

# The screening length of charge-asymmetric electrolytes: A hypernetted chain calculation

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The screening length of the charge-asymmetric electrolyte is calculated in the hypernetted chain approximation. Results are presented for 1:1, 2:1, 3:1, and 4:1 electrolyte with concentrations ranging from  $10^{-5}$  to 1 M. A number of analytic approximations for the screening length are compared to the hypernetted chain data. We find that the second moment approach of Attard [Phys. Rev. E **48**, 3604 (1993)] gives good results for monovalent but not asymmetric electrolyte. A nonlinear version of the second moment approach is found to give good results for asymmetric electrolytes. We also find that the asymptotic formula of Mitchell and Ninham [Chem. Phys. Lett. **53**, 397 (1978)], although giving a null result for monovalent electrolyte, is a satisfactory estimate for asymmetric electrolytes. © 1998 American Institute of Physics. [S0021-9606(98)52030-2]

## I. INTRODUCTION

The interaction of charged surfaces in electrolyte solutions is crucial to the behavior of many physical, chemical, and biological processes. The stability of biological membranes, DNA folding, cellular fusion, the swelling of clays, and the clarification of drinking water are some of the phenomena that depend on forces between charged surfaces. It is therefore important to investigate accurately those properties of electrolyte solutions which influence these forces.

When a charged surface is immersed in an electrolyte solution, ions of opposite charge to the surface (counter-ions) are electrostatically attracted to the surface whilst ions of like charge (co-ions) are repelled. However, due to thermal motions, the counter-ions are not bound to the surface but rather remain dispersed and mobile in the vicinity of the surface. This spatial separation of charge is denoted the electric double layer.

If two similar electric double layers overlap a repulsive force is generated. Along with the attractive van der Waals force that exists between all surfaces, the electric double layer repulsion forms the basis of the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of colloidal interactions.<sup>1</sup> According to this theory, the balance between the repulsive electric double layer force and the van der Waals attraction is what determines the stability or otherwise of colloidal systems.

The properties of the electric double layer have long been subject to theoretical modeling, ranging from the seminal mean-field approach of Debye and Hückel through to the modern liquid state theories which use the full apparatus of statistical mechanics (see the review by Attard<sup>2</sup> for a survey of these modern theories). There have also been many experimental studies of electric double layer forces, especially since the advent of techniques such as the surface force apparatus<sup>3</sup> and the atomic force microscope.<sup>4</sup> Despite their

differences, all these theories predict, and experiment has established, that at sufficiently large distances the electric double layer force is described by an exponential function of distance. Furthermore, the decay constant  $\kappa$  (known as the inverse screening length) depends only on the properties of the bulk electrolyte, not on the surface properties.

The classical prediction for the screening length is the Debye length, Eq. (2.5) below. It arises from the linearized Poisson–Boltzmann equation, which is a mean-field approximation that is expected to be valid at low electrolyte concentrations for monovalent ions. In recent decades, however, various theoretical corrections to the screening length have been proposed,<sup>5–9</sup> corrections which depend on parameters such as ion size and charge asymmetry. There have been several experimental investigations<sup>10–12</sup> aimed at testing the validity of these corrections, although the conclusions remain somewhat controversial. In this paper, we investigate the effect of charge asymmetry on the screening length and compare a number of analytic approximations against accurate numerical calculations.

The departures from the Debye length are relatively small, and it is difficult to obtain the screening length accurately from computer simulations. Hence we use the hypernetted chain calculations as benchmarks to test the more approximate theories, which include asymptotic expansions,<sup>6,8</sup> self-consistent second-moment approaches,<sup>7</sup> and the well-known mean spherical approximation.<sup>5,13</sup> We use the original version of the latter, although a number of successful modifications have been developed, including self-consistent versions<sup>14,15</sup> (see the tests for monovalent electrolyte by Lee *et al.*<sup>16</sup>). Of course the structural properties of colloids and polyelectrolytes with very high charge and size asymmetries have been studied by simulation and integral equation methods<sup>17–21</sup> but our concern here is with the screening

length in the monotonic regime for primitive model ions with equal diameters and charge asymmetries up to 4:1.

## II. THEORETICAL BACKGROUND

The classical theory of electrolytes is the mean-field approach of Debye and Hückel. In the Debye–Hückel theory, the electrolyte is modelled as point ions in a dielectric continuum. The radial distribution function  $g_{\alpha\gamma}(r)$  (proportional to the probability of finding ions of type  $\alpha$  and  $\gamma$  separated by a distance  $r$ ) follows a Boltzmann distribution

$$g_{\alpha\gamma}(r) = e^{-\beta q_\alpha q_\gamma \phi_\alpha(r)}, \quad (2.1)$$

where  $\phi_\alpha(r)$  is the mean electrostatic potential due to the ion  $\alpha$ ,  $q_\alpha$  is the charge of ion species  $\alpha$ , and  $\beta = 1/k_B T$  ( $k_B$  is Boltzmann's constant and  $T$  is temperature). This potential is given by Poisson's equation

$$\nabla^2 \phi_\alpha(r) = \frac{-1}{\epsilon_0 \epsilon} Q_\alpha(r), \quad (2.2)$$

$\epsilon$  is the total permittivity,  $\epsilon = 4\pi\epsilon_0\epsilon_r$ ,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is relative permittivity, where  $Q_\alpha(r)$  is the mean charge density about ion  $\alpha$ ,

$$Q_\alpha(r) = \sum_\gamma q_\gamma \rho_\gamma Q_{\alpha\gamma}(r).$$

Combining Poisson's equation, Eq. (2.2), with the Boltzmann equation, Eq. (2.1), gives the famous Poisson–Boltzmann equation

$$\nabla^2 \phi_\alpha(r) = \frac{-1}{\epsilon_0 \epsilon} \sum_\gamma q_\gamma \rho_\gamma e^{-\beta q_\gamma \phi_\alpha(r)}. \quad (2.3)$$

For weak potentials, the exponential arising from the Boltzmann equation can be linearized. In bulk electrolyte, the potential is spherically symmetric and only depends on the radial coordinate  $r$  so the linearized Poisson–Boltzmann equation becomes a simple differential equation for the potential  $\phi_\alpha(r)$ . The resultant Debye–Hückel total correlation function,  $h_{\alpha\gamma}(r) = g_{\alpha\gamma}(r) - 1$ , is

$$h_{\alpha\gamma}(r) = \frac{-\beta q_\alpha q_\gamma}{\epsilon} \frac{e^{\kappa_D r}}{r}. \quad (2.4)$$

We see that the classical theory predicts that ions are screened from each other at distances greater than  $\kappa_D^{-1}$ . This characteristic length scale of the system is the classical screening length, the Debye length, and is given by

$$\kappa_D^2 = \frac{4\pi\beta}{\epsilon} \sum_\alpha \rho_\alpha q_\alpha^2. \quad (2.5)$$

The Debye–Hückel theory is fundamentally approximate in two ways. First, being a mean-field theory, it does not recognize that the electrostatic potential at  $r$  due to ion  $\alpha$  is affected by the presence of ion  $\gamma$  and that the true potential is in fact determined by complex local rearrangement of the ions. Second, the original Debye–Hückel theory is for point-sized ions, an obvious approximation since ions do have finite size.

We use the so-called primitive model, in which the electrolyte is represented as hard-sphere ions immersed in a continuum dielectric background. The potential between ions of species  $\alpha$ ,  $\gamma$  is thus considered to be the sum of Coulomb's law in media

$$u_{\alpha\gamma}^{\text{coul}}(r) = \frac{1}{4\pi\epsilon_0\epsilon} \frac{q_\alpha q_\gamma}{r},$$

and the hard-sphere potential

$$u_{\alpha\gamma}^{\text{hs}}(r) = \begin{cases} \infty & r < d_{\alpha\gamma} \\ 0 & r > d_{\alpha\gamma} \end{cases}.$$

The primitive model excludes effects such as ionic polarizability and solvent structure.

The fundamental equation of liquid-state theory is the Ornstein–Zernike equation, which is (for a multicomponent fluid)

$$h_{\alpha\gamma}(r) = c_{\alpha\gamma} + \sum_\lambda \rho_\lambda \int h_{\alpha\lambda}(s) c_{\lambda\gamma}(|\mathbf{r}-\mathbf{s}|) ds, \quad (2.6)$$

where  $h_{\alpha\gamma}(r)$  is the total correlation function,  $c_{\alpha\gamma}(r)$  the direct correlation function, with  $\rho_\gamma$  the density of ion species  $\gamma$ . In view of the fact that the direct correlation function approaches the Coulomb potential asymptotically, it is convenient to define a short-ranged function  $\chi_{\alpha\gamma}(r)$  such that

$$\chi_{\alpha\gamma}(r) = c_{\alpha\gamma}(r) + \beta u_{\alpha\gamma}^{\text{coul}}(r).$$

The Ornstein–Zernike equation is an equation for two unknowns; the total correlation function,  $h_{\alpha\gamma}(r)$ , and the direct correlation function  $c_{\alpha\gamma}(r)$  [equivalently  $\chi_{\alpha\gamma}(r)$ ]. In order to solve for these, we must have another equation, the closure relation

$$h_{\alpha\gamma}(r) = -1 + \exp\{h_{\alpha\gamma}(r) - \chi_{\alpha\gamma}(r) + b_{\alpha\gamma}(r)\}, \quad (2.7)$$

where  $b_{\alpha\gamma}(r)$  is the so-called bridge function. The closure relation is exact. However, the bridge function is generally extremely difficult to evaluate, if not intractable. The hypernetted chain (HNC) approximation consists of neglecting the bridge function entirely, that is  $b_{\alpha\gamma}(r) = 0$ . The Ornstein–Zernike equation and the HNC closure are then solved for the correlation functions  $h_{\alpha\gamma}(r)$  and  $\chi_{\alpha\gamma}(r)$ .

Exact asymptotic analysis of the Ornstein–Zernike shows that total correlation function takes on a Debye–Hückel-type form as  $r \rightarrow \infty$ ,<sup>7,8</sup>

$$h_{\alpha\gamma}(r) \sim \frac{-\beta \tilde{q}_\alpha \tilde{q}_\gamma}{\epsilon \nu} \frac{e^{\kappa r}}{r} \quad (2.8)$$

with the screening length,  $\kappa^{-1}$  formally given by

$$\kappa^2 = \frac{4\pi\beta}{\epsilon} \sum_\alpha \rho_\alpha \tilde{q}_\alpha q_\alpha. \quad (2.9)$$

The scaling factor  $\nu$  and the effective charge  $\tilde{q}_\alpha$  are functionals of  $\hat{\chi}_{\alpha\gamma}(k)$ , the Fourier transform of  $\chi_{\alpha\gamma}(r)$ , evaluated at  $k = i\kappa$ . Note that  $\kappa$  may be complex, which corresponds to oscillatory asymptotic decay of the total correlation function. The HNC approximation is very reliable, and the results for the screening length can be considered to be exact, with little

difference in the results upon inclusion of the first bridge diagram.<sup>7</sup> The HNC results shall therefore be taken as the benchmark for the purposes of this paper.

The Ornstein–Zernike equation implies that the total correlation function must satisfy moment conditions, the two most important of which are (see Ref. 7 for a derivation) the zeroth moment, or electroneutrality condition,

$$q_\alpha = - \sum_\gamma \rho_\gamma q_\gamma \int h_{\alpha\gamma}(r) d\mathbf{r}, \quad (2.10)$$

and the second moment or Stillinger–Lovett condition,

$$1 = \frac{-4\pi\beta}{6\epsilon} \sum_{\gamma,\lambda} q_\gamma q_\lambda \rho_\gamma \rho_\lambda \int h_{\gamma\lambda}(r) r^2 d\mathbf{r}. \quad (2.11)$$

The linearized Debye–Hückel theory is obtained when the short-ranged part of the direct correlation function is neglected,  $\chi_{\alpha\gamma}(r) = 0$ . However, the linearized Debye–Hückel theory will only obey the two moment conditions, Eqs. (2.10), (2.11) if we have point-sized ions.<sup>7</sup> Furthermore, the linearized Debye–Hückel theory is only expected to hold for low charge electrolytes (i.e., monovalent electrolyte), since it neglects higher-order electrostatic effects. Both of these shortcomings are due to the neglect of the short-ranged part of the direct correlation function,  $\chi_{\alpha\gamma}(r) = 0$ . Nonetheless, the exponential form of the correlation function is still useful and convenient, especially in light of the fact that the exact asymptote of the Ornstein–Zernike equation is of exponential form.<sup>2,7</sup> Much theoretical effort has therefore been expended obtaining expressions for the screening length that differ from the Debye length but also include effects due to moment condition constraints and higher-order electrostatic effects. The analytic result of Attard<sup>7</sup> reflects the moment conditions constraint. It is obtained by substituting the Debye–Hückel functional form

$$h_{\alpha\gamma}(r) = \frac{-\beta q_\alpha q_\gamma e^{\kappa r}}{\epsilon \nu r}$$

into the moment conditions Eqs. (2.10), (2.11). A cubic equation for the screening length  $\kappa^{-1}$  in terms of the Debye length  $\kappa_D^{-1}$  and the hard-sphere diameter  $d$  is then obtained (see Ref. 7 for details). This cubic equation has the solution, correct to third-order,

$$\frac{\kappa}{\kappa_D} = \frac{1}{\sqrt{1 - (\kappa_D d)^2/2 + (\kappa_D d)^3/6}}. \quad (2.12)$$

Note that there is no extra dependence on the charge of the ions, beyond that in the Debye length.

Another analytical approach that will be investigated in this paper is that of Mitchell and Ninham.<sup>6</sup> These authors expand the short range part of the direct correlation diagrammatically and find an expression for the screening length (for binary electrolyte) given by

$$\frac{\kappa}{\kappa_D} = 1 + \frac{\Lambda \ln 3}{8} \frac{(\rho_1 z_1^3 + \rho_2 z_2^3)^2}{(\rho_1 z_1^2 + \rho_2 z_2^2)^2}, \quad (2.13)$$

where  $\rho_{1,2}$ ,  $z_{1,2}$  are the densities and valences of the two components of the electrolyte, and where  $\Lambda = \kappa_D \beta q^2 / \epsilon$ . Note that the correction to the Debye length vanishes for symmetric electrolytes.

In contrast to the above result of Attard, the Mitchell and Ninham formula does not depend on the hard-sphere diameter of the ions but does include an extra dependence on the ion valences. The result of Mitchell and Ninham was extended by Kjellander and Mitchell<sup>8</sup> to include a term for symmetric electrolyte

$$\begin{aligned} \frac{\kappa}{\kappa_D} = 1 + \frac{\Lambda \ln 3}{8} (|z_1| - |z_2|)^2 \\ + \frac{\Lambda^2 \ln \Lambda}{12} (|z_1|^2 - |z_1||z_2| + |z_2|^2)^2. \end{aligned} \quad (2.14)$$

It should be noted that both the Mitchell and Ninham and the Kjellander and Mitchell equations are asymptotic formulae, derived on the premise of an infinitely dilute electrolyte and so may not be expected to hold for finite concentrations.

It is worth mentioning that Stell and Lebowitz<sup>22</sup> have also obtained asymptotic expressions for the screening length. Their result depends upon a certain integral of the radial distribution function of the reference hard-sphere fluid. To leading order their correction to the Debye length vanishes for an electrolyte with equal sized ions, but they also give higher order terms that survive in this case.

Another, relatively simple, numerical approach to estimation of the screening length is what we shall term the nonlinear Debye–Hückel approach. Like the analytic approach of Attard, Eq. (2.12), the nonlinear Debye–Hückel approximation used in this paper consists of a specified functional form of the total correlation function under the constraint that it must obey the moment conditions. However, instead of imposing the exponential form upon the correlation function we assume that potential of mean force has the form

$$w_{\alpha\gamma}(r) = \frac{q_\alpha q_\gamma e^{\kappa r}}{\epsilon \nu r}, \quad r > d \quad (2.15)$$

and seek values for  $\kappa$  and  $\nu$  such that the correlation function  $h_{\alpha\gamma}(r) = -1 + \exp(-\beta w_{\alpha\gamma}(r))$  satisfies the two moment conditions, Eqs. (2.10) and (2.11).<sup>7</sup> Through a numerical approach like the HNC approximation, it is much easier to implement computationally than the hypernetted chain theory.

We shall also consider the well-known mean spherical approximation (MSA).<sup>5,13</sup> In this approach, the short-range part of the direct correlation function is set to zero outside of the hard-sphere additive diameter, that is,  $\chi_{\alpha\gamma}(r) = 0$ ,  $r > d_{\alpha\gamma}$ . Like all the theories considered, MSA predicts that the total correlation function is exponentially screened. However, unlike the other theories considered, the MSA predicts that the inverse screening length  $\kappa$  approaches the inverse Debye length  $\kappa_D$  from below in the limit of infinite dilution.

### III. RESULTS AND DISCUSSION

The Ornstein–Zernike equation was solved for a binary primitive model electrolyte using the standard Fourier trans-

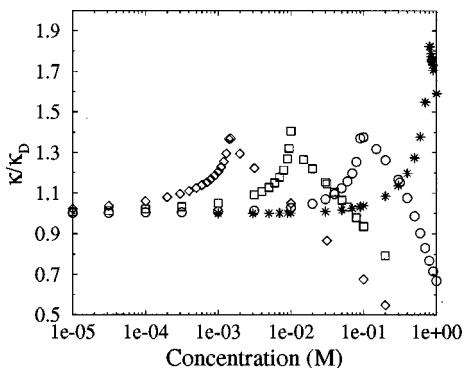


FIG. 1. HNC screening length results. Plotted is the ratio of the inverse screening length,  $\kappa$ , to the inverse Debye length,  $\kappa_D$ , against concentration. The stars, circles, squares, and diamonds are 1:1, 2:1, 3:1, and 4:1 electrolyte, respectively.

form approach.<sup>2,7</sup> Once the short-ranged part of the direct correlation function  $\chi_{\alpha\gamma}(r)$  was obtained, Eq. (2.9) was used to get the screening length. Since the expression for  $\kappa$ , Eq. (2.9), requires  $\tilde{q}(k)$  evaluated at  $i\kappa$ , this equation must be solved iteratively. This was done, starting with an initial guess of  $\kappa = \kappa_D$  and iterating until convergence to at least six significant figures.

Figure 1 shows the ratio of the inverse screening length to the inverse Debye length vs concentration for 4:1, 3:1, 2:1, 1:1 electrolytes in the HNC calculation. Unless otherwise indicated all the following results are for ions with equal hard-sphere diameters of  $d = 4.5 \text{ \AA}$ . The cusp in these curves shows the concentration at which  $\kappa$  becomes complex and an oscillatory, decaying correlation function ensues.<sup>7</sup> Since it only makes sense to discuss an effective screening length in the monotonic regime, particularly with reference to experimental results, we shall focus on this regime here.

Figure 2 shows  $\kappa/\kappa_D$  vs concentration for a 1:1 electrolyte comparing the HNC, nonlinear Debye–Hückel, and the various analytical approximations. We see that the nonlinear Debye–Hückel numerical result and Attard’s third-order equation, Eq. (2.12), are in good agreement with the HNC

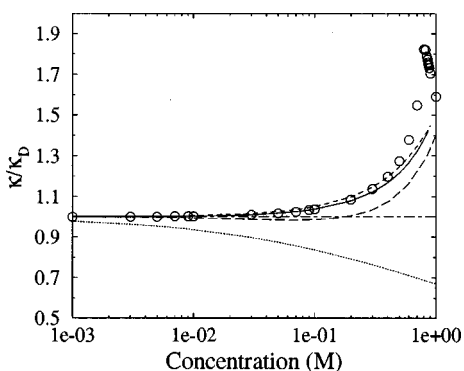


FIG. 2. Screening length, 1:1 electrolyte. As in the preceding figure, the ratio of the inverse screening length,  $\kappa$ , to the inverse Debye length,  $\kappa_D$ , against concentration is plotted. From top to bottom, the symbols are the HNC results, the short-dashed line is Attard’s formula, Eq. (2.12), the solid line the numerical nonlinear Debye–Hückel-type result, the dot–dashed line the Mitchell and Ninham formula, Eq. (2.13), the long-dashed line is Kjellander and Mitchell’s formula, Eq. (2.14), and the dotted line the MSA expression.

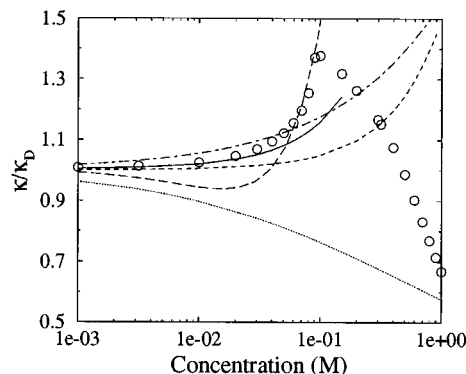


FIG. 3. As in the preceding figure but for the 2:1 electrolyte.

result. As noted above the Mitchell and Ninham correction to the Debye length, Eq. (2.13), vanishes for a symmetric electrolyte. Unlike any of the other results which predict a monotonic variation in  $\kappa/\kappa_D$  for all concentrations considered, the Kjellander and Mitchell result, Eq. (2.14), predicts that  $\kappa < \kappa_D$  in the regime  $10^{-2} \text{ M} \sim 10^{-1} \text{ M}$  and thereafter  $\kappa > \kappa_D$ , with the crossover at around  $0.1 \text{ M} \sim 0.2 \text{ M}$ . The MSA result predicts that  $\kappa < \kappa_D$ , in complete contrast to the HNC result which has  $\kappa > \kappa_D$  for all concentrations considered. Modified versions of the MSA (Refs. 14–16) will likely show better agreement with the HNC, although we have not tested these here.

Figure 3 shows results for a 2:1 electrolyte. Once again the nonlinear Debye–Hückel result agrees reasonably well with the HNC results. The deviation predicted by the Mitchell and Ninham formula, Eq. (2.13), is now nonzero and, although somewhat overestimating the deviation, does exhibit the general behavior of the HNC result, that  $\kappa > \kappa_D$ . On the other hand, the Kjellander and Mitchell result, Eq. (2.14), again predicts that  $\kappa < \kappa_D$  initially before crossing over to  $\kappa > \kappa_D$ , which is in complete contrast to the HNC and nonlinear Debye–Hückel results. The analytical result of Attard, Eq. (2.12), does not show any extra deviation due to the charge-asymmetry, yet there clearly is such an effect in the HNC results. Consequently, Attard’s result will not be compared in the further cases investigated. The MSA result again predicts that  $\kappa < \kappa_D$  for all concentrations considered.

Figures 4 and 5 plot  $\kappa/\kappa_D$  vs concentration for the 3:1

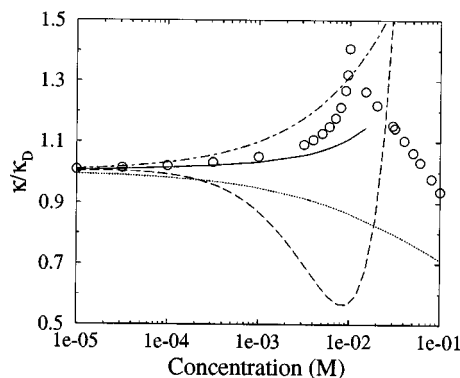


FIG. 4. As for the preceding figure except for the 3:1 electrolyte and Attard’s formula is no longer plotted.

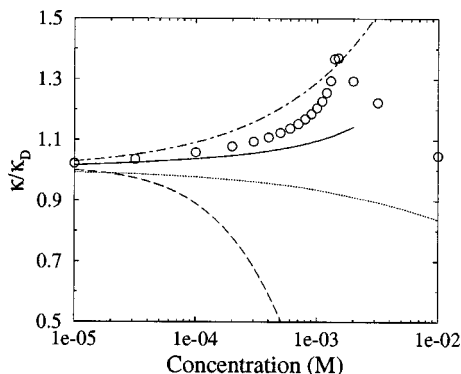
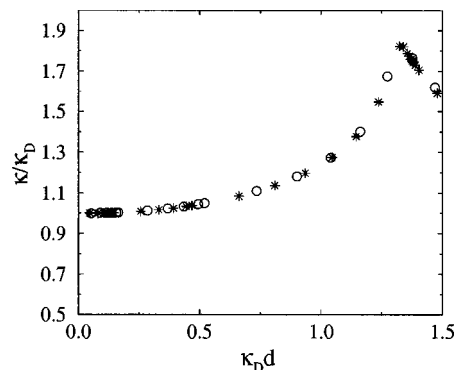


FIG. 5. As in the preceding figure but for the 4:1 electrolyte.

and 4:1 electrolyte, respectively. The results are much the same as for the previous cases. The numerical nonlinear Debye–Hückel results agree best with the HNC result, although the agreement becomes progressively worse as the valence asymmetry increases. The Mitchell and Ninham result once again, if not quantitatively, at least qualitatively agrees with the HNC data. The MSA results are still in contrast to the HNC data, with  $\kappa/\kappa_D$  monotonic and less than unity for all concentrations considered for both the 3:1 and 4:1 electrolyte. For the 3:1 electrolyte, the Kjellander and Mitchell formula shows even more striking nonmonotonic behavior whilst for the 4:1 case the Kjellander and Mitchell formula becomes completely unphysical, with  $\kappa/\kappa_D$  passing through zero and turning negative (not shown on the graph).

These results show that the nonlinear Debye–Hückel approach to the screening length agrees reasonably well with the hypernetted chain theory. Of the analytical approaches, Attard’s result, Eq. (2.12), is successful for the monovalent case but not for the 2:1, 3:1, and 4:1 electrolytes. On the other hand, the result of Mitchell and Ninham does not predict a correction for the monovalent electrolyte, but gives a fair estimate of the screening length for the asymmetric electrolytes. It is no surprise that the Kjellander and Mitchell formula completely breaks down at the electrolyte concentrations considered in this paper, since it was derived at infinite dilution. What is surprising is that the Mitchell and Ninham formula gives such a reasonable result, since it too was derived at infinite dilution.

As noted in Sec. II, the analytical result of Attard, Eq. (2.12), depends on the hard-sphere diameter of the ions  $d$ , indeed predicting that  $\kappa/\kappa_D$  is a function of  $\kappa_D d$  only. If this is true then we should find that a plot of  $\kappa/\kappa_D$  vs  $\kappa_D d$  gives the same curve, regardless of the size of the ions. Figure 6 is such a plot of the HNC results for a 1:1 electrolyte at two different hard-sphere diameters, 4.5 Å and 5.0 Å. We see that the two cases do indeed lie on the same curve, a result already established by Ennis *et al.*<sup>23</sup> and by Attard.<sup>7</sup> However, given that we have already established that Attard’s approach fails for an asymmetric electrolyte, it is by no means obvious that  $\kappa/\kappa_D$  will show similar dependence on  $\kappa_D d$  for asymmetric electrolytes. In order to test this,  $\kappa/\kappa_D$  against  $\kappa_D d$  for a 2:1 electrolyte at two different hard-sphere diameters, 4.5 Å and 5.0 Å, was calculated in the HNC approximation. The results are plotted in Fig. 7.

FIG. 6.  $\kappa/\kappa_D$  vs  $\kappa_D d$  for the 1:1 electrolyte. The stars are for  $d=4.5$  Å and the circles  $d=5.0$  Å.

We see that the two cases lie on the same curve, as in the monovalent case. These results indicate that the screening length has the functional form

$$\frac{\kappa}{\kappa_D} = f(q_\alpha, q_\gamma, \kappa_D d). \quad (3.1)$$

Furthermore, it seems, given the success of the numerical nonlinear Debye–Hückel-type approximation, compared to the linear version, that the influence of charge-asymmetry on the screening length is an essentially nonlinear effect.

#### IV. CONCLUSION

We have examined the effect of charge-asymmetry on the screening length of electrolytes using the HNC approximation. We found that the simpler nonlinear Debye–Hückel-type numerical scheme gives good results. We found that the analytical result of Attard<sup>7</sup> gives good results for the monovalent but not the asymmetric electrolyte. On the other hand, we have shown that the Mitchell and Ninham asymptotic formula,<sup>6</sup> although giving a null result for the monovalent electrolyte, is a satisfactory estimate for asymmetric electrolytes. We have also shown that the asymptotic expansion of Kjellander and Mitchell is inapplicable at realistic concentrations, and that the original MSA is likewise inaccurate. It is possible that more sophisticated, self-consistent versions of the MSA will give a more reliable estimate of the screening length of asymmetric electrolytes.

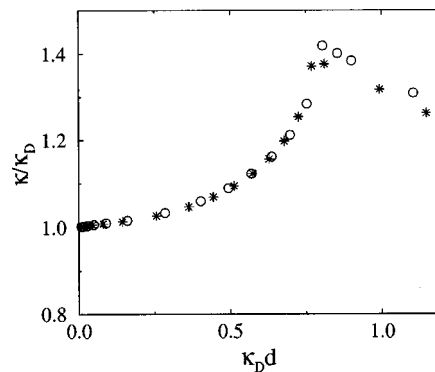


FIG. 7. As in the preceding figure but for the 2:1 electrolyte.

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