratio \(\tilde{Z}_{\text{eff}} = Z_{\text{eff}}\lambda_B/a\) instead of the valency itself. In
Fig. 3 we show the results of $\tilde{Z}_{\text{eff}}$ as obtained from fitting the scattering data with our OZ-RY scheme (same symbols as in Fig. 2). Furthermore, in Fig. 3 we compare the data with results of the PM simulations described above (solid circles in the Inset), where $Z_{\text{bare}}/a = 40.0$ and the $\tilde{Z}_{\text{eff}}$ are extracted following the same protocol as in the experiments. Both sets of data show a pronounced minimum of the effective charge at $\varphi \approx 10^{-2}$.

The behavior of $\tilde{Z}_{\text{eff}}$ in the range $\varphi \lesssim 10^{-2}$ stems from the variation of the mean counterion concentration. Upon increasing $\varphi$, counterions in average get closer to the colloidal surface thus leading to a gradual decrease of $\tilde{Z}_{\text{eff}}$. At $\varphi > 10^{-2}$, in contrast, the effective charge starts increasing because the average electrostatic potential in the bulk, or at least at $r \geq r_m$, becomes comparable to that on the colloid surface thus making the counterion condensation less favorable. In Fig. 3 we also present results from two models, which predict a similar density dependence for $\tilde{Z}_{\text{eff}}$: renormalized jellium [14] and Poisson-Boltzmann cell model (PB-cell) [11]. We used $c_s = 2 \times 10^{-7}$ M in the experiments (main figure) and $c_s = 0$ in the simulations (Inset). These models correctly reproduce the qualitative behavior of the effective charge, although the values corresponding to the saturation regime are too high. This quantitative disagreement might be caused by various reasons. First, the best fit in our procedure corresponds to slightly lower effective charges than those in the jellium model. Moreover, the values are affected by the actual surface charge density on the colloids in experiment and ionic correlation effects in the simulations [28]. The charge dissociation in water-alcohol mixtures is expected to be lower than in pure water. Our present data suggest the dissociation on the level of ca. 20% of that in water, which means the actual charges are below the saturation values for these particles at some volume fractions. Finally, we should note that the non-monotonic behavior of $\tilde{Z}_{\text{eff}}$ is characteristic for the counterion-dominated screening regime. Our numerical estimations show that already amounts of salt comparable to the effective counterion concentration, ca. 1µM in our systems, might lead to disappearance of the minimum in the effective interaction and effective charge as function of colloidal volume fraction.

In summary, we have studied the variation of the colloidal structure factor in charged deionized colloidal dispersions and demonstrated that its density dependence corresponds to a non-monotonic variation of the mean interparticle interaction and particle effective charge, with a minimum at about a volume fraction of 1%. Our results cover a wider range of particle concentrations than in any previous study thus giving an excellent benchmark for models of electrostatic screening in colloidal dispersions. Furthermore, our findings are confirmed by computer simulations in the counterion dominated regime of both primitive and one-component models.

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[1] T. Palberg et al., J. Phys.: Condens. Matter 16, S4039 (2004).
[2] L. Shapran et al., J. Chem. Phys. 125, 194714 (2006).
[3] C. Haro-Pérez et al., J. Phys.: Condens. Matter 18, L363 (2006).
[4] E. Trizac and Y. Levin, Phys. Rev. E 69, 031403 (2004).
[5] R. Castañeda-Priego et al., Phys. Rev. E 74, 051408 (2006).
[6] E. Trizac et al., Phys. Rev. E 75, 011401 (2007).
[7] V. Lobaskin et al., Phys. Rev. Lett. 98, 176105 (2007).
[8] C. P. Royall et al., J. Chem. Phys. 124, 244706 (2006).
[9] B. V. R. Tata et al., Solid State Comm. 139, 562 (2006).
[10] B. Beresford-Smith et al., J. Colloid Interface Sci. 105, 216 (1984).
[11] S. Alexander et al., J. Chem. Phys. 80, 5776 (1984).
[12] L. Belloni, J. Phys.: Condens. Matter 12, R549 (2000); Y. Levin, Rep. Prog. Phys. 65, 1577 (2002).
[13] T. Gisler et al., J. Chem. Phys. 101, 9924 (1994).
[14] R. R. Netz and H. Orland, Eur. Phys. J. E 11, 301 (2003).
[15] L. F. Rojas et al., Europhys. Lett. 60, 802 (2002); L. F. Rojas et al., Faraday Discuss. 123, 385 (2003).
[16] L. F. Rojas-Ochoa et al., Phys. Rev. Lett. 93, 073903 (2004).
[17] D. Bertolini et al., J. Chem. Phys. 78, 365 (1983).
[18] P. Schurtenberger and M. E. Newman, in Environmental Particles, edited by J. Buffe and H. P. van Leeuwen, Boca Raton; Lewis Publishers (1993), pp. 37-115; F. Scheffold and R. Cerbino, Curr. Opin. Coll. Int. Sci. 12, 50 (2007).
[19] 3D-DLS is an extension of traditional SLS/DLS to the regime of weak and moderate multiple scattering based on a cross-correlation scheme [C. Urban and P. Schurtenberger, J. Colloid Interface Sci. 207, 150 (1998)].
[20] L. F. Rojas-Ochoa et al., Phys. Rev. E 65, 051403 (2002).
[21] C. F. Wu and S. H. Chen, J. Chem. Phys. 87, 6199 (1987).
[22] B. D’Aguanno and R. Klein, Phys. Rev. A 46, 7652 (1992); G. Nägele, Phys. Rep. 272, 215 (1996).
[23] M. Brunner et al., Europhys. Lett. 58, 926 (2002); V. Lobaskin et al., J. Phys.: Condens. Matter 15, 6693 (2003).
[24] V. Lobaskin et al., Phys. Rev. E 63, 020401(R) (2001).
[25] M. Evers et al., Phys. Rev. E 57, 6774 (1998); D. Hesseinger et al., Phys. Rev. E 61, 5493 (2000).
[26] J. G. Barker et al., J. Appl. Cryst. 28, 105 (1995).
[27] J. P. Hansen and L. Verlet, Phys. Rev. 184, 151 (1969).
[28] V. Lobaskin and P. Linse, J. Chem. Phys. 111, 4300 (1999).