

Interaction forces in charged colloids: Inversion of static structure factors

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(Received 6 November 1996)

A simple, easily usable “predictor-corrector” inversion method is presented for extracting the effective pair potential $u(r)$ from static structure factor $S(q)$ of colloidal dispersions and liquids. The method, based on the Ornstein-Zernike integral equation, replaces the unknown bridge function $B(r)$ in the closure with an iteratively obtained hard-sphere bridge function $B_d(r)$. The accuracy of the method is examined by direct determination of $B(r)$ using simulations for extreme examples of pair potential appropriate for charged dispersions. An example of the application of the method to liquid metals is also presented. The results demonstrate the need for using $S(q)$ over the full range of q 's [especially $S(q)$'s for sufficiently low values of q] for obtaining the crucial details of $u(r)$. They further show the fallacies associated with the previous analyses of $S(q)$ that have fueled the controversy concerning the nature of interaction forces in charged colloids and suggest the types of data needed for extracting $u(r)$ for colloidal, Coulombic, and simple fluids.

[S1063-651X(97)04404-8]

PACS number(s): 82.70.Dd, 05.40.+j, 61.25.Hq

I. INTRODUCTION

Interaction forces in charged colloidal dispersions have received much attention recently because of their broad significance to liquid-state physics and other branches of materials and condensed-matter physics. Colloidal dispersions mimic atomic systems in a number of ways; e.g., they exhibit gas, liquid, glass, and crystalline phases, serve as models of Coulombic crystals, and display a rich variety of structural transitions when confined between two surfaces [1,2]. Moreover, one of the field variables driving the transitions is the ionic strength of the dispersion, which offers a better control over the strength and the range of interaction forces than possible in atomic fluids. Further, because the microstructure of these dispersions is optically resolvable and since the dynamics of the phase transitions is very slow, these colloids serve as excellent model systems for studying a broad class of condensed-matter phenomena at convenient spatial and temporal scales, as has been demonstrated beautifully in a number of recent studies [1,2]. The details of the interaction forces, particularly in charged colloids (“macroions”), are of interest for a number of reasons. (i) Such dispersions represent highly asymmetric electrolytes and open up interesting opportunities for studying Coulombic systems. (ii) As we shall note shortly, a drastic rescaling of the actual number of charges on the macroions is needed to explain the observed behavior and properties. Moreover, many recent experimental studies suggest the presence of long-range attraction in situations where classical arguments would predict only repulsive forces. (iii) In view of the above, and since not all the experimental parameters can be controlled precisely, it is important to be able to extract the details of the interaction forces unambiguously and without restrictive assumptions so that the experimental observations can be interpreted in a self-consistent manner. The purpose of the present paper is to provide and illustrate a readily usable method to address item

(iii) above. In doing so, we shall also clarify the reasons for some of the conflicting results that have appeared in the literature on the nature of interaction forces in charged dispersions.

The paper is organized as follows. In Sec. II, we present a brief discussion of the pair potentials for charge-stabilized colloids and the controversy surrounding their validity, since these motivate, partly, our interest in the interpretations of static structure factor data. This is followed in Sec. III by the details of the inversion method proposed here. First, a brief introduction to the so-called *single-step* inversions based on the Ornstein-Zernike integral equation is presented. The details of our “predictor-corrector” inversion scheme and its relation to a more accurate, but more involved, computer-simulation-based corrector are then discussed. In Sec. IV, we consider a set of experimental data that appears to lead to conflicting results for $u(r)$. These data correspond to an extreme case of charge interactions and serve to illustrate the potential pitfalls of the traditional trial-and-error analyses of $S(q)$ to extract $u(r)$. We first test the proposed inversion scheme using Monte Carlo simulations corresponding to the above data and demonstrate that the proposed method, despite the approximation involved in the corrector step, can distinguish *qualitative* differences in the potentials accurately and, moreover, can provide *quantitative* results within about 3–7 % error, i.e., well within typical experimental errors. The implications of these results to the previously advanced interpretation of the data are also discussed in this section. Finally, we illustrate the ease of application of the method and the quality of the results that can be obtained by using scattering data for liquid Cu and compare our result with the potential obtained previously by other means. Some closing remarks and a brief discussion of the types of data needed for extracting $u(r)$'s for highly charged dispersions follow in Sec. V.

II. INTERACTION POTENTIALS IN CHARGE-STABILIZED COLLOIDAL DISPERSIONS

The classical form of the potential between two macroions, formulated by Derjaguin, Landau, Verwey, and Overbeek (DLVO) using the Debye-Hückel linearization of the Poisson-Boltzmann equation, is purely repulsive and is given by the Yukawa form [3]

$$u_{\text{DLVO}}(r) = \begin{cases} \infty & \text{if } r < \sigma \\ \frac{(Ze)^2}{4\pi\epsilon} \frac{e^{\kappa\sigma}}{(1+\kappa\sigma)} \frac{e^{-\kappa r}}{r} & \text{if } r \geq \sigma, \end{cases} \quad (1)$$

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 DLVO potential has been used for explaining a variety of experimental observations ranging from sedimentation data, phase boundaries in phase diagrams, osmotic

pressures, and elastic constants. In general, Eq. (1) has been the standard choice even under conditions at which the assumptions underlying its derivation break down. However, in most such cases it has been necessary to replace the bare charge Ze by a significantly smaller ‘‘renormalized’’ charge Z^*e , with the justification that the renormalization accounts for the nonlinear screening of the macroions by the counterions and coions.

However, there have been a number of recent experimental observations, such as the existence of *vapor-liquid* transitions in charged dispersions [4] and stable voids in macroscopically homogeneous dispersions (see Ref. [1]), that have led some to question the validity of Eq. (1) from a fundamental standpoint. Further, recent two-dimensional (2D) experiments (based on confining a single layer of particles between two charged plates) also suggest the existence of long-range attraction [5,6]. Numerous attempts have been made to explain such results using a potential derived by Sogami [7], which has been the focus of much controversy [8]:

$$u_{\text{Sog}}(r) = \begin{cases} \infty & \text{if } r < \sigma \\ \frac{(Ze)^2}{2\epsilon} \frac{2 \sinh^2(\kappa\sigma/2)}{\kappa\sigma} \left(\frac{2 + \kappa\sigma \coth(\kappa\sigma/2)}{r} - \kappa \right) e^{-\kappa r} & \text{if } r \geq \sigma. \end{cases} \quad (2)$$

Equation (2) includes a long-range, counterion-mediated attractive component (in addition to a short-range repulsion) and has been used to explain the vapor-liquid transition and the smaller than expected lattice constants in colloidal crystals observed in experiments with charged dispersions [1].

The basis of the derivation of the Sogami potential and the origin of the counterion-mediated attraction have come under criticism in the literature. It is not our objective in this paper to either elaborate on or resolve the controversies concerning the DLVO and Sogami potentials. However, because these two potentials have been used to interpret the types of data we use in the present paper and motivate, partly, the focus on the inverse problem addressed in this paper, a brief mention of the source of the controversies is in order. First, it may be noted that the classical DLVO potential is the potential of mean force between two interacting particles in a *canonical* ensemble; i.e., the potential represents the Helmholtz free energy for the interacting electrical double layers. In contrast, Sogami’s derivation resorts to a ‘‘Gibbsian’’ description of the interaction potential—an approach that has its origin in Sogami’s division of the volume around each macroion into two regions, one containing the relatively tightly bound counterions close to the macroion and the other containing the rest. To account for the differential accessibility of the total volume to the counterions, Sogami defines a fictitious membrane (i.e., for mathematical purposes only) around each macroion to separate the bound counterions from those in the bulk solution. The long-range attraction is a result of this mathematical construction, and the validity, implications, and consequences of such a construction have come under criticism and have been the focus of much debate in the literature. The pros and cons of the Sogami for-

malism are discussed in detail by Jönsson *et al.* and Smalley [8], and we refer the readers to those discussions and the references therein.

Because of their insensitivity to the details of the potential, many of the properties mentioned earlier (e.g., osmotic compressibility and elastic constants) can be described satisfactorily using either Eq. (1) or Eq. (2) (or others). Moreover, in fitting such properties one introduces another level of arbitrariness by treating Z and κ as adjustable parameters [9] (in addition to the *a priori* assumptions that are already made concerning the forms of the potentials). As a result, such procedures for extracting $u(r)$ from $S(q)$ severely restrict (and clearly bias) the results obtained and are *indirect* and *unreliable* probes of $u(r)$.

A more direct probe of the interaction potential is possible through the use of the positional correlations among the particles, obtained from the static structure factor $S(q)$ measured through radiation scattering techniques or equivalently from $g(r)$ measured using optical microscopy. The latter method, made possible because the positions of the particles can be resolved and recorded optically in the case of colloids in the appropriate size range, has been used recently to probe the potentials in three-dimensional [10] and two-dimensional [5,6] systems. For example, Crocker and Grier [10] record the trajectory of a charged particle in the vicinity of a second particle held stationary with an optical trap in a dilute dispersion. The pair potential is then given simply by $\beta u(r) = -\ln g(r)$, where $\beta^{-1} = k_B T$. Pair correlation functions at larger concentrations are accessible in 2D experiments, since, in this case, the dispersion is confined to a single layer between two charged plates (although the use of charged confining plates does introduce an uncertainty in the inter-

pretation of the data). Kepler and Fraden [5] have recently obtained $g(r)$'s from such experiments and use a fitting procedure based on a preselected form of the potential to obtain $u(r)$ —an approach that is similar to that of Tata *et al.* [9] and, as a result, carries with it the biases or assumptions implicit in the selected potential. The experiments of Carbajal-Tinoco *et al.* [6] are similar to those of Kepler and Fraden [5], but the data analysis used by Carbajal-Tinoco *et al.* differs from those used by Tata *et al.* [9] and Kepler and Fraden [5] and is related to some of the methods we shall discuss in the following section.

III. INVERSION BASED ON THE ORNSTEIN-ZERNIKE EQUATION

Extracting information on $u(r)$ from $S(q)$ has been a problem of long-standing interest in physics. The classical approach to this problem is the one we have alluded to in the previous section, namely, to fit the experimentally observed $S(q)$ using a *preselected* potential and a suitable theory that relates $u(r)$ to $S(q)$ —an approach that we refer to as the *forward* formalism. In this approach one usually seeks the *parameters* of an assumed potential rather than the potential itself. This approach has been very popular in the analysis of the experimental $S(q)$'s for micellar solutions and charged colloids [11–13]. As already noted, a major drawback of this method is that it requires *a priori* information on the functional form of the potential; any assumptions made for this purpose clearly bias the results of the analysis. A classic case of such a bias and the resulting contradictions in the extracted potentials are evident from the results reported by Tata *et al.* [9], who find that their experimental data on charged latex dispersions can be fitted, within statistical accuracy, using two *qualitatively* different potentials, one purely repulsive (of the DLVO form) and the other with a long-range *attraction* (a Sogami potential). We shall defer further comments on this contradictory observation to Sec. IV.

An alternative route to the analysis is to devise a scheme to “invert” the $S(q)$ data without making any assumption about the form or the parameters of the pair potential. This *inverse* problem is the one that forms the focus of this paper. For reasons that will become clear shortly, we choose the integral-equation method based on the Ornstein-Zernike equation for this purpose.

As is well known, the structure factor $S(q)$ is given by the Fourier transform of the total correlation function $h(r)$ [$=g(r)-1$]:

$$S(q) = 1 + \rho \int h(r) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}, \quad (3)$$

with ρ being the number density of the particles. The function $h(r)$ can be written in terms of the direct correlation function $c(r)$ using the Ornstein-Zernike (OZ) equation

$$h(r) = c(r) + \rho \int h(r') c(|r-r'|) d\mathbf{r}', \quad (4)$$

which can be solved, in principle, using the following exact closure relation:

$$c(r) = -\beta u(r) + h(r) - \ln[h(r) + 1] + B(r), \quad (5)$$

where $B(r)$ is the so-called *bridge function* representing the sum of an infinite series of elementary clusters in terms of h bonds [14]. Since $B(r)$ is analytically intractable, a number of approximations to Eq. (5) are normally used in the forward methods based on Eq. (4). Despite the attendant limitations, the relative convenience and successes of approximate closures [such as the Percus-Yevick (PY) and the hypernetted-chain (HNC) approximations] in the study of simple fluids and liquid metals have largely been the reason for the popularity of the Ornstein-Zernike equation in liquid-state physics.

A. Single-step inversions based on the OZ equation

Not surprisingly, for the same reasons, the OZ formalism also lends itself naturally to the solution of the inverse problem, as illustrated by the pioneering work of Johnson *et al.* [15] for rare-gas liquids and liquid metals. The approach of Johnson *et al.* is based on the PY and HNC approximations to the closure equation (5). The PY and HNC closures represent specific approximations for the bridge function (see, for example, Hansen and McDonald [14]) and restrict the accuracy of the results of the inversion severely at liquid densities (although they have been used recently by Carbajal-Tinoco *et al.* [6] to analyze their 2D data on dispersions). For example, the HNC closure corresponds to taking $B(r)$ in Eq. (5) to be identically equal to zero. The extracted potentials under such assumptions sometimes do not bear any resemblance to the original potentials, as has been demonstrated by Ailawadi [16]. However, formal inversion schemes based on approximate closures relate the structure factor $S(q)$ [or, equivalently, $g(r)$] to $u(r)$ in a simple fashion, and the pair potential can be obtained in a straightforward manner from a given experimental $S(q)$. Therefore, inversion schemes that rely on such simple rearrangements of the closure equation are often called “single-step” inversions, as opposed to the “predictor-corrector” schemes, which seek iterative corrections to the closure at each step.

One can achieve a significant improvement over the PY and HNC predictions by substituting $B_d(r)$, the bridge function for a hard-sphere fluid with a suitably chosen hard-sphere diameter d , for the actual unknown $B(r)$ in Eq. (5). The choice of d is usually based on a criterion suggested by Lado in his *reference hypernetted-chain* (RHNC) theory [17]:

$$\int \frac{\partial B_d(r)}{\partial d} [g(r) - g_d(r)] dr = 0. \quad (6)$$

We shall refer to this as the *single-step RHNC inversion*.

B. The proposed “predictor-corrector” method

If one is willing to sacrifice the convenience of single-step inversions for a significant improvement in accuracy, the *exact* closure can be incorporated in the inversion by employing an *iterative* scheme in combination with computer simulations at each iteration, as first illustrated by Reatto *et al.* [18]. In order to place the iterative methods [19], including

the simpler one we propose in this paper, within a unified framework, it is convenient to recast the OZ equation and its closure as follows.

The basic idea behind any inversion scheme based on the OZ equation is to use Eq. (4) in combination with Eq. (5) to extract $u(r)$ from the experimental $S(q)$ at the known density ρ of the system. Since the OZ equation can be used to relate $c(r)$ in the closure to the experimental data $S(q)$ through

$$c(q) = \frac{1}{\rho} \left[1 - \frac{1}{S(q)} \right] \quad (7)$$

it is the lack of a direct link between the experimental data and $B(r)$ that prevents one from using Eq. (5) to obtain $u(r)$ directly from $S(q)$. The single-step inversion methods circumvent this problem by either neglecting $B(r)$ altogether (as in the HNC inversion) or approximating it in terms of known information (as in the PY and in the single-step RHNC inversions).

We begin our discussion of iterative methods by first writing Eq. (5) relative to the corresponding closure for a fluid of as-yet-unknown potential $u'(r)$ as follows:

$$\beta u(r) = \ln \left(\frac{y'(r)}{[h(r)+1]} \right) + [h(r) - h'(r)] - [c(r) - c'(r)] + \Delta[u(r), u'(r)], \quad (8)$$

where the prime identifies the functions corresponding to $u'(r)$, and

$$y'(r) = g'(r) e^{\beta u'(r)} \quad (9)$$

is the *cavity function*. The task of obtaining the required $u(r)$ now reduces to choosing $u'(r)$ such that $\Delta[u(r), u'(r)] \rightarrow 0$, where $\Delta[u(r), u'(r)] = [B(r) - B'(r)]$. In an iterative scheme, one starts with a suitably chosen initial guess for $u'(r)$ and computes the corresponding $y'(r)$, $h'(r)$, and $c'(r)$ to obtain an improved $u(r)$, with Δ set to zero. In this sense, Eq. (8) becomes the *predictor*. The *corrector* step involves refining this prediction using $y(r)$, $h(r)$, and $c(r)$ based on the result of the previous step in place of the primed quantities. How one obtains the correlation functions in the corrector step distinguishes the different ‘‘predictor-corrector’’ formalisms. One can use computer simulations at each step to obtain $y'(r)$, $h'(r)$, and $c'(r)$ as suggested first by Reatto *et al.* [18]. However, for reasons that will be discussed later, we propose the following, simpler ‘‘predictor-corrector’’ formalism based on a hard-sphere potential $u'(r) = u_d(r)$, where d is the hard-sphere diameter. We shall use an iterative scheme to obtain the fixed point d , and hence $u(r)$, with Eq. (8) [with Δ set to zero] serving as the ‘‘predictor.’’ The primary advantage for replacing $u'(r)$ with $u_d(r)$ is the availability of an extremely accurate parametrized form for $y_d(r)$, the hard-sphere cavity function [20] [and, hence, $B_d(r)$]. At first glance, using a hard-sphere reference might appear to be a severe approximation; however, it is well known that, at high densities, the short-range repulsive core of $u(r)$ determines the behavior of the structure factor and the bridge function of the fluid. Further, computer simulations show that even the $B(r)$ ’s for full potentials dif-

fer from $B_d(r)$ ’s for suitably chosen d ’s by at most 10% in the regions of interest in the inversion [21]. We shall discuss the accuracy of this choice further in Sec. IV.

In the inversion proposed here, we first obtain an initial estimate of d using the relation between the isothermal compressibility and $S(q=0)$, viz.,

$$\frac{1}{S(0)} = \left[\frac{\partial(\beta P)}{\partial \rho} \right]_T \quad (10)$$

in which an equation such as the Carnahan-Starling equation [22] is sufficient for relating the pressure P to d . The first approximation to $u(r)$ based on this d is then split into a core part $u_c(r)$ and a perturbation $u_p(r)$ according to the Weeks-Chandler-Andersen criterion [23]:

$$u(r) = u_c(r) + u_p(r). \quad (11)$$

The above core part of the potential is then used in the corrector step to refine the correlation functions $y'(r)$, $h'(r)$, and $c'(r)$ [or, equivalently, $B'(r)$]. Therefore, the requirement that $\Delta \rightarrow 0$ is sought by obtaining an improved d based on $u_c(r)$, using a criterion such as

$$\int \frac{\partial y_d(r)}{\partial d} [e^{-\beta u_c(r)} - e^{-\beta u_d(r)}] dr = 0, \quad (12)$$

which minimizes the difference between the free energies of two fluids (at the given density ρ) interacting through $u_d(r)$ and $u_c(r)$, respectively [24]. This new diameter is now used in Eq. (8) to improve $u(r)$, and the procedure is repeated until d and $u(r)$ converge. Notice that the above *iterative* improvement of the hard-sphere diameter distinguishes this method from the single-step RHNC method mentioned earlier.

C. Computation of hard-sphere correlation functions

There are two items that require attention in using the hard-sphere reference as the corrector. The first is the accuracy of replacing the actual bridge function $B'(r)$ of the iterate $u'(r)$ with the hard-sphere bridge function corresponding to $u_c(r)$, and the second is the calculation of $B_d(r)$ for a given diameter d . We shall defer the discussion of the first item to Sec. IV and focus on the second here.

It follows from Eq. (5) that the hard-sphere bridge function $B_d(r)$ is given by

$$B_d(r) = c_d(r) + \ln y_d(r) - h_d(r). \quad (13)$$

We have used the Henderson and Grundke [20] correlation for $y_d(r)$, which is based on a cubic polynomial fit for $\ln y(r)$ for $r < d$, for obtaining $B_d(r)$. The coefficients of the cubic polynomial are determined using the well-known macroscopic properties of the hard-sphere fluid and the Verlet and Weis [25] semiempirical pair-distribution function $g_d(r)$. The accuracy of the Henderson-Grundke parametrization of $y_d(r)$ is estimated to be within about 3% of the exact values even for a reduced density, ρd^3 , as large as 0.8. The correlation for $\ln y_d(r)$ is in principle sufficient for calculat-

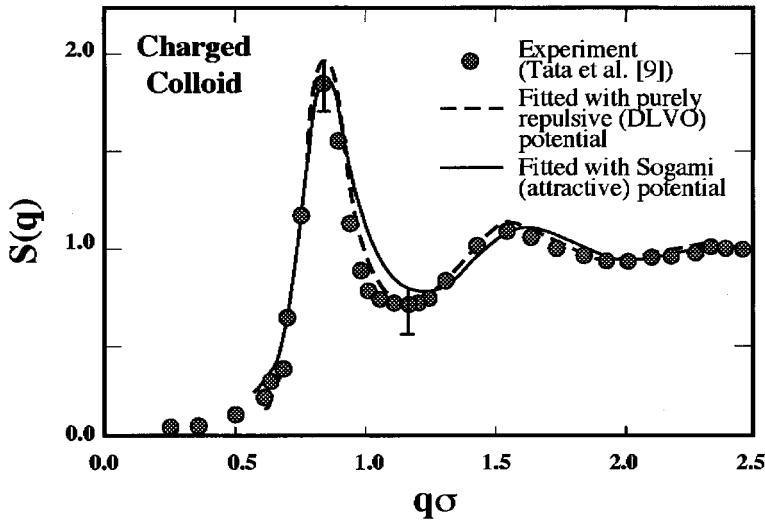


FIG. 1. The experimental structure factor for a charged dispersion along with the calculated $S(q)$ based on the DLVO and Sogami potentials shown in Fig. 2. See Tata *et al.* [9] and Salgi *et al.* [28] for the parameters.

ing $B_d(r)$ from Eq. (13) since one can use the OZ equation to evaluate $c_d(r)$ from the parametrized $y_d(r)$, which is equal to $[h_d(r)+1]$ for $r>d$. However, it is well known that even small changes in $h_d(r)$ can cause large changes in the tail of $c_d(r)$. Therefore using the Henderson-Grundke $y_d(r)$ for calculating $c_d(r)$ is not advisable. Instead, we have used the correlation for $c_d(r)$ given by Groot *et al.* [26]; unlike the Verlet-Weis correlation, which is based on Monte Carlo simulation results with 108 particles, the correlation of Groot *et al.* is based on simulations of fairly large-size systems (number of particles around 2500) with corrections for the finite size of the simulation box. The error involved in the resulting parametrization of $c_d(r)$ is less than 1% for $\rho d^3 < 0.9$ and $r < d$. The absolute error in $c_d(r)$ is estimated to be about 1–2% for $r > d$ in the same range of densities.

IV. DISCUSSION

In this section, we shall use a typical set of experimental structure factor data reported in the literature to examine the potential pitfalls of using forward schemes for extracting pair potentials and to test the accuracy of the hard-sphere-corrector-based inversion method presented in Sec. III B. Following this, an application of the inversion method for liquid metals is discussed in order to illustrate the ease of application and the larger utility of the proposed method.

A. Fitting methods for obtaining $u(r)$ from $S(q)$

In the following, we use the scattering data reported by Tata *et al.* [9] for a charged dispersion of polystyrene spheres of diameter $\sigma=0.109 \mu\text{m}$. Although the volume fraction of the dispersion corresponding to the data is 0.9×10^{-3} , the *effective* volume fraction is rather large (~ 0.4) because of the strong excluded-volume effect due to

the long range of the repulsion and is close to the “solid-liquid” boundary. Tata *et al.* fit the experimental $S(q)$ over a limited range of q ’s (near the primary peak) quite satisfactorily with Eq. (1) and Eq. (2), but using κ as an adjustable parameter; see Fig. 1. The resulting potentials, shown in Fig. 2, differ significantly from each other for $r \geq 9\sigma$, which corresponds to $q\sigma \leq 0.6$ in the Fourier space. As can be seen from Fig. 1, this range of $q\sigma$ coincides with the range *not* included in the fitting procedure used by Tata *et al.*, and has a bearing on the apparently contradictory results of the analysis, as we shall see shortly.

The fact that the data shown in Fig. 1 can be fitted using the Sogami potential equally acceptably has been used to question the validity or the adequacy of the DLVO potential for highly charged dispersions. We shall use the above set of data as a reference for testing our inversion method and, in that process, for shedding some further light on the above contradictory results.

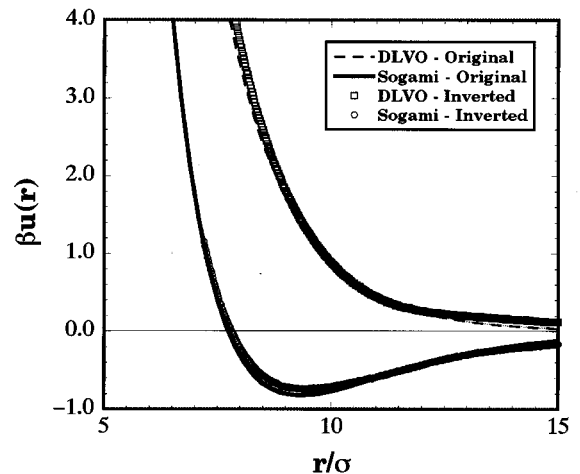


FIG. 2. The theoretical DLVO and Sogami potentials used in Fig. 1 (solid and dashed lines). Also shown are results obtained from the inversion of $S(q)$ ’s shown in Fig. 4 (symbols).

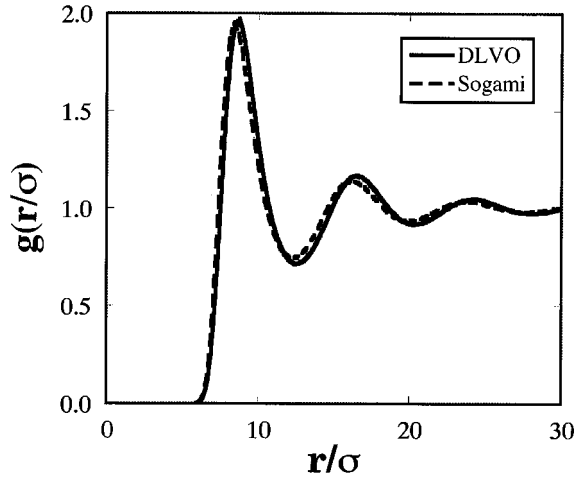


FIG. 3. The radial distribution function $g(r)$ from Monte Carlo simulations for a charged dispersion with the DLVO and Sogami potentials shown in Fig. 2. See Tata *et al.* [9] and Salgi *et al.* [28] for the parameters.

B. The accuracy of the predictor-corrector inversion method

Although the experimental data in the above example are available down to $q\sigma=0.25$, because estimates of experimental errors are not available and since data below $q\sigma < 0.25$ are needed, we resort to Monte Carlo simulations to test the inversion method.

Standard canonical Monte Carlo simulations based on the Metropolis algorithm are used to generate $S(q)$ using (typically) 2048 particles and periodic boundary conditions. Simulations with a larger number of particles lead to the same results within statistical accuracy. The radial distribution function $g(r)$ is obtained as an average over at least 4000 Monte Carlo steps (i.e., about 8×10^6 configurations) after equilibration. The radial distribution functions thus obtained for both the DLVO and the Sogami potentials in Fig. 2 are shown in Fig. 3. As can be noted, the $g(r)$'s for these two (even *qualitatively* different) potentials are almost identical (except for a small out-of-phase oscillation) since the repulsive core dominates the spatial structure of the fluid at the high effective volume fractions corresponding to the conditions used. Such a situation should be expected whenever the mean interparticle distance (as determined by the overall density) is about the same as the location of the minimum in the potential. In such cases, the presence of the attractive minimum in the pair potential does not lead to quantitative differences in $g(r)$ that are easily distinguishable. [As a result, fitting $g(r)$'s theoretically by adjusting parameters of an assumed $u(r)$ is highly unreliable.] In addition, the ‘‘core’’ of $u(r)$ ($r \leq 9\sigma$ in this case) has a significant influence on the long-wavelength oscillations in $g(r)$. This effect is usually obscured in $g(r)$ and is most easily seen in $S(q)$ in the low- q region [i.e., for $q < q_{\max}$, where q_{\max} is the location of the primary peak in $S(q)$]. The low- q region of the structure factor is, therefore, a better measure of order in the system in such instances and is very important in the inversions.

As noted in Eq. (3), $S(q)$ is obtained by Fourier transforming $g(r)$, but, in the case of $g(r)$'s obtained from simulations, Eq. (3) leads to accurate results only for $S(q)$ near and beyond the primary peak. The magnitude of $S(q)$ in the

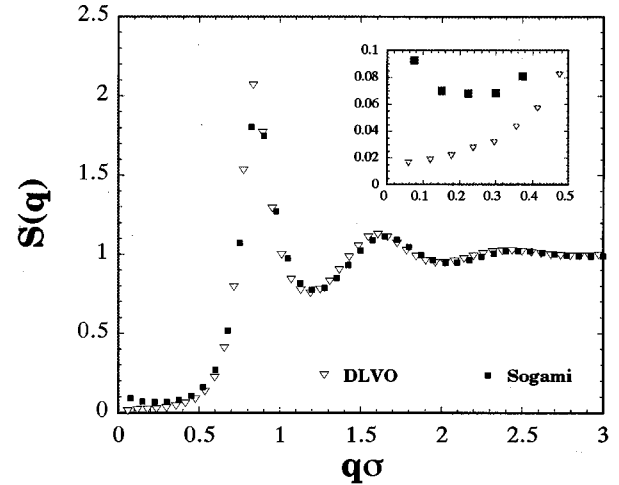


FIG. 4. The structure factors for the DLVO and the Sogami potentials obtained from simulations. The inset shows the low- q results.

low- q region is very noisy because of the finite size of the simulation box. Therefore it is necessary to calculate $S(q)$ in the low- q region by the direct-averaging procedure suggested by Frenkel *et al.* [27]. The $S(q)$'s for the two potentials shown in Fig. 2 have been generated for $q\sigma \geq 0.075$ using the above procedure and are shown in Fig. 4. Additional details on the simulations and estimates of statistical errors are available elsewhere [28]. Figure 4 shows that the magnitudes of $S(q)$ at low q are quite low; i.e., the isothermal compressibility is very low, as one would expect for strongly repulsive interactions. Also, the simulated $S(q)$'s for the two potentials are practically the same near and beyond q_{\max} and are essentially the same as the experimental $S(q)$ shown in Fig. 1. It is, therefore not surprising that the experimental $S(q)$ can be described using the two potentials shown in Fig. 2 with the same level of accuracy [29]. However, a careful examination of the low- q region reveals differences between the two $S(q)$'s that are significant for the interpretation of interaction forces (see the inset in Fig. 4). In particular, $S(q)$ of the Sogami potential shows an upward turn for $q\sigma < 0.25$, consistent with the fact that the attractive component in $u_{\text{Sogami}}(r)$ renders the system more compressible.

We have used the $g(r)$'s and $S(q)$'s obtained from the simulations to test the inversion scheme. The systems represented by these data provide a very rigorous test of the method since the *effective* volume fraction of the dispersion is near freezing (as evident from the range of the repulsion in the potentials). The result for the potential with long-range attraction is shown in Fig. 3, along with the original potential, and it is evident that the inversion recovers both the repulsive core and the attractive tail with excellent accuracy. The steep repulsive core of the potential can be recovered up to about $10k_B T$ (although only a portion of the results near the core is shown). In the case of $u_{\text{DLVO}}(r)$, which offers a much more stringent test of the inversion, the potential does not have a minimum nor does it cross zero, and the separation of the iterates has to be done at some arbitrary point. One choice is to select a point r_s such that $10k_B T < u(r_s) < 2k_B T$. Separation points with $u(r_s) > 10k_B T$ are not useful since $g(r)$ is insensitive to the potential in this

region. The inverted potential in this case is also shown in Fig. 2 along with the original. Again, excellent agreement between the two is obtained.

Somewhat more accurate results can be obtained if one uses a rigorous calculation of the bridge function at each iteration using simulations as the “corrector” for the iterate $u'(r)$ from the previous step, as proposed first by Reatto *et al.* [18]. This procedure can lead to a final potential with about less than 2–3% error if sufficiently accurate structure factors (equivalently, bridge functions) are calculated in the simulations at each step in the iteration. However, such a procedure is quite time consuming and cannot be used easily since extensive simulations are needed at each iteration [with accompanying extension and refinement of the $g(r)$ for obtaining $S(q)$]. For example, for the results presented in this paper, about 20 iterations will be required, with each iteration requiring many hours of computer simulations and extensions. Further, in applying the method to real data, it is unreasonable to demand a level of accuracy in the corrector beyond what is justified by the errors in experimental $S(q)$'s. Our objective in this paper has been to seek a method that avoids the use of computer simulations at every step in the iteration while restricting the error in the extracted potential to an acceptable level. To this end, the procedure we suggest takes advantage of the availability of a parametrized correlation for hard-sphere bridge function and provides a scheme for the selection of the best hard-sphere diameter under a few minutes of calculations. In addition, the error in the inverted potential is under 6–7% even in extreme cases such as the ones illustrated here. However, if further improvements are warranted and are justified by the quality of the experimental data, one can use our results as the starting point in the simulation-based corrector of Reatto *et al.* to fine-tune the result.

C. Accuracy of replacing $B(r)$ with $B_d(r)$

In order to better understand the error arising from the use of the hard-sphere corrector, we have calculated the bridge functions for the actual potentials and for the corresponding hard-sphere fluids with d determined by Eq. (12). Although, in principle, the bridge function can be calculated for a given $u(r)$ [or $h(r)$] in terms of an infinite series of h -bonded elementary diagrams, the convergence of such a series is too slow for such an approach to be of any practical use. Computer simulations, on the other hand, provide a better and a highly accurate route to the calculation of the bridge function. A rearrangement of Eq. (5) shows how one can calculate $B(r)$ if $u(r)$ and $g(r)$ are known:

$$B(r) = c(r) + \ln y(r) - h(r). \quad (14)$$

The calculation is straightforward for radial distances near and beyond the first peak in $g(r)$ since $y(r)$ in Eq. (14) can be calculated easily from the computed $g(r)$ and the known $u(r)$ using Eq. (9). [The direct correlation function $c(r)$ needed in Eq. (14) follows from the OZ equation; see Eq. (7).] However, this procedure is inadequate in the core region of the potential, where $g(r) \approx 0$; in particular, a direct, more accurate determination of $y(r)$ is needed.

We use the Henderson method [30,21] to calculate the cavity function directly using simulations. The cavity func-

tion in the canonical ensemble is given by

$$y(r) = e^{\beta\mu} \langle e^{-\beta\sum_{j=2}^{N+1} u(r_{1j})} \rangle, \quad (15)$$

where $\langle \rangle$ represents the ensemble average and μ is the residual chemical potential. Equation (15) relates $y(r)$ to the interaction potential between a “ghost” particle labeled “1” and the N real particles in the simulation box. The ghost particle is so named since it does not influence the movement of the other particles. The exponent of the Boltzmann factor in Eq. (15) is the sum of the potential of interaction of the ghost particle with all particles “ j ” other than a “second” particle fixed at a distance of r . Since the labeling of the *real* particles is arbitrary, any of the N particles can serve as the “second” particle. This implies that each configuration generated in the simulation provides the Boltzmann factor in Eq. (15) for N values of r . The residual chemical potential μ in Eq. (15) can also be calculated as a part of the same simulation using the Widom test-particle insertion method [31]. Since the presence of the ghost particle does not disturb the equilibrium configurations generated by the Metropolis algorithm, the calculation of $g(r)$ also can be carried out simultaneously.

Although the cavity function can be calculated for all interparticle distances using the above procedure, for the region beyond the core of the potential it is much more efficient to calculate $y(r)$ from $g(r)$ and $u(r)$ using Eq. (9), as noted earlier. For inside the core, however, the use of Eq. (15), or appropriate alternatives [21], is essential.

We have calculated $y(r)$ from simulations using $N=2048$ real particles and one ghost particle for the potentials considered in this paper. The corresponding hard-sphere fluids do not require simulations, as parametrized correlating equations for both $y_d(r)$ and $B_d(r)$ are available in the literature [20,32,33], as already noted in Sec. III C. An accurate determination of $B(r)$ allows one to examine the percentage error in the inverted potential since

$$\frac{\beta u_{\text{inv}}(r) - \beta u_{\text{actual}}(r)}{\beta u_{\text{actual}}(r)} = \frac{B_d(r) - B_{\text{exact}}(r)}{\beta u_{\text{actual}}(r)}. \quad (16)$$

The results show that the percentage error is negligible inside the core and that the only significant difference occurs just outside the core in the case of both the DLVO and the Sogami potentials. [The largest absolute differences between $B(r)$ and $B_d(r)$ occur for (r/d) less than about 0.2—a distance so far inside the core that those differences have no significance to the extracted potentials. Therefore, the comments below refer to $r \geq d$.] For the DLVO potential, the maximum difference between the actual and the extracted potential occurs at a distance r of about 10σ , where σ is the actual diameter of the particle. The magnitude of the difference is about $0.06k_B T$, compared to the actual potential of about $0.9k_B T$, corresponding to an error of about 7%. In the case of the Sogami potential, again the difference is about $0.08k_B T$, at the minimum in the potential; this also corresponds to an error of about 8%. Sample results for the case of the Sogami potential are shown in Fig. 5 for r near the core and beyond.

As noted earlier, the use of simulations as the corrector at each iteration will improve the accuracy of the extracted po-

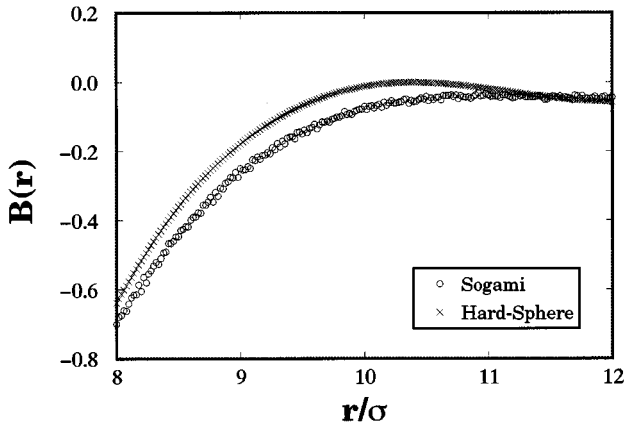


FIG. 5. The bridge function for the Sogami potential and the hard-sphere fluid with diameter determined by Eq. (12).

tential, although the final error is typically about 2–3%—a reduction of about 5% from what was obtained using the iterated $B_d(r)$. Exact correctors require, especially for the types of long-range interactions considered in this paper, extensive simulations to reduce the statistical errors and large box sizes (and hence large N 's) to obtain $S(q)$'s for low enough q 's. However, in most cases, the above-mentioned small further reduction in the error does not justify the computational effort involved in using a simulation-based corrector. Nevertheless, the possibility of using simulations as corrector does leave open the option of further refining our results if a higher level of accuracy is needed or justified.

D. Application to a liquid metal

As an example of how our method can be used to predict the potential as well as the properties of liquids using actual scattering data, we consider a case of liquid Cu examined by Arai and Yokoyama [34].

Arai and Yokoyama have used a trial-and-error fitting method for the experimental structure factor data for liquid Cu (at $T=1423$ K and $\rho=0.07554 \text{ \AA}^{-3}$) measured by Waseda and Ueno [36] in the low- q region ($0.1 \text{ \AA}^{-1} \leq q \leq 2.3 \text{ \AA}^{-1}$) and by Waseda [35] over a larger range ($0.5 \text{ \AA}^{-1} \leq q \leq 17 \text{ \AA}^{-1}$). Their goal was to extract the long-range attractive tail of the effective potential, about which very little is known for liquid metals. It is not our objective here to present a detailed analysis of the method used by Arai and Yokoyama or to examine the potential they have obtained. Rather, our primary objective is to illustrate the simplicity of our method relative to the one used by Arai and Yokoyama and to show that results of comparable quality (or better) can be obtained without much effort.

In order to provide an appreciation for how effective potentials are usually extracted and ‘‘pieced together’’ from $S(q)$ data, it is instructive to present some background details on the approach used by Arai and Yokoyama. To separate the effects of the core of the potential from those of the tail, Arai and Yokoyama first separate $u(r)$ into a ‘‘reference’’ part, $u_{\text{ref}}(r)$, and a perturbation, $u_p(r)$, representing the long-range attraction:

$$u(r) = u_{\text{ref}}(r) + u_p(r). \quad (17)$$

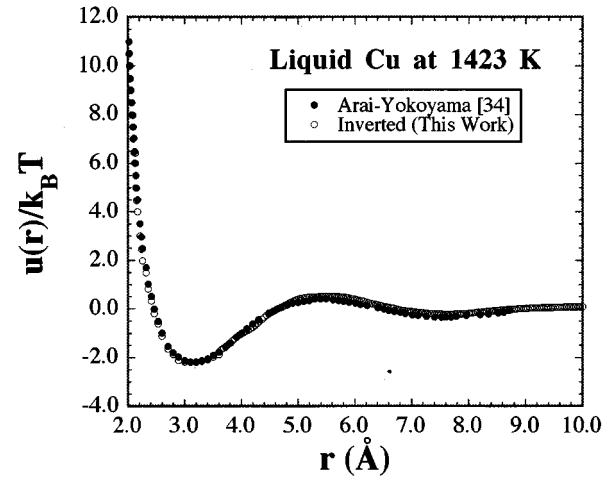


FIG. 6. The inverted potential for liquid Cu at $T=1423$ K obtained from neutron scattering data reported in Waseda [35]. Also shown is the potential based on the work of Arai and Yokoyama [34].

Since purely repulsive u_{ref} 's overestimate the primary peak in $S(q)$ significantly, $u_{\text{ref}}(r)$ is further decomposed into a purely repulsive $u_0(r)$ and an attractive tail $u_{\text{attr}}(r)$. Arai and Yokoyama approximate $u_0(r)$ by an inverse twelfth-power potential whose parameters they determine by trial and error (using simulations) such that the experimental structure factor data can be fitted well in the large- q region. The long-range attractive tail $u_p(r)$ is then obtained using the random-phase approximation from the low- q scattering data via

$$\beta u_p(r) = [(2\pi)^3 \rho]^{-1} \int_0^{q_0} 4\pi q^2 \left[\frac{1}{S(q)} - \frac{1}{S_0(q)} \right] \left(\frac{\sin qr}{qr} \right) dq, \quad (18)$$

where $q_0 = (18\pi^2 \rho)^{1/3}$ and $S_0(q)$, the structure factor corresponding to $u_0(r)$, is determined again using simulations. Notice that this prescription for $u_p(r)$ corresponds to equating $u_p(r)$ to $c_0(r) - c(r)$, and ignores the effect of $u_{\text{attr}}(r)$. For $u_{\text{attr}}(r)$, Arai and Yokoyama have assumed a negative inverse sixth-power potential with the same parameters as those of $u_0(r)$. The effect of $u_{\text{attr}}(r)$ on $S_{\text{ref}}(q)$, again examined using molecular dynamics, is to lower the magnitude of the primary peak. This fitting method is a quite time-consuming, laborious, piecewise ‘‘reconstruction’’ of the potential and is based at least partly on *ad hoc* reasoning. However, the structure factor calculated from their potential via molecular dynamics is in good agreement with the experimental one except in the region delimited by the first and second diffraction peaks, and the total potential reproduces the low- q experimental data well. The resulting effective pair potential of Arai and Yokoyama also predicts the heat capacity, self-diffusion coefficient, and shear viscosity in very good agreement with experimental data.

When applied to the same set of $S(q)$ data, the predictor-corrector method we have described in Sec. III leads to a potential that is in very good agreement with the result of Arai and Yokoyama; see Fig. 6. Moreover, in contrast to the assumptions, trial-and-error calculations and computational

effort involved in the Arai-Yokoyama method, our predictor-corrector method converges within four or five iterations, and the resulting structure factor and properties are within about a few percent of the results reported by Arai and Yokoyama. We shall examine this and additional applications of the present method to liquid metals in a future publication.

V. CLOSING REMARKS

We have presented a simple, readily usable “predictor-corrector” based on well characterized hard-sphere correlation function for the extraction of interaction potential from the structure factor data. The previous analyses of interactions in charged colloids based on experimental $S(q)$'s and $g(r)$'s are highly unreliable. In fact, the currently available data are *insufficient* to resolve the controversies concerning interaction potentials in charged dispersions, *despite* numerous claims to the contrary. However, both the conventional analyses *and* inversion methods require very accurate data at low values of $q\sigma$. The lowest q at which $S(q)$ can be mea-

sured in scattering experiments is restricted by experimental limitations. Moreover, the rather low values of $S(q \rightarrow 0)$ in strongly repulsive systems makes accurate measurement of $S(q)$ difficult as they correspond to low intensities in the scattered radiation and, hence, to relatively high statistical errors. On the other hand, direct imaging experiments of the type described in Refs. [1, 5, 6, 10] offer an opportunity to measure $g(r)$'s and $S(q)$'s much more accurately, even at very low q 's, and open up new avenues for studying interactions in dispersions and, by extension, phase behavior in a large class of condensed-matter systems. The proposed method can therefore serve as a tool for systematic analyses of experimental data in colloids as well as Coulombic systems and liquid metals.

ACKNOWLEDGMENTS

We thank the National Science Foundation and the Texas Higher Education Coordinating Board for partial support of the research reported here.

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