On the nature of long-range contributions to pair interactions between charged colloids in two dimensions

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Abstract
We perform a detailed analysis of solutions of the inverse problem applied to experimentally measured two dimensional radial distribution functions for highly charged latex dispersions. The experiments are carried out at high colloidal densities and under low-salt conditions. At the highest densities studied, the extracted effective pair potentials contain a long-range attractive part. At the same time, we find that for the best distribution functions available the range of stability of the solutions is limited by the nearest neighbour distance between the colloidal particles. Moreover, the measured pair distribution functions can be explained by purely repulsive pair potentials contained in the stable part of the solution.

The machinery of statistical mechanics is designed to provide information on the structure of liquids from given interparticle interaction potentials. When solving the inverse problem of statistical mechanics, one hopes to find a unique interaction potential reproducing a measured distribution function [1, 2]. There are, however, always obstacles such as limited range and finite accuracy of the measured distributions, but also a number of numerical difficulties. No numerical procedure is able to fit the reference distribution exactly. Therefore, in practice, the inverse problem is always ill-posed and the uniqueness of the solution is not guaranteed. The problem becomes even more complicated at high particle densities where the spatial distributions are governed by packing effects. In this case, a wide range of effective potentials are projected onto a very tight space of radial distribution functions (rdfs), thus making it impossible to distinguish between the potentials of different shapes by comparing the pair distributions only.

Another problem that occurs is particularly virulent in dense suspensions of charged colloids. It is related to the fact that a colloidal system is not a simple liquid with state-independent pair interactions, but rather a complex system in which the colloidal interaction results from integrating out the microionic degrees of freedom [3–6]. As a result, a description

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in terms of pair potentials becomes inadequate at higher volume fractions when many-body interactions between the colloids come into play. If this is the case, an inversion of the rdfs results in density-dependent pair potentials which contain contributions of the many-body interactions and which are thus different from the true (density-independent) pair potentials acting between the particles.

In an attempt to explore the density dependence of the effective interactions between charged colloids, we have recently made progress in the experimental as well as the theoretical approach [7, 8]: (i) a much improved range and precision in measuring rdfs at high colloidal number densities was achieved, (ii) control of the colloidal densities became possible, and (iii) advanced inversion tools were used. In our previous papers we have focused our analysis on the behaviour of the pair potentials at short distances where ambiguities due to the inversion procedure can be safely ruled out. We have found that the pair potentials show a density-dependent deviation from the expected Yukawa form which can best be explained in terms of many-body interactions. We only mentioned that at larger distances and high densities we have found attractive parts in the pair potential. The present paper now concentrates on the analysis of this attraction.

From the beginning, we should make a distinction between the phenomenon that we discuss here and the attraction observed between charged colloids confined by two narrowly spaced glass plates ($<20\,\mu$m) or located at the air–water interface [9–15]. These latter potentials were obtained at low densities for which different inversion procedures gave almost identical results. In particular the latest studies [14, 15] show very clearly that pair potentials between colloids in weakly confined suspensions are purely repulsive, while more strongly confined suspensions display attractions at the same density; so confinement is obviously an essential requirement for the observed attraction in those studies [14, 15]. We did not detect any similar confinement effects since the spacing between the two glass plates of our sample cell was an order of magnitude larger than in all the other experiments [14, 15] ($>200\,\mu$m).

In the present work, we consider a 2D charge stabilized colloidal dispersion of $\sigma = 2.4\,\mu$m diameter polystyrene sulfonate particles taken at 2D packing fractions $\rho\sigma^2$ ranging between 0.1 and 0.23, where ρ is the particle number density in two dimensions. More precisely, we should call our system a *quasi-2D* system since the electric double layers around the colloids preserve their three dimensional character while the centres of the colloids are effectively confined to a plane. The colloidal 2D rdfs were measured as described in [7, 8], but with a higher spatial resolution than in the previous works. As previously, an Ornstein–Zernike (OZ) equation based inversion routine with Percus–Yevick (PY) and hypernetted-chain (HNC) closures as well as inverse Monte Carlo (IMC) method were used to extract the effective pair potentials between the colloids from the measured rdfs [7, 8, 16–18]. Figure 1 shows the rdfs for the 2D latex dispersion. One can readily observe that the position of the initial peak shifts slightly towards smaller r when the density is increased and that its height grows with the concentration. The results of the inversion are presented in figure 2. Since the potentials are defined by the inversion procedure up to an additive constant and thus subject to vertical shifts, it is more convenient to compare force curves, which in figure 2 are plotted for various concentrations, obtained using different inversion methods. In the IMC method, the cut-off radius within the inversion scheme (defined in [8, 16, 18]) has been varied in order to study its effect on the final result. The collection of IMC curves in figure 2 thus gives an idea of the error produced by the cut-off. A finite cut-off also implies that different lengths of the rdf are used for the analysis. We thus model the experimental situation where the range of accessible rdfs is shortened. For comparison, we also plotted the best Yukawa fit for the IMC result at the lowest density 0.098, denoted as the 'reference Yukawa interaction' in the following (pair potential in units of kT: $u(r)/kT = 35\,000\sigma \exp(-5r/\sigma)/r$).
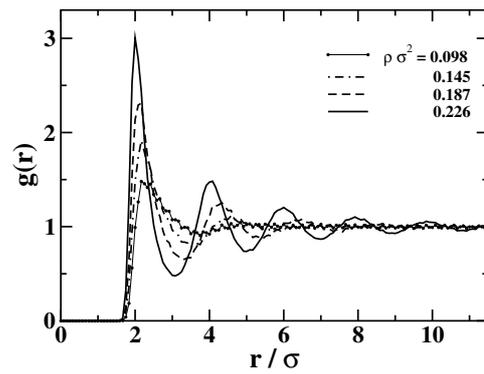
Figure 1. Radial distribution functions for charged colloids in a 2D suspension at different colloidal densities, measured in a video-microscopy experiment. σ is the diameter of a colloidal sphere.
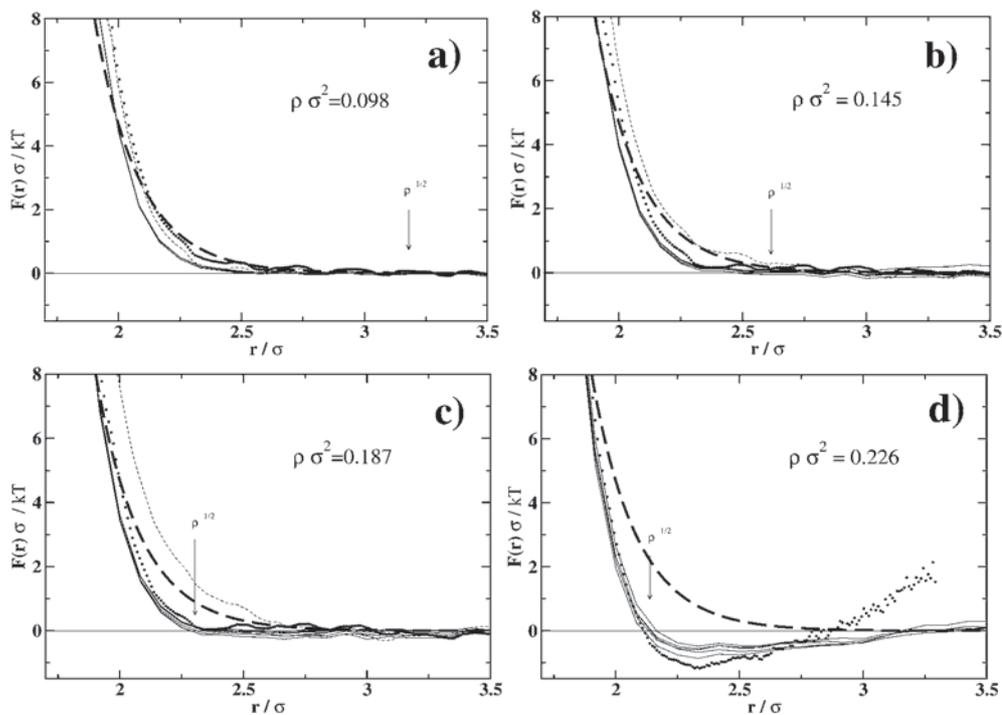
Figure 2. Effective pair forces between two macroions in a 2D colloidal suspension at the indicated colloid densities, as obtained from experimentally measured rdfs using the IMC method (thin solid curves) as well as the integral equation scheme with HNC (dashed curve) and PY (dotted curve) closures and subsequent numerical differentiation of the effective pair potentials. To estimate the error, the IMC inversion has been carried out using different cut-off distances at 3σ, 5σ, 8σ and 12.5σ; each of these calculations is represented by one of the thin solid curves. A reference Yukawa potential is given as a thick dashed curve.

The effective pair forces shown in figure 2 display a very steep repulsive part at short distances, whereas their long-range part beyond 2.5σ is close to zero. The potentials extracted from the OZ based method with PY and HNC closures differ form each other. The HNC
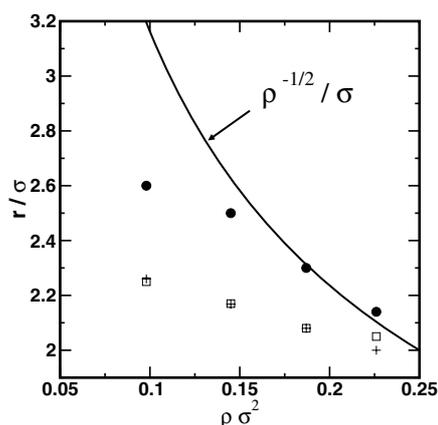
Figure 3. The point of zero force (filled circles), the branching point (open squares), and the position of the first peak in $g(r)$ (crosses) versus the reduced densities, compared to the mean distance $d_m/\sigma = \frac{1}{\sqrt{\rho\sigma}}$ (solid curve) between two colloids in a suspension at density ρ.

result approaches the reference Yukawa derivatives, while the PY forces stay closer to the IMC data. At densities above 0.187 for HNC no meaningful solution of the OZ based method could be found. Some of the curves are slightly attractive at larger separations. The depth of the minimum reaches $0.25kT$ for the potential and $0.2\sigma kT$ for the force. At the highest density, the uncertainty of the result is fairly large in the long-range part. It is important to note that the distances at which the force reaches zero correspond roughly to the position of the main peak of the rdf at $r \leqslant \rho^{-1/2}$ (arrows in figure 2 indicate the mean interparticle distance $\rho^{-1/2}$). This may be seen in figure 3 where we compare the mean distance with (i) the distance of the first peak in the rdf and (ii) the distance where the force reaches zero.

The important new message of figure 2 is that the effective pair potential decomposes into two parts: a short-ranged and cut-off-independent repulsive part and a long-ranged part, which can show an attraction. This attraction depends sensitively on the chosen cut-off. We call the crossover point dividing the potential into a cut-off-dependent and a cut-off-independent part the 'branching point' because beyond this point a noticeable branching of the different IMC curves sets in. Figure 3 demonstrates that the position of this branching point scales with the density, and that it is always at shorter distances than the point of zero force. The force value at which it starts characterizes the sensitivity threshold of the inversion procedure in use. We have to conclude that the limitations of the inversion procedure allow us to make firm statements only about the short-ranged repulsive parts of the pair potential, but not about the 'attractive' forces observed at larger distances. We stress that at distances smaller than the branching point, the effective forces are clearly seen to be less repulsive than expected for a Yukawa-like interaction, an effect which increases with the concentration. This feature, observed also in 3D suspensions [19–21], is discussed in [7, 8, 21] in terms of a macroion shielding effect [22]; this result is obviously not affected by the uncertainty of the inversion procedure.

The fact of branching manifests the apparent degeneration of the solution to the direct problem, i.e., the calculation of the rdf. The consequences of this degeneration of the problem at hand are further illustrated by figure 4, which demonstrates the insensitivity of the structure to the long-range part of the effective pair potential. We show two potentials obtained from inverting the $g(r)$ measured at $\rho\sigma^2 = 0.187$, using cut-offs at 3σ and 8σ, together with the rdfs generated from these potentials. To facilitate comparison between the range of the two
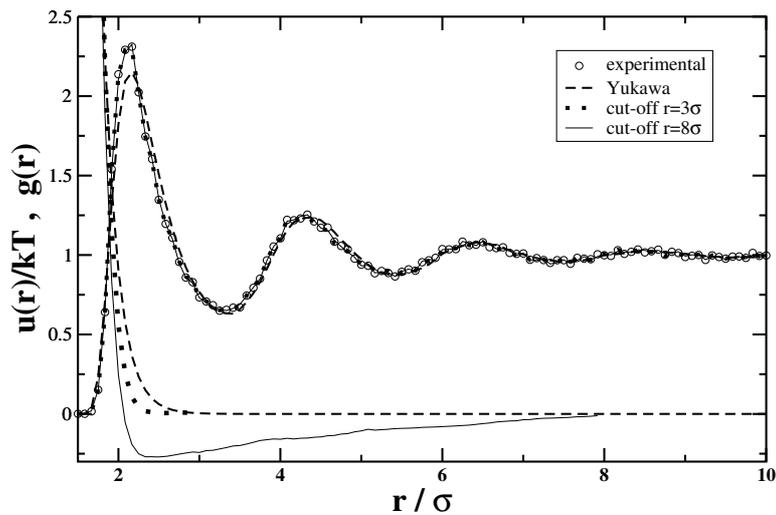
Figure 4. Radial distribution functions and corresponding effective pair potentials for charged colloids in a 2D suspension at a colloid density of $\rho\sigma^2 = 0.187$. The potentials are obtained from experimental rdfs (circles) by means of the IMC method using different cut-off distances, $r = 3\sigma$ (dotted curve) and $r = 8\sigma$ (solid curve). These two potentials lead to almost identical rdfs (solid and dotted rdf curves) that agree perfectly with the experimental rdf; their difference is comparable to the line thickness. Also shown is the reference Yukawa potential and its corresponding rdf (thick dashed curves).

potentials and the distribution functions, we present both quantities in the same plot. While the potentials show a significant discrepancy, the difference between calculated rdfs is smaller than the statistical uncertainty (the sum of relative deviations from the reference rdf did not exceed 0.5% in either case) and show an excellent agreement with the experimental data. The potential with the short cut-off turns to zero at $r > 3\sigma$ while that with the long cut-off leads to a minimum of about $-0.25kT$ at $r = 2.5\sigma$. This corroborates our conclusions (pointed out above) that the features of the effective pair interaction in a distance regime beyond the first layer of neighbouring particles cannot be resolved for the present system. Certainly, these conclusions do not apply to dilute systems where the effective potential is close to the potential of mean force; then the inversion gives unambiguous results [11, 14, 15].

One should note that for the observations made in this work, the geometry of the system is essential. In all the above mentioned quasi-2D colloidal dispersions, only the colloidal particles are confined by the external forces while the ionic clouds remain essentially three dimensional. A certain fraction of counterions escape into the bulk and thus do not participate in the in-layer screening, which is confirmed by the extremely large Debye screening length (about 500 nm) obtained for these systems. As the double layers thicken, we have a chance to probe their nonlinear parts and the many-body contributions to the interparticle interaction [22]. For comparison, in an unconstrained suspension of the same particles at volume fraction of 0.1 (giving a similar mean interparticle distance), the deviation of the full electrostatic potential from its far-field Debye–Hückel asymptote would already be less than 5% at $r = 1.5\sigma$, while in our 2D system we still see significant deviation from the Yukawa shape even at $r \approx 2\sigma$.

Despite the apparent failure of our efforts to find the unique solution of the inverse problem, this study still arrives at a useful result. As is seen in figure 4, we were able to reproduce the rdf to a very high accuracy using only the short-range part of the effective potential. We compare
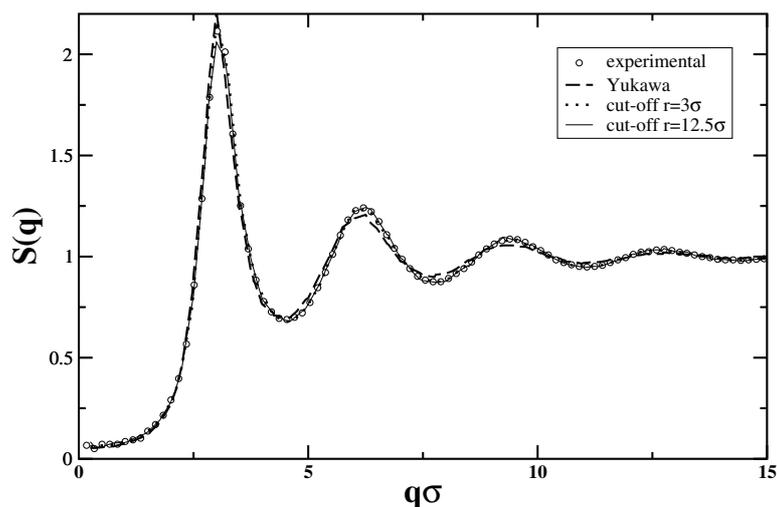
Figure 5. Structure factors for charged colloids in a 2D suspension at a colloid density of $\rho\sigma^2 = 0.187$ as obtained using different effective potentials: the IMC result with cut-offs at $r = 3\sigma$ (dotted curve) and $r = 12.5\sigma$ (solid curve); the reference Yukawa potential (thick dashed curve). The cut-off potentials improve the Yukawa result both at high q and in the limit $q \to 0$.

in figure 4 the rdf obtained using the reference Yukawa potential with that obtained using the IMC result. One can see that the model with the Yukawa potential predicts the rdf notably less well. The deviation from the reference rdf in this case is caused by the too strong repulsion at the mean interparticle distance. On the basis of the comparison to the IMC curves that give excellent fits, one can impose a simple correction on the reference Yukawa potential to improve the agreement with the experimental rdf. The Yukawa potential can be truncated at the position of the main rdf peak and then shifted down so that the new potential is zero at and beyond this distance. Since the position of the peak scales as shown in figure 3, the new effective potential reflects the density change. This idea of using a truncated Yukawa potential as a model for colloidal pair potentials has been tested in more detail in [20, 21].

It is also instructive to have a look at the osmotic coefficients of our colloidal suspension. These coefficients have been obtained for $\rho\sigma^2 = 0.187$ from the virial equation, where we used the various potentials discussed above. The IMC potential with a long cut-off ($r = 12.5\sigma$) gives 1.35 while the potential with the shorter cut-off ($r = 3\sigma$) leads to a much larger osmotic coefficient of 3.93, which is somewhat lower than that for the reference Yukawa potential which is 4.48. The agreement between the results from using the latter two, on the one hand, and the large difference from the result obtained with the long-cut-off potential, on the other hand, marks a trend that does not match our observations made in figure 4 where the two cut-off potentials agree while showing differences from the rdf of the reference Yukawa potential. As for the structure factor (see figure 5), one again observes the opposite trend: the two cut-off potentials lead to almost identical results, which are clearly different from the structure factor that one obtains using the pure Yukawa potential. This applies especially to the $q \to 0$ behaviour. For $S(q)|_{q\to 0}$ we find 0.074 and 0.066 for the potentials with the longer and the shorter cut-offs, respectively, and 0.054 for the Yukawa potential. Thus, although with the cut-off procedure we obtained improvement over the Yukawa potential in all properties studied, there arises a potential dilemma: corrections of the pair potentials leading to improvements concerning the structure of the liquid may spoil a possible agreement on the thermodynamic

side. In other words, the contribution of the many-body interactions to the effective pair potential strongly depends on the property that one uses to detect these contributions [23]. In view of this fact, one could consider alternative ways to correct the effective potential—for example, one which would correct not for the structure (compressibility) but for the equation of state.

We close with the statement that the best available structure data do not provide sufficient accuracy for finding the unique solution of the inverse problem for two dimensional colloidal dispersions at high densities. Although we are able to deduce the pair potential at short distances ($r < \rho^{-1/2}$), the rdfs, being of limited accuracy, do not provide unambiguous information about the long-range part of the pair potential ($r > \rho^{-1/2}$). To narrow the range of the possible solutions, we suggest applying an additional constraint on the potential, i.e. choosing the potential that is equal to zero beyond the first nearest neighbour layer. We have shown that this choice produces satisfactory pair distributions and improves the description of thermodynamic properties.

Acknowledgments

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