

## HIGHLY ASYMMETRIC ELECTROLYTES: A MODEL FOR STRONGLY INTERACTING COLLOIDAL SYSTEMS

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Dilute but strongly interacting colloidal systems are investigated using a highly asymmetric primitive model electrolyte. An analytic expression for an effective pair potential which is dependent on the colloidal particle density is obtained. Solutions in the hypernetted chain approximation to the asymmetric electrolyte and to the effective one-component model are compared.

### 1. Introduction

According to the classical theory of the stability of colloidal systems [1], the electrostatic interaction between charged colloidal particles is screened by the presence of counterions and added electrolyte. That is, the colloidal system is assumed to be in osmotic equilibrium with a reservoir of ions of known fixed concentration and the strength of the screening is determined by the usual Debye screening length of this reservoir. However, in many instances, 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 concentration. For such cases every part of the solvent is under the electrical influence of the colloidal particles and nowhere in the suspension would the equilibrium concentration be present. A familiar 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. This system has been studied extensively by conventional and dynamic light scattering [2]. The experimental results have been interpreted using Monte Carlo [3] and brownian dynamics [4] simulations in which the colloidal particles are assumed to interact via a linear Debye-Hückel (screened Coulomb) pair potential. This pair potential is characterised by the surface po-

tential (or equivalently the charge) on the colloidal particles and the screening length of the dispersion. Both of these parameters were difficult to determine experimentally [5]. Although the composition (and hence the screening length) of the reservoir that is in equilibrium with the dispersion can, in principle, be determined by dialysis, its properties will in general be a function of the concentration of colloidal particles in the system [6,7]. In the simulation studies, values for the surface potential and screening length were chosen to give agreement with experiment and these were taken to be independent of particle number concentration.

In this communication we model a strongly interacting colloidal system by a highly asymmetric primitive model electrolyte in which the ions and colloidal particles are given equal emphasis. For example, in treating the polystyrene dispersion referred to above [2], we may, if we neglect the presence of excess electrolytes, regard the colloidal particles and their associated counter-ions as a 1 : Z electrolyte in which  $|Z| \approx 10^2$ . An approximate analytic expression is derived for the effective pair potential between colloidal particles with or without added electrolyte. It is the appropriate effective pair potential to employ if the colloidal particles are to be regarded as an effective one-component system. This potential contains many-body effects in that it is a function of the concentra-

tion of colloidal particles. The predictions of this effective pair potential are compared with the solution of the (1 : Z) + (1 : 1) electrolyte in the hypernetted chain approximation.

## 2. The model and the effective pair potential

We model the colloidal system as a highly asymmetric electrolyte comprised of ions of number density  $\rho_i$ , valence  $Z_i$  ( $i = 0, 1, 2, \dots$ ) obeying the electroneutrality condition  $\sum_i \rho_i Z_i = 0$ . The subscript  $i = 0$  refers to the colloidal particle and  $i = 1, 2, \dots$  refer to small ions — counter-ions and added electrolyte. The interaction between all charged species is taken to be of the form

$$U_{ij}(r) = \infty, \quad r < d_{ij}, \\ = Z_i Z_j e^2 / \epsilon r, \quad r > d_{ij}, \quad (1)$$

where  $d_{ij} = (d_i + d_j)/2$  and  $d_i$  is the ionic diameter. The solvent is simply characterised as a dielectric continuum of dielectric constant  $\epsilon$ . In choosing parameters for the model we use values that are appropriate to those in the study of Brown et al. [2]. Since the colloidal particles are small,  $d_0 \approx 500 \text{ \AA}$ , and the dispersion is dilute, van der Waals interactions between the colloidal particles are negligible.

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

$$\tilde{h}_{ij}(k) = \tilde{C}_{ij}(k) + \sum_n \tilde{C}_{in}(k) \tilde{h}_{nj}(k), \\ i, j = 0, 1, 2, \dots, \quad (2)$$

where the Fourier transforms are defined by

$$\tilde{h}(k) = \int dr \exp(-ik \cdot r) h(r)$$

and the colloid–colloid structure factor is

$$S_{00}(k) = 1 + \rho_0 \tilde{h}_{00}(k). \quad (3)$$

The hypernetted chain approximation is defined by supplementing (2) with the conditions ( $\beta = 1/k_B T$ )

$$C_{ij}(r) = -\beta U_{ij}(r) + h_{ij}(r) - \ln[1 + h_{ij}(r)], \\ r > d_{ij}, \quad (4a)$$

$$h_{ij}(r) = -1, \quad r < d_{ij}. \quad (4b)$$

This approximation has proved successful for systems involving coulombic interactions [8].

We now derive the effective pair potential between colloidal particles for the situation in which only colloidal particles and counterions are present (excess electrolyte being removed by ion-exchange resins and the effects due to the dissociation of water being neglected). This case is equivalent to a  $Z_1 : Z_0$  electrolyte. From (2) we can write

$$\tilde{h}_{00}(k) = \tilde{C}_{00}^{\text{eff}}(k) + \rho_0 \tilde{C}_{00}^{\text{eff}}(k) \tilde{h}_{00}(k), \quad (5)$$

where

$$\tilde{C}_{00}^{\text{eff}} = \tilde{C}_{00} + \rho_1 \tilde{C}_{01} \tilde{C}_{10} / (1 - \rho_1 \tilde{C}_{11}) \quad (6)$$

is the *effective* colloid–colloid direct correlation function. If we now approximate the ion–ion and ion–colloid direct correlation functions by their asymptotic forms [9]

$$C_{11}(r) = -\beta Z_1^2 e^2 / \epsilon r, \quad 0 < r < \infty, \quad (7)$$

$$C_{10}(r) = C_{01}(r) = -\beta Z_1 Z_0 e^2 / \epsilon r, \quad 0 < r < \infty, \quad (8)$$

and put

$$C_{00}(r) = C_{00}^s(r) - \beta Z_0^2 e^2 / \epsilon r, \quad 0 < r < \infty, \quad (9)$$

we find from (6) that

$$\tilde{C}_{00}^{\text{eff}}(k) = \tilde{C}_{00}^s(k) - \frac{4\pi\beta Z_0^2 e^2 / \epsilon}{k^2 + 4\pi\beta Z_1^2 e^2 / \epsilon} \quad (10)$$

or

$$C_{00}^{\text{eff}}(r) = C_{00}^s(r) - (\beta Z_0^2 e^2 / \epsilon r) \exp(-\kappa^{\text{eff}} r), \\ 0 < r < \infty, \quad (11)$$

with

$$\kappa^{\text{eff}} = (4\pi\beta e^2 \rho_1 Z_1^2 / \epsilon)^{1/2}. \quad (12)$$

Eq. (11) suggests the definition of an effective colloid–colloid pair potential of the form

$$U^{\text{eff}}(r) = (Z_0^2 e^2 / \epsilon r) \exp(-\kappa^{\text{eff}} r). \quad (13)$$

Note that  $U^{\text{eff}}(r)$  has the form of a screened Coulomb potential and only the counter-ions contribute to the

screening parameter  $\kappa^{\text{eff}}$ . However, because of the electroneutrality condition  $\rho_0 Z_0 + \rho_1 Z_1 = 0$ ,  $\kappa^{\text{eff}}$  is a function of colloid number density. Indeed, for  $|Z_0/Z_1| \gg 1$ ,  $\kappa^{\text{eff}}$  is much smaller than the Debye parameter of the  $Z_1 \cdot Z_0$  electrolyte given by  $\kappa^2 = (4\pi\beta e^2/\epsilon) \times (\rho_0 Z_0^2 + \rho_1 Z_1^2)$ .

In the presence of added electrolyte (ionic species  $i = 2, 3, \dots$ ) the effective colloid-colloid pair potential is still given by (13) except  $\kappa^{\text{eff}}$  is now

$$\kappa^{\text{eff}} = \left[ 4\pi\beta e^2 \epsilon^{-1} \sum_{i=1} \rho_i Z_i^2 \right]^{1/2} \quad (14)$$

where the summation is taken over all ions - counterions and added electrolyte. The screening parameter given by (14) is still a function of the colloid number density because of the electroneutrality condition  $\sum_i \rho_i Z_i = 0$ . However, in the dilute limit  $\rho_0 \rightarrow 0$ , the screening is determined solely by the added electrolyte concentration as expected from the classical theory.

### 3. Numerical results

As an example of our numerical calculations, we choose parameters that are representative of the systems of deionized polystyrene particles mentioned earlier [2]. The following input data were chosen:  $T = 298$  K,  $\epsilon = 78.4$ ,  $d_0 = 500$  Å,  $d_1 = 4$  Å,  $Z_1 = 1$ ,  $Z_0 = -120$  (i.e. a 1 :  $Z_0$  electrolyte),  $\rho_0 = 8.46 \times 10^{12}$  cm $^{-3}$  which is the highest density considered in the experiment [2] and corresponds to a colloid volume fraction  $\phi = \frac{1}{6} \pi \rho_0 d_0^3 = 5.54 \times 10^{-4}$ . In presenting our results we scaled all lengths to the so-called ion sphere radius  $r_s$  for the colloidal particles which is defined by  $\frac{4}{3} \pi \rho_0 r_s^3 = 1$ ,

and gives, for  $\rho_0 = 8.46 \times 10^{12}$  cm $^{-3}$ ,  $r_s = 3040$  Å.

Eqs. (2) and (4) were solved by the usual iterative scheme using fast Fourier transform methods [10,11]. Previous work on highly asymmetric electrolytes which are also based on the same equations have considered charge asymmetries of 6 : 1 and a size ratio of 2 : 1 between oppositely charged species [10]. For ions with the same size, charge asymmetries of up to 20 : 1 have been studied [11]. In the present work, truncations of the integrals in real space at  $r \approx 34r_s$  and a uniform step size  $\Delta r = 8.28 \times 10^{-3} r_s$  was sufficient to give an estimated error < 1%. A logarithmic distribution of

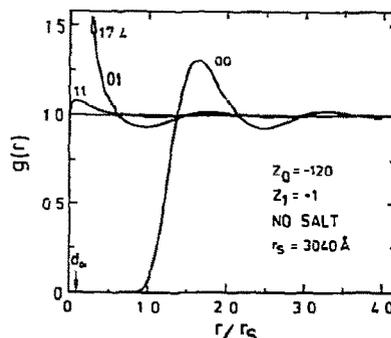


Fig. 1 The radial distribution functions for a 1 : 120 electrolyte: ion-ion,  $g_{11}$ ; colloid-ion,  $g_{01}$ ; colloid-colloid,  $g_{00}$ . The contact value of  $g_{01}$  is given in the diagram and  $\rho_0 = 8.46 \times 10^{12}$  cm $^{-3}$ .

integration points [12,13] was also used and it gave the same results as that using a uniform set of grid points.

In fig. 1 are shown the various radial distribution functions for a 1 : 120 "electrolyte". We note the significant correlation between the colloidal particles ( $g_{00}$ ) at a separation of  $\approx 1.6r_s \gg d_0$  (the particle diameter) which is a result of strong coulombic repulsion. Oscillations in the ion-colloid distribution function ( $g_{01}$ ) are a result of the correlations in  $g_{00}$ . The classical double layer theory (Poisson Boltzmann or Debye-Huckel) with an infinite electrolyte reservoir would have predicted  $g_{01}(r)$  to be a monotonic decaying function of  $r$ . The shoulder at  $r/r_s \approx 0.2$  in the ion-ion correlation function ( $g_{11}$ ) reflects the high

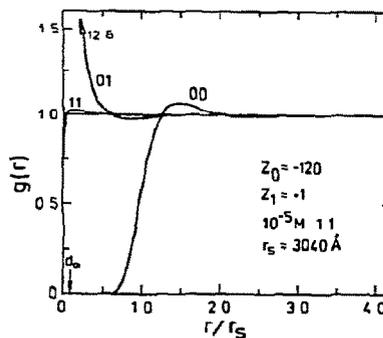


Fig. 2. The radial distribution functions corresponding to fig. 1 for a 1 : 120 electrolyte with  $10^{-5}$  M 1 : 1 electrolyte present.

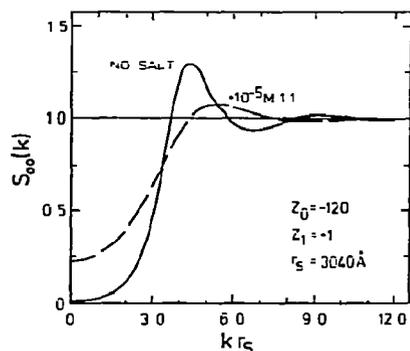


Fig. 3. The colloid-colloid structure factor corresponding to the results in figs. 1 and 2 1:120 electrolyte —, 1:120 +  $10^{-5}$  M 1:1 electrolyte ---.

accumulation of counterions in the vicinity of a colloidal particle.

The screening effects due to the addition of  $10^{-5}$  M 1:1 electrolyte (ionic diameter  $d_i = 4$  Å,  $i = 3, 4$ ) can be seen in fig. 2. The correlations seen in fig. 1 are diminished as one would expect intuitively.

The colloid-colloid structure factor (see eq. (3)) corresponding to the results in figs. 1 and 2 are shown in fig. 3. It was found that the position of the main peak in  $S_{00}(k)$  occurs at  $kr_s \approx 4.4$ , close to that found in the experiments [2]. It should be noted that the non-linear effects included in the hypernetted chain approximation are very important. Indeed, the (linear) mean spherical approximation [14] (i.e. with the rhs of eq. (4a) replaced by  $-\beta U_{ij}$ ) predicts the main peak in  $S_{00}(k)$  to occur at  $kr_s \approx 18$ .

Given the colloid-colloid radial distribution functions shown in figs. 1 and 2, one can ask the following question: If the colloidal particles were regarded as a one-component system, what pair potential  $U^*(r)$  between the colloidal particles would give the same radial distribution function? We have found  $U^*(r)$  by inverting  $g_{00}(r)$  in figs. 1 and 2 using a one-component hypernetted chain equation. That is, given  $\tilde{h}_{00}(k)$  we solved the following equations for  $U^*(r)$ :

$$\begin{aligned} \tilde{h}_{00}(k) &= \tilde{C}^*(k) + \rho_0 \tilde{C}^*(k) \tilde{h}_{00}(k), \\ h_{00}(r) &= -1, \quad r < d_0, \\ C^*(r) &= -\beta U^*(r) + h_{00}(r) - \ln[1 + h_{00}(r)], \\ & \quad r > d_0. \end{aligned} \quad (15)$$

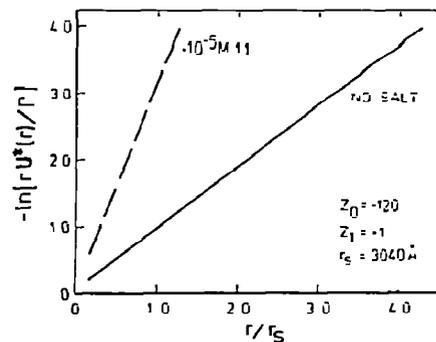


Fig. 4. The colloid-colloid pair potential  $U^*(r)$  as obtained from the results of figs. 1 and 2 using eq. (15). 1:120 electrolyte —; 1:120 +  $10^{-5}$  M 1:1 electrolyte ---.  $\Gamma = \beta Z_0^2 e^2 / \epsilon$

The results for  $U^*(r)$  are shown in fig. 4. The effective pair potential  $U^{\text{eff}}(r)$  (13) agrees with  $U^*(r)$  to better than 3%. However, when we use  $U^{\text{eff}}(r)$  to calculate  $S_{00}(k)$  (assuming we are dealing with a one-component system) in the hypernetted chain approximation, the result is practically identical to the corresponding result from the 1:  $Z_0$  electrolyte. For instance, the height and position of the main peak in  $S_{00}(k)$  are in agreement to better than 1%. This good agreement demonstrates the validity and utility of the effective pair potential  $U^{\text{eff}}(r)$ . Moreover, it contains no adjustable parameters. We note that  $U^*(r)$  given by (15) is only defined to be the effective pair potential that would generate the colloid-colloid radial distribution (in the hypernetted chain approximation). If the triplet colloid distribution function was available, one should in principle be able to deduce an effective triplet potential which, in general, will *not* be simply a sum of pair potentials obtained herein.

The one-component plasma (OCP) — colloidal particles carrying a charge ( $Z_{\text{OCP}}e$ ) in a uniform neutralizing background — had been used as a model for strongly interacting colloidal systems [15]. It turns out that the colloid-colloid radial distribution function can be fitted quite well by a OCP provided the value of  $Z_{\text{OCP}}$  is suitably chosen. In general,  $Z_{\text{OCP}}$  is an adjustable parameter which is a function of  $Z_0$  and the added electrolyte concentration. While it may be interesting to be able to obtain a good fit to the colloid-colloid radial distribution function using a OCP, there is no guarantee that the dynamical behaviour will be equally well represented by a OCP.

#### 4. Conclusion

By treating a strongly interacting colloidal system as a highly asymmetric electrolyte in which both the ions and colloidal particles are placed on an equal footing, we have derived an appropriate effective pair potential,  $U^{\text{eff}}(r)$  (13), between the colloidal particles. The colloidal particles may then be regarded as an effective one-component system. The long-ranged [ $\approx 1/k^{\text{eff}}$  cf. (12) and (14)] nature of the effective pair potential had been observed in related problems [16,17]. The analytic result for  $U^{\text{eff}}(r)$  provides a considerable simplification of a complicated multicomponent problem and should be a useful starting point for simulation studies on such systems. However, this effective pair potential contains many-body effects in that it is a function of the number density of colloidal particles in the system. As a result, the point of the onset of the disorder-to-order transition predicted by this density-dependent effective pair potential would be at a higher density than that predicted by a density-independent pair potential [3,18].

In a forthcoming paper we shall compare the predictions from our model with some experimental results.

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