

# Electrical Double-layer Interactions in Concentrated Colloidal Systems

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In this paper we compare three methods for deducing the effective pair potential that describes the double-layer interaction between colloidal particles in a concentrated dispersion. The structure factors and small-time behaviour of the intermediate scattering function predicted by these models are compared with results obtained from laser and neutron-scattering experiments.

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## 1. INTRODUCTION

The study of the structure of colloidal suspensions has a long history which dates back to Langmuir,<sup>1</sup> who put forward the idea that the electrostatic or electrical double-layer interactions between colloidal particles are responsible for giving rise to long-range structures or order in such systems. Kirkwood and Mazur<sup>2</sup> made the first attempt to treat colloidal particles as an effective one-component 'fluid' in which the colloidal particles interact via pair potentials (of mean force) which depend on the properties and ionic composition of the solvent. Using the Debye-Hückel expression for the double-layer interaction, they produced colloid-colloid pair correlation functions which resemble those found between atoms in a simple monatomic fluid. Their results demonstrated that the repulsive double-layer interaction between the colloidal particles can be responsible for the observed structure in colloidal systems.

Recent experimental advances in light- and neutron-scattering techniques, together with the application of modern concepts of liquid-state physics, have seen a revival of interest in the subject. In modelling the properties of a dispersion as an effective one-component fluid of colloidal particles, computer-simulation techniques<sup>3,4</sup> or the integral equation methods<sup>5-7</sup> of liquid-state physics have been used. However, both of these approaches require, as input, the form of the interaction potential between the colloidal particles. The remaining task, therefore, is to construct the colloid-colloid interaction potential in terms of the physico-chemical properties of the particles and the composition of the dispersion medium such as pH, electrolyte concentration etc.

In the conventional treatment<sup>8</sup> of the interaction between colloid particles, the colloidal system is assumed to be in osmotic equilibrium with a large electrolyte reservoir of known fixed composition. The screening of the electrostatic interaction between the particles is controlled by the ionic strength of this reservoir. However, in order to maximize the electrostatic repulsion, colloidal systems are often treated with ion-exchange resins to remove all excess electrolytes. The concentration of added

electrolytes is then controlled by the addition of known amounts of salt. As a consequence, the properties of the electrolyte reservoir which is supposed to be in equilibrium with the system are left undetermined, although in principle they can be determined by equilibrium dialysis. The theoretical analysis outlined in this paper is developed with a view to circumvent this problem. The basic idea is to regard the colloidal system as a collection of ions and colloidal particles of known valence and number concentration. The solvent is taken to be a dielectric continuum. The next step is to exploit the obvious asymmetry in charge and size between the ions and colloidal particles and formally regard the colloidal particles as a 'solute' in a 'solvent' of small ions. Using the McMillan–Mayer picture, we can obtain the free energy of a configuration of the system in which the colloidal particles have been held fixed but the small ions have been averaged over all allowed positions. Obviously some approximations must be made to effect this average. The resultant free energy of this configuration of colloidal particles is the  $N$ -body colloid–colloid potential of mean force. In general this is a many-body potential. However, within our approximation scheme this many-body potential of mean force can be written as a sum of *pair* interactions between the colloidal particles. This effective pair potential turns out to be dependent on the concentration of colloidal particles and it is the appropriate potential to employ if one wishes to regard the colloidal system as an effective one-component system. The usefulness of the effective pair potential will be tested against measurements on polystyrene dispersions based on dynamic light scattering and neutron scattering.

The idea of treating a colloidal system as a highly asymmetric electrolyte comprised of ions and colloidal particles has been used to model the dynamical properties of dense colloidal systems.<sup>9,10</sup> The analyses were made in the linear Debye–Hückel limit, which is only capable of yielding 'limiting-law' behaviour. However, because of the high charge on the colloidal particles, the weak interaction assumption implicit in the Debye–Hückel treatment cannot be applied to the colloid–colloid interaction. The equilibrium properties of highly asymmetric electrolytes have been investigated by integral equation<sup>11,12</sup> and Monte Carlo<sup>13</sup> methods for a charge asymmetry of up to 20 to 1.

## 2. THE EFFECTIVE PAIR POTENTIAL

By modelling a colloidal dispersion as a highly asymmetric electrolyte, we have obtained an analytical expression for the effective pair potential which describes the double-layer interaction between the colloidal particles.<sup>14</sup> As mentioned in the Introduction, this result is applicable to situations in which the composition of the colloidal system is known but the properties of the electrolyte reservoir that is in osmotic equilibrium with the dispersion remain undetermined. (As a consequence, conventional double-layer theory cannot be applied.) In the original derivation<sup>14</sup> the effective pair potential was obtained from an asymptotic analysis of the Ornstein–Zernike equations for the colloid–colloid, colloid–ion and ion–ion pair correlation functions. By replacing the ion–ion and ion–colloid direct correlation functions by their limiting forms which are valid for large separations, one readily obtains simple analytic expression for the effective colloid–colloid pair potential. The same result can be obtained from a derivation based on the McMillan–Mayer formalism for studying solutions. Here the colloidal particles are regarded as 'solutes' in a 'solvent' of small ions.<sup>15</sup> The colloid–colloid potential of mean force was obtained by averaging over all configurations of the ions. This averaging process

is achieved by invoking the same approximations for the ion–ion and ion–colloid interaction as in the Debye–Hückel theory of electrolytes.

Our expression for the effective pair potential between two colloid particles, each having a charge ( $z_0e$ ), at a distance  $r$  apart is<sup>14</sup>

$$U^{\text{eff}}(r) = \frac{(z_0e)^2}{\epsilon r} \exp(-\kappa r) \quad (2.1)$$

where  $\epsilon$  is the dielectric constant of the solvent and  $\kappa$  is defined by

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} \sum_i n_i z_i^2 \quad (2.2)$$

The summation in eqn (2.2) is to be taken over all species of counterions necessary to balance the colloidal charge as well as over all species of added salt (mean concentration  $n_i$ , valence  $z_i$ ). In the absence of added salt, where the system is made up of colloidal particles and counterions (a limit which has no counterpart in conventional double-layer theory), eqn (2.2) becomes

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} n_1 z_1^2 \quad (2.3)$$

where  $z_1$  is the valence of the counterions and  $n_1$ , the concentration of counterions, is related to the concentration of colloidal particles,  $n_0$ , by the electroneutrality condition

$$n_0 z_0 + n_1 z_1 = 0. \quad (2.4)$$

Thus we can see from eqn (2.4) or its generalization in the presence of added salt that the screening parameter  $\kappa$  in  $U^{\text{eff}}$  will be a function of the number density of colloidal particles. In the limit of low concentration of colloidal particles or swamping added salt,  $\kappa$  will only be determined by the added salt concentration.

To obtain an appreciation of the relative magnitudes of contributions to  $\kappa$  from the counterions and from the added salt, let us consider a colloidal dispersion of 8% volume fraction of spherical particles of 160 Å radius, each carrying 840 elementary charges (this corresponds to a surface charge density of 4.2  $\mu\text{C cm}^{-2}$ ) with univalent counterions (see later). Let there be  $10^{-3}$  mol  $\text{dm}^{-3}$  of 1:1 added salt. From eqn (2.2) the screening parameter for  $U^{\text{eff}}$  can be written as

$$\kappa^2 = \kappa_{\text{counterion}}^2 + \kappa_{\text{added salt}}^2. \quad (2.5)$$

For the above data we find

$$\kappa_{\text{counterion}}^2 / \kappa_{\text{added salt}}^2 = 3.3.$$

In a previous paper<sup>14</sup> the colloid–colloid structure factor and pair distribution function were obtained by solving the multicomponent Ornstein–Zernike equation for the asymmetric electrolyte in the hypernetted-chain approximation. By treating the colloidal particles as an effective one-component system an effective pair potential was obtained from the colloid–colloid pair distribution function by inverting the one-component hypernetted-chain equation. The effective pair potential so obtained was in very good agreement with the result given by eqn (2.1) and (2.2). The colloid–colloid pair correlation functions calculated according to eqn (2.1) and the hypernetted-chain approximation are also in good agreement with the corresponding quantities obtained by a Monte Carlo simulation<sup>13</sup> of the asymmetric 1:  $z_0$  electrolyte.

In deriving eqn (2.1) we have assumed that the particle radius is small compared with the mean interparticle spacing and with  $\kappa^{-1}$ . Moreover, the linearity assumption in treating the ion–colloid interactions imposes the condition  $(z_0 z_1 e^2 / \epsilon k T a) < 1$  where  $a$  is the distance of closest approach between a colloidal particle and a counterion. For systems where the above assumptions do not hold we propose the following generalization to the effective pair potential given by eqn (2.1).<sup>15</sup>

We model the colloidal dispersion as a multicomponent electrolyte in which the ions and colloidal particles all interact via  $r^{-1}$  coulomb potentials. The Ornstein–Zernike equations for the pair distribution functions  $g_{ij}(r) = 1 + h_{ij}(r)$  have the form ( $i, j, k = 0, 1, 2, \dots$ )

$$h_{ij}(r) = c_{ij}(r) + \sum_k n_k \int c_{ik}(|r - s|) h_{kj}(s) ds. \quad (2.7)$$

From eqn (2.7) we can write down a formal one-component equation for the colloid–colloid correlation function (component 0)

$$\tilde{h}_{00}(k) = \tilde{c}_{00}^{\text{eff}}(k) + n_0 \tilde{c}_{00}^{\text{eff}}(k) \tilde{h}_{00}(k) \quad (2.8)$$

where the Fourier transforms are defined by ( $f = h$  or  $c$ )

$$\tilde{f}(k) = \frac{4\pi}{k} \int_0^\infty dr r \sin(kr) f(r). \quad (2.9)$$

The effective colloid–colloid direct correlation function  $\tilde{c}_{00}^{\text{eff}}(k)$  is related to the direct correlation in eqn (2.7) by

$$\tilde{c}_{00}^{\text{eff}} = \tilde{c}_{00} + \tilde{c}_0^T \cdot [\mathbf{I} - \tilde{\mathbf{c}}^*]^{-1} \cdot \tilde{c}_0 \quad (2.10)$$

where the column matrix  $\tilde{c}_0$  has elements

$$(\tilde{c}_0)_i = n_i^{\frac{1}{2}} \tilde{c}_{i0}(k), \quad i = 1, 2, \dots \quad (2.11)$$

and the matrix

$$(\tilde{\mathbf{c}}^*)_{ij} = (n_i n_j)^{\frac{1}{2}} \tilde{c}_{ij}(k), \quad i, j = 1, 2, \dots \quad (2.12)$$

The effective pair potential is then defined by

$$U^{\text{eff}}(r) = -kT \lim_{r \rightarrow \infty} c_{00}^{\text{eff}}(r). \quad (2.13)$$

To obtain  $c_{00}(r)$  via eqn (2.10) we replace the ion–ion direct correlation functions  $c_{ij}(r)$  by their asymptotic forms

$$c_{ij}(r) = -\frac{z_i z_j e^2}{\epsilon k T r}, \quad 0 < r < \infty \quad (2.14)$$

which is reasonable for univalent ions. We obtain the ion–colloid direct correlation functions  $c_{i0}(r)$  by solving the Ornstein–Zernike equation

$$h_{i0}(r) = c_{i0}(r) + \sum_{j=1} n_j \int c_{ij}(|r - s|) h_{j0}(s) ds + n_0 \int c_{i0}(|r - s|) h_{00}(s) ds \quad (2.15)$$

using eqn (2.14) together with

$$h_{i0}(r) = -1, \quad r < a \quad (2.16)$$

$$c_{i0}(r) = -\frac{z_i z_0 e^2}{\epsilon k T r} + h_{i0}(r) - \ln[1 + h_{i0}(r)], \quad r > a \quad (2.17)$$

$$h_{00}(r) = 0. \quad (2.18)$$

The assumptions embodied in eqn (2.14)–(2.17) are identical to those needed to derive the Poisson–Boltzmann equation for the potential distribution near charged interfaces. The use of eqn (2.18) assumes that as far as determining  $c_{i0}(r)$  is concerned, the remaining colloidal particles are treated as a uniform jellium. This is the simplest way to handle the last term in eqn (2.15) while maintaining electroneutrality. For later reference we shall call this the jellium approximation. With the substitution

$$h_{i0}(r) = \exp[-z_i y(r)] - 1 \quad (2.19)$$

eqn (2.15)–(2.18) are equivalent to solving the differential equation

$$\frac{d^2 y}{dr^2} + \frac{2}{r} \frac{dy}{dr} = -\frac{4\pi e^2}{\epsilon kT} \left( n_0 z_0 + \sum_{i=1} n_i z_i \exp(-z_i y) \right), \quad r > a \quad (2.20)$$

with boundary conditions

$$y \rightarrow 0, \quad r \rightarrow 0 \quad (2.21)$$

$$\frac{dy}{dr} = -\frac{z_0 e^2}{\epsilon kT a^2} (1 + \varphi), \quad r = a \quad (2.22)$$

where  $\varphi = 4\pi a^3 n_0/3$ . The effective pair potential determined from eqn (2.13) still has the same functional form as eqn (2.1) but with the constant  $(z_0 e)^2$  replaced by a constant which is a function of  $a$ ,  $z_0$  and  $\kappa$ , and hence the volume fraction of colloidal particles.

### 3. THE CELL MODEL

An alternative approach to evaluating the double-layer interaction in concentrated dispersions is to deduce the properties of the ‘fictitious’ electrolyte reservoir which would be in osmotic equilibrium with the colloidal system in terms of the composition of the system. Conventional double-layer theory can then be applied to determine the pair interaction. The properties of the electrolyte reservoir can be determined using a cell model for the dispersion.<sup>16</sup> In this model each colloidal particle is assumed to be in the centre of a spherical cell of radius  $r_s$  ( $4\pi r_s^3 n_0/3 = 1$ ) with one particle per cell. The cell also contains the average number of counterions and added electrolyte ions so that it is electrically neutral.

The potential distribution within the cell is assumed to be given by the Poisson–Boltzmann theory:

$$\nabla^2 \psi = -\frac{4\pi}{\epsilon} \sum_i n_i^R z_i \exp(-z_i e\psi/kT) \quad (3.1)$$

where the ionic composition of the electrolyte reservoir is given by  $\{n_i^R\}$ . The concentrations  $\{n_i^R\}$  can be determined from the conditions that (i) the ionic composition within the cell is known, (ii) the cell is overall neutral and (iii) there is no surface charge density at the cell boundary. In general,  $\{n_i^R\}$  has to be determined by numerical iteration.<sup>16</sup> We note, however, that the cell model approach cannot be applied to ‘salt-free’ dispersions comprised only of colloidal particles and counterions.

If one further assumes that the exponential factor in eqn (3.1) may be linearized, the quantities  $\{n_i^R\}$  may be determined analytically. In this linear approximation the

result for the effective screening parameter for the 'fictitious' electrolyte reservoir is

$$\begin{aligned}\kappa_{\text{R}}^2 &\equiv \frac{4\pi e^2}{\epsilon k T} \sum_i n_i^{\text{R}} z_i^2 \\ &= \kappa^2\end{aligned}\quad (3.2)$$

where  $\kappa^2$  is given by eqn (2.2). Thus we see that our expression for the effective pair potential  $U^{\text{eff}}$  given by eqn (2.1) is equivalent to the interaction between two point charges ( $z_0 e$ ) in an electrolyte which has a screening parameter given by  $\kappa$ .

From the above observation one might expect the non-linear version of the cell model<sup>16</sup> to give better agreement with experimental measurement. However, as we shall see in the next section, this does not appear to be the case.

#### 4. COMPARISON WITH SCATTERING MEASUREMENTS

##### STRUCTURE FACTOR

The structure of a dispersion can be probed by scattering measurements. The relevant experimental quantity is the colloid–colloid structure factor

$$S(k) = 1 + \frac{4\pi n_0}{k} \int_0^\infty r \sin kr [g_{00}(r) - 1] dr \quad (4.1)$$

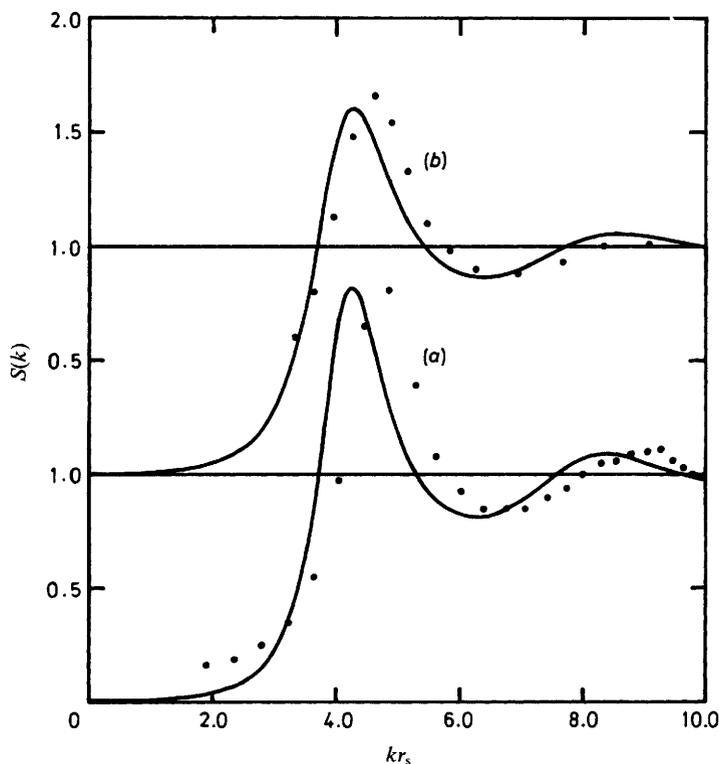
where  $g_{00}(r)$  is the colloid–colloid pair correlation function. The scattering vector,  $k$ , is related to the scattering angle,  $\theta$  by the usual formula

$$k = \frac{4\pi}{\lambda} \sin(\theta/2) \quad (4.2)$$

where  $\lambda$  is the wavelength of the radiation in the dispersion medium.

For a potential of the form given by eqn (2.1) the structure factor,  $S(k)$ , obtained by solving the one-component Ornstein–Zernike equation in the hypernetted-chain approximation is, in general, found to be in good agreement with that obtained by Monte Carlo simulations<sup>17</sup> for almost all values of  $k$ . However, when the height of the first peak in  $S(k)$  is large (ca. 2) the hypernetted-chain approximation tends to underestimate this peak height by ca. 15%. Nevertheless, there is still good agreement with regard to the location of the peak position. These observations are very similar to those found for one-component plasmas.<sup>18</sup>

While light-scattering studies have been carried out on numerous systems, few of these are sufficiently well characterized to permit detailed comparison with theory. One notable exception is the light-scattering data of Brown et al.<sup>19</sup> on dispersions of polystyrene spheres. These particles carry 500 elementary charges and a mean radius of 230 Å. The system was treated with ion-exchange resin to remove all excess electrolyte, leaving only univalent counterions. In fig. 1 a comparison between the experimental and theoretical structure factors is shown. The theoretical results are obtained by solving the one component Ornstein–Zernike equation in the hypernetted-chain approximation using the effective pair potential in eqn (2.1). The system was taken to be salt free but the particles only carry 235 instead of 500 elementary charges. However, since the presence of small amounts of added 1:1 electrolyte (ca.  $10^{-6}$  mol dm<sup>-3</sup>) can significantly affect the theoretical results there is a fair amount of leeway in obtaining a fit between theory and experiment. Indeed the quality of fit is comparable to those obtained using different theoretical models.<sup>3,6,20</sup>



**Fig. 1.** Structure factor for a dispersion of polystyrene spheres, radius 230 Å, at particle number concentrations: (a)  $8.46 \times 10^{12} \text{ cm}^{-3}$  and (b)  $1.67 \times 10^{12} \text{ cm}^{-3}$ . (•••) Experimental points;  $\text{---}$  calculated according to eqn (2.1) and (2.2) for a particle charge of 235 (see text).

It has been observed experimentally that the location ( $k_{\text{max}}$ ) of the first peak in  $S(k)$  is related to the particle number density by the simple empirical result<sup>19</sup>

$$k_{\text{max}} r_s = 4.6 \quad (4.3)$$

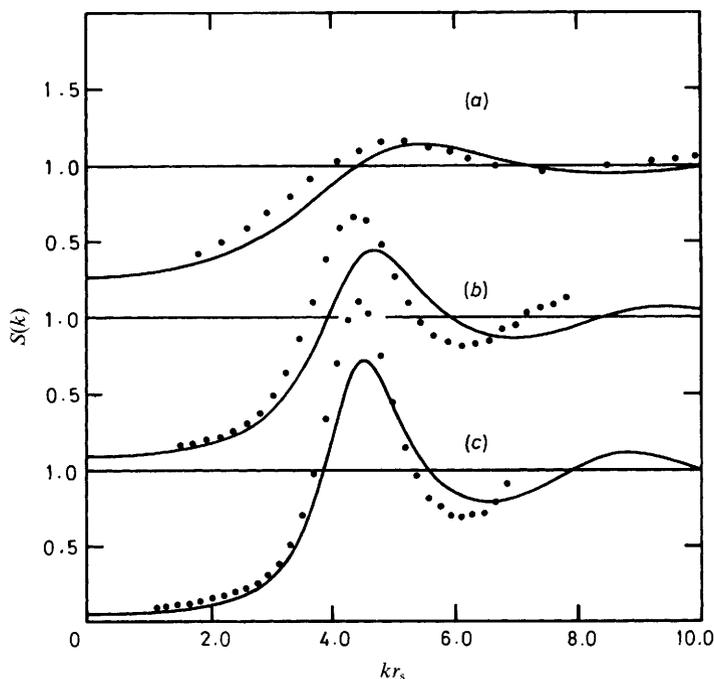
where  $r_s = (3/4\pi n_0)^{1/3}$ . In our calculations this product is

$$k_{\text{max}} r_s = 4.4 \quad (4.4)$$

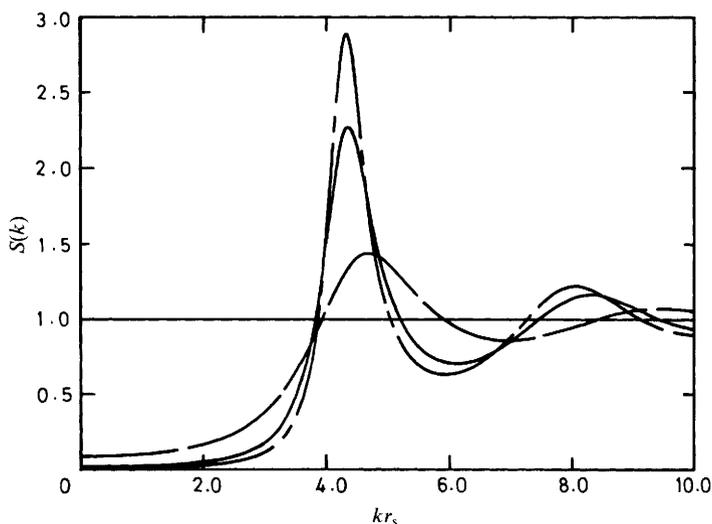
which is almost identical to the value obtained by an analysis based on Bragg diffraction assuming the colloidal particles are in a body-centred cubic lattice.<sup>21</sup>

Another comparison between theory and experiment is afforded by recent neutron-scattering experiments on dispersions of polystyrene spheres.<sup>22</sup> Here the particles are of radius  $a = 160 \text{ Å}$  and carry 840 elementary charges. The dispersion was treated with ion-exchange resin to remove excess electrolytes, but subsequently sodium chloride was added to the dispersion to make up added salt concentrations of  $10^{-3} \text{ mol dm}^{-3}$ . An effective one-component pair potential of the form given by eqn (2.1) was used to calculate the structure factor. The screening parameter  $\kappa$  was calculated according to eqn (2.2). However, because of the high charge and  $\kappa a$  (ca. 3) values of these systems, the pre-exponential factor in eqn (2.2) was replaced by

$$(z_0 e)^2 \rightarrow A^2. \quad (4.5)$$



**Fig. 2.** Structure factor for a dispersion of polystyrene spheres, radius  $160 \text{ \AA}$ , with  $10^{-3} \text{ mol dm}^{-3}$  added sodium chloride and 840 elementary charges per particle. Points, experimental data [ref. (22)] (—) calculated according to the jellium model (see text). Volume fraction: (a) 2, (b) 8 and (c) 13%.



**Fig. 3.** Structure factor calculated according to three different forms of  $U^{\text{eff}}$ : (a) as obtained from conventional double-layer theory assuming  $\kappa$  is determined only by added salt (—); (b) as above but with  $\kappa$  determined by cell model (---); (c) as obtained from the jellium model (- - -). The particle volume fraction is 8%, all other data as for fig. 2.

The coefficient  $A$  in eqn (4.5) is obtained by using the jellium approximation described in section 2. In fig. 2 a comparison is given for the structure factor obtained by using the jellium approximation and the hypernetted-chain approximation and that obtained by small-angle neutron-scattering studies.<sup>22</sup> In fig. 3 are shown the structure factors obtained from the present theory, the cell model and from a model which assumes that the screening parameter is determined solely by the added salt (i.e. neglect the contribution of the counterions to the screening). These results illustrate the need to account for the contribution of the counterions to the screening length in the effective colloid-colloid pair potential. In view of the comments in sections 2 and 3 the disagreement between the experiment and the cell model is unexpected.

From the discussion so far, it is clear that it is fairly easy to obtain good fits to the structure factor especially if a theory has an adjustable parameter. Indeed, even a hard-sphere model with a suitably chosen hard-sphere radius can provide a reasonable fit to  $S(k)$ . However, a more stringent test can be provided by examining temporal correlations.

#### THE INTERMEDIATE SCATTERING FUNCTION

From dynamic light-scattering experiments it is possible to extract the small-time behaviour of the intermediate scattering function  $G(k, t)$ .<sup>19</sup> When hydrodynamic interactions between colloidal particles are negligible, an acceptable approximation at low volume fractions, we have the result<sup>23</sup>

$$Q(k) = \left[ \left( \frac{\partial^2 \ln G(k, t)}{\partial t^2} \right) / \left( \frac{\partial \ln G(k, t)}{\partial t} \right)^2 \right]_{t=0} \quad (4.6)$$

$$= S(k) - 1 + k^{-2} S(k) B(k) \quad (4.7)$$

where

$$B(k) = (n_0/kT) \int g_{00}(r) (1 - \cos \mathbf{k} \cdot \mathbf{r}) (\mathbf{k} \cdot \nabla)^2 U^{eff}(r) dr. \quad (4.8)$$

Here we see that the quantity  $Q(k)$  is given in terms of the colloid-colloid pair correlation function  $g_{00}(r)$  and the effective pair potential,  $U^{eff}(r)$ . In fig. 4 we see

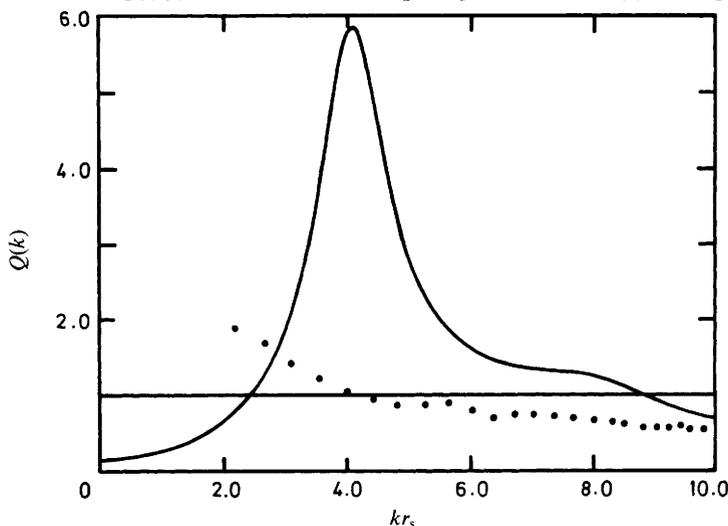


Fig. 4. Comparison of experimental values [ref. (19)] (•) and theoretical predictions (—) of  $Q(k)$  for the system described in fig. 1(a).

that the same input data that were able to give a reasonable fit to  $S(k)$  in fig. 1 predict quite different forms for the function  $Q(k)$ . In particular, the theoretical  $Q(k)$  contains a fair amount of structure with a dominant peak in the same position as the main peak in  $S(k)$ . This observation is in agreement with that found for the one-dimensional harmonic lattice for which an exact analytic solution for  $S(k)$  and  $Q(k)$  have been obtained.<sup>23</sup>

A possible source for the disagreement between theory and experiment may perhaps be found in the magnitude of  $Q(k)$ . The experimental values of  $Q(k)$  were obtained by a truncated cumulant analysis in which the intermediate scattering function,  $G(k, t)$ , is assumed to have the form

$$\ln[G(k, t)/S(k)] = 1 - \Gamma(k)t + \frac{1}{2}Q(k)[\Gamma(k)t]^2. \quad (4.9)$$

In the original analysis<sup>19</sup> it was noted that this assumption was expected to be accurate for small  $Q(k)$  ( $< 0.5$ ), but for larger  $Q(k)$  the truncation in eqn (4.9) will introduce systematic errors.

## 5. DISCUSSION

In this paper we have outlined and compared approximate methods for determining the effective pair potential which characterises the electrical double-layer interaction between particles in concentrated colloidal systems. The input data required are the particle number concentration, the particle charge and the amount of added salt in the dispersion. These are quantities that experimentalists should determine in the process of characterising their system in order to eliminate unknown or fitting parameters in a comparison with theory.

From earlier work, as well as from the results given here, it is clear that a knowledge of the structure factor alone does not provide very stringent constraints on the theoretical model. However, when combined with temporal measurements there appear to be disagreements which require clarification.

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