Renormalization in charged colloids: non-monotonic behaviour with the surface charge

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Abstract

The static structure factor $S(q)$ is measured for a set of deionized latex
dispersions with different numbers of ionizable surface groups per particle and
similar diameters. For a given volume fraction, the height of the main peak of
$S(q)$, which is a direct measure of the spatial ordering of latex particles, does
not increase monotonically with the number of ionizable groups. This behaviour
cannot be described using the classical renormalization scheme based on the cell
model. We analyse our experimental data using a renormalization model based
on the *jellium* approximation, which predicts the weakening of the spatial order
for moderate and large particle charges.

A long-standing issue in colloid science is the precise understanding of the electrostatic forces
in charge-stabilized dispersions. According to the widely known Derjaguin–Landau–Verwey–
Overbeek (DLVO) theory, the interaction potential $u(r)$ of charged spherical colloidal particles
is

$$u(r) = \frac{(Ze)^2}{4\pi \varepsilon_0 \varepsilon_{\mathrm{r}}} \frac{\exp(2\kappa a)}{(1 + \kappa a)^2} \frac{\exp(-\kappa r)}{r}. \tag{1}$$

Here, Z is the number of charges per colloidal particle, e is the elementary charge, κ is the
Debye–Hückel screening parameter, $\varepsilon_0 \varepsilon_{\mathrm{r}}$ is the dielectric permittivity of the solvent and a is
the colloidal particle radius. This expression was derived assuming small surface charges.
However, a large number of theoretical works state that equation (1) could be valid if Z and κ
are considered as *renormalized* parameters rather than the actual ones (see [1–3] and references
cited therein). Some theories have been devised for predicting renormalized parameters in a

Table 1. Latexes used in this work.

Latex	Diameter (nm)	Surface charge density ($\mu C\ cm^{-2}$)	Number of ionizable groups per particle
L1	82	0.63	425
L2	80	1.51	2100
L3	80	2.97	4210
L4	80	7.86	11140

numerical way. In the middle 1980s Alexander *et al* proposed the cell model [4], which has been widely used since then. Accordingly, the dimensionless solution (Ψ) to the Poisson–Boltzmann (PB) equation is asymptotically approximated at the boundary of the so-called Wigner–Seitz (WS) cell by the solution of the linearized PB equation (Ψ_0), where the size of the WS cell is determined by the particle concentration. At small distances from the surface, Ψ_0 underestimates the magnitude and the slope of Ψ. This underestimation is interpreted in terms of charge renormalization [4].

At the same time, Beresford-Smith and co-workers [5] developed a renormalization scheme based on the so-called *jellium* approximation. The theory proposed by these authors is also based on the approximation of Ψ by Ψ_0 but at large distances in this case. Also in contrast with the cell model, the dispersion is supposed to be completely disordered. In other words, this theory assumes that there are no correlations between the particles, i.e. the colloid–colloid radial distribution function is $g(r) = 1$. Although this approach was proposed two decades ago, only recently have a few works emphasized its more peculiar and characteristic predictions. Rojas and co-workers find in their experiments that the amplitude of the first peak of the structure factor does not increase monotonically with the volume fraction (φ) but shows a minimum [6], which had already been predicted by Beresford-Smith [5]. Another of its predictions is the behaviour of the structure with particle charge; they reported that the first peak of the structure factor should exhibit a maximum with increasing particle charge. Trizac and Levin propose a *renormalized jellium* model and argue as to why the effective charge obtained from it is more relevant for studying colloidal interactions [7].

We should also point out that, in a recently published work, fairly good agreement between the above mentioned prediction of Beresford-Smith's approach (non-monotonic behaviour with the surface charge) and experimental results was found for a set of liposome vesicles with different numbers of ionizable groups [8]. However, only moderately structured samples were observed for such systems and the probable failure of the theoretical model in the case of highly structured dispersions was claimed.

The aim of this work is to look into the non-monotonic behaviour of the spatial ordering with the surface charge in a set of model colloids and find out to what extent Beresford-Smith's approach can explain the observed structure factors in highly ordered systems. In order to characterize the evolution of static properties with the particle charge, we have studied several colloidal dispersions with similar particle size but different charges. The remainder of the work is organized as follows. First, the experimental systems and methods are described in some detail. Then, the experimental results are presented and compared to the theoretical predictions.

In our experiments, four latexes supplied by Ikerlat Polymers were used. Their sizes and numbers of ionizable sulfate groups (determined by means of transmission electron microscopy and titration, respectively) are shown in table 1. As can be seen, all these latexes have practically the same diameter. Their spherical form and monodispersity were also confirmed by fitting the corresponding form factors with the expression provided by the Rayleigh–Gans–Debye theory for spheres of identical size.
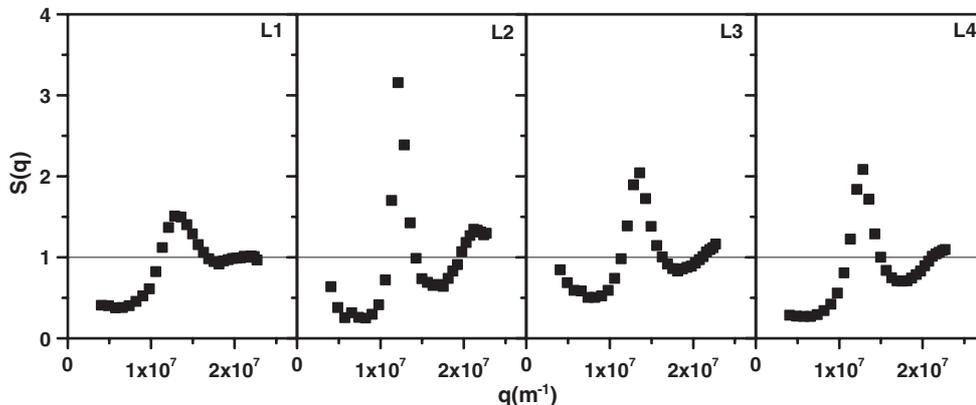
Figure 1. Experimental structure factors for latex systems at a volume fraction around 0.15%.

The dependence on q of the average scattered intensity was measured with a 3D-DLS system (LS Instruments) for angles from 15° to 135°. The 3D cross-correlation scheme allows correcting the effect of multiple scattering on the scattered light intensity and can be used to successfully characterize turbid suspensions with transmission values, of the singly scattered light, as low as 0.01 [9, 10]. The light source was a diode laser working at 680.4 nm and the device is provided with a *multitau* correlator (Flex). A complete description of the technique has been given elsewhere [9]. The different samples were prepared at 0.15% in volume fraction by dilution of stock solutions and kept for at least 20 days in a mixed bed of ion exchanger resin in sealed cylindrical quartz cuvettes. During this period, the scattered intensity was monitored and when no significant changes were observed, the deionization process was supposed to be completed. In figure 1, the structure factors observed for the four latexes are shown. First, the appearance of a re-entrant fluid–crystal–fluid phase upon increase of the number of charged groups per particle should be pointed out. Sample L2 shows crystallization. Nevertheless, in this work we focus on the metastable state of the samples. Due to the low particle number density of the system, of order 6×10^{13} cm^{-3}, the metastable state is obtained by tumbling the sample before each measurement [11]. Another striking feature of the measured $S(q)$ is the upturn at low values of q for samples L2 and L3. In our case, the multiple scattering effects can be safely ruled out since the singly scattered light represents more than 90% of the measured intensity. Furthermore, even if the particle concentration in all the samples is very similar, the uprising only appears in these two samples. Rojas *et al* have observed a similar upturn in the static structure factor for latex samples at similar and higher concentrations, a feature that is also reflected in the dynamics [12].

Structure factors in figure 1 show that spatial correlation first increases with the number of ionizable groups (N) and then seems to decrease. This non-monotonic behaviour can also be graphically illustrated by plotting the height of the first peak of $S(q)$, S_{max}, as a function of N (see figure 2). S_{max} clearly exhibits a maximum versus N (as predicted by Beresford-Smith *et al*; see figure 8 in [5]). However, it should be stressed that the value of S_{max} for the sample corresponding to this maximum (L2) is extremely large. In fact, this sample crystallizes after tumbling if we wait enough time, as mentioned above. According to the Verlet's rule, the crystallization takes place for $S_{max} > 2.8$ and this system is just over this threshold. In addition, we should mention that the crystallization of latex L2 was also observed (with the naked eye) for other particle concentrations.
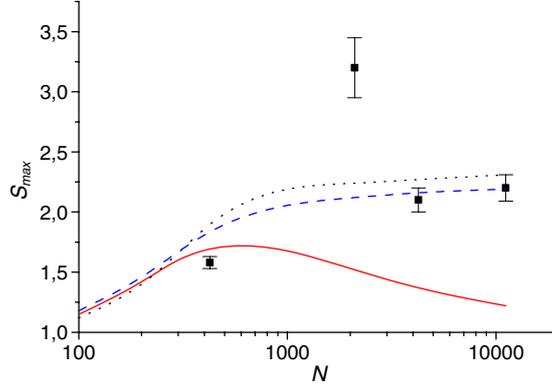
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Figure 2. Height of the main peak of the structure factor, S_{max}, as a function of the number of ionizable groups per particle. Squares denote the experimental results whereas solid, dotted and dashed lines indicate the predictions obtained from the jellium approximation, the cell model and the self-consistent modified jellium model (see equation (5)) respectively.

(This figure is in colour only in the electronic version)

As first attempt to explain our results we have applied the jellium renormalization scheme to our colloidal systems. In order to do that, the normalized electrostatic potential Ψ must be calculated from the Poisson–Boltzmann (PB) equation assuming that: (i) colloidal particles are treated on the same footing as small ions; (ii) the spatial ordering is completely neglected, i.e. $g(r) = 1$. Under these assumptions and for spherical particles, the PB equation then reads

$$\Psi''(r) + \frac{2}{r}\Psi'(r) = -4\pi l_B \left[(Zn_P + n_S)\exp(-\Psi) - n_S\exp(\Psi) - Zn_P \right] \qquad (r \geqslant a) \qquad (2)$$

where l_B is the so-called Bjerrum length (0.713 nm for water at 25 °C), and n_P and n_S are the concentrations of colloidal particles and monovalent salt, respectively. Equation (2) is solved together with the boundary conditions $\Psi'(a) = Zl_B/a^2$, which is Gauss's law applied to the particle surface, and $\Psi(\infty) = 0$. The far-field solution of equation (2) can be matched by the linearized solution

$$\Psi_0(r) = l_B \frac{Z_{ren}\exp(\kappa_{ren}a)}{1 + \kappa_{ren}a} \frac{\exp(-\kappa_{ren}r)}{r} \qquad (3)$$

where Z_{ren} and κ_{ren} are the renormalized parameters. In the application of this procedure one could be tempted to identify the particle charge (Z) with the total number of ionizable groups (N). This assumption seems reasonable since we are dealing with strong acid groups (sulfate). However, in highly deionized suspensions the proton concentration close to the particle surface could be so extremely large that the local pH would even be comparable to the $pK_{sulfate}$, as other authors pointed out [13]. Consequently, the *actual* number of dissociated surface groups (Z) would be considerably smaller than the total one (N), which can be estimated implementing a mass equation in our calculations. Accordingly, the *mass* equation for the dissociation of the surface sulfate groups would be $K_{sulfate} = [H^+]_0 Z/(N - Z)$, where $[H^+]_0$ is the proton concentration at the particle surface. As this quantity depends on the surface electrostatic potential, this condition must be consistently applied together with the boundary condition derived from Gauss's law. Following some studies [13–15] $K_{sulfate} \approx 2$ was assumed. It should also be mentioned that, although our experiments are carried out with highly deionized samples, we have assumed a residual ion concentration of 10^{-6} M, following the estimations done by Evers *et al* [16]. In table 2, the results for Z calculated from this procedure are

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Table 2. Values obtained for Z (actual charge), Z_{ren} (renormalized charge) and $\kappa_{ren}a$ from the jellium approximation and cell model.

Latex	Z (in elementary charges per particle)		Z_{ren} (in elementary charges per particle)		$\kappa_{ren}a$	
	Jellium	Cell model	Jellium	Cell model	Jellium	Cell model
L1	407	411	285	352	0.224	0.240
L2	1153	1020	342	468	0.331	0.250
L3	1672	1326	345	482	0.389	0.251
L4	2780	1833	359	493	0.498	0.253

shown. The values for κ are also included. It should be noted that κ is not renormalized in the jellium approach, in contrast to the cell model, and it depends on the bare charge Z, $\kappa = \sqrt{4\pi l_B(2n_S + Zn_P)}$. This is the key point for understanding our results. After having calculated the parameters characterizing the interaction, Z_{ren} and κ_{ren}, which are displayed in table 2, the structure factor and, more specifically, S_{max} can be computed. In our study, we applied the hypernetted chain (HNC) approximation where the input parameters are the renormalized charge Z_{ren} (obtained from the dissociated charge, Z), κ_{ren} and the volume fraction. In figure 2 the resulting S_{max} for a suspension of particles with $a = 40$ nm and $\varphi = 0.0015$ is plotted to be compared with the experimental data. As can be seen, the prediction of the jellium approximation does not reproduce the experimental results. A non-monotonic behaviour with N is obtained but a quantitative description is not possible. On the one hand, it significantly underestimates the values of S_{max}. Other authors have also reported such underestimation of the dependence of the spatial ordering on the volume fraction (or particle concentration) [6, 17]. In other words, this theory overestimates the screening effect of the particles and/or underestimates the particle–particle spatial ordering. This is not surprising since the particle–particle structure has been completely neglected in this model, $g(r) = 1$. On the other hand, certain disagreement between theory and experiment on the position of the maximum is also found.

At this point, we will also probe to what extent the classical Alexander cell model can capture the main features of the $S_{max}-N$ plot. According to this model, Ψ is computed solving the PB equation in a cell of radius R (depending on the volume fraction):

$$\Psi''(r) + \frac{2}{r}\Psi'(r) = -4\pi l_B \left[(Zn_P + n_S)\exp(-\Psi) - n_S\exp(\Psi)\right] \qquad (a \leqslant r \leqslant R). \qquad (4)$$

In this case, the presence of the other colloidal particles is considered, introducing the cell of finite volume. Again one assumes at $r = a$ that $\Psi'(a) = Zl_B/a^2$, whereas the electric field vanishes at the cell boundary (i.e., $\Psi'(R) = 0$), which guarantees electroneutrality. The renormalized parameters were calculated again approximating asymptotically the numerical solution of equation (4) at the WS cell boundary with a linearized solution of the PB equation. The dissociation of sulfate groups was taken into account as well. At any rate, it should be mentioned that Trizac *et al* have revisited the renormalization prescription of Alexander, suggesting an efficient way to apply such a scheme in practice [18]. Moreover, these authors have shed light on the definition and calculation of κ, which sometimes seems to be confused.

The results for the dissociated charge Z and the renormalized charge Z_{ren} obtained with the cell model are also shown in table 2. It should be emphasized that the Debye screening parameter is also renormalized, κ_{ren}, which did not occur in the case of the jellium approximation. Furthermore, κ_{ren} seems to saturate with increasing Z. The predictions obtained for S_{max} (with $a = 40$ nm and $\varphi = 0.0015$) are also plotted in figure 2. As expected, this

quantity increases monotonically with increasing particle charge and, consequently, this model also fails to fully describe our data. From a quantitative viewpoint, these predictions seem to be somewhat successful, with the clear exception of the crystallizing sample ones.

Certainly, figure 2 suggests that the jellium approximation overestimates the screening of the macroions (whose actual charge is Z), so we intended to apply a modified jellium model improving this picture and inspired by an idea put forward by Trizac and Levin [7]. According to these authors, one should suppose that colloidal particles screen with their renormalized (or effective) charge instead of the actual one. Consequently, equation (2) could be rewritten as

$$\Psi''(r) + \frac{2}{r}\Psi'(r) = -4\pi l_B \left[(Z_{ren} n_P + n_S) \exp(-\Psi) - n_S \exp(\Psi) - Z_{ren} n_P \right] \qquad (r \geqslant a)$$

(5)

and $\kappa = \sqrt{4\pi l_B (2n_S + Z_{ren} n_P)}$. Obviously, the problem then is that Z_{ren} is unknown *a priori*. In fact, we must solve equation (5) (and then apply equation (3)) to determine the renormalized charge. In other words, this parameter is calculated self-consistently (together with the corresponding boundary conditions and the *mass* equation for the dissociation of the surface sulfate groups). First, a trial value for Z_{ren} is chosen (as input). After solving the previous differential equation, this guess is compared with the *output* value. This procedure is repeated until both coincide. The results are also plotted in figure 2. As can be seen, the behaviour is quite similar to that reported for the cell model, although the quantitative agreement with experimental data is better. In any case, this self-consistent jellium model cannot explain the crystallization of sample L2 either.

Other authors have also investigated the influence of the particle charge on the solid–liquid phase transition for silica and polymer latex dispersions [19], although for a narrow range of surface charge densities ($<1~\mu$C cm^{-2}). They also reported a re-entrant transition with increasing surface charge density and claimed that such behaviour is not explicable in terms of a purely repulsive Yukawa potential complemented with a charge renormalization scheme. This study seems to support this conclusion from an analysis in which we have explicitly considered: (i) the measure of the structure factor for characterizing the spatial ordering; (ii) two models for predicting renormalized interaction parameters. The theory proposed by Beresford-Smith *et al* is able to predict the weakening of the spatial correlation with increasing particle charge but the jellium approximation is inadequate for highly structured samples. As regards the cell model, this scheme cannot predict the crystallization of one of the samples. In our opinion, the existence of an attractive contribution to the interaction potential is still a controversial issue. For instance, Roij *et al* have shown that the observation of a fluid–fluid phase separation in a charge-stabilized colloidal dispersion does not necessarily imply such attractive component in the effective pair interaction between highly charged particles [20]. On the other hand, some of the same authors have considered three-body forces finding attractive triplet interactions [21]. Nevertheless, the structure factors reported here show a feature that could be attributed to an attractive component, i.e. the increase in $S(q)$ for low q (see figure 2). In a previous work, polydispersity and the presence of large aggregates were also considered causes for such increase [22]. However, the latexes used here are quite monodisperse, less than 5%. Concerning the existence of aggregation, it should be noted that the increase in $S(q)$ for low q is also present (and even more noticeable) for the crystallizing sample (L2). As the crystallization in this sample is the result of very intense electrostatic forces, aggregation due to electrostatic destabilization does not seem feasible. Consequently, this phenomenon should also be rejected as the cause for the behaviour of the structure factor at low q.

In our opinion, the rise of the intensity observed for small scattering vectors may be related to the proximity of the phase transition mentioned above (fluid–crystal). The presence of small

domains of crystals in the micron size range may result in an additional low q contribution to the scattered intensity. Whichever is the case, our finding confirms the existence of spatial heterogeneities. Extensive studies in the low q regime should be carried out in order to rule out this scenario.

We have observed a non-monotonic dependence of the local order on the particle charge, which has been analysed in terms of two renormalization schemes. The jellium approximation explains qualitatively the existence of a certain charge where the correlation among particles is maximum but it underestimates the height of the structure factor main peak. In contrast, the cell model, which seems to improve the prediction of the experimental S_{max} values at larger particle charges, cannot explain the non-monotonic behaviour.

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