

# The Electrostatic Interaction in Colloidal Systems with Low Added Electrolyte

BRYAN BERESFORD-SMITH, DEREK Y. C. CHAN,<sup>1</sup> AND D. JOHN MITCHELL

*Department of Applied Mathematics, Research School of Physical Sciences, Australian National University,  
Canberra, Australia 2600*

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In a colloidal system in which the amount of added electrolyte is sufficiently low (e.g., nonaqueous dispersions or aqueous dispersions that have been treated by ion-exchange resins or micellar systems with no added electrolyte) conventional double-layer theory cannot be used to describe the electrostatic interaction between the particles. A theoretical treatment of such systems which takes into account the contribution of the counterions derived from the colloidal particles in screening the coulombic repulsion, is proposed. This leads to an effective colloid-colloid pair potential which varies with the volume fraction of the colloidal particles present in the system. A striking consequence of the theory is that under certain conditions, correlations in the spatial distribution of particles can persist over four orders of magnitude of the volume fraction. Moreover, these correlations, as measured by the height of the first peak of the structure factor, may not be a monotonically increasing function of the particle charge. These theoretical predictions are compared with neutron and light-scattering studies on the structure of colloidal systems. © 1985 Academic Press, Inc.

## 1. INTRODUCTION

In the conventional description of a colloidal system (1), the colloidal particles are treated as a one-component system with a given pair potential (of mean force). This pair potential is assumed to be independent of particle number concentration. For instance, the electrostatic interaction between each pair of particles is taken to be only a function of the particle charge and the ionic composition of the electrolyte reservoir which is in osmotic equilibrium with the system. The ionic strength of this reservoir determines the magnitude of the Debye screening length. In many situations, the nature of this reservoir is not immediately apparent due either to the high-volume fraction of colloidal particles in the dispersion or low added electrolyte concentrations. An example is that of a dilute dispersion of charged polystyrene particles at low ionic strengths where excess electrolytes

have been removed by ion-exchange resins (2). Other examples may be found in nonaqueous dispersions or micellar systems in which the only charged species are the colloidal particles and their counterions (3). For such cases, every part of the solvent is under the electrical influence of the colloidal particles and it is not obvious that a concentration-independent pair potential can be used to characterize the electrostatic interaction between the particles.

In an earlier note (4), we considered a strongly interacting colloidal dispersion as a highly asymmetric electrolyte in which the ions and colloidal particles are treated on an equal footing. That is, like the small ions, the colloidal particles are treated as an ionic species with a very large "ionic" size and a very high valence. By starting with the Ornstein-Zernike equations for the various correlation functions, and then replacing the ion-ion and ion-colloid direct correlation functions by their asymptotic forms, we obtained an approximate analytic expression

<sup>1</sup> To whom correspondence should be addressed. Present address: Department of mathematics, University of Melbourne, Parkville, Australia 3052.

for the effective pair potential which characterizes the electrostatic interaction between the colloidal particles. This effective pair potential turned out to depend on the colloidal particle concentration. Unfortunately, the physical content of this result is not very obvious from its original derivation. In this paper, we begin with the McMillan–Mayer (5) picture of the colloidal dispersion where we formally regard the particles as the “solute” and the ions as the “solvent” species. Our earlier result can be obtained by using approximations that are similar to those used in deriving the Debye–Hückel theory of electrolytes. Although the resulting effective pair potential between colloidal particles *looks* exactly like the simple Debye–Hückel pair potential it is by no means identical. The screening parameter  $\kappa$  of the Debye–Hückel theory is *independent* of the particle-volume fraction, being determined by the electrolyte reservoir with which the system is in osmotic equilibrium. The screening parameter  $\kappa$  of our result is a function of the colloid particle-volume fraction, and hence so is the effective pair potential.

From our analysis, it is evident that the form of the simple effective pair potential we obtained earlier (4) is only valid when the colloidal charge and size are not too large. In this paper, we propose an approximation that yields the effective pair potential in the regime of large colloidal charges and sizes found in existing experimental systems. We also give predictions of the structure of colloidal systems that interact via such a density-dependent effective pair potential. The structure of such systems is markedly different from systems which interact via density-independent pair potentials. For example, under experimentally realizable conditions, our theory predicts that a system of colloidal particles can retain a liquid-like structure, with significant correlations between the positions of nearest neighbors, over four orders of magnitude in the particle volume fraction. By contrast, a system with a density-*independent* pair potential at a volume fraction which

exhibits a liquid-like structure would certainly solidify within an order-of-magnitude increase in the volume fraction. Furthermore, because of the nature of the volume fraction-dependent pair potential between the particles, a *decrease* in the particle charge can result in an *increase* in the structure of the colloidal systems. Such observations, which are supported by available experimental data, are of course contrary to the predictions of the conventional DLVO (1) picture of volume fraction-independent pair potentials.

This paper is organized as follows. In Section 2, we specify our model of the colloidal system and recapitulate the method by which the simple effective pair potential can be obtained by an asymptotic analysis of the Ornstein–Zernike equations. In Section 3, we give an alternative derivation of the same result using the McMillan–Mayer picture. This calculation establishes the fact that the simple effective pair potential is only valid in the regime of small colloidal sizes and charges. It gives a better physical insight into how the effective pair potential arises and suggests the later approximate extensions to the nonlinear regime, which is of more relevance to real colloidal systems. It also provides a ready illustration of how the effective one- and two-body colloid potentials combine to yield the Debye–Hückel limiting law for the thermodynamic behavior of the whole colloidal system. In Section 4, we propose an approximate method—the Jellium Approximation—to determine the effective pair potential for large colloidal sizes and charges. Results and predictions based upon this effective pair potential, together with comparisons with available experimental data, will be given in Section 5.

## 2. THE MODEL AND THE SIMPLE EFFECTIVE PAIR POTENTIAL

We model the ions and particles in a colloidal system as a highly asymmetric electrolyte comprised of ions of number density  $n_i$ , valence  $z_i$  ( $i = 0, 1, 2, \dots$ ) obeying the electroneutrality condition  $\sum_i n_i z_i = 0$ . The

subscript  $i = 0$  refers to the colloidal particles and  $i = 1, 2, \dots$  refer to the small ions—counterions and added electrolyte. In this model the interactions between all charged species are taken to have the form

$$u_{ij}(r) = \infty, \quad r < d_{ij} \\ = \frac{z_i z_j e^2}{\epsilon r}, \quad r > d_{ij} \quad [2.1]$$

where  $d_{ij} = (d_i + d_j)/2$  and  $d_i$  is the ionic diameter. The solvent is simply characterized as a dielectric continuum of dielectric constant  $\epsilon$ .

Previous studies of highly asymmetric electrolytes have been carried out in the hypernetted chain approximation for charge asymmetries of up to 20 to 1 (6, 7). Comparisons between Monte Carlo simulations, integral equation approximations, and the cell model have recently been made at a colloidal charge of 12 with univalent and divalent counterions (8).

The structure of the asymmetric electrolyte can be described by the pair distribution functions  $g_{ij}(r) = 1 + h_{ij}(r)$ . The total correlation functions  $h_{ij}(r)$  obey the Ornstein-Zernike equations

$$\tilde{h}_{ij}(k) = \tilde{c}_{ij}(k) + \sum_l n_l \tilde{c}_{il}(k) \tilde{h}_{lj}(k) \\ i, j, l = 0, 1, 2, \dots, \quad [2.2]$$

where the Fourier transforms are defined by  $\tilde{h}(k) = \int dr \exp(-i\mathbf{k} \cdot \mathbf{r}) h(r)$ . From [2.2], we can write down a formal equation for the colloid-colloid correlation functions (component 0)

$$\tilde{h}_{00}(k) = \tilde{c}_{00}^{\text{eff}}(k) + n_0 \tilde{c}_{00}^{\text{eff}}(k) \tilde{h}_{00}(k) \quad [2.3]$$

with

$$\tilde{c}_{00}^{\text{eff}} = \tilde{c}_{00} + \tilde{\mathbf{c}}_0^T \cdot [\mathbf{I} - \tilde{\mathbf{c}}^*]^{-1} \cdot \tilde{\mathbf{c}}_0 \quad [2.4]$$

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

$$(\tilde{\mathbf{c}}_0)_i = n_i^{1/2} \tilde{c}_{i0}(k), \quad i = 1, 2, \dots \quad [2.5]$$

and the matrix  $\tilde{\mathbf{c}}^*$  is given by

$$(\tilde{\mathbf{c}}^*)_{ij} = (n_i n_j)^{1/2} \tilde{c}_{ij}(k), \quad i, j = 1, 2, \dots \quad [2.6]$$

Equation [2.3] suggests that one can formally

regard the asymmetric electrolyte system as an effective one-component system of colloidal particles (component 0) with an effective direct correlation function  $\tilde{c}_{00}^{\text{eff}}$  given by [2.4] (9).

The large  $r$  form of the direct correlation functions is given by (10) ( $\beta = 1/k_B T$ )

$$c_{ij}(r) \rightarrow -\beta u_{ij}(r), \quad r \rightarrow \infty. \quad [2.7]$$

We now approximate the ion-ion and ion-colloid direct correlation functions by their asymptotic forms at all separations, that is,

$$c_{ij}(r) = \frac{-\beta z_i z_j e^2}{\epsilon r}, \quad 0 < r < \infty \quad [2.8]$$

$$c_{i0}(r) = c_{0i}(r) = \frac{-\beta_i z_0 z e^2}{\epsilon r}, \quad 0 < r < \infty \quad [2.9]$$

and put

$$c_{00}(r) \equiv c_{00}^s(r) - \frac{\beta z_0^2 e^2}{\epsilon r}, \quad 0 < r < \infty. \quad [2.10]$$

We find from [2.4] that

$$\tilde{c}_{00}^{\text{eff}}(k) = \tilde{c}_{00}^s(k) - \frac{(4\pi\beta z_0^2 e^2/\epsilon)}{k^2 + \kappa^2} \quad [2.11]$$

or upon taking the inverse Fourier transform

$$c_{00}^{\text{eff}}(r) = c_{00}^s(r) - \frac{\beta z_0^2 e^2}{\epsilon r} e^{-\kappa r}, \\ 0 < r < \infty \quad [2.12]$$

with

$$\kappa = [(4\pi\beta e^2/\epsilon) \sum_{i=1} n_i z_i^2]^{1/2}. \quad [2.13]$$

From [2.7] and [2.12] we can identify an effective colloid-colloid pair potential

$$U^{\text{eff}}(r) = \frac{(z_0 e)^2}{\epsilon} \frac{e^{-\kappa r}}{r}. \quad [2.14]$$

Note that  $U^{\text{eff}}(r)$  has the form of a screened Coulomb potential. However, only the small ions contribute to the screening parameter  $\kappa$ . That is, the summation in [2.13] is taken over all small ions in the system—counterions and added electrolyte. However, because of the electroneutrality condition

$$n_0 z_0 + \sum_{i=1} n_i z_i = 0 \quad [2.15]$$

$\kappa$  is a function of the colloid number density,  $n_0$ . When the amount of added salt is low,  $\kappa$  can be much smaller than  $\kappa_D$ , the Debye parameter for the total asymmetric electrolyte system

$$\kappa_D^2 \equiv \kappa^2 + (4\pi\beta e^2/\epsilon)n_0 z_0^2. \quad [2.16]$$

At high concentrations of added electrolyte or at low colloid concentrations ( $n_0 \rightarrow 0$ ) in the presence of added salt,  $\kappa \rightarrow \kappa_D$  and the screening is determined solely by the added electrolyte concentration as expected from the classical theory.

The utility of the effective pair potential,  $U^{\text{eff}}(r)$  in predicting the colloid-colloid structure factor has been considered in an earlier paper (4). Next we give an alternative derivation of  $U^{\text{eff}}(r)$  that is based upon the McMillan-Mayer theory of solutions. Such a derivation reveals more of the physical content subsumed in the effective pair potential.

### 3. AN ALTERNATIVE DERIVATION OF $U^{\text{eff}}(r)$

Consider for simplicity an idealized colloidal system which consists only of colloidal particles and counterions—excess electrolyte being removed by ion-exchange resins and effects due to the dissociation of water being neglected. The inclusion of added salt only complicates the notation and does not affect the physical arguments in the discussion. Let there be  $N_0$  colloids of valence  $z_0$  and  $N_1$  counterions of valence  $z_1$  confined in a volume  $V$ . This system is a  $z_1:z_0$  electrolyte. Electroneutrality requires that

$$z_1 N_1 + z_0 N_0 = 0. \quad [3.1]$$

The Hamiltonian for this system can be written as

$$H = \frac{1}{2M} \sum_{i=1}^{N_0} P_i^2 + \frac{1}{2m} \sum_{i=1}^{N_1} p_i^2 + U(\{\mathbf{R}\}, \{\mathbf{r}\}), \quad [3.2]$$

where  $\mathbf{P}_i$ ,  $\mathbf{R}_i$  ( $\mathbf{p}_i$ ,  $\mathbf{r}_i$ ) are the momenta and

position coordinates of the colloids (ions). We have made the tacit assumption that all species have spherical symmetry and that there are no internal degrees of freedom. In a classical system, the Helmholtz free energy,  $F$ , can be written as

$$F = F^{\text{id}} + F^{\text{int}}, \quad [3.3]$$

where  $F^{\text{id}}$ , the Helmholtz free energy of ( $N_0 + N_1$ ) ideal particles in a volume  $V$ , is obtained by integrating the partition function over the momentum coordinates. The interaction term  $U$  in the Hamiltonian gives rise to the interaction part,  $F^{\text{int}}$ , of the free energy,

$$\exp(-\beta F^{\text{int}}) = \frac{1}{V^{N_0+N_1}} \int \int d\{\mathbf{R}\} d\{\mathbf{r}\} \times \exp(-\beta U(\{\mathbf{R}\}, \{\mathbf{r}\})) \quad [3.4]$$

$$= \frac{1}{V^{N_0}} \int d\{\mathbf{R}\} \exp(-\beta W(\{\mathbf{R}\})), \quad [3.5]$$

where

$$\exp(-\beta W(\{\mathbf{R}\})) \equiv \frac{1}{V^{N_1}} \int d\{\mathbf{r}\} \exp(-\beta U(\{\mathbf{R}\}, \{\mathbf{r}\})). \quad [3.6]$$

The quantity  $W(\{\mathbf{R}\})$  is the  $N_0$ -body colloid potential of mean force and is obtained by fixing  $N_0$  colloids at positions  $\{\mathbf{R}\} = \{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_0}\}$  and integrating over all configurations of the counterions (cf. [3.6]). Thus from [3.4] we see that the system of colloidal particles may be formally regarded as a one-component system with a temperature- and density-dependent effective Hamiltonian  $W(\{\mathbf{R}\})$ . In general,  $W(\{\mathbf{R}\})$  will be a sum of one-, two-, three-, ..., etc. body interactions; but under certain conditions, only a sum of one- and two-body terms will suffice to represent  $W(\{\mathbf{R}\})$ .

For interaction potentials of the type given by [2.1] the interaction part of the Hamiltonian,  $U$  can be written as

$$U = U^{\text{SR}} + U^{\text{ES}}, \quad [3.7]$$

where  $U^{\text{SR}}$  denotes short-ranged (in this case, hard sphere) interactions and  $U^{\text{ES}}$  electrostatic interactions.  $U^{\text{ES}}$  can be written in the form

$$U^{ES} = \frac{1}{2} \int \hat{\rho}(\mathbf{r})\hat{\psi}(\mathbf{r})d\mathbf{r} - E_S, \quad [3.8]$$

where the total charge density operator  $\hat{\rho}(\mathbf{r})$  is defined by

$$\hat{\rho}(\mathbf{r}) = z_1e \sum_i \delta(\mathbf{r} - \mathbf{r}_i) + z_0e \sum_i \delta(\mathbf{r} - \mathbf{R}_i) \quad [3.9]$$

$$\equiv \hat{\rho}_1(\mathbf{r}) + \hat{\rho}_0(\mathbf{r}) \quad [3.10]$$

with separate contributions from the counterions,  $\hat{\rho}_1(\mathbf{r})$  and the colloid particles,  $\hat{\rho}_0(\mathbf{r})$  defined by [3.10]. The potential operator  $\hat{\psi}(\mathbf{r})$  is given by

$$\hat{\psi}(\mathbf{r}) = \int \frac{\hat{\rho}(\mathbf{r}')d\mathbf{r}'}{\epsilon|\mathbf{r} - \mathbf{r}'|} \quad [3.11]$$

$$= \sum_i \frac{z_1e}{\epsilon|\mathbf{r} - \mathbf{r}_i|} + \sum_i \frac{z_0e}{\epsilon|\mathbf{r} - \mathbf{R}_i|} \quad [3.12]$$

The quantity  $E_S$  is the electrostatic self-energy of both species.

We now proceed to obtain an approximate expression for the  $N_0$ -body colloid potential of mean force  $W(\{\mathbf{R}\})$ . From [3.6] to [3.8] it follows that

$$\frac{\partial[\beta W(\{\mathbf{R}\})]}{\partial\beta} = \langle U(\{\mathbf{R}\}, \{\mathbf{r}\}) \rangle \quad [3.13]$$

$$= \langle U^{SR} \rangle - E_S + \frac{1}{2} \int \langle \hat{\rho}(\mathbf{r})\hat{\psi}(\mathbf{r}) \rangle d\mathbf{r}, \quad [3.14]$$

where

$$\langle A \rangle \equiv \frac{\int d\{\mathbf{r}\} A(\{\mathbf{r}\}) \exp(-\beta U(\{\mathbf{R}\}, \{\mathbf{r}\}))}{\int d\{\mathbf{r}\} \exp(-\beta U(\{\mathbf{R}\}, \{\mathbf{r}\}))} \quad [3.15]$$

denotes an average over all configurations of the counterions using the Boltzmann factor  $\exp(-\beta U(\{\mathbf{R}\}, \{\mathbf{r}\}))$ . From the definition of

$\hat{\psi}(\mathbf{r})$  [3.11], the last term in [3.14] can be written as

$$\int \langle \hat{\rho}(\mathbf{r})\hat{\psi}(\mathbf{r}) \rangle d\mathbf{r} = \int d\mathbf{r} \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\psi}(\mathbf{r}) \rangle + \int d\mathbf{r} \int d\mathbf{r}' \frac{[\langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle - \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\rho}(\mathbf{r}') \rangle]}{\epsilon|\mathbf{r} - \mathbf{r}'|} \quad [3.16]$$

The quantity  $\langle \hat{\rho}(\mathbf{r}) \rangle$  is the average charge density at position  $\mathbf{r}$ , given the  $N_0$  colloids are held fixed at  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_0}$  and the average is taken over all configurations of the counterions;  $\langle \hat{\psi}(\mathbf{r}) \rangle$  is the corresponding average electrostatic potential and is related to  $\langle \hat{\rho}(\mathbf{r}) \rangle$  by Poisson's equation. From the definition of  $\hat{\rho}(\mathbf{r})$  we see that the contribution from the colloidal particles,  $\hat{\rho}_0(\mathbf{r})$ , will be unaffected by the averaging process over the counterions, hence

$$\langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle - \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\rho}(\mathbf{r}') \rangle = \langle \hat{\rho}_1(\mathbf{r})\hat{\rho}_1(\mathbf{r}') \rangle - \langle \hat{\rho}_1(\mathbf{r}) \rangle \langle \hat{\rho}_1(\mathbf{r}') \rangle \quad [3.17]$$

$$= z_1^2 e^2 n_1(\mathbf{r})[\delta(\mathbf{r} - \mathbf{r}') + h(\mathbf{r}, \mathbf{r}')] n_1(\mathbf{r}') \quad [3.18]$$

The right-hand side of [3.17] is the charge correlation among the counterions given the colloidal particles are at a fixed configuration  $\{\mathbf{R}\} = \{\mathbf{R}_1, \mathbf{R}_2, \dots\}$ . In [3.18],  $n_1(\mathbf{r})$  is the number density of counterions—it is a function of position because the colloids are held at a fixed configuration  $\{\mathbf{R}\}$  and [3.18] defines the correlation function  $h(\mathbf{r}, \mathbf{r}')$ . Combining [3.14], [3.16], and [3.18] we have the exact result

$$\frac{\partial[\beta W(\{\mathbf{R}\})]}{\partial\beta} = \frac{1}{2} \int \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\psi}(\mathbf{r}) \rangle d\mathbf{r} + \frac{1}{2} z_1^2 e^2 \int d\mathbf{r} \int d\mathbf{r}' \times \frac{n_1(\mathbf{r})[\delta(\mathbf{r} - \mathbf{r}') + h(\mathbf{r}, \mathbf{r}')n_1(\mathbf{r}')] }{\epsilon|\mathbf{r} - \mathbf{r}'|} - E_S + \langle U^{SR} \rangle. \quad [3.19]$$

So far we have only made formal manipulations and all results are exact. Our objective

is to determine the two integrals in [3.19] by using certain approximations.

Consider the first integral. As mentioned earlier, the average charge density,  $\langle \hat{\rho}(\mathbf{r}) \rangle$  and the average electrostatic potential  $\langle \hat{\psi}(\mathbf{r}) \rangle$ , are related by Poisson's equation

$$\nabla^2 \langle \hat{\psi}(\mathbf{r}) \rangle = -\frac{4\pi}{\epsilon} \langle \hat{\rho}(\mathbf{r}) \rangle \quad [3.20]$$

with

$$\begin{aligned} \langle \hat{\rho}(\mathbf{r}) \rangle &= z_1 e n_1(\mathbf{r}) + z_0 e \sum_i \delta(\mathbf{r} - \mathbf{R}_i) \\ &\equiv z_1 e n_1(\mathbf{r}) + z_0 e n_0(\mathbf{r}). \end{aligned} \quad [3.21]$$

To close [3.20] we assume the Boltzmann distribution for the ion number density

$$n_1(\mathbf{r}) = \bar{n}_1 \exp[-\beta z_1 e (\langle \hat{\psi}(\mathbf{r}) \rangle - \bar{\psi})], \quad [3.22]$$

where  $\bar{n}_1 \equiv N_1/V$  is the mean density of counterions and the constant  $\bar{\psi}$  is defined to be the potential where  $n_1(\mathbf{r}) = \bar{n}_1$ . In writing [3.22] we have, as in the derivation of the Debye-Hückel limiting law, omitted short-ranged, noncoulombic interactions between the ions and colloidal particles. Setting

$$\psi(\mathbf{r}) \equiv \langle \hat{\psi}(\mathbf{r}) \rangle - \bar{\psi} \quad [3.23]$$

and retaining only linear terms in  $\beta e \psi(\mathbf{r})$ , [3.20] simplifies to

$$\begin{aligned} \nabla^2 \psi(\mathbf{r}) - \kappa^2 \psi(\mathbf{r}) &= -\frac{4\pi z_1 e \bar{n}_1}{\epsilon} \\ &\quad - \frac{4\pi z_0 e}{\epsilon} \sum_i \delta(\mathbf{r} - \mathbf{R}_i), \end{aligned} \quad [3.24]$$

where (cf. [2.13])

$$\kappa^2 \equiv 4\pi \beta e^2 \bar{n}_1 z_1^2 / \epsilon. \quad [3.25]$$

Since [3.24] is linear, we approximate the potential outside the colloidal particles as

$$z_1 \beta e \psi(\mathbf{r}) = 1 + \sum_i \Phi(|\mathbf{r} - \mathbf{R}_i|), \quad [3.26]$$

where

$$\Phi(r) = \frac{\beta e^2 z_1 z_0}{\epsilon} \frac{e^{-\kappa r}}{r} \quad [3.27]$$

is the dimensionless potential around each colloidal particle. The solution given by [3.26]

and [3.27] is valid only in the limit  $\kappa d_{01} \ll 1$ , where  $d_{01}$  is the distance of closest approach between the centers of an ion and a colloidal particle, otherwise we shall have to include polarization effects due to having to solve the Laplace equation for  $\langle \hat{\psi} \rangle$  ( $\nabla^2 \langle \hat{\psi} \rangle = 0$ ) in the interior of the particles.

To linear order, the average charge density becomes

$$\begin{aligned} \langle \hat{\rho}(\mathbf{r}) \rangle &= -z_1 e \bar{n}_1 \sum_i \Phi(|\mathbf{r} - \mathbf{R}_i|) \\ &\quad + z_0 e \sum_i \delta(\mathbf{r} - \mathbf{R}_i). \end{aligned} \quad [3.28]$$

Thus combining [3.23], [3.26], and [3.28] we find

$$\begin{aligned} \frac{1}{2} \int \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\psi}(\mathbf{r}) \rangle d\mathbf{r} &= \frac{(z_0 e)^2}{2\epsilon} \sum_{\substack{i,j \\ i \neq j}} \frac{e^{-\kappa R_{ij}}}{R_{ij}} \\ &\quad - \frac{\kappa (z_0 e)^2}{4\epsilon} \sum_{i,j} e^{-\kappa R_{ij}} - \frac{N_0 \kappa (z_0 e)^2}{2\epsilon} + E_S^c, \end{aligned} \quad [3.29]$$

where  $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$  and  $E_S^c$  is the electrostatic self-energy of the colloidal particles. In obtaining [3.29] we have noted that because of electroneutrality viz.  $\int \langle \hat{\rho}(\mathbf{r}) \rangle d\mathbf{r} = 0$ , constant terms in  $\langle \hat{\psi}(\mathbf{r}) \rangle$  do not contribute to the integral in [3.29].

We turn now to the second integral in [3.19]. Poisson's equation for the potential  $\phi(\mathbf{r}, \mathbf{r}')$  at  $\mathbf{r}$  given an ion (charge  $z_1 e$ ) is held at  $\mathbf{r}'$ , has the form

$$\begin{aligned} \nabla^2 \phi(\mathbf{r}, \mathbf{r}') &= -\frac{4\pi z_0 e}{\epsilon} n_0(\mathbf{r}) \\ &\quad - \frac{4\pi z_1 e}{\epsilon} n_1(\mathbf{r}) g(\mathbf{r}, \mathbf{r}') - \frac{4\pi z_1 e}{\epsilon} \delta(\mathbf{r} - \mathbf{r}'). \end{aligned} \quad [3.30]$$

The  $\phi(\mathbf{r}, \mathbf{r}')$  is sometimes referred to as the fluctuation potential. If we use the linearized Boltzmann approximation

$$\begin{aligned} g(\mathbf{r}, \mathbf{r}') &\equiv 1 + h(\mathbf{r}, \mathbf{r}') \\ &= \exp[-z_1 \beta e \phi(\mathbf{r}, \mathbf{r}')] \\ &\approx 1 - z_1 \beta e \phi(\mathbf{r}, \mathbf{r}') \end{aligned} \quad [3.31]$$

with the simplifying assumptions

$$\begin{aligned} n_0(\mathbf{r}) &\approx N_0/V = \bar{n}_0 \\ n_1(\mathbf{r}) &\approx N_1/V = \bar{n}_1 \end{aligned} \quad [3.32]$$

we find

$$\begin{aligned} \nabla^2 \phi(\mathbf{r}, \mathbf{r}') \\ = \kappa^2 \phi(\mathbf{r}, \mathbf{r}') - \frac{4\pi z_1 e}{\epsilon} \delta(\mathbf{r} - \mathbf{r}') \end{aligned} \quad [3.33]$$

with the solution

$$\phi(\mathbf{r}, \mathbf{r}') = \frac{z_1 e}{\epsilon} \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad [3.34]$$

and hence

$$h(r, r') = -\frac{\beta z_1^2 e^2}{\epsilon} \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}. \quad [3.35]$$

Combining [3.32] and [3.35] we find for the second integral in [3.19]

$$\begin{aligned} \frac{1}{2} z_1^2 e^2 \int d\mathbf{r} \\ \times \int d\mathbf{r}' \frac{n_1(\mathbf{r})[\delta(\mathbf{r}-\mathbf{r}') + h(\mathbf{r}, \mathbf{r}')]n_1(\mathbf{r}')}{\epsilon|\mathbf{r}-\mathbf{r}'|} \\ = E_S^i - N_1 \frac{\kappa z_1^2 e^2}{2\epsilon}, \end{aligned} \quad [3.36]$$

where  $E_S^i$  is the electrostatic self-energy of the counterions.

We now assemble the results in [3.19], [3.29], and [3.36] to find

$$\begin{aligned} \frac{\partial[\beta W(\{\mathbf{R}\})]}{\partial\beta} &= \langle U^{SR} \rangle - N_1 \frac{\kappa z_1^2 e^2}{2\epsilon} \\ &- N_0 \frac{\kappa(z_0 e)^2}{2\epsilon} + \frac{(z_0 e)^2}{2\epsilon} \sum_{\substack{i,j \\ i \neq j}} \frac{e^{-\kappa R_{ij}}}{R_{ij}} \\ &- \frac{\kappa(z_0 e)^2}{4\epsilon} \sum_{i,j} e^{-\kappa R_{ij}}. \end{aligned} \quad [3.37]$$

Recognizing the temperature dependence in  $\kappa$  we integrate this result from  $\beta = 0$  to  $\beta$  to find

$$W(\{\mathbf{R}\}) = W^{SR} + N_0 W_1 + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} W_2(R_{ij}), \quad [3.38]$$

where  $W^{SR}$  results from integrating the contribution from short-ranged interactions  $\langle U^{SR} \rangle$ . In addition to this, we see that within our approximations, the  $N_0$ -body colloid-colloid potential of mean force,  $W(\{\mathbf{R}\})$ , can be written as a sum of one-body,  $W_1$ , and two-body,  $W_2(r)$ , terms. There are no explicit three- or higher body interactions within our approximations. The (constant) effective one-body potential for the colloidal particles has the form

$$W_1 = -\frac{\kappa(z_0 e)^2}{2\epsilon} + \frac{\kappa z_0 z_1 e^2}{3\epsilon} + \frac{1}{2} \frac{z_0}{z_1} kT \quad [3.39]$$

and the effective pair potential between the colloidal particles is given by

$$W_2(r) = \frac{(z_0 e)^2}{\epsilon} \frac{e^{-\kappa r}}{r} \quad [3.40]$$

Point particles, linear approximation

which is identical to the effective pair potential given by [2.14]. Again we note that  $W_2(r)$  is a function of the number density of colloidal particles through the parameter  $\kappa$  defined in [3.25].

Having obtained an approximate expression for the effective pair potential, one can determine certain properties of the colloidal system by treating it as a one-component fluid with this pair potential. In closing this section, we shall illustrate how the one- and two-body potentials may be used to obtain some familiar results. From [3.5] and [3.38] we can write the interaction part of the free energy as

$$F^{\text{int}} = F^{SR} + N_0 W_1 + F_2, \quad [3.41]$$

where  $F^{SR}$  is the free energy due to the short-ranged part of the potential  $U^{SR}$  when all the particles are uncharged. The term  $F_2$  is the contribution from the effective pair potential and can be obtained via the coupling constant integration process

$$F_2 = \int_0^1 \frac{d\lambda}{\lambda} \left\{ \frac{1}{2} N_0 \bar{n}_0 \int d\mathbf{r} [\lambda W_2(r)] g(r|\lambda) \right\}, \quad [3.42]$$

where  $g(r|\lambda)$  is the pair correlation of a *one*-component system that interacts via a pair potential  $[\lambda W_2(r)]$ . If we now calculate  $g(r|\lambda) = 1 + h(r|\lambda)$  by summing only simple chains with  $(-\lambda\beta W_2)$  bonds (10), that is, we use

$$\tilde{h}(k|\lambda) = \frac{\tilde{c}(k|\lambda)}{1 - \bar{n}_0 \tilde{c}(k|\lambda)} \quad [3.43]$$

with

$$c(r|\lambda) = -\lambda\beta W_2(r), \quad 0 < r < \infty \quad [3.44]$$

we find

$$g(r|\lambda) = 1 - \frac{\lambda\beta(z_0 e)^2 e^{-\kappa_D(\lambda)r}}{\epsilon r}, \quad [3.45]$$

where

$$\kappa_D^2(\lambda) = \frac{4\pi\beta e^2}{\epsilon} (\bar{n}_1 z_1^2 + \lambda \bar{n}_0 z_0^2). \quad [3.46]$$

Note that for  $\lambda = 1$ , the correlation function given by [3.45] is the same as that given by the Debye-Hückel theory with  $\kappa_D(\lambda = 1)$  being the Debye screening parameter for the  $z_1:z_0$  electrolyte. Using [3.45] in [3.42] we find

$$F_2 = -N_0 W_1 - \frac{\kappa_D e^2}{3\epsilon} (N_1 z_1^2 + N_0 z_0^2), \quad [3.47]$$

which when combined with [3.39] and [3.41] yields the Debye-Hückel limiting law for the interaction free energy,  $F^{\text{int}}$ .

An observation regarding the above example is that if one wishes to obtain the thermodynamic properties of the colloidal system by treating it as an effective one-component fluid, it is necessary to have compatible expressions for the effective one- and two-body potentials as there are mutually cancelling contributions to the total free energy from the two potentials. For, while the effective pair potential between colloidal particles is purely repulsive (cf. [3.40]), the excess free energy of the colloidal system due to electrostatic interactions is negative.

In connection with the calculation outlined in this section, we should point out that Sogami (11) had made a similar calculation to determine the Helmholtz free energy of a

colloidal system in which all the colloidal particles are held fixed at a given configuration. Using the same set of approximations as we have, he found that the Helmholtz free energy could be written as a sum of one- and two-body terms. The form of his two-body potential is identical to that given by [3.40], that is the effective interaction is purely repulsive. However, his expression for the one-body term is incorrect. In particular, the second and third terms in [3.39] have been omitted. The cause of this omission can be traced to his definition of the total electrostatic energy—he has omitted to include the correlation terms (cf. [3.19]). As a consequence Sogami's result cannot reproduce the Debye-Hückel limiting law for the excess free energy of the colloidal system.

Sogami also gave an expression for the Gibbs free energy of the colloidal system in which all the colloidal particles have been held at fixed positions. From this Gibbs free energy he concluded that the effective pair potential in the Gibbs ensemble has a minimum—that is, it is repulsive at small interparticle separations but is *attractive* at large separations. We believe that this result may be an artifact of his definition of the Gibbs free energy. The reason is that the pressure of the system (which is only due to the small ions since the particles are held fixed) is not isotropic. Indeed, in evaluating the pressure as the negative derivative of the Helmholtz free energy, one must specify precisely how the volume of the system is being changed relative to the positions of the fixed colloidal particles. For the present problem, we feel that the Gibbs free energy is not a useful quantity.

#### 4. EXTENSION TO LARGE COLLOIDAL SIZE AND CHARGE

From the derivations given in Sections 2 and 3 we can see that the effective pair potential given by [2.14] and [3.40] is strictly a linearized result because of the linearity assumptions embodied in [2.9] and [3.24]. Consequently, it is only valid provided  $(\beta z_0 e^2 /$

$\epsilon a$ ) is not too large. (Here  $a$  is the distance of closest approach between the colloidal particle and a counterion.) However, we have found that [2.14] remains accurate up to  $(\beta z_0 e^2 / \epsilon a) \sim 3$  (4). Also from the discussion following the derivation of [3.26] and [3.27], we can see that [3.40] is only valid in the limit  $\kappa a \ll 1$ , that is it is a leading order result in the colloidal size. In this section, we shall derive expressions for  $U^{\text{eff}}$  which will go beyond the above limitations.

Consider as in the previous section a  $z_1:z_0$  electrolyte. The expression for the effective colloid–colloid direct correlation function is (cf. [2.2]–[2.6])

$$\tilde{c}_{00}^{\text{eff}}(k) = \tilde{c}_{00}(k) + \frac{n_1 \tilde{c}_{01}(k) \tilde{c}_{10}(k)}{1 - n_1 \tilde{c}_{11}(k)}. \quad [4.1]$$

In order to obtain an expression for  $\tilde{c}_{10}$  in [4.1] we examine the ion–colloid Ornstein–Zernike equation

$$h_{10}(r) = c_{10}(r) + n_1 \int c_{11}(|\mathbf{r} - \mathbf{s}|) h_{10}(s) ds + n_0 \int c_{10}(|\mathbf{r} - \mathbf{s}|) h_{00}(s) ds. \quad [4.2]$$

Motivated by the approximation [3.32] used to derive the linearized version of the effective pair potential [3.40], we propose the following approximation for calculating the direct correlation function,  $c_{01}$ , between an ion and a colloidal particle. Assume that all the small ions (species 1) remain mobile but that the charges on the remaining  $(N_0 - 1)$  colloidal particles (those other than the one being considered) are replaced by a uniform continuum of charge—a jellium—having the same average charge per unit volume. This approximation ensures overall electroneutrality but otherwise neglects the contribution of other colloidal particles to the direct correlation function between an ion and a given colloidal particle. This Jellium Approximation is equivalent to assuming that, for the purpose of calculating the ion–colloid direct correlation function, the colloid–colloid distribution function may be considered as uni-

form, that is  $g_{00}(r) = 1$  for all  $r > 0$ . Thus [4.2] is replaced by

$$h_{00}(r) = 0 \quad [4.3]$$

Jellium Approximation

$$h_{10}(r) = c_{10}(r) + n_1 \int c_{11}(|\mathbf{r} - \mathbf{s}|) h_{10}(s) ds. \quad [4.4]$$

It should be reemphasized that [4.4] is used *only* for determining  $c_{10}(r)$ , which is subsequently used, in conjunction with [4.1], for the calculation of an effective pair potential for the one-component colloidal system.

We shall first investigate the form of  $U^{\text{eff}}$  taking into account the colloidal size effect within the linear approximation.

#### a. Size Effect in the Linear Approximation

To solve [4.4] for  $c_{10}(r)$  we supplement the exact condition

$$h_{10}(r) = -1, \quad r < a \quad [4.5]$$

which is a consequence of the hard-sphere interaction between an ion and a colloidal particle, with the approximate closures

$$c_{11}(r) = -\frac{\beta e^2 z_1^2}{\epsilon r}, \quad 0 < r < \infty \quad [4.6]$$

$$c_{10}(r) = -\frac{\beta e^2 z_1 z_0}{\epsilon r}, \quad r > a. \quad [4.7]$$

Equation [4.6] states that the ion–ion interaction is treated in the linearized point ion limit and that for  $r > a$ ,  $c_{10}(r)$  is still assumed to have its asymptotic form. The solution to [4.4]–[4.7] is

$$h_{10}(r) = -\frac{\beta e^2 z_1 z_0}{\epsilon} \frac{e^{\kappa a}}{(1 + \kappa a)} (1 + \phi) \frac{e^{-\kappa r}}{r}, \quad r > a \quad [4.8]$$

$$c_{10}(r) = -1 - \frac{1}{2} (\kappa a)^2 + \frac{1}{6} (\kappa r)^2 - \frac{\beta e^2 z_1 z_0 \kappa}{\epsilon} \frac{(1 + \phi)}{(1 + \kappa a)}, \quad r < a \quad [4.9]$$

with  $\phi$  being the colloid volume fraction

$$\phi = \frac{4\pi}{3} n_0 a^3 \quad [4.10]$$

and

$$\kappa^2 = 4\pi\beta e^2 n_1 z_1^2 / \epsilon. \quad [4.11]$$

Combining [2.10], [4.1], and [4.9] we find

$$c_{00}^{\text{eff}}(r) = c_{00}^s(r) - \frac{\beta e^2 z_0^2}{\epsilon} \frac{e^{2\kappa a}}{(1 + \kappa a)^2} \times (1 + \phi)^2 \frac{e^{-\kappa r}}{r} \quad [4.12a]$$

$$= c_{00}^s(r) - \beta U^{\text{eff}}(r). \quad [4.12b]$$

Thus we can identify the effective colloid-colloid pair potential

$$U^{\text{eff}}(r) = \frac{(z_0 e)^2}{\epsilon} \frac{e^{2\kappa a}}{(1 + \kappa a)^2} (1 + \phi)^2 \frac{e^{-\kappa r}}{r}.$$

Linearized Jellium Approximation, finite particles size  
[4.13]

We observe that apart from the factor  $(1 + \phi)^2$ ,  $U^{\text{eff}}(r)$  is superficially identical to the familiar expression for the double-layer interaction between two colloidal particles in osmotic equilibrium with an electrolyte reservoir characterized by the screening parameter  $\kappa$ , calculated according to the linearized Debye-Hückel theory in the superposition or weak overlap approximation (1). Equation [4.13] is an extension of [2.14] to include particle-size effects. It can be seen that given all other parameters being equal, an increase in particle size will increase the double-layer interaction. In the limit  $a \rightarrow \infty$ , [4.13] obeys the Derjaguin approximation as one would expect. Since  $\kappa$  is determined by the counterion concentration (see [4.4]), it will be a function of the concentration of colloidal particles. From [4.13] we can then see that the variation of  $U^{\text{eff}}(r)$  with particle concentration is similar to the variation of the classical double-layer pair potential with reservoir salt concentration.

It is straightforward to repeat the above derivation in the presence of added salt. The final form of the effective pair potential is still given by [4.13] but the screening parameter will now be given by

$$\begin{aligned} \kappa^2 &= \frac{4\pi\beta e^2 n_1 z_1^2}{\epsilon} + \frac{4\pi\beta e^2}{\epsilon} \sum_{i=2} n_i z_i^2 \\ &= \kappa_{\text{counterions}}^2 + \kappa_{\text{added salt}}^2, \end{aligned} \quad [4.14]$$

where the summation on the right-hand side is to be taken over all species of added electrolyte.

We now move on to derive an expression for the effective pair potential for high colloidal charges.

### b. Large Colloidal Charge—Nonlinear Effects

When the colloidal charge is high, nonlinear effects, which have up until now been neglected, must be taken into account. We shall consider this problem for a system of colloidal particles with counterions together with a known amount of added salt. The generalization of the ion-colloid Ornstein-Zernike equation in the Jellium Approximation for the colloidal particles ( $h_{00}(r) = 0$ ) is given by (cf. [4.4])

$$h_{i0}(r) = c_{i0}(r) + \sum_j n_j \int c_{ij}(|\mathbf{r} - \mathbf{s}|) h_{j0}(s) ds. \quad [4.15]$$

To obtain the nonlinear form of  $U^{\text{eff}}$ , we solve [4.15] together with

$$h_{i0}(r) = -1 \quad r < a \quad i = 1, 2, \dots \quad [4.16]$$

$$c_{ij}(r) = -\frac{\beta e^2 z_i z_j}{\epsilon r}, \quad 0 < r < \infty \quad i, j = 1, 2, \dots \quad [4.17]$$

$$c_{i0}(r) = -\frac{\beta e^2 z_i z_0}{\epsilon r} + h_{i0}(r) - \ln(1 + h_{i0}(r)), \quad r > a, \quad i = 1, 2, \dots \quad [4.18]$$

Equation [4.16] is exact, [4.17] should be reasonable for univalent ions, and [4.18] is the hypernetted chain closure. The assumptions embodied in [4.16]–[4.18] are identical to those needed to derive the nonlinear Pois-

son-Boltzmann equation for ionic distributions (12). Using the substitution

$$h_{i0}(r) = e^{-z_i y(r)} - 1 \quad [4.19]$$

Eqs. [4.15]–[4.18] are equivalent to the differential equation

$$\frac{d^2 y(r)}{dr^2} + \frac{2}{r} \frac{dy(r)}{dr} = - \frac{4\pi\beta e^2}{\epsilon} (n_0 z_0 + \sum_{i=1} n_i z_i e^{-z_i y(r)}), \quad r > a \quad [4.20]$$

with boundary conditions

$$y(r) \rightarrow 0, \quad r \rightarrow \infty \quad [4.21]$$

$$\frac{dy}{dr} = - \frac{\beta z_0 e^2 (1 + \phi)}{\epsilon a^2}, \quad r = a. \quad [4.22]$$

This differential equation has to be solved numerically.

The effective pair potential  $U^{\text{eff}}$  is defined in the same way as in [4.12] but [2.4] has to be used to evaluate the effective colloid–colloid direct correlation function  $c_{00}^{\text{eff}}(r)$ . Again this has to be carried out numerically.

However, it is possible to extract the asymptotic form of  $U^{\text{eff}}(r)$  for  $r \rightarrow \infty$ . We shall do this for a three component asymmetric electrolyte made up of colloidal particles (component 0), counterions (component 1), and coions (component 2), so that

$$n_0 z_0 + n_1 z_1 + n_2 z_2 = 0. \quad [4.23]$$

For this case, [2.4] for  $\tilde{c}_{00}^{\text{eff}}(k)$  becomes

$$\tilde{c}_{00}^{\text{eff}} = \tilde{c}_{00} + \frac{(n_1 \tilde{c}_{01}^2 (1 - n_2 \tilde{c}_{22}) + n_2 \tilde{c}_{02}^2 (1 - n_1 \tilde{c}_{11}) + 2n_1 n_2 \tilde{c}_{01} \tilde{c}_{02} \tilde{c}_{12})}{((1 - n_1 \tilde{c}_{11})(1 - n_2 \tilde{c}_{22}) - n_1 n_2 \tilde{c}_{12}^2)}. \quad [4.24]$$

Using [2.10], [4.17] together with the definition

$$c_{0i}(r) \equiv c_{0i}^s(r) - \frac{\beta e^2 z_i z_0}{\epsilon r}, \quad 0 < r < \infty, \quad i = 1, 2, \quad [4.25]$$

where  $c_{0i}^s(r)$  is short-ranged, we find

$$\tilde{c}_{00}^{\text{eff}}(k) = \tilde{c}_{00}^s(k) + n_1 [\tilde{c}_{01}^s(k)]^2 + n_2 [\tilde{c}_{02}^s(k)]^2 - \frac{4\pi\beta e^2}{\epsilon} \frac{[f(k)]^2}{k^2 + \kappa^2}, \quad [4.26]$$

where

$$\kappa^2 = \frac{4\pi\beta e^2}{\epsilon} (n_1 z_1^2 + n_2 z_2^2) \quad [4.27]$$

and

$$f(k) = z_0 + n_1 z_1 \tilde{c}_{01}^s(k) + n_2 z_2 \tilde{c}_{02}^s(k). \quad [4.28]$$

The asymptotic form of  $U^{\text{eff}}(r)$  is determined by the pole at  $k = i\kappa$  in the last term of the rhs of [4.26]. Thus by an inverse Fourier transform, we find

$$U^{\text{eff}}(r) = \frac{e^2}{\epsilon} [f(i\kappa)]^2 \frac{e^{-\kappa r}}{r}. \quad [4.29]$$

Thus the effective pair potential retains the form of a screened Coulomb function with a coefficient that depends on the colloidal particle size and number density.

In practice, a fair amount of numerical effort is needed to determine the coefficient  $f(i\kappa)$ . In the next section, we give a less rigorous but perhaps more intuitive derivation of the same result which involves considerably less computation.

### c. The Superposition Approximation

Consider the mean electrostatic potential  $\psi(r)$  about a given colloidal particle. Poisson's equation for the reduced potential  $y(r) = \beta e\psi(r)$  is

$$\nabla^2 y(r) = - \frac{4\pi\beta e^2}{\epsilon} [n_0 z_0 g_{00}(r) + n_1 z_1 g_{10}(r) + n_2 z_2 g_{20}(r)].$$

If we invoke the Jellium Approximation ( $g_{00}(r) = 1$ ) for the colloid–colloid distribution function together with the Boltzmann approximation ( $g_{i0}(r) = \exp(-z_i y(r))$ ,  $i = 1, 2$ ) for the ion–colloid distribution functions, Poisson's equation for  $y(r)$  becomes

$$\begin{aligned} \nabla^2 y &= -\frac{4\pi\beta e^2}{\epsilon} n_0 z_0, \quad r < a \\ &= -\frac{4\pi\beta e^2}{\epsilon} [n_0 z_0 + n_1 z_1 e^{-21y} + n_2 z_2 e^{-22y}], \\ & \quad r > a \end{aligned} \quad [4.30]$$

and we have the boundary conditions

$$\begin{aligned} y(r) &\rightarrow 0, \quad r \rightarrow \infty \\ y'(a^+) - y'(a^-) &= -\frac{4\pi\beta e\sigma}{\epsilon} \end{aligned} \quad [4.31]$$

where  $\sigma$  is the colloid surface charge density

$$\sigma = \frac{z_0 e}{4\pi a^2}. \quad [4.32]$$

The solution for  $r < a$  is

$$y(r) = \frac{4\pi\beta e^2}{\epsilon} \frac{n_0 z_0}{6} (a^2 - r^2) + y(a) \quad [4.33]$$

and the boundary condition [4.31] becomes

$$y'(a^+) = \frac{4\pi\beta e}{\epsilon} \sigma(1 + \phi). \quad [4.34]$$

Notice that [4.30]–[4.34] are identical to [4.20]–[4.22]. The factor  $(1 + \phi)$  in the boundary condition comes from the nonzero distribution of charge inside the fixed colloidal particle as a result of the Jellium Approximation.

For large  $r$ , the solution to [4.30] and [4.31] has the form

$$y(r) \rightarrow \frac{\beta e^2}{\epsilon} \bar{y} \frac{e^{-\kappa r}}{r}, \quad r \rightarrow \infty \quad [4.35]$$

with  $\kappa$  given by [4.27]. The constant  $\bar{y}$  can be determined numerically by solving [4.30] and matching the boundary condition at  $r = a$  (Eq. [4.34]). The effective pair potential between two colloidal particles can be obtained using the following argument. We bring together two particles while the remaining  $(N_0 - 2)$  colloidal particles are treated in the Jellium Approximation. The interaction is taken to arise from the overlap of the mean electrostatic potential profile or equivalently the ionic atmosphere around each particle. In the superposition approximation,

the interaction potential is given by the usual formula

$$U^{eff}(r) = \frac{e^2 \bar{y}^2}{\epsilon} \frac{e^{-\kappa r}}{r}. \quad [4.36]$$

Nonlinear Jellium Approximation, finite particle size

To establish the equivalence between [4.36] and [4.29] we note that from the solutions  $c_{i0}(r)$  to [4.15]–[4.18], the Fourier transform of the potential  $y(r)$  can be written in terms of  $\tilde{c}_{i0}^s(k)$  as

$$\begin{aligned} \tilde{y}(k) &= \frac{4\pi\beta e^2}{\epsilon} \frac{z_0 + \sum_{i=1} n_i z_i \tilde{c}_{i0}^s(k)}{(k^2 + \kappa^2)} \\ & \quad + \frac{z_0 \beta e^2}{\epsilon} \tilde{p}(k), \end{aligned} \quad [4.37]$$

where  $\tilde{p}(k)$  is the Fourier transform of

$$\begin{aligned} p(r) &= \frac{1}{a} - \frac{1}{r}, \quad r < a \\ &= 0, \quad r > a. \end{aligned} \quad [4.38]$$

Assuming as before that the pole that contributes to the asymptotic form of  $y(r)$  is that at  $k = i\kappa$ , we establish the required result, namely,

$$\bar{y} = f(i\kappa). \quad [4.39]$$

We can see that the effective pair potential derived from the Jellium model using either the Ornstein–Zernike equations or a superposition argument lead to identical results. However, the superposition approach is much easier to implement in practice. Indeed the effective pair potentials for the linearized cases, [3.40] and [4.13], follow immediately from solving the linearized form of [4.30].

## 5. RESULTS AND DISCUSSIONS

Having obtained an effective colloid–colloid pair potential, [4.36], the multicomponent colloidal system can now be treated as an effective one-component fluid consisting of colloidal particles. Certain properties of the system can be determined from the effective one-component fluid but we reiterate that the calculation of the thermodynamics of the multicomponent system requires a

knowledge of the effective *one-body* potentials arising from ion-ion and ion-colloid interactions, as demonstrated for the linear case in Section 3. However, the colloid-colloid pair distribution function  $g_{00}(r) = 1 + h_{00}(r)$  or equivalently the structure factor

$$\begin{aligned} S(k) &= 1 + \frac{4\pi}{k} n_0 \int_0^\infty \sin krh(r)rdr \\ &= 1 + n_0 \tilde{h}_{00}(k) \end{aligned} \quad [5.1]$$

can be obtained using the effective one-component fluid and methods of liquid-state physics. The particle-particle structure factor of strongly interacting colloidal systems has been measured by both light and neutron scattering. In this section we compare some of these measurements with predictions based on the Jellium Approximation. Due to the difference in the wavelength of the radiation, light ( $\lambda \sim 5000 \text{ \AA}$ ) and neutron ( $\lambda \sim 10 \text{ \AA}$ ) scattering can be combined to examine the structure of a colloidal system over four orders of magnitude in the volume fraction.

The experimental systems we have chosen to examine in detail are aqueous dispersions of charged polystyrene spheres (2, 13, 14). These dispersions are first prepared at various known particle-volume fractions and are then treated with ion-exchange resin to remove excess electrolytes. Ideally such systems would then only contain charged colloidal particles and their counterions. In practice, there will be small amounts of residual electrolyte present. The added electrolyte concentration of the system is then controlled by adding known amounts of salt. Provided the amount of added salt is significant, the small quantity of residual electrolyte present in the ion-exchanged system may be neglected. With this procedure, the total ionic composition of a given colloidal system is known. In the case of the ionic composition of a colloidal system which has been dialyzed against an electrolyte reservoir of given concentration is known without a further determination of the electrolyte concentration within the colloidal system. This distinction is important since the parameters needed for the theory are the

particle size, charge, and volume fraction as well as the molarity of added salt in the colloidal system, which in general is not the same as the ionic strength of the equilibrium electrolyte reservoir. This difference is a consequence of the Donnan equilibrium which results in the familiar coion exclusion effect.

The theory we have presented predicts, without any adjustable parameters, an effective colloid-colloid pair potential of the form  $Ar^{-1}e^{-\kappa r}$ . The parameters  $A$  and  $\kappa$  depend only on certain measurable properties of the multicomponent colloidal system, such as the colloid particle size, charge, and concentration and the amount of added electrolyte. Having obtained an expression for the effective pair potential we can determine the structure factor by using one of the many approximate methods of liquid-state physics. Our model of the colloidal system as an asymmetric electrolyte has an analytic solution in the Mean Spherical Approximation but, as we noted in a previous paper (4), this gives nonsensical results. The Hypernetted Chain Approximation gives sensible results but requires a time-consuming iterative procedure for its solution. For an effective pair potential of the form  $\sim r^{-1}e^{-\kappa r}$ , the Rescaled Mean Spherical Approximation (RSMSA) (15) is a rapid, convenient, and reasonably accurate method for calculating the structure factor  $S(k)$ . All structure factors in this paper are calculated using the RSMSA. The RSMSA is *not* a predictive theory but an ingenious algorithm for calculating the structure factor between particles when the particle-particle interaction potential is of the screened Coulomb form. By comparing with Monte Carlo simulations of the same potential (15), it has been found that the RSMSA (as with the hypernetted chain approximation) underestimates the fluid structure. That is, the height of the first peak of the structure factor can be too small by as much as 20% when  $S(k_{\max}) \sim 2$ ,  $k_{\max}$  being the position of the first peak. This point must be kept in mind when comparing theory with experiments.

In the experimental system considered here

(13, 14) the polystyrene particles have a mean radius of  $a = 160 \text{ \AA}$  and a charge of  $z_0 = 840$  (surface charge density  $4.2 \mu\text{C cm}^{-2}$ ), which is obtained by conductometric titration.

In Fig. 1 we can see the variation of the effective colloid–colloid pair potential  $U^{\text{eff}}$  (cf. [4.36], with particle charge. The colloidal system is at volume fraction  $\phi = 10^{-3}$  and contains  $5 \times 10^{-7} M$  1:1 added electrolyte. We note that upon decreasing the particle charge  $z_0$  from 840 to 300, the effective pair potential increases in range. The reason for this behavior is that at high charges,  $z_0$ , the constant  $\bar{y}$  in  $U^{\text{eff}}$  is insensitive to the value of  $z_0$ . Therefore the dominant effect of decreasing the particle charge is to decrease the magnitude of  $\kappa$  and this results in an increase in the range of  $U^{\text{eff}}$  (cf. [4.23], [4.27], and [4.36]). On further decreasing  $z_0$  from 300 to 100, the magnitude of  $U^{\text{eff}}$ , through its dependence on  $\bar{y}$ , is seen to decrease with particle charge (cf. [4.13]). At the same time, the range of the pair potential still increases because  $\kappa$  decreases with particle charge.

The variation of the effective pair potential with volume fraction is illustrated in Fig. 2. We note that an increase in the particle number density is accompanied by an increase in the counterion concentration which then results in an increase in the screening between the particles. As a consequence the range of the effective pair potential becomes

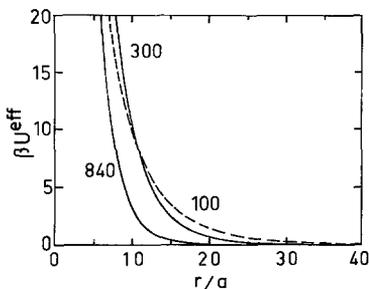


FIG. 1. The effective pair potential,  $U^{\text{eff}}(r)$ , at various particle charges: particles radius  $a = 160 \text{ \AA}$ , volume fraction  $\phi = 10^{-3}$ ,  $5 \times 10^{-7} M$  1:1 added electrolyte, temperature  $298^\circ\text{K}$ , dielectric constant  $\epsilon = 78$ .

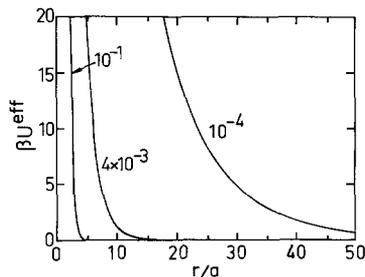


FIG. 2. The effective pair potential,  $U^{\text{eff}}(r)$ , at various particle-volume fractions: particle charge,  $z_0 = 300$ , other details as in Fig. 1.

shorter. This phenomenon is similar to the intuitively more familiar situation in which excess electrolyte is added to the system at constant-volume fraction, see Fig. 3.

We have seen so far that the effective pair potential is dependent on the particle number density, the particle charge and the amount of added salt. If we rewrite [4.36] as

$$U^{\text{eff}}(r) = U_0 a e^{-\kappa r} / r \quad [5.2]$$

the constant  $U_0$  will depend on the following independent dimensionless parameters:  $\phi$ —the volume fraction of colloidal particles;  $(e^2 z_0 / \epsilon k T a)$ —the reduced particle charge; and  $(\kappa_{\text{salt}} a)$ , where

$$\kappa_{\text{salt}}^2 = \frac{4\pi\beta e^2}{\epsilon} \sum_{\text{added salt}} n_i z_i^2 \quad [5.3]$$

is the Debye parameter for the *added salt*, and  $a$  is the particle radius. The dependence of  $U_0$  on these three parameters is summarized in Fig. 4. This figure permits a quick estimate of the volume fraction-dependent

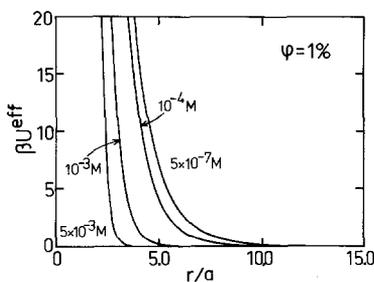


FIG. 3. The effective pair potential,  $U^{\text{eff}}(r)$ , at various amounts of added 1:1 electrolyte: particle charge  $z_0 = 300$ , volume fraction  $\phi = 1\%$ , other data as in Fig. 1.

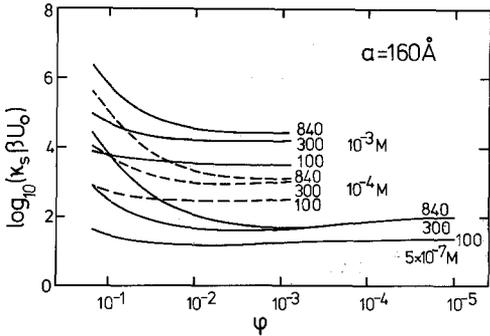


FIG. 4. The variation of the coefficient,  $U_0$ , of the effective pair potential with volume fraction, particle charge, and added electrolyte concentration. (See Eqs. [5.2] and [5.3].)  $\kappa_s = \kappa_{\text{salt}}a$ .

pair potential without having to carry out the numerical calculations described in Section 4.

In Fig. 5 we compare the colloid particle structure factor  $S(k)$  obtained by small-angle neutron scattering (SANS) (14) with our theoretical predictions. The experimental system has been described briefly at the beginning of this section (see original paper for more details). For the theory we use the effective pair potential given in Section 4, [4.36], which is based on the nonlinear Jellium Approximation. As discussed earlier the structure factors were then obtained from this effective pair potential using the RMSA. The input parameters are: particle radius  $a = 160 \text{ \AA}$ , and particle charge  $z_0 = 300$ . The reason for using the value for the particle charge will be discussed below. Apart from the assumptions in the Jellium Approximation, the theory contains *no* other adjustable parameters. The agreement between theory and experiment is only fair. The theory tends to underestimate the height of the first peak. This discrepancy can be accounted for by the fact that the RMSA tends to underestimate the height of the peak of  $S(k)$ —by  $\sim 20\%$  when  $S(k) \sim 2$ . Beyond the first peak, there are considerable differences between theory and experiment.

It should be said that the ability to match the structure factor does not constitute a

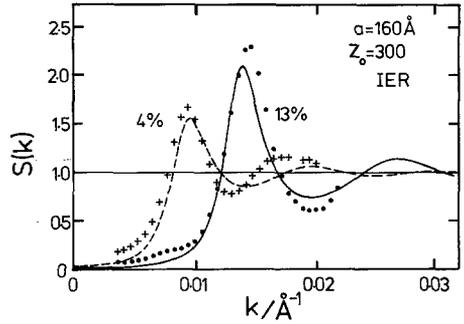


FIG. 5. The colloid structure factor  $S(k)$  of polystyrene particles that have been treated with ion-exchange resins (IER) at volume fractions of 4 and 13%. Points—experimental small-angle neutron scattering (14). Curves—theory based on the effective pair potential given by Eq. [4.36] and a particle charge  $z_0 = 300$ . Other data as in Fig. 1, see text for details.

strong test of a given theory. Indeed, a hard-sphere model, with an *adjustable* hard-sphere diameter that varies with volume fraction can also provide a good fit to the measured  $S(k)$ . The important observation here is that the use of the pair potentials obtained by conventional double-layer theory, which takes no account of the role of the counterions in screening the electrostatic interaction, or that obtained by the cell theory (16) will result in considerable disagreement with the experimental structure factor (17). Indeed both theories cannot be applied to an ion-exchanged system which contain no added electrolyte.

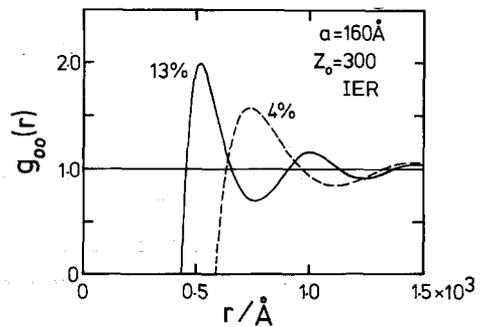


FIG. 6. The colloid pair correlation  $g(r)$  corresponding to the theoretical results in Fig. 5.

The colloid–colloid pair correlation functions corresponding to the cases shown in Fig. 5 are given in Fig. 6. For such systems, the distance between nearest neighbors can be much larger than the physical size of the particles because of the strong electrostatic repulsion. For a continuous potential of the form given by [4.36] one expects the function  $g_{00}(r)$  to approach zero smoothly at small values of  $r$  (17). The cusps at  $g_{00}(r) = 0$  observed in Fig. 6 are artifacts of the approximations of the RMSA.

As a summary of all available experimental results we have plotted in Fig. 7 the height of the first peak of the structure factor,  $S(k_{\max})$  as a function of particle-volume fraction for various amounts of added salt. The magnitude of  $S(k_{\max})$  can be regarded as a measure of the degree of interparticle structure in the system. The theoretical curves are calculated using the effective pair potential given by [4.36] with a particle charge  $z_0 = 840$ , which corresponds to the titratable charge. There is only qualitative agreement between theory and experiment. However, we do observe that for an ion-exchange system at a volume fraction of  $\phi = 5 \times 10^{-4}$ , there is still considerable structure between the particles even though the volume fraction

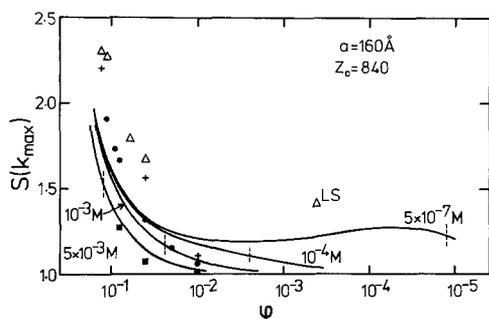


FIG. 7. The height of the first peak of the colloid structure factor,  $S(k_{\max})$ , of a polystyrene-latex dispersion as a function of volume fraction at various amounts of added salt. Points—experimental results from neutron (14) and light (13) scattering (the latter indicated by LS):  $\Delta$ , ion-exchange resins; +,  $10^{-4}$  M;  $\bullet$ ,  $10^{-3}$  M; and  $\blacksquare$ ,  $5 \times 10^{-3}$  M. Curves—theory based on the effective pair potential of Eq. [4.36] with  $z_0 = 840$  and RMSA. Other data as in Fig. 1, see text for details.

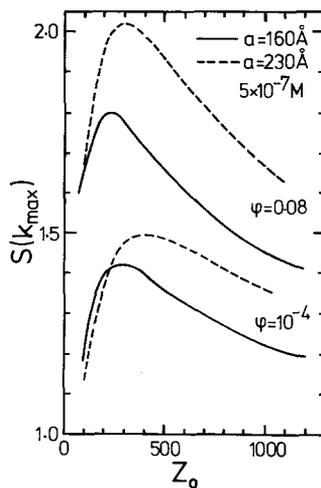


FIG. 8. Variations of the first peak of the colloid structure factor  $S(k_{\max})$  with particle charge for particle radius  $a = 160$  and  $230$  Å. The calculations are based on the effective pair potential given by Eq. [4.36].

has been lowered by about two orders of magnitude. Due to the large interparticle spacing at this low-volume fraction, the measurement was taken by light (13) rather than neutron scattering. This feature is predicted, qualitatively at least, by our theory. The explanation of this observation can be found in Fig. 2 in which a reduction in volume fraction results in a decrease in the counterion concentration so that the range of the electrostatic interaction then increases, thereby maintaining the interparticle structure in spite of the increase in the interparticle spacing. The small vertical lines in Fig. 7 indicate the volume fractions at which the contribution to the screening parameter,  $\kappa$ , from the counterions is equal to that from the added salt, cf. [4.14].

Before we discuss the discrepancies between theory and experiment shown in Fig. 7, let us first examine the behavior of  $S(k_{\max})$  as a function of particle charge and particle size (Figs. 8 and 9). From the result in Fig. 1 we have already seen that a reduction of the particle charge from 840 can actually result in an increase in the effective interparticle repulsion. This observation is again reflected in the behavior of  $S(k_{\max})$  with particle charge,

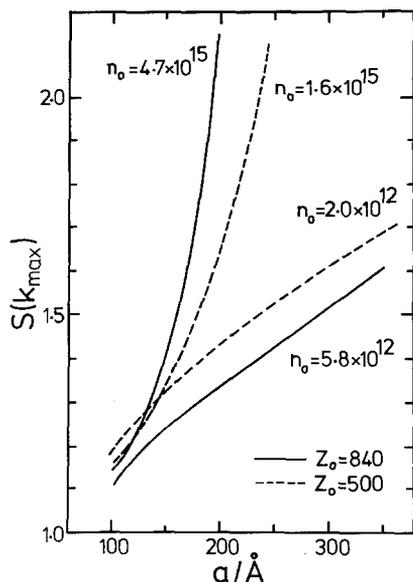


FIG. 9. Variations of the first peak of the colloid structure factor  $S(k_{\max})$  with particle size at various colloid particle number densities,  $n_0$  ( $\text{cm}^{-3}$ ). The calculations are based on the effective pair potential given by Eq. [4.36].

$z_0$  (Fig. 8). As the charge is reduced from a high value, the interparticle structure initially increases. There must, however, be a maximum (at  $z_0 \sim 300$ ) since at zero charge, the interparticle correlation must be negligible at such low-volume fractions.

The results in Fig. 10 are identical to those in Fig. 7 except we have used a particle charge of  $z_0 = 300$  (with a corresponding reduction in counterion concentration to maintain electroneutrality) instead of 840.

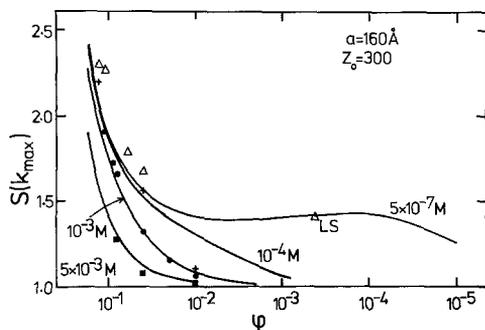


FIG. 10. As with Fig. 7 except a particle charge  $z_0 = 300$  was used to calculate the theoretical curves.

The resultant improvement in the agreement between theory and experiment is evident on comparing Figs. 7 and 10 (see also Fig. 5). The use of a lower particle charge may be explained in somewhat vague terms such as "counterion binding." However, it may not be easy to justify this in terms of the chemistry of the strongly acidic surface sulfonate groups. We shall not attempt to do so here. Before we adjusted the particle charge our theory contained no adjustable parameters as all input parameters can be determined experimentally. The use of a lower charge represents the introduction of a single parameter which does *not* vary with particle size, charge, volume fraction, or electrolyte concentration. Its use may be mitigated against the fact that it can improve agreement between theory and experiment over a range of electrolyte concentrations and over a very wide range of volume fractions. The discrepancy in  $S(k_{\max})$  for volume fractions  $\phi \sim 0.1$  can be largely explained by the slight errors in the use of the RMSA to calculate the structure factors.

In Fig. 11 we show the variation of the position of the first peak of the structure factor,  $k_{\max}$ , as a function of volume fraction for various amounts of added salt. The particle charge was taken to be  $z_0 = 300$ . In

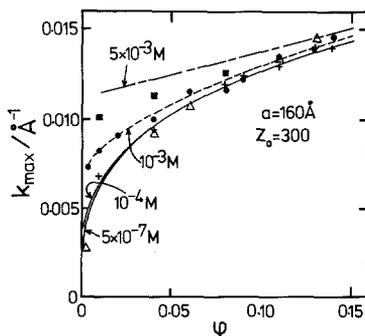


FIG. 11. Location of the first peak,  $k_{\max}$  of the colloid structure factor as a function of particle-volume fraction  $\phi$  for various amounts of added NaCl. Experimental points are from neutron scattering (14) (see Fig. 7), theoretical curves are based on Eq. [4.36]. The ion-exchanged system is modeled with  $5 \times 10^{-7} M$  of added electrolyte.

general, there is good agreement between theory and experiment except for the salt concentration of  $5 \times 10^{-3} M$ . At this highest electrolyte concentration, the peak of the structure factor is very small  $S(k_{\max}) \approx 1$  (cf. Fig. 10) and is also very broad. As a result, it may be difficult to determine the experimental peak position to the same accuracy as for those at lower salt concentrations.

Thus far it may be argued that the experimental support for the existence of our volume fraction-dependent potential may be somewhat tenuous in that there is only one set of light-scattering studies (13) (see Figs. 7 or 10). However, there is an earlier light-scattering study on the structure of a similar polystyrene-latex system which seems to support our prediction of colloidal structuring over a large-volume fraction range (2). The system in question consists of polystyrene spheres,  $a = 230 \text{ \AA}$  radius, particle charge  $z_0 = 500$  ( $1.2 \text{ \mu C/cm}^2$  as determined by conductometric titration), treated by ion-exchange resins. The structure factors were determined both by static and dynamic light-scattering methods. Although there was some scatter in the peak height,  $S(k_{\max})$ , it can be seen in Fig. 12 that there is better than qualitative agreement between theory and experiment. In this case it is not possible to improve the agreement between theory and

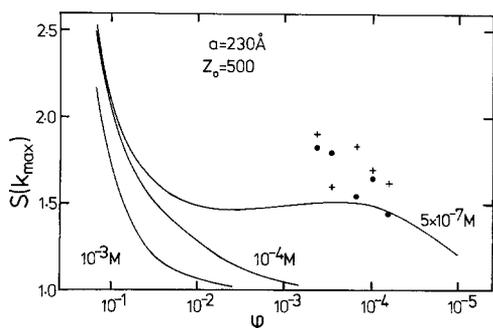


FIG. 12. The height of the first peak in the colloid structure factor,  $S(k_{\max})$  of a polystyrene-latex dispersion as a function of volume fraction. The system has been treated by ion-exchange resins. Points—experimental results from light scattering (2). Curves—theory based on Eq. [4.36].

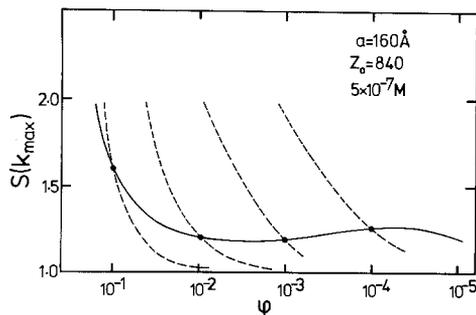


FIG. 13. An illustration of the volume fraction dependence of  $S(k_{\max})$  for density-dependent and -independent potentials. Solid curves—density-dependent potential, Eq. [4.36]. Broken curves—density-independent potentials chosen to coincide with Eq. [4.36] at  $\phi = 10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ , and  $10^{-4}$ .

experiment by adjusting the particle charge. The titratable charge  $z_0 = 500$  is already very close to the maximum of the  $S(k_{\max})$  vs  $z_0$  curve shown in Fig. 8.

From a theoretical viewpoint, the difference between the predictions of a density-dependent and density-independent pair potential can be quite marked. In Fig. 13 we have reproduced the behavior of  $S(k_{\max})$  as a function of volume fraction,  $\phi$  for an ion-exchanged system which is characterized by a volume fraction-dependent pair potential. Superimposed on this curve are the variations of  $S(k_{\max})$  with  $\phi$  for various volume fraction-independent potentials. These volume fraction-independent potentials are chosen to be the same as the volume fraction-dependent pair potential at various fixed volume fractions. The general observation is that with volume fraction-independent pair potentials, the particle structure only persists over about 1 decade of volume fraction. However, with the volume fraction-dependent potential, interparticle correlations can remain significant over four orders of magnitude in the volume fraction.

In summary, we have demonstrated theoretically that the effective double-layer pair interaction between highly charged particles in a low-salt environment can be quite different from that predicted by conventional

double-layer theory. The reason is that one must take into account the role of the counterions associated with the colloidal particles in screening the electrostatic interaction. One interesting result of the theory is that the effective pair interaction between colloidal particles in such situations will only increase with the particle charge when the latter is small. At sufficiently high charges, the associated increase in the counterion concentration can actually screen to reduce the electrostatic repulsion between the particles. Another consequence of screening due to the counterion is that the pair interaction becomes dependent on the volume fraction of particles in the system, with the result that interparticle correlations can persist over 4 decades of variation in the volume fraction. While available experimental support for this prediction is reasonably convincing, there remains a strong case for a detailed investigation of a single well-characterized system over a wide range of conditions.

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