Interaction forces in quasi-two-dimensional charged dispersions

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A ''predictor-corrector'' inversion of the Ornstein-Zernike equation has been presented for extracting the pair potential $u(r)$ between colloidal particles from the radial distribution function $g(r)$ or the static structure factor $S(q)$ of dispersions confined to a single layer. The method, an extension of the three-dimensional analog presented earlier, is used to obtain $u(r)$'s for recently published experimental data on confined dispersions. The results confirm unambiguously the existence of an attractive force in $u(r)$, even for a set of data that has been described using a purely repulsive $u(r)$ previously. We also illustrate the potential effect of experimental artifacts in imaging experiments that can lead to an apparent attraction in $u(r)$ and offer an explanation for the persistence of attraction or its disappearance as a function of the distance between the plates used to confine the dispersions in the experiments. [S1063-651X(98)09703-7]

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I. INTRODUCTION

It has been well established in the past decade that colloidal dispersions serve as excellent models of condensed matter as they exhibit phases very similar to those of atomic systems [1,2]. Because of the relatively large size and the slow dynamics of the particles, the motion of the particles can be tracked in real time and recorded using video microscopy. Recent experiments on charged dispersions confined to a single layer [1,3,4] have further shown that these systems are also ideal for studying two-dimensional (2D) phases. In fact, the use of colloids as model systems allows one to study phenomena that are not easily accessible in atomic systems [2]. The analyses of the resulting experimental observations, however, require self-consistent effective pair potentials between the particles, for a number of reasons. For instance, in the case of charged particles the effective charge on the particles often differs significantly from the charge estimated from titration experiments. The exact electrolyte concentration in the dispersion is also difficult to estimate in many cases. In addition, there is a strong likelihood of many-body effects on the potential at conditions close to phase transitions. Finally, as we shall see later in this paper, the effective interaction potentials between particles confined between two plates differ from the corresponding potentials at bulk conditions and remain ill-understood currently.

The macroscopic properties of charge-stabilized colloidal dispersions are usually understood using a theory of interaction potential formulated by Derjaguin, Landau, Verwey, and Overbeek about 50 years ago [5]. The effective pair potential between two charged particles (''macroions'') in the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is dominated by a repulsive interaction given by the Yukawa form for low elecrostatic screening:

$$u_{DLVO}(r)=\begin{cases}\infty, & r<\sigma \\ \dfrac{(Ze)^2}{4\pi\epsilon}\dfrac{e^{\kappa\sigma}}{(1+\kappa\sigma)}\dfrac{e^{-\kappa r}}{r}, & r\geqslant\sigma,\end{cases} \tag{1}$$

where r is the distance between the macroions of diameter σ, κ^{-1} is the Debye screening length, ϵ is the dielectric constant of the suspending medium, and Ze is the charge of the macroion. The above form of the DLVO potential is valid only for low surface charges and for dilute dispersions. Nevertheless, the DLVO potential has been used to explain a variety of experimental observations ranging from sedimentation data, phase boundaries in phase diagrams, osmotic pressures, and elastic constants, at least qualitatively [6]. In contrast, there is very little information currently on the pair potential appropriate for charged colloids confined between two charged plates.

The objective of this paper is to outline a method for extracting effective pair potentials from positional correlation functions obtained from 2D experiments using colloids and to shed some light on the interpretation of the extracted potentials. In Sec. II, we review some recent experimental studies designed to probe the microscopic structure of confined fluids. In Sec. III, we discuss a 2D version of the inversion of Ornstein-Zernike equation for extracting effective potentials from positional correlations among the particles. This method is then applied in Sec. IV to computer-generated data for a 2D Lennard-Jones fluid at a large area fraction of 0.5 to examine the accuracy of the method and then to the experimental $g(r)$ measured using digital video microscopy by Kepler and Fraden [3] and Carbajal-Tinoco *et al.* [4]. We conclude Sec. IV with a discussion of the influence of experimental artifacts on the interpretation of the experimental data in terms of effective interaction potentials. We conclude with a summary in Sec. V.

II. QUASI-2D SYSTEMS OF CHARGED PARTICLES

A number of papers have appeared in recent years [1,3,4,7,8] on structural transitions in quasi-2D systems of charged colloidal dispersions. Some of these studies reveal the existence of a long-range attractive component in the effective pair potential and raise interesting questions on the physical origin of such an attraction. We shall review some

of these studies in this section in order to motivate the focus of the present paper.

Recently, Kepler and Fraden [3] have examined systems consisting of aqueous dispersions of negatively charged polystyrene particles of diameter $\sigma=1.27\ \mu$m confined between two glass plates (also negatively charged) separated by a gap of 2–6 μm at relatively low number densities of the particles (corresponding to area fractions ranging from 0.007 to 0.03). The instantaneous configurations of the particles are then recorded using time-lapse video microscopy. The experiments provide the radial distribution function $g(r)$, constructed from averaging over 500–5000 ''snapshots'' (configurations). We refer to these systems as *quasi*-2D systems since the particles are not strictly confined to a 2D plane but can wander away from the plane (even if such ''excursions'' are small). The implications of such excursions to the interpretation of effective potentials will be addressed in Sec. IV C.

The experiment of Kepler and Fraden focuses on interaction forces in confined dispersions, but the analysis of the data is not straightforward since some of the crucial parameters needed in the analysis are not accessible through direct measurements. For example, the effective charge on the particles is one such quantity and remains an unknown in *both* 2D and 3D experiments. In addition, in the case of quasi-2D systems such as the one in the Kepler-Fraden experiments, the narrow spacing between the confining plates makes the ionic strength of the dispersion an unknown as well because of the significant plate-solution interfacial area relative to the volume of the solution and the possible leaching and ionic association or dissociation effects. In the absence of any reasonable guidance as to the form of the potential, Kepler and Fraden resorted to a modified Lennard-Jones potential of the type shown below since a purely repulsive potential failed to predict the experimental $g(r)$'s adequately. Kepler and Fraden have fitted the experimentally measured $g(r)$'s using Brownian dynamics simulations and a modified Lennard-Jones potential given by

$$u(r)=4\epsilon\left[\left(\frac{\alpha}{\zeta}\right)^{2a}-\left(\frac{\alpha}{\zeta}\right)^{a}\right], \tag{2}$$

where $\zeta=r/\sigma-1$, ϵ is the depth of the potential minimum, and α and a are empirical fitting parameters. This analysis shows the existence of a long-range attractive component in $u(r)$ and a minimum in the potential of about $0.2k_BT$, which vanishes as the electrolyte concentration goes down.

The Kepler-Fraden potentials have been reinterpreted by Tata and Arora [9] in terms of the so-called Sogami potential [10]

$$u_{Sog}(r)=\begin{cases}\infty, & r<\sigma\\ \dfrac{(Ze)^2}{2\epsilon}\dfrac{2\sinh^2(\kappa\sigma/2)}{\kappa\sigma}\left(\dfrac{2+\kappa\sigma\coth(\kappa\sigma/2)}{r}-\kappa\right)e^{-\kappa r}, & r\geqslant\sigma,\end{cases} \tag{3}$$

where all the symbols retain their meanings as in Eq. (1). The analysis of Tata and Arora consists of adjusting the parameters of the Sogami potential to fit the potentials of Kepler and Fraden [3] by fixing the magnitude and the position of the minimum. This amounts to adjusting the values for the charge Ze of the particle and the dimensionless Debye screening length $\kappa\sigma$ so as to make the Sogami form of the potential fit the Kepler-Fraden results. More importantly, to be able to do this successfully, Tata and Arora had to scale the charge on the particle with respect to the concentration of the added salt in an arbitrary fashion.

The experiments of Kepler and Fraden have been extended to larger particle concentrations (i.e., dimensionless number density $\rho\sigma^2$ from 0.023 to 0.48, close to freezing conditions) by Carbajal-Tinoco *et al.* [4]. The measured $g(r)$'s, however, have been analyzed somewhat more formally using some of the approximate closures to the Ornstein-Zernike equation, such as the mean spherical approximation (MSA), the Percus-Yevick (PY) approximation and the hypernetted-chain (HNC) approximation. We shall comment on such ''single-step'' inversions later in this paper. The analysis of Carbajal-Tinoco *et al.* also reveals the existence of a long-range attraction in confined dispersions even at large particle densities.

Since the experimental measurements of Kepler and Fraden and Carbajal-Tinoco *et al.* yield *effective* potentials (rather than *bare* pair potentials) because of either many-body effects or the effects of the confining plates or (as we discuss in Sec. IV C) the excursions of the particles away from the 2D layer, attempts have also been made to measure the potentials in very dilute dispersions or between isolated pairs of particles. Notable among such experiments is the one by Crocker and Grier [8], who have employed two optical traps to hold an isolated pair of particles at a known distance from each other and to record their mutual distances of separation after release, from which the pair potential has been obtained using Boltzmann distribution. Crocker and Grier have also corrected for the out-of-plane motions of the particles so that the actual distances between the particles can be measured accurately. The result of Crocker and Grier also reveals an effective attraction between the particles when the distance between the plates confining the particles is of the order of a few particle diameters. The attraction, however, vanishes for smaller distances between the plates. We shall return to this in Sec. IV C.

III. INVERSION BASED ON INTEGRAL-EQUATION FORMALISM

A. Structure factor $S(q)$ for 2D liquids

The Ornstein-Zernike integral equation theory of fluids in three dimensions reduces formally to the same form in the

case of 2D liquids with all the correlations retaining their physical meaning [11]. The only significant differences occur in the volume integral, which now becomes an area integral, and in the manner in which the 2D Fourier transforms are carried out. The static structure factor $S(q)$ for an isotropic system is related to the radial distribution function $g(r)$ by

$$S(q)=1+\rho\int e^{-i\mathbf{q}\cdot\mathbf{r}}[g(r)-1]d\mathbf{r}. \tag{4}$$

Carrying out the integral over angle θ leads to [12]

$$S(q)=1+2\pi\rho\int r[g(r)-1]J_0(qr)dr, \tag{5}$$

where $J_0(qr)$ is the zeroth-order Bessel function given by the defining relation

$$J_0(qr)=\frac{1}{2\pi}\int e^{-i\mathbf{q}\cdot\mathbf{r}}d\theta. \tag{6}$$

The occurrence of the Bessel function in Eq. (5) leads to a crucial difference in the way the integral transform is evaluated by discretization in the 2D space. The discrete Fourier integral transform is given by [for N data points, with $g(r)$ available for $r\leqslant R$]

$$S(q_i)=1+2\pi\rho\sum_{j=1}^{N} r_j[g(r_j)-1]J_0(q_i r_j)dr_j, \tag{7}$$

where $r_j=\mu_j R/\mu_N$, μ_i's being the roots of the Bessel function, and $q_i=\mu_i/R$. For given R and N, the r_i's and q_i's are fixed and equispaced in the 3D discrete transform. On the other hand, in the 2D version, once R and N are fixed, r_i's and q_i's are determined by the zeros of the Bessel function $J_0(qr)$, a requirement needed to satisfy the orthogonality property of the Fourier transform. Therefore, the discrete version of the integral given in Eq. (7) takes the form of the trapezoidal rule with unequal intervals [although, in the limit of large N, the discretization in Eq. (7) becomes almost equally spaced]. The importance of satisfying the orthogonal property when evaluating the Fourier integral transforms has been demonstrated by Lado [12] for simple Gaussian functions.

B. Ornstein-Zernike inversion of $S(q)$

The ''predictor-corrector'' method we shall use here for the extracting $u(r)$ for a given experimental $g(r)$ or $S(q)$ is identical in concept to the one proposed by Reatto *et al.* [13] for 3D systems. We briefly summarize the steps involved.

The Ornstein-Zernike equation is given by

$$g(r)-1=c(r)+\rho\int c(r')[g(|r-r'|)-1]d\mathbf{r}' \tag{8}$$

and the exact closure relation required for solving Eq. (8) is written as

$$g(r)=e^{-\beta u(r)+g(r)-1-c(r)+B(r)}, \tag{9}$$

where $c(r)$ is the direct correlation function and $B(r)$ is the so-called bridge function for given $u(r)$ and ρ. It follows from Eq. (8) that

$$c(r)=\frac{1}{2\pi\rho}\int\left(1-\frac{1}{S(q)}\right)e^{-i\mathbf{q}\cdot\mathbf{r}}dq. \tag{10}$$

As $B(r)$ in Eq. (9) is generally analytically intractable and is difficult to evaluate numerically, one often resorts to approximations for $B(r)$ in solving the Ornstein-Zernike equation for determining $S(q)$'s for given $u(r)$'s. The approximations to the closure equation leading to integral-equation theories (such as the HNC equation, the PY equation, and the MSA) for 2D cases remain identical to the 3D counterparts [11].

The pair potential $u(r)$ can be determined uniquely from known $g(r)$ and/or $S(q)$ by rewriting Eq. (9) as

$$\beta u(r)=-\ln g(r)+g(r)-1-c(r)+B(r) \tag{11}$$

if one can evaluate $B(r)$. However, since $B(r)$ cannot be computed unless $u(r)$ is already known, approximations are usually made for $B(r)$ so that Eq. (11) can be used directly to obtain $u(r)$. The simplest approximation, namely, ignoring $B(r)$ in Eq. (11), corresponds to the HNC approximation, which we shall comment on in Sec. IV B. Notice that a direct use of Eq. (11) with approximations that allow the right-hand side of the equation to be determined explicitly in terms of experimentally accessible quantities does not require any iterative corrections to $B(r)$ and hence is known as *single-step* inversion.

As we have discussed for the case of 3D systems [14], Eq. (11) can also be solved iteratively by writing it relative to the closure for a suitably chosen ''reference'' potential $u'(r)$ as

$$\beta u(r)=\beta u'(r)+\ln\left(\frac{g'(r)}{g(r)}\right)+[g(r)-g'(r)]-[c(r)-c'(r)]+[B(r)-B'(r)], \tag{12}$$

where the prime on $g'(r)$, $c'(r)$, and $B'(r)$ identifies them as the ones corresponding to the reference potential $u'(r)$.

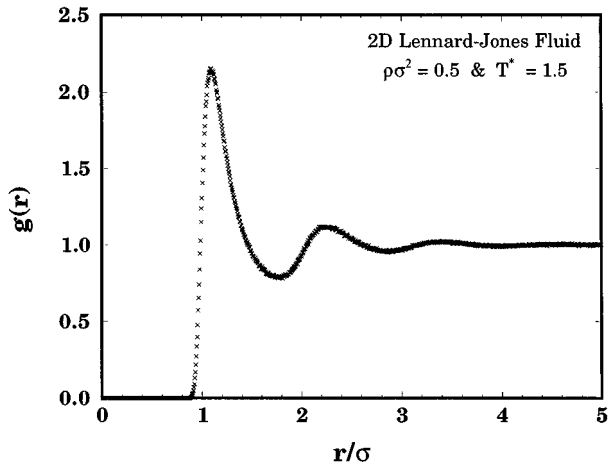

FIG. 1. The radial distribution function $g(r)$ from Monte Carlo simulations for a 2D Lennard-Jones fluid at $\rho\sigma^2=0.5$.

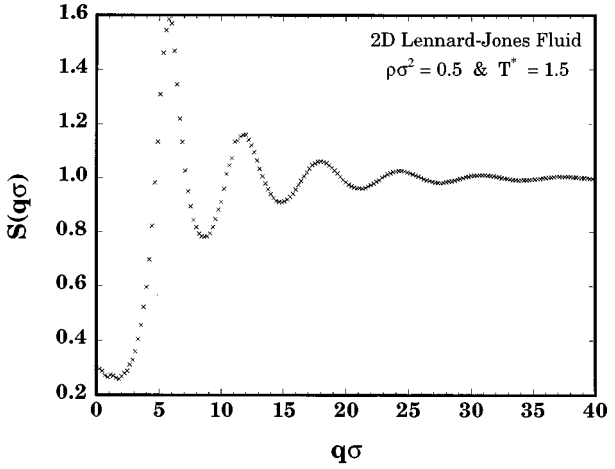

FIG. 2. Structure factor $S(q)$ for the Lennard-Jones fluid obtained by a 2D Bessel transform of $g(r)$ shown in Fig. 1. The low-q results for $S(q)$ are obtained directly from the Monte Carlo simulations.

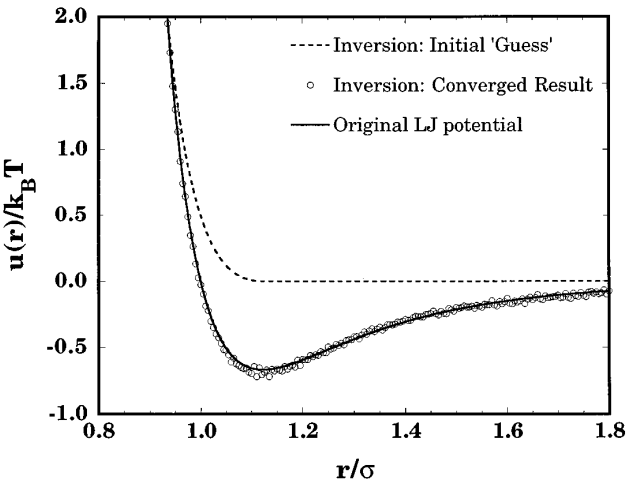

FIG. 3. The potential based on the iterative ''predictor-corrector'' method for the Lennard-Jones fluid shown along with the original potential. The initial potential used in the iteration is also shown.

An iterative predictor-corrector method that refines $u'(r)$ at each step such that $B'(r)\rightarrow B(r)$ then leads to the following predictor for $u(r)$:

$$\beta u_i(r)=\beta u_{i-1}(r)+g(r)-g_{i-1}(r)+\ln\left(\frac{g_{i-1}(r)}{g(r)}\right)+\frac{1}{2\pi\rho}\int\left[\frac{1}{S(q)}-\frac{1}{S_{i-1}(q)}\right]e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{q}, \qquad (13)$$

where we have used Eq. (10) to write the $c(r)$'s in terms of the corresponding $S(q)$'s. The subscripts i and $i-1$ in the above equation denote the results of the corresponding iterations. If the functions $g_{i-1}(r)$ and $S_{i-1}(q)$ are computed exactly in each iteration in the corrector step [i.e., for the iterate $u_{i-1}(r)$], the prediction $u_i(r)$ will converge to the potential $u(r)$ corresponding to the given $g(r)$ and $S(q)$. An approximate corrector sufficient for most practical cases (for 3D systems) has been presented elsewhere [14]; here we shall use a computer-simulation-based corrector.

IV. RESULTS AND DISCUSSION

A. Inversion for a Lennard-Jones fluid

We begin with a test case based on simulated data in order to illustrate the quality of the results that can be expected from the inversion and the quality of the data needed. This is important for interpreting the results based on real data and for determining the quality of data one needs to demand from physical experiments. The test case we have chosen is a 2D Lennard-Jones (LJ) fluid at $\rho\sigma^2=0.5$ and $T^*=k_BT/\epsilon=1.5$. A canonical Monte Carlo simulation with 225 particles has been used for obtaining $g(r)$ and $S(q)$, with an equilibration run of 5000 Monte Carlo steps (MCS) and a subsequent run of 10 000 MCS for the averages. The resulting $g(r)$ and $S(q)$ are shown in Figs. 1 and 2, respectively, and the extracted pair potential is shown in Fig. 3 along with the original potential. The result in Fig. 3 shows that the inversion can extract very accurate potentials (within 2–3% error) even under extreme conditions. (In contrast, the single-step HNC inversion underestimates the minimum by about 20%, although the location of the minimum is overestimated by only about 5%.)

B. Inversion for confined dispersions

We now examine a few typical sets of experimental data reported by Kepler and Fraden [3] and Carbajal-Tinoco *et al.* [4]. First we consider case c of Kepler and Fraden, which corresponds to a density $\rho\sigma^2$ of 0.0194 (area fraction of 0.015). This is one of the cases for which the analysis of Kepler and Fraden indicates a long-range attraction. The corrector steps in the inversions reported in this section use Monte Carlo simulations with 400 particles, an equilibration run of 5000 MCS, and an averaging run of 50 000 MCS. A larger number of MCS is used for the averages here (relative to the averages here LJ case) to minimize the statistical noise: a problem usually common in the simulation of dilute systems. The result for $u(r)$, shown in Fig. 4 along with the result of Kepler and Fraden, is practically identical to the potential obtained by Kepler and Fraden and confirms the accuracy of their trial-and-error analysis in this case. This is not the case for the data set corresponding to $\rho\sigma^2=0.0307$ (case f of Kepler and Fraden), the result for which is shown in Fig. 5. In this instance, the Kepler-Fraden analysis leads to an essentially purely repulsive potential, while our inversion indicates that the effective potential still shows a minimum, with a fairly substantial attractive tail. In both cases, the inverted potentials reproduce the experimentally observed radial distribution functions very well, as shown in Fig. 6 for case f of Fraden and Kepler.

It is instructive to examine the equivalent Sogami potentials obtained by Tata and Arora [9] for the Kepler-Fraden data. As mentioned in Sec. II, Tata and Arora have reinterpreted the results of Kepler and Fraden using the Sogami potential in an attempt to account for the physical origin of the attractive tail. The Sogami forms of the potentials obtained by Tata and Arora are also shown in Figs. 4 and 5 and are based on fitting the Kepler-Fraden results by adjusting the parameters of the Sogami potential [10]. The potentials

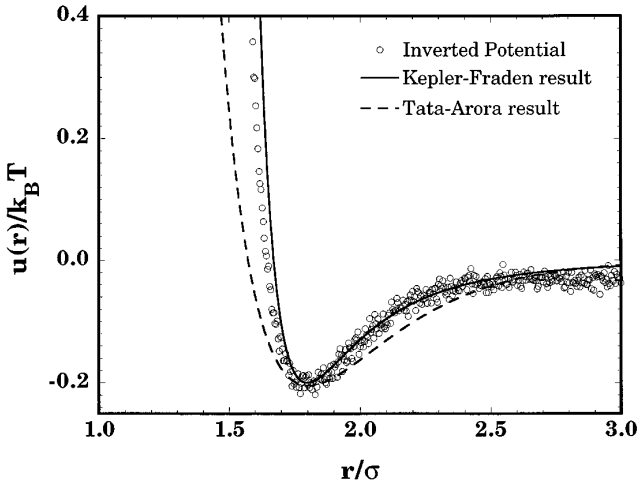

FIG. 4. Pair potential based on the predictor-corrector method for case c ($\rho\sigma^2=0.0194$) of Kepler and Fraden [3] along with the Kepler-Fraden result. The result of Tata and Arora [9] is also shown.

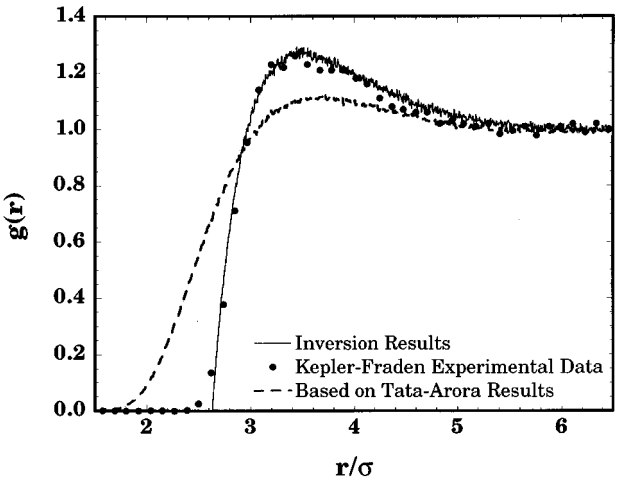

FIG. 6. Radial distribution function $g(r)$ obtained from the extracted potential for case f of Kepler and Fraden [3]. The original data and $g(r)$ based on the Tata-Arora potential are also shown.

thus obtained, however, differ noticeably from the Kepler-Fraden results and ours, as evident from Figs. 4 and 5. More importantly, the Tata-Arora results do *not* reproduce the experimental $g(r)$'s, as illustrated for $\rho\sigma^2=0.0307$ (case f of Kepler and Fraden) in Fig. 6, which shows a significant difference in $g(r)$ near the first-coordination shell. In particular, the differences observed in $u(r)$ and $g(r)$ are substantial enough to affect those properties of the system (e.g., osmotic pressure) that depend on the core of $u(r)$ and $g(r)$ [15].

As mentioned earlier, Carbajal-Tinoco *et al.* [4] have extended the Kepler-Fraden experiments to larger particle concentrations, up to near-freezing conditions ($\rho\sigma^2=0.48$). Carbajal-Tinoco *et al.*, however, analyze their data using single-step inversion methods (e.g., MSA, PY, and HNC) mentioned in Sec. III to obtain $u(r)$. Because such methods resort to severe approximations of the bridge function, the inversion can lead to even qualitatively incorrect potentials (particularly at large particle concentrations or when the interactions are strong), as we have noted elsewhere [14,16]. Under such conditions, the rigorous inversion that we have outlined in Sec. III becomes indispensable. In order to examine the effect of using approximate closure relations, we have inverted the data corresponding to the highest particle concentration used by Carbajal-Tinoco *et al.* ($\rho\sigma^2=0.48$) using the predictor-corrector method and the HNC approximation [which corresponds to taking $B(r)=0$ in Eq. (11)]. The results are shown in Fig. 7. While the exact inversion demonstrates the existence of attraction in the potential, one can also see that the hypernetted-chain approximation leads to quantitatively incorrect results.

C. Source of attraction in confined charged colloids

While the inversion method described here clearly establishes the existence of an effective attraction in confined charged dispersions, it of course cannot provide a physical basis for such an attraction [17]. In this section, we comment

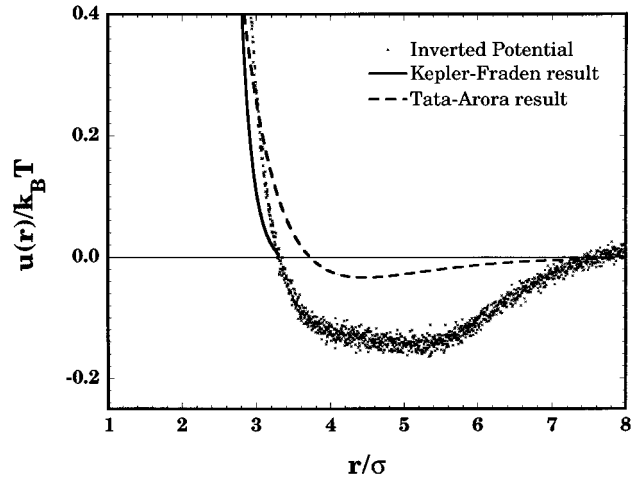

FIG. 5. Pair potential based on the predictor-corrector method for case f of Kepler and Fraden [3] ($\rho\sigma^2=0.0307$) along with the Kepler-Fraden result. The result of Tata and Arora [9] is also shown.

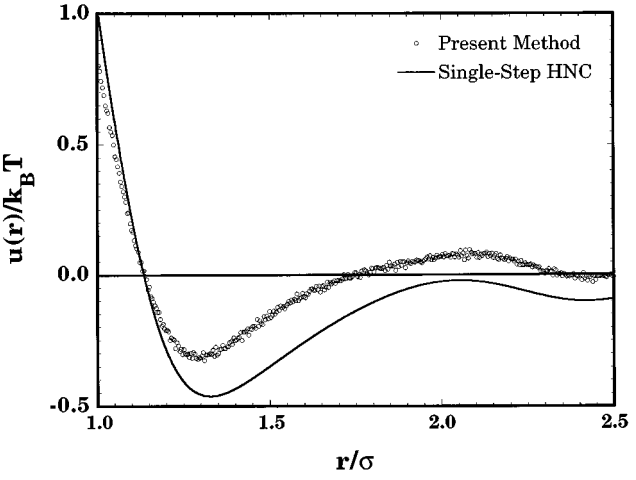

FIG. 7. Pair potential based on the predictor-corrector method for $\rho\sigma^2=0.48$ using the data of Carbajal-Tinoco *et al.* [4], along with the inversion based on the hypernetted-chain closure.

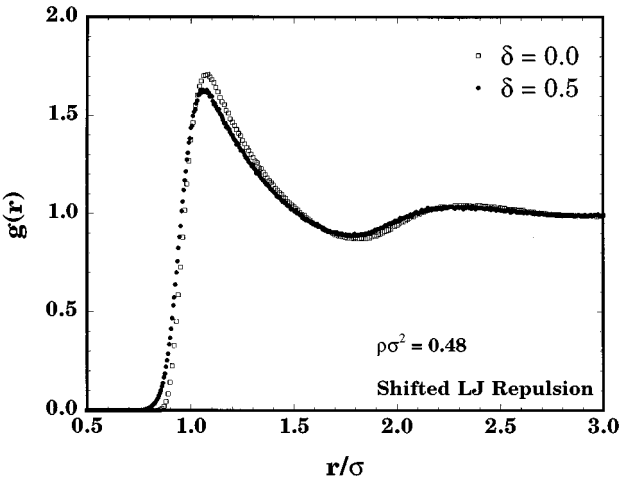

FIG. 8. Radial distribution functions $g(r)$ from Monte Carlo simulations for 2D (i.e., $\delta=0$) and quasi-2D (i.e., $\delta=0.5$) dispersions.

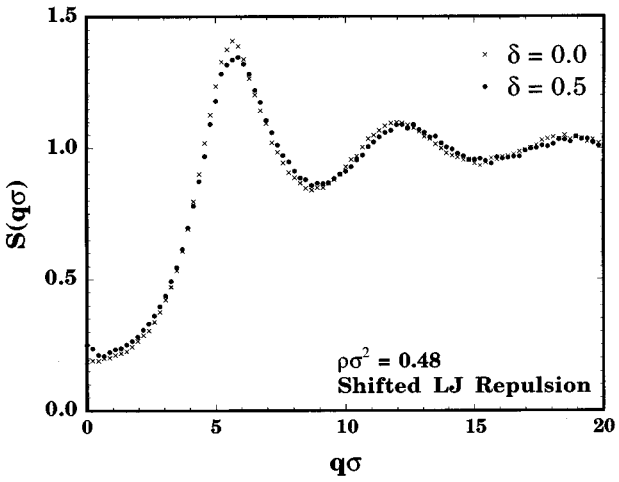

FIG. 9. Structure factors $S(q)$ from Monte Carlo simulations for 2D (i.e., $\delta=0$) and quasi-2D (i.e., $\delta=0.5$) dispersions.

on an important experimental artifact in imaging experiments that can lead to an *apparent* attraction in the pair potential. We also comment on one possible source of the attraction when the artifact is corrected in the experiments [8].

The analyses of Refs. [3,4] assume that the excursions of the particles away from the image plane are negligible. However, even small displacements away from the plane can skew the observed $g(r)$ sufficiently to introduce an apparent attraction in $u_{eff}(r)$. Out-of-plane displacements do not necessarily appear to be negligible in the above experiments of Kepler and Fraden and Carbajal-Tinoco *et al.* as can be noted, for example, from case *a* in Ref. [3], which shows noticeable deviations of $g(r)$ from zero even *inside the core*. Similar situations are also apparent from the data of Carbajal-Tinoco *et al.*

We illustrate our point using Monte Carlo simulations of particles confined between two hard plates separated by $(1+\delta)\sigma$, where $\delta=0$ for a strictly 2D system. The particles are assumed to interact through the repulsive part of a LJ potential shifted up by the magnitude of the LJ minimum. Figure 8 shows $g(r)$'s for $\delta=0$ and 0.5. The $g(r)$ for the *quasi-2D* case (i.e., $\delta>0$) is obtained from particle positions projected onto the image plane, i.e., the x-y plane (as done in the experiments [3,4]). The differences in $g(r)$ for $\delta>0$, particularly the broadening of the primary peak, are indicative of the softening of $u_{eff}(r)$ and of the possibility of attraction. The differences of importance in the extraction of the pair potential show up in the limit of $q\rightarrow 0$ in the structure factor $S(q)$, as shown in Fig. 9. Therefore, it often becomes important to use both good quality $g(r)$ *and* $S(q)$ in the inversion (see also [16]). The potentials inverted using the method of Sec. III and the data in Figs. 8 and 9 are shown in Fig. 10 and clearly demonstrate the influence of out-of-plane excursions of the particles on the effective potential. In particular, the effective potential has an attraction, although the actual potential is purely repulsive.

These results do *not* rule out other sources of attraction. In an attempt to correct for the out-of-plane movements of the particles, Crocker and Grier [8] have conducted a series of experiments in which the z-directional displacements of the particles have been estimated using variations in the image intensity. The Crocker-Grier experiments isolate a pair of particles using two optical tweezers and follow the interparticle separation as a function of time once the particles are released. The pair potential $u(r)$ can then be obtained from the tranjectories of the particles. The results of Crocker and Grier show that $u(r)$ is purely repulsive when the charged glass plates confining the dispersion are far apart. However, $u(r)$ shows attraction for smaller separations δ between the plates and the attraction vanishes on further reductions in the plate separation.

Because the z-directional displacements have been accounted for in the Crocker-Grier experiments, the attraction in $u(r)$ in this case cannot be attributed to the out-of-plane excursions of the particles. It is likely that the effective attraction here arises from the repulsion of the wandering particle by the charged, confining plates toward the other particle when the plates are far enough to allow excursions but close enough to exert influence. However, when δ is very small, the particles are essentially confined to the midplane and the attraction would be expected to vanish. The magnitudes and shapes of $u_{eff}(r)$'s, of course, will depend on the

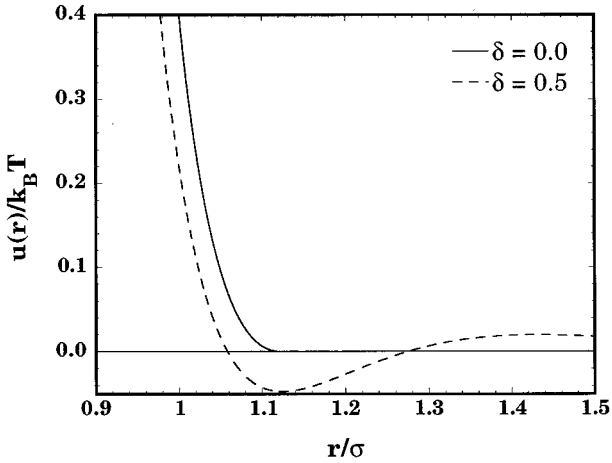

FIG. 10. Inverted potentials for the data shown in Figs. 8 and 9.

experimental conditions (e.g., charges on the plates and the particles, ionic equilibria, etc.) and the quantitative details will depend on more than the above geometric argument.

V. CONCLUDING REMARKS

We have presented a 2D extension of the computer-simulation-based predictor-corrector inversion method for the extraction of the interaction potential from structural data [$g(r)$ or $S(q)$]. When applied to the data of Kepler and Fraden [3] and Carbajal-Tinoco *et al.* [4], the method confirms the appearance of attraction in $u(r)$ unambiguously. Moreover, even in the one case for which Kepler and Fraden report only repulsion, the predictor-corrector inversion shows the existence of attraction. We have pointed out the need for correcting for the out-of-plane motions of the particles in imaging experiments and suggest a reason for the appearance of attraction (and its subsequent disappearance) even when the experiments account for the excursions of the particles.

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[1] C. A. Murray and D. G. Grier, Am. Sci. **83**, 238 (1995).
[2] A. K. Arora and R. Rajagopalan, Curr. Opin. Colloid Interface Sci. **2**, 391 (1997).
[3] G. M. Kepler and S. Fraden, Phys. Rev. Lett. **73**, 356 (1994).
[4] M. D. Carbajal-Tinoco, F. Castro-Román, and J. L. Arauz-Lara, Phys. Rev. E **53**, 3745 (1996).
[5] E. J. W. Verwey and J. Th. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).
[6] *Ordering and Phase Transitions in Charged Colloids*, edited by A. K. Arora and B. V. R. Tata (VCH, New York, 1996).
[7] J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **73**, 352 (1994).
[8] J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **77**, 1897 (1996).
[9] B. V. R. Tata and A. K. Arora, Phys. Rev. Lett. **75**, 3200 (1995).
[10] I. Sogami, Phys. Lett. **96A**, 199 (1983).
[11] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
[12] F. Lado, J. Comput. Phys. **8**, 417 (1971); J. Chem. Phys. **49**, 3092 (1968).
[13] L. Reatto, D. Levesque, and J. J. Weis, Phys. Rev. A **33**, 3451 (1986); L. Reatto, Philos. Mag. A **58**, 37 (1988).
[14] R. Rajagopalan and K. Srinivasa Rao, Phys. Rev. E **55**, 4423 (1997).
[15] It does not, however, seem to be the intention of Tata and Arora [9] to suggest that the Sogami versions of the Kepler-Fraden results presented by them fully explain the experimental data. What they do suggest is that the general shapes of the Kepler-Fraden potentials are consistent with the Sogami form.
[16] R. Rajagopalan, Langmuir **8**, 2898 (1992).
[17] Notice that the situation in quasi-2D systems differs from the similar one in favor of attraction in bulk (i.e., 3D) systems. Until recently, a compelling argument in favor of attraction in 3D systems has focused on the appearance of ''vapor-liquid'' transitions in bulk charged colloids without any added electrolytes (or at very low electrolyte concentrations). However, van Roij and Hansen [R. van Roij and J.-P. Hansen, Phys. Rev. Lett. **79**, 3082 (1997)] have demonstrated recently that the above is a special case that does *not* require attraction in the pair potential to explain the vapor-liquid transition.