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

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(Dated: January 8, 2022)

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 studied densities, the extracted effective pair potentials contain 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 obtain 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 is projected onto a very tight space of radial distribution functions (rdf), 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 micro-ionic degrees of freedom \([3, 4, 5, 6]\). As a result, a description 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 behavior 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 be best 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 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 \([8, 10, 11, 12, 13, 14, 15]\). These latter potentials were obtained at low densities for which different inversion procedures gave almost identical results. Especially 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 \(\rho\) 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 centers of the colloids are effectively confined to a plane. The colloidal 2D rdf’s were measured as described in \([8, 10]\), but with a higher spatial resolution than in the previous works. As previously, an Ornstein-Zernike equation (OZ)-based inversion routine with Percus-Yevick (PY) and hypernetted-chain (HNC) closures as well as inverse Monte Carlo method (IMC) were used to extract the...
effective pair potentials between the colloids from the measured rdfs \[ g \]. Figure 1 shows the rdfs for the 2D latex dispersion. One can easily 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 Fig. 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 Fig. 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 \[ g \]) has been varied in order to study its effect on the final result. The collection of IMC curves in Fig. 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 $kT$:

\[
\frac{u(r)}{kT} = \frac{35000\sigma}{r} \exp\left(-\frac{5r}{\sigma}\right).
\]

The effective pair forces shown in Fig. 2 display a very steep repulsive part at short distances, whereas their long-range part beyond 2.5$\sigma$ is close to zero. The potentials extracted from the OZ-based method with PY and HNC closures differ from each other. The HNC 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 0.25$kT$ 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 $r \leq \rho^{-1/2}$ (arrows in Fig. 2 indicate the mean interparticle distance $\rho^{-1/2}$). This may be seen in Fig. 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 Fig. 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 cross-over 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. Fig. 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 allows 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, 20, 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 Fig. 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 a cut-off at $3\sigma$ and $8\sigma$, together with the rdfs generated from these potentials. To facilitate comparison between the range of both the 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 form the reference rdf did not exceed 0.5% in both cases) and show an excellent agreement with the experimental data. The potential with the short cut-off turns to zero at $r > 3\sigma$ while the long cut-off leads to a minimum of about $-0.25kT$ at
FIG. 3: The point of zero force (filled circles), the branching point (open squares) and the position of the first peak in $g(r)$ (crosses) vs the reduced densities, compared to the mean distance $d_m/\sigma = \sqrt{\rho \sigma}$ (solid line) between two colloids in a suspension at density $\rho$.

FIG. 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 inverse Monte Carlo 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 lines).
Experimental Yukawa cut-off $r=3\sigma$ 

\begin{align*}
S(q) &= \text{experimental} \\
\text{Yukawa} &\quad \text{solid curve} \\
\text{cut-off } r=3\sigma &\quad \text{dotted curve} \\
\text{cut-off } r=12.5\sigma &\quad \text{dashed curve}
\end{align*}

FIG. 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: IMC result with a cut-offs at $r = 3\sigma$ (dotted curve) and $r = 12.5\sigma$ (solid curve), the reference Yukawa potential (thick dashed curve). The cut potentials improve the Yukawa result both at high $q$ and in the limit $q \to 0$. 

$r = 2.5\sigma$. This corroborates our conclusions (pointed out above) that the features of the effective pair interaction in a distance regime beyond the first layer of neighboring 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 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 escapes into the bulk and thus does 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 be less than 5% already 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 it is seen in Fig. 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 in Fig. 4 the rdf obtained using the reference Yukawa potential with that using the IMC result. One can see that the model with the Yukawa potential predicts the rdf notably worse. The deviation from the reference rdf in this case is caused by the too strong repulsion at the mean interparticle distance. Based on 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 it is shown in Fig. 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 of the latter two, on the one hand, and the large difference to the result of the long cut-off potential, on the other hand, marks a trend that does not match our observations made in
Fig. 4 where the two cut potentials agree while showing differences to the rdf of the reference Yukawa potential. As for the structure factor (see Fig. 5), one again observes the opposite trend: the two cut potentials lead to almost identical results, which are clearly different from the structure factor one obtains using the pure Yukawa potential. This applies, especially, to the $q \rightarrow 0$ behavior. For $S(q)|_{q \rightarrow 0}$ 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 studied properties, 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 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 yet 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 limited accuracy of the rdfs 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. to choose the potential that is equal to zero beyond the first nearest neighbor layer. This cut-off procedure is justified by the form of the pair potential, which is measured at low densities where the many-body effects are minimal and thus is closest to the true pair potential. We have shown that this choice produces satisfactory pair distributions and improves description of thermodynamic properties.

Authors thank David Grier for the valuable comments on the manuscript. VL thanks the Swiss National Science Foundation for financial support during his stay in the University of Fribourg.

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