A model for association in electrolytes. Analytic solution of the hypernetted-chain/mean spherical approximation

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We study the structural and thermodynamic properties of electrolytes in which the association between oppositely charged ions $(A^+ + B^- \rightleftharpoons AB)$ is represented by a sticky electrolyte model (SEM) which allows positive and negative ions of diameter σ to be bonded at a distance $L \leqslant \sigma/2$. The model is solved for a 2–2 electrolyte at concentrations up to 2 M and for $L = \sigma/2$ using the hypernetted-chain (HNC) approximation for the correlation functions within the spherical core and the mean spherical (MS) approximation outside. The number of AB dimers at a separation L is found to increase with concentration while there is a reduction in the number of contact ion pairs below that predicted by the restricted primitive model (RPM) from which stickiness is absent. The structural and thermodynamic properties of the SEM and RPM prove to be significantly different and sufficiently interesting to justify future applications of the SEM to molten salts and molecular solvents, especially if the ion–ion interactions can be treated with greater accuracy. The equilibrium properties of the fully associated system of extended dipoles with charges separated at a distance $L = \sigma/2$ are also given in the mean spherical approximation.

I. INTRODUCTION

In a series of papers,[1,2] Cummings and Stell have discussed a novel analytic approach to the study of chemical reactions in nonideal systems; statistical mechanical studies of chemical bonding have also been reported earlier by Andersen[3] and Høye and Olaussen.[4] Cummings and Stell studied the simplest association reaction[1]

$$A + B \rightleftharpoons AB \qquad (1.1)$$

by considering a model equimolar mixture of A and B atoms in which the three pair potentials $\phi_{AA}(r)$, $\phi_{AB}(r)$, and $\phi_{BB}(r)$ are given by

$$
\begin{aligned}
\phi_{AA}(r) = \phi_{BB}(r) &= \infty \quad r < \sigma \\
&= 0 \quad r > \sigma
\end{aligned} \right\} , \qquad (1.2a)
$$

$$
\begin{aligned}
\phi_{AB}(r) &= \epsilon_1 & 0 < r < L - w/2 \\
&= -\epsilon_2 & L - w/2 < r < L + w/2 \\
&= \epsilon_1 & L + w/2 < r < \sigma \\
&= 0 & r > \sigma
\end{aligned} \right\} , \qquad (1.2b)
$$

where ϵ_1 is the height of the potential mound which models the repulsion between the unlike species atoms and ϵ_2 is the depth of a deep attractive well of width w centered at interparticle separation L. As argued in detail in Ref. 1 [referred to throughout this paper as I, with Eq. (i.j) from I being denoted by (I.i.j)], the pair potentials (1.2) define a mixture in which type A atoms can "react" with type B atoms to form AB diatomics when a suitable definition for the existence of AB pairs is chosen: an appropriate such definition studied in I is to consider two atoms as "bound" into a diatomic if the interaction energy is large and negative, and $L + w/2 < \sigma/2$. The pair potentials (1.2) exhibit the property of *steric saturation*,[4,5] i.e., given the above definition of binding, each A and B atom should belong to *at most* one diatomic molecule.

By considering the Hamiltonian model (1.2) in the limit $w \rightarrow 0$, $\epsilon_2 \rightarrow \infty$ while holding the second virial coefficient fixed, Cummings and Stell were able to solve the Percus–Yevick (PY)[6] approximation analytically. They showed that when $\epsilon_1/k_B T$ (where k_B is Boltzmann's constant and T is absolute temperature) is greater than ~ 3, the results for the mass action association constant k defined are qualitatively and quantitatively close to those for $\epsilon_1 \rightarrow \infty$, a limit in which the analysis becomes considerably simpler and the definition of associated pairs is conceptually unambiguous. The mass action association constant k is given by

$$k = \rho_{AB}/\rho_A \rho_B , \qquad (1.3a)$$

where ρ_{AB} is the number density of AB dimers, defined by

$$\rho_{AB} = \rho_{A0}\rho_{B0} \int_{L^-}^{L^+} g_{AB}(r)\, d\mathbf{r}, \qquad (1.3b)$$

where ρ_i, ρ_{i0} $(i = A,B)$ are the monomer density and the total density, respectively, of species i, and $g_{AB}(r)$ is the distribution function for the pair AB.

In this paper, we turn our attention to the problem of ion pairing in electrolytes by studying the association reaction

$$A^+ + B^- \rightleftharpoons AB \qquad (1.4)$$

in a continuum dielectric solvent. The prototypes of the pair potentials assumed are given by

$$
\begin{aligned}
\phi_{AA}(r) = \phi_{BB}(r) &= \infty & r < \sigma \\
&= \frac{e^2}{\epsilon r} & r > \sigma
\end{aligned} \right\} , \qquad (1.5a)
$$

$$
\begin{aligned}
\phi_{AB}(r) &= \epsilon_1 & 0 < r < L - w/2 \\
&= -\epsilon_2 & L - w/2 < r < L + w/2 \\
&= \epsilon_1 & L + w/2 < r < \sigma \\
&= -\frac{e^2}{\epsilon r} & r > \sigma
\end{aligned} \right\} , \qquad (1.5b)
$$

where ϵ is the dielectric constant of the (continuum) solvent and e is the magnitude of the charge on the ions. The pair potentials (1.5), which are shown schematically in Fig. 1, make it clear that we are studying a symmetric electrolyte (1–1 or 2–2) for which electroneutrality demands that an equimolar mixture of ions be considered. We discuss the solution to this model for electrolytes in the limit when the width of the well $w\rightarrow 0$ and the height ϵ_1 and the depth ϵ_2 both tend to infinity. Unlike the uncharged system studied by Cummings and Stell,[1,2] however, we employ the hypernetted-chain (HNC) closure for the correlation functions within the spherical core of diameter σ and the mean spherical approximation (MSA) for the essentially electrostatic part of the correlation functions outside the core diameter. The Hamiltonian model (1.5) becomes identical to the restricted primitive model (RPM) for electrolytes when the well is removed ($w = \epsilon_2 = 0$) and ϵ_1 is maintained at infinity.

The RPM for the electrolytes, which has been the subject of extensive study, has been reviewed by Friedman,[7,8] Rasaiah,[9] and, more recently, by Hafksjold and Stell,[10] and is defined by the following expression for the pair potentials:

$$\phi_{AA}(r) = \phi_{BB}(r) = \infty \qquad r < \sigma$$
$$= \frac{e^2}{\epsilon r} \qquad r > \sigma \qquad (1.6a)$$

$$\phi_{AB}(r) = \infty \qquad r < \sigma$$
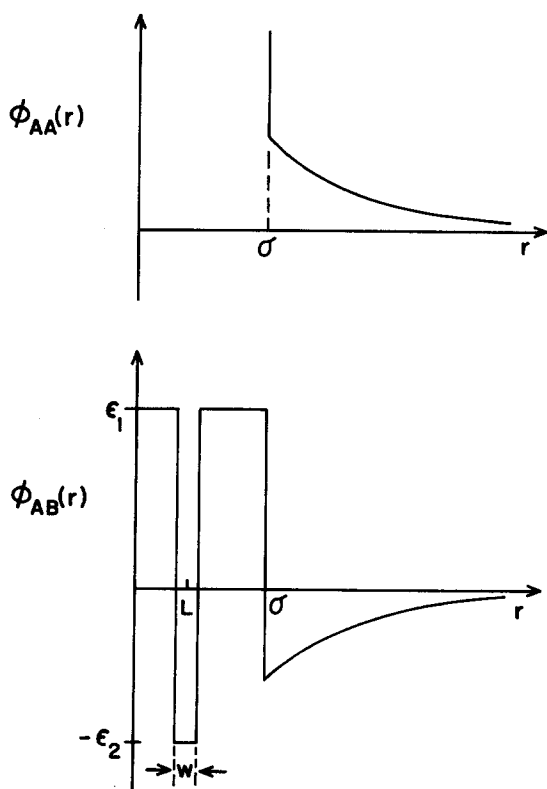$$= -\frac{e^2}{\epsilon r} \qquad r > \sigma \qquad (1.6b)$$

FIG. 1. The pair potential for the sticky electrolyte model (SEM) studied in this paper, and defined by Eqs. (1.5). The model parameters used are $w = 0.1\sigma$, $\epsilon_2/k_B = 4000$ K, and $L = \sigma/2$ for a 2–2 electrolyte ($e = 2$ esu) in a solvent of dielectric constant $\epsilon = 78.358$.

The model has provoked a great deal of study over the years for a number of reasons, the foremost being that it is a conceptually simple prototypical model for electrolytes that possess two features of such systems: a harsh repulsive core at sufficiently short separations and a Coulombic interaction which is asymptotically correct at large separations. The most accurate integral equation approximation for the RPM is the hypernetted-chain approximation (HNC), and considerable effort has been expended over the past decade in obtaining solutions to this approximation numerically.[11–16] The mean spherical approximation (MSA)[17] is also of considerable interest for this model since it was shown to be analytically solvable by Waisman and Lebowitz.[18] The extension of this analysis to ions of arbitrary sizes by Blum[19] enables the thermodynamic properties of low molarity 1–1 electrolytes to be fitted quite accurately and routinely.[20]

When the charges on the ions are increased, however, even the hypernetted-chain equation fails to provide a completely reliable description of the equilibrium properties of 2–2 electrolytes at low concentrations. This failure is accompanied by a dramatic rise in the magnitude of the pair correlation functions at contact, $g_{+-}(\sigma)$, between oppositely charged ions,[16] a clear manifestation of the tendency to form ion pairs. At a concentration of 10^{-4} molar, e.g., $g_{+-}(\sigma)$ is nearly 715 for a 2–2 aqueous electrolyte solution at 25 °C when the system is treated according to the RPM. The problem of highly charged electrolytes at room temeprature, or equivalently moderately charged ions at low temperature or in solvents with low dielectric constants—the relevant parameter in the RPM is $e^2/(\epsilon k_B T\sigma)$—is the problem of treating ion pairing and more complex association effects. The appearance of a low-density phase transition for ionic systems below a certain critical temperature[21] has been discussed recently in terms of this tendency to ion association.[7,22] One example is the work of Ebeling and Grigo,[23] which is a modification of the classical Bjerrum theory[24,25] with the free ions treated according to the mean spherical approximation and the equilibrium constant for association defined by splitting the second virial coefficient arbitrarily into hard sphere, long-range, and bound parts. The ratio of free ions to ion pairs is obtained by minimizing the free energy. All of this work and recent extensions to the hypernetted-chain equation[26] treat the ions in the RPM. Our discussion, however, applies to a different Hamiltonian model which includes "stickiness" between oppositely charged ions leading to association effects quite distinct from those expected in the RPM. Since the free ions of our system are treated in the MSA, a comparison of our results with the corresponding MSA calculations for the RPM should provide an indication of how stickiness or bonding between oppositely charged ions affects the thermodynamic and structural properties of the system.

The definition of ion pairing that we use in our calculation of the equilibrium constant corresponds exactly to the definition of dimerization used in I for the corresponding uncharged system, with $L = \sigma/2$ in Eq. (1.3b). These dimers are not the contact ion pairs, at $r = \sigma$, referred to earlier in this section nor do they correspond to the definitions of ion pairing introduced by Bjerrum.[24] Accordingly, the associ-

ation constants k that are calculated in this paper are not strictly comparable to the association constants often discussed in the electrochemical literature.[25] By using the same definitions of ρ_{AB} and k for the charged and uncharged systems, however, we can determine how these quantities are changed when the system is charged. Conversely adding stickiness to the interactions already present in the restricted primitive model for electrolytes produces changes in the number of contact ion pairs, which can also be calculated by us. Our analysis also provides the equilibrium properties of the fully associated system of extended dipoles in the mean spherical approximation for $L = \sigma/2$.

This paper is organized as follows: Section II contains the details of the Hamiltonian models employed, the approximation used and the analytic solution using Wiener–Hopf factorization.[27,28] Results for the structural, association, and thermodynamic properties are presented and discussed in Sec. III.

II. FURTHER DETAILS OF THE MODEL AND ITS ANALYTIC SOLUTION IN THE HYPERNETTED-CHAIN/MEAN SPHERICAL APPROXIMATION

We now consider the limiting process $w \to 0$, $\epsilon_1, \epsilon_2 \to \infty$ more carefully. When we begin by taking the limit $\epsilon_1 \to \infty$ for the unlike pair potential (1.5b), we are led to consider the second virial coefficient $B_{2,AB}$, defined by

$$B_{2,AB} = -(1/2)\int f_{AB}(r)d\mathbf{r}, \qquad (2.1)$$

where $f_{ij}(r)$, the Mayer f function is given by

$$f_{ij}(r) = \exp[-\phi_{ij}(r)/k_B T] - 1.$$

In this limit, $B_{2,AB}$ is given by

$$B_{2,AB}(T) = \frac{2\pi\sigma^3}{3} - 2\pi\left(L^2 w + \frac{w^3}{12}\right)\exp(\epsilon_2/k_B T)$$
$$- 2\pi\int_\sigma^\infty \{\exp[e^2/(\epsilon k_B T r)] - 1\}r^2\, dr.$$
$$(2.2)$$

In the limit $\epsilon_2 \to \infty$, $w \to 0$, we follow Baxter[30] and define another Mayer f function

$$f^*_{AB}(r) = -1 + \frac{L}{12\tau}\delta(r - L) \quad 0 < r < \sigma$$
$$= -1 + \exp[e^2/(\epsilon k_B T r)] \quad r > \sigma \qquad (2.3)$$

with second virial coefficient

$$B^*_{2,AB}(\tau) = \frac{2\pi\sigma^3}{3} - \frac{2\pi L^3}{12\tau}$$
$$- 2\pi\int_\sigma^\infty \{\exp[e^2/(\epsilon k_B T r)] - 1\}r^2\, dr. \quad (2.4)$$

The constant τ is obtained by equating $B^*_{2,AB}(\tau)$ and $B_{2,AB}(T)$:

$$\tau = \frac{L^3}{12L^2 w + w^3}\exp(-\epsilon_2/k_B T). \qquad (2.5)$$

Thus, in the computations to be reported in this paper, we will consider the Hamiltonian model for which the Mayer function is defined by Eq. (2.3) to be an approximation for

the model (1.5) in the limit $\epsilon_1 \to \infty$. By choosing fixed values of ϵ_2, w, and L, we find the temperature dependence of τ from Eq. (2.5).

The integral equation approximation to be used is defined in terms of the radial distribution function $g_{ij}(r)$ (proportional to the probability density of finding ions i and j separated by distance r), the total correlation function $h_{ij}(r) = g_{ij}(r) - 1$, and the direct correlation function $c_{ij}(r)$ defined by the Ornstein–Zernike (OZ) equation[31] for mixture of m species

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^m \rho_{k0}\int c_{ik}(s)h_{kj}(|\mathbf{r} - \mathbf{s}|)d\mathbf{s}, \qquad (2.6)$$

where ρ_{k0} is the *total* number density of species k ions (i.e., counting free ions as well as ions associated into pairs). The HNC approximation[6] is given by

$$c_{ij}(r) = -\beta\phi_{ij}(r) + h_{ij}(r) - \ln[1 + h_{ij}(r)] \qquad (2.7)$$

while the MSA for systems with hard core potentials is given by[17]

$$h_{ij}(r) = -1, \quad r < \sigma_{ij},$$

$$c_{ij}(r) = -\beta\phi_{ij}(r), \quad r > \sigma_{ij}, \qquad (2.8)$$

where σ_{ij} is the diameter for the hard core interaction between species i and j ions and $\beta = 1/k_B T$. (In the case under consideration in this paper, $\sigma_{ij} = \sigma$.) For our model, we propose a hybrid approximation obtained by using the HNC approximation inside the core ($r < \sigma$) and the MSA outside the core ($r > \sigma$). Thus, for our binary mixture of A and B ions of equal diameter we have

$$c_{ij}(r) = -\beta\phi_{ij}(r) + h_{ij}(r) - \ln[1 + h_{ij}(r)], \quad r < \sigma_{ij}, \quad (2.9a)$$
$$c_{ij}(r) = -\beta\phi_{ij}(r), \quad r > \sigma_{ij} \qquad (2.9b)$$

which we refer to as the hypernetted-chain/mean spherical approximation (HNC/MSA). Equation (2.9a) implies that $h_{AB}(r)$ contains a delta function at $r = L$, so that in the HNC/MSA,

$$h_{AB}(r) = -1 + \frac{\lambda L}{12}\delta(r - L), \quad 0 < r < \sigma, \qquad (2.10a)$$

$$h_{AA}(r) = h_{BB}(r) = -1, \quad 0 < r < \sigma. \qquad (2.10b)$$

The parameter λ which measures the extent of association between oppositely charged ions is related to the parameter τ (a dimensionless measure of the temperature T and the well depth ϵ) through Eq. (2.9a). The average number $\langle N \rangle$ of ions "bonded" to a chosen ion is given by

$$\langle N \rangle = \rho_{A0}\int_{L-}^{L+} g_{AB}(r)d\mathbf{r} = \eta\lambda\left(\frac{L}{\sigma}\right)^3, \qquad (2.10c)$$

where $\eta = \pi\rho_{A0}\sigma^3/3$ and we expect $0 \leqslant \langle N \rangle \leqslant 1$.

Thus, the mathematical problem to be solved consists of the mixture OZ equation (2.6) for $m = 2$ species subject to the closure (2.10) inside the core ($r < \sigma$) and (2.9b) outside the core. As we shall see, this problem has some features similar to the problem solved in I, and for notational continuity with that paper, it is useful to label A (B) ions as species 1 (2) particles. For the equimolar ($\rho_{10} = \rho_{20} = \rho/2$) associating electrolyte, we can define the sum (S) and difference (D) correlation functions by

$$h_S(r) = \frac{h_{12}(r) + h_{11}(r)}{2}, \quad h_D(r) = \frac{h_{12}(r) - h_{11}(r)}{2}$$

$$(2.11)$$

and similarly for $c_S(r)$ and $c_D(r)$. The OZ equations for the mixture are then found to be equivalent to the decoupled equations

$$h_S(r) = c_S(r) + \rho \int c_S(s) h_S(|\mathbf{r} - \mathbf{s}|) d\mathbf{s}, \qquad (2.12a)$$

$$h_D(r) = c_D(r) - \rho \int c_D(s) h_D(|\mathbf{r} - \mathbf{s}|) d\mathbf{s}, \qquad (2.12b)$$

subject to closures

$$h_S(r) = -1 + \frac{\lambda L}{24} \delta(r - L), \quad 0 < r < \sigma, \qquad (2.13a)$$

$$c_S(r) = 0, \quad r > \sigma, \qquad (2.13b)$$

$$h_D(r) = \frac{\lambda L}{24} \delta(r - L), \quad 0 < r < \sigma, \qquad (2.14a)$$

$$c_D(r) = e^2/(\epsilon k_B T r), \quad r > \sigma. \qquad (2.14b)$$

We limit our attention in this paper to $L = \sigma/2$ and consider the sum and difference equations separately. For this choice of L it follows from Eq. (2.10c) that $\langle N \rangle = \eta\lambda /8$.

A. The sum equations

Since from Eq. (2.13b) the sum direct correlation function $c_S(r)$ is zero beyond $r = \sigma$, Baxter factorization of the OZ equation (2.12a) is straightforward, yielding[27]

$$r h_S(r) = -q_S'(r) + 2\pi\rho \int_0^\sigma dt\, q_S(t)(r - t) h_S(|r - t|), \qquad (2.15a)$$

$$r c_S(r) = -q_S'(r) + 2\pi\rho \int_r^\sigma dt\, q_S(t - r) q_S'(t), \qquad (2.15b)$$

where $q_S(r)$, the Baxter q function, is zero for $r < 0$ and $r \geqslant \sigma$ and $q_S'(r)$ is the derivative of $q_S(r)$ with respect to r. Application of the closure condition (2.13a) on $0 < r < \sigma$ results in the following differential-difference equation for $q_S(r)$:

$$q_S'(r) + p[q_S(r + \sigma/2) - q_S(r - \sigma/2)] + \frac{\lambda\sigma^2}{96} \delta(r - \sigma/2)$$

$$= ar + b, \qquad (2.16)$$

where

$$p = \frac{2\pi\rho\lambda L^2}{24} = \frac{\pi\rho\sigma^2\lambda}{48}, \qquad (2.17)$$

$$a = 1 - 2\pi\rho \int_0^\sigma q_S(t) dt, \qquad (2.18a)$$

and

$$b = 2\pi\rho \int_0^\sigma t q_S(t) dt. \qquad (2.18b)$$

As discussed in detail in I, the solution to Eq. (2.16) is given by

$$q_S(r) = -\frac{a}{p} r + \frac{a}{p^2}\left(1 - \frac{v}{2}\right) - \frac{b}{p}$$

$$+ A\cos(pr) + B\sin(pr), \quad 0 < r < \sigma/2$$

$$= \frac{a}{p} r + \frac{a}{p^2}\left(1 - \frac{v}{2}\right) + \frac{b}{p} + A\sin[p(r - \sigma/2)]$$

$$- B\cos[p(r - \sigma/2)], \quad \sigma/2 < r < \sigma, \qquad (2.19)$$

where $v = p\sigma = \eta\lambda/8$, $\eta = \pi\rho\sigma^3/6$ being the dimensionless density, and a, b, A, B are obtained from the solution of the matrix equation

$$\mathbf{M} \begin{bmatrix} a \\ b/\sigma \\ A/\sigma^2 \\ B/\sigma^2 \end{bmatrix} = \begin{bmatrix} -\lambda/96 \\ 0 \\ 1 \\ 0 \end{bmatrix}. \qquad (2.20)$$

The elements of the matrix $\mathbf{M}$ are found by substituting $f = 1$ into Eqs. (I.3.27). The solution to Eq. (2.20) is given by

$$a = \frac{1}{\Delta}\left(\frac{-\lambda}{96} T_{11} + T_{31}\right), \qquad (2.21a)$$

$$\frac{b}{\sigma} = \frac{1}{\Delta}\left(\frac{-\lambda}{96} T_{12} + T_{32}\right), \qquad (2.21b)$$

$$\frac{A}{\sigma^2} = \frac{1}{\Delta}\left(\frac{-\lambda}{96} T_{13} + T_{33}\right), \qquad (2.21c)$$

$$\frac{B}{\sigma^2} = \frac{1}{\Delta}\left(\frac{-\lambda}{96} T_{14} + T_{34}\right). \qquad (2.21d)$$

In Eqs. (2.21), Δ is the determinant of the matrix $\mathbf{M}$ and is given by Eq. (I.A 1) with $f = 1$; similarly, $T_{11}, T_{12}, ..., T_{34}$ are cofactors of the matrix $\mathbf{M}$ and are given by Eqs. (I.A 2) through (I.A 9) with $f = 1$.

B. The difference equations

The Baxter factorization of Eq. (2.12b) with $c_D(r)$ given by Eq. (2.14b) is somewhat more involved than that required by the sum equations. Following the method of Blum[19,20] and Thompson,[29] it is necessary to write

$$c_D(r) = c_D^0(r) + \frac{e^2}{\epsilon k_B T} \frac{e^{-zr}}{r} \qquad (2.22a)$$

and perform the factorization of $[1 + \rho\tilde{c}_D(k)] = \tilde{q}_D(k)\tilde{q}_D(-k)$ assuming no zeros on the real axis. The function $\tilde{c}_D(k)$ is the Fourier transform of $c_D(r)$ with z finite. We then consider the limit $z \to 0$, and find in this case that in real space,

$$q_D(r) = M, \quad r \geqslant \sigma \qquad (2.22b)$$

with

$$M = -\left(\frac{e^2}{\pi\rho\epsilon k_B T}\right)^{1/2}. \qquad (2.23)$$

Thus, defining $q_D^0(r)$ by

$$q_D(r) = q_D^0(r) + M, \quad r > 0 \qquad (2.24)$$

so that $q_D^0(r) = 0, r \geqslant \sigma$, Baxter factorization yields

$$r h_D(r) = q_D^{0'}(r) + 2\pi\rho \int_0^\infty dt$$

$$\times [M + q_D^0(t)](r - t) h_D(|r - t|), \qquad (2.25a)$$

$$rc_D^0(r) = q_D^{0\prime}(r) + 2\pi\rho M q_D^0(r)$$

$$- 2\pi\rho \int_0^\infty dt\, q_D^0(t) q_D^{0\prime}(t - r). \qquad (2.25b)$$

Note that from Eq. (2.23),

$$M = -\frac{\kappa}{2\pi\rho},$$

where κ is the inverse Debye screening length for the electrolyte defined by

$$\kappa^2 = \frac{4\pi}{\epsilon k_B T} \sum_i e_i^2 \rho_i.$$

In this expression, e_i and ρ_i are the charge and number density, respectively, of ion i. The functional form of $q_D^0(r)$ is now obtained by substituting the closure (2.14a) into Eq. (2.25a) on the domain $0 < r < \sigma$. This yields the differential-difference equation

$$q_D^{0\prime}(r) - p[q_D^0(r + \sigma/2) - q_D^0(r - \sigma/2)] + \frac{\lambda\sigma^2}{96}\delta(r - \sigma/2)$$

$$= pM[1 - \theta(r - \sigma/2)] - H, \qquad (2.26)$$

where H, a constant, is given by

$$H = -2\pi\rho M \int_\sigma^\infty sh_D(s)ds \qquad (2.27)$$

and $\theta(x)$ is the Heaviside function

$$\theta(x) = 0 \quad x < 0,$$

$$= 1 \quad x > 0.$$

The parameter p is defined in Eq. (2.17) above. The solution to Eq. (2.26) is found to be

$$q_D^0(r) = -\frac{H}{p} + E\cos(pr) + F\sin(pr), \quad 0 < r < \sigma/2,$$

$$= -M + \frac{H}{p} - E\sin[p(r - \sigma/2)]$$

$$+ F\cos[p(r - \sigma/2)], \quad \sigma/2 < r < \sigma. \qquad (2.28)$$

The boundary conditions on $q_D^0(r)$ are

$$q_D^0(\sigma) = 0, \qquad (2.29a)$$

$$q_D^0(\sigma^+/2) = q_D^0(\sigma^-/2) + \frac{\lambda\sigma^2}{96}. \qquad (2.29b)$$

These conditions result in two simultaneous linear equations for E and F whose solution is given by

$$E' = \frac{E}{\sigma^2}$$

$$= \frac{(H'/v)(2c + s - 1) + M'(1 - c - s) - (v/12\eta)c}{1 - s}, \qquad (2.30a)$$

$$F' = \frac{F}{\sigma^2} = \frac{(H'/v)(2s - c) + M'(c - s) - (v/12\eta)s}{1 - s}, \qquad (2.30b)$$

where

$$s = \sin\left(\frac{v}{2}\right), \quad c = \cos\left(\frac{v}{2}\right),$$

$$\eta = \frac{\pi}{6}\rho\sigma^3, \quad H' = \frac{H}{\sigma}, \quad M' = \frac{M}{\sigma^2}.$$

In order to determine the parameter H, it is necessary to consider the integrated form of Eq. (2.25a) given by

$$J(r) = -q_D(r) + 2\pi\rho \int_0^\infty dt\, q_D(t) J(|r - t|), \qquad (2.31)$$

where

$$J(r) = \int_r^\infty sh_D(s)ds. \qquad (2.32)$$

From the definition of H, Eq. (2.27),

$$H = -2\pi\rho M J(\sigma) = \kappa J(\sigma). \qquad (2.33)$$

Now, it follows trivially from Eq. (2.14a) that

$$J(r) = J(0), \qquad\qquad 0 < r \leqslant \sigma^-/2, \qquad (2.34a)$$

$$= J(\sigma) = J(0) - \frac{p}{2\pi\rho}, \quad \sigma^+/2 \leqslant r \leqslant \sigma. \qquad (2.34b)$$

Additionally, the Stillinger–Lovett zeroth moment (electroneutrality) condition[32] can be written in terms of $J(r)$ as

$$\int_0^\infty J(t)dt = \frac{1}{4\pi\rho}. \qquad (2.35)$$

Thus, evaluating Eq. (2.31) at $r = 0$, we obtain

$$J(0) = -[q_D^0(0) + M] + 2\pi\rho M \int_0^\infty dt\, J(t)$$

$$+ 2\pi\rho \int_0^\sigma dt\, q_D^0(t) J(t)$$

$$= -[q_D^0(0) + M] + \frac{M}{2}$$

$$+ 2\pi\rho\left[J(0)\int_0^{\sigma/2} dt\, q_D^0(t) + J(\sigma)\int_{\sigma/2}^\sigma dt\, q_D^0(t)\right], \qquad (2.36)$$

where use has been made of Eq. (2.35). Evaluating the integrals in Eq. (2.36) and making use of Eqs. (2.30), (2.33), and (2.34), we obtain the quadratic equation for H:

$$\frac{8\pi\rho}{p^2}(1 - c)H^2 + \left[c - 2 + \frac{4\pi\rho M}{p}(-3 + 3c + s)\right]H$$

$$+ [p(1 - c) + \pi\rho M(5 - 4c - 3s)]M = 0. \qquad (2.37)$$

The requirement that $H \to 0$ as $\rho^{1/2}M \to 0$ dictates the choice of the root in Eq. (2.37):

$$H = \frac{(2 - c) + 2\kappa(-3 + 3c + s)/p - [(2 - c)^2 - 4\kappa(-c^2 - c + 2 - 2s + cs)/p]^{1/2}}{16\pi\rho(1 - c)/p^2}. \qquad (2.38)$$

A parameter similar to H arises in the analytic solution of the MSA for the RPM[18–20]:

$$H(\text{RPM}) = \frac{(1 + \kappa\sigma) - (1 + 2\kappa\sigma)^{1/2}}{2\pi\rho\sigma^2} \qquad (2.39)$$

and, as required, the expression for H given in Eq. (2.38) reduces to the RPM result (2.39) in the limit $\lambda \to 0$.

C. Determining the parameter λ and the mass action association constant

As a result of the analyses of Secs. II A and II B, all the parameters in the analytic solution are now determined as functions of the temperature-dependent parameter τ, reduced density η and the parameter λ which determine the equilibrium mass action association constant. To specify the parameter λ as a function of τ and η, it is necessary to apply the closure (2.9a) inside the core. Defining $y_{12}(r)$ by

$$g_{12}(r) = \exp[-\beta\phi_{12}(r)] \, y_{12}(r)$$

and using Eqs. (2.3) and (2.10a) at $r = L = \sigma/2$, we find, quite generally,

$$\lambda\tau = y_{12}(\sigma/2), \tag{2.40}$$

where τ is defined by Eq. (2.5). As $\rho \to 0$, $y_{12}(r) \to 1$ so that $\lambda \to 1/\tau$. The HNC closure (2.9a) implies that

$$\ln y_{12}(\sigma/2) = h_{12}(\sigma/2) - c_{12}(\sigma/2). \tag{2.41}$$

Writing this in terms of the sum and difference equations and substituting into Eq. (2.38) leads to the relationship between λ and τ in the HNC approximation which is given by

$$\lambda\tau = \exp\left[h_S(\sigma/2) - c_S(\sigma/2) + h_D(\sigma/2) - c_D(\sigma/2)\right]. \tag{2.42}$$

We find from our analysis that

$$h_S(\sigma/2) - c_S(\sigma/2)$$

$$= -1 + \frac{2a}{v} + 2vA' - 24\eta\left[\frac{a^2}{2v^3} - \frac{3a^2}{8v^2} - \frac{ab'}{2v^2}\right.$$

$$- \frac{A'b'}{v}s - \frac{B'b'}{v}(1-c)$$

$$+ \frac{A'a}{v^2}(1 - c + 2s - vs) + \frac{B'a}{v^2}$$

$$\times\left(2 - 2c - s + vc - \frac{v}{2}\right) + \frac{A'^2}{4}(v + \sin v)$$

$$\left. + \frac{A'B'}{2}(1 - \cos v) + \frac{B'^2}{4}(v - \sin v)\right] \tag{2.43a}$$

and

$$h_D(\sigma/2) - c_D(\sigma/2)$$

$$= 12\eta M'^2 + 2vE' - 24\eta\left[M'\left(\frac{H'}{v} + F'\right)\right.$$

$$- \frac{H'}{v}(E's - F'c + F') + \frac{E'^2}{4}(v + \sin v)$$

$$\left. + \frac{E'F'}{2}(1 - \cos v) + \frac{F'^2}{4}(v - \sin v)\right], \tag{2.43b}$$

where b', A', and B' are the dimensionless quantities

$$b' = \frac{b}{\sigma}, \quad A' = \frac{A}{\sigma^2}, \quad B' = \frac{B}{\sigma^2}.$$

Thus, the analytic solution of the HNC/MSA for the associating electrolyte reduces to the solution of a single nonlin-

ear equation for the parameter λ. Numerically, we begin at low density using a series expansion for λ in powers of density and solve Eq. (2.42) at successively higher densities using the bisection method.

The expression for the dimensionless association constant K, when $L = \sigma/2$ which implies $\langle N \rangle = \eta\lambda/8$, follows from Eqs. (1.3a) and (1.3b) and is given by

$$K = \frac{k}{\sigma^3} = \frac{\pi\lambda}{24(1 - \eta\lambda/8)^2}. \tag{2.44}$$

The parameter λ is necessarily positive when the HNC/MSA is used for the correlation function as described in our discussion. If instead the Percus–Yevick approximation is substituted for the HNC closure within the spherical core, negative values of λ, which are physically unacceptable, are found to occur for 2–2 electrolytes at room temperature. In the limit as $\eta \to 0$, the mass action association constant reduces to its zero density limit, $\pi/(24\tau)$, denoted by K_0. When $\lambda = 8/\eta$ and $K = \infty$ the system is devoid of free ions and contains extended dipoles.

Although it is customary to call K the mass action association constant, it is constant (dependent on temperature but independent of density) only for an ideal system. The equilibrium constant, which depends only on temperature, is defined by Eq. (1.3a) with the densities ρ_i replaced by the activities a_i of the reactants and products. Since $a_i \to \rho_i$ as $\rho_i \to 0$, K_0 is the equilibrium constant and K/K_0 measures the deviation of the system from ideality.

D. Thermodynamic properties

We choose to calculate the thermodynamic properties using the energy route, extending the methods developed by Barboy and Tenne for the adhesive hard sphere model.[33] Starting with the expression

$$\beta E^{ex}/V = -\frac{1}{2}\beta\sum_{i,j}\rho_i\rho_j\int_0^\infty \frac{\partial \exp[-\beta\phi_{ij}(r)]}{\partial\beta}$$

$$\times y_{ij}(r)4\pi r^2 \, dr \tag{2.45}$$

for the excess internal energy E^{ex}, and ignoring the temperature dependence of the dielectric constant,[13] we find that for our system

$$\beta E^{ex}/N = -\frac{\lambda\eta\beta\epsilon_2}{16} - \frac{\kappa H}{2}, \tag{2.46}$$

which, as expected, reduces to the energy in the MSA for the RPM when $\lambda \to 0$. The other thermodynamic properties are given by the standard thermodynamic relations

$$\beta A^{ex} = \beta A^{ex,0} + \int_0^\beta E^{ex}(\beta')d\beta', \tag{2.47}$$

$$\beta p^{ex} = \beta p^{ex,0} - \int_0^\beta \frac{\partial E^{ex}(\beta')}{\partial V}d\beta', \tag{2.48}$$

$$\phi \equiv 1 + \frac{\beta p^{ex}}{\rho} = \phi^0 - \frac{1}{\rho}\int_0^\beta \frac{\partial E^{ex}(\beta')}{\partial V}d\beta', \tag{2.49}$$

and

$$\beta A^{ex} = N[\ln\gamma_\pm + (1 - \phi)], \tag{2.50}$$

where A^{ex}, p^{ex}, $\ln\gamma_\pm$, and ϕ are, respectively, the excess Helmholtz free energy, the excess pressure, the mean ionic
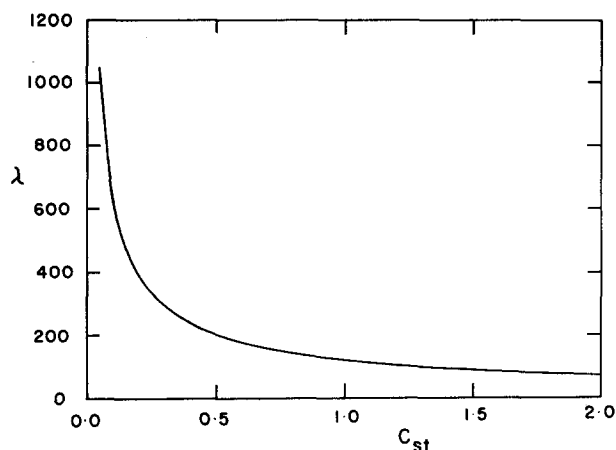
FIG. 2. The parameter λ as a function of the electrolyte concentration c_{st} for a 2–2 electrolyte using the SEM. The temperature $T = 298$ K, the dielectric constant $\epsilon = 78.358$, and the ionic diameter $\sigma = 4.2$ Å.

FIG. 4. The average number $\langle N \rangle$ of oppositely charged ions at distance $\sigma/2$ from the center of a given ion for a 2–2 electrolyte in the SEM. The distribution functions at contact for oppositely charged ions in the RPM and the SEM are also shown ($T = 298$ K, $\epsilon = 78.358$, and $\sigma = 4.2$ Å).

activity coefficient, and the osmotic coefficient, and the superscript zero refers to our uncharged sticky reference system at infinite temperature ($\beta = 0$). Although the excess internal energy can be calculated directly, the other properties must be calculated numerically since a closed form expression for λ cannot generally be found.

However, when association is complete ($\lambda = 8/\eta$) and the system contains just extended dipoles, we find from Eqs. (2.38) and (2.46) that the excess energy E^{ex}, excluding the binding energy of the dipoles, is given in the MSA by

$$\frac{\beta E^{ex}}{N_D} = -\frac{x(c_1 + c_2 x - (c_1^2 + c_3 x)^{1/2})}{96(c_1 - 1)\eta}, \qquad (2.51)$$

where N_D is the number of dipoles,

$$c_1 = 2 - \cos(1/2), \qquad (2.52)$$

$$c_2 = 6[\cos(1/2) - 1] + 2 \sin(1/2), \qquad (2.53)$$

$$c_3 = -4\{[\cos(1/2) - 2][\sin(1/2) - 1] - \cos^2(1/2)\}, \qquad (2.54)$$

and $x = \kappa\sigma$ is related to the dipole moment $\mu = e\sigma/2$ by

$$x = \kappa\sigma = 4(\pi\rho/\epsilon k_B T)^{1/2}\mu, \qquad (2.55)$$

where ρ is twice the density of dipoles and ϵ is the dielectric

constant of the continuum background which is unity for a vacuum.[34] Using Eq. (2.47) the excess Helmholtz free energy A^{ex} of this system is found to be given by

$$\frac{\beta(A^{ex} - A^{ex,HD})}{N_D}$$

$$= -\frac{1}{288c_3(c_1 - 1)\eta}$$

$$\times [3c_3 c_2 x^2 + 6c_3 c_1 x - 4(c_1^2 + c_3 x)^{3/2} + 4c_1^3],$$

$$(2.56)$$

where $A^{ex,HD}$ is the excess Helmholtz free energy of the hard diatomic system.

III. RESULTS AND DISCUSSION

The results of our calculations for the sticky electrolyte model (SEM) using the HNC/MSA are presented in this section along with comparisons against some of the properties of the RPM electrolyte using the MSA. We confine ourselves here to studying only a 2–2 electrolyte at stoichiometric concentrations $c_{st}(=\rho/2)$ ranging from 0.05 to 2.0 molar; the ionic diameter $\sigma = 4.2$ Å. The temperature is as-
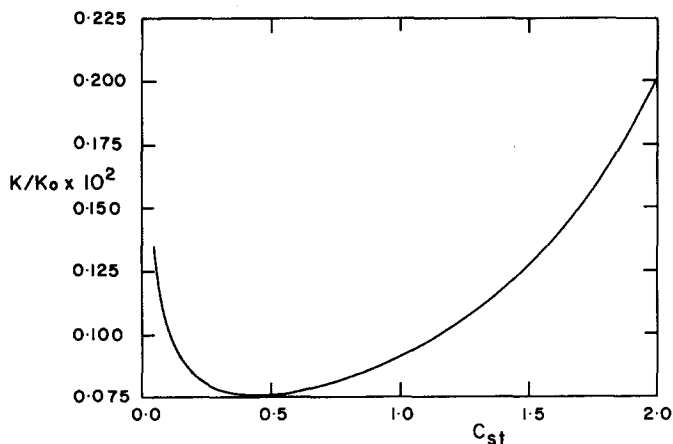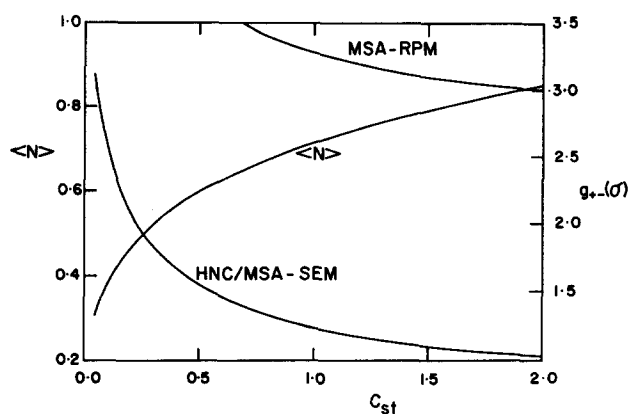

FIG. 3. The reduced mass action association constant K/K_0 for a 2–2 electrolyte as a function of stoichiometric concentration c_{st} in the SEM ($T = 298$ K, $\epsilon = 78.358$, and $\sigma = 4.2$ Å).
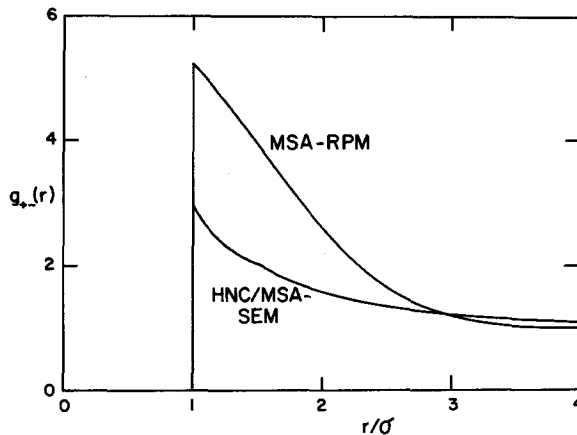

FIG. 5. The pair distribution function $g_{+-}(r)$ for oppositely charged ions of a 2–2 electrolyte at a concentration $c_{st} = 0.0625$ M according to two different models—SEM and RPM ($T = 298$ K, $\epsilon = 78.358$, and $\sigma = 4.2$ Å).
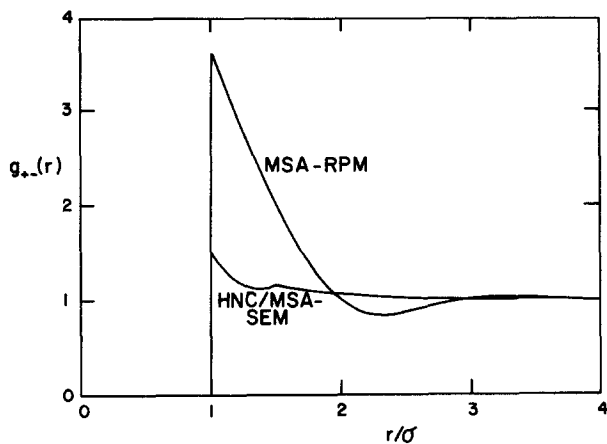
FIG. 6. The pair distribution function $g_{+-}(r)$ for the system depicted in Fig. 5 except that $c_{st} = 0.5625$ M.

FIG. 8. The distribution functions $g_{++}(r)$ and $g_{+-}(r)$ for a 2–2 electrolyte at $c_{st} = 2.0$ M using the SEM according to the HNC/MSA. All of the other model parameters and solution parameters are the same as for the preceding figures.

sumed to be 25 °C and the dielectric constant ϵ is taken to be 78.358 which is the value for water at this temperature. The width w and depth ϵ_2/k_B of the sticky well are assumed to be 0.1σ and 4000 K, respectively; the latter corresponds to an energy of about $13k_B T$ at room temperature (25 °C).

The parameter λ and the ratio K/K_0 are plotted against the electrolyte concentration in Figs. 2 and 3. The average number of oppositely charged ions distance L away from any given ion $\langle N \rangle = \eta\lambda/8$ as a function of c_{st} appears in Fig. 4 which also shows the distribution functions $g_{+-}(\sigma)$ for oppositely charged ions at contact in the SEM and the RPM. Although λ decreases with concentration, $\langle N \rangle$ increases to the extent that 83% of the ions at a concentration of 2 molar have formed dipolar diatomics for the model parameters (ϵ_2, w) assumed in this study. The decrease in the number of contact ion pairs, as measured by the difference between $g_{+-}(\sigma)$ for the SEM and the RPM, is apparently caused by a depletion of counterions at the surface of an ion that is already bonded to an oppositely charged ion. In Figs. 5 to 7 the distribution functions $g_{+-}(r)$ for oppositely charged ions calculated for the RPM and the SEM are plotted as functions of r, showing the pronounced differences in the structural properties of these two systems. The appearance of a cusp at $r = 3\sigma/2$ is noteworthy, and Fig. 8 shows a maxi-
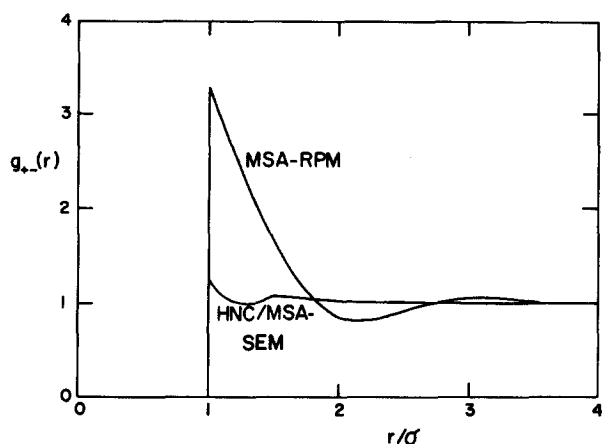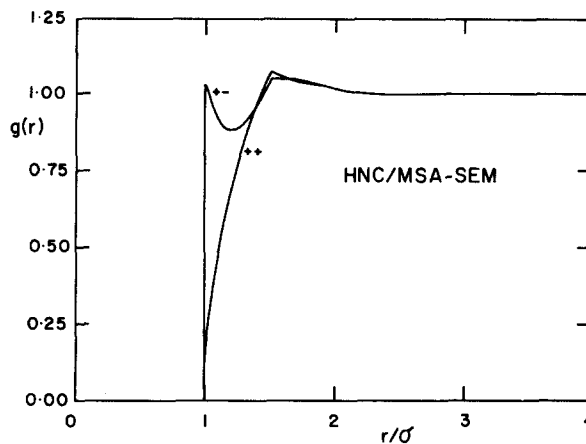
mum cusp in the distribution functions $g_{++}(r)$ for ions of the same sign at $r = 3\sigma/2$ in the SEM. This implies that positive and negative ions have nearly equal probabilities of appearing at the end of a bonded ion pair or dipole, and may be a reflection of the failure of the MSA to differentiate strongly enough between the two extremes, or it may arise from the heavy shielding of ions at high concentrations which reduces the effective charge. (The Debye length $1/\kappa \approx 1.07$ Å at $c_{st} = 2.0$ molar for this system.)

Our calculations of the thermodynamic properties are confined to the excess energy E^{ex} presented in Fig. 9 in dimensionless units of $Nk_B T$ where N is the total number of particles. The energy for the SEM is more negative than that for the MSA because the energy of pair formation $-\langle N \rangle\beta\epsilon_2/2$ overshadows the increase in electrostatic energy caused by the reduction in concentration of free ions due to pair formation.

The results obtained for the sticky electrolyte model (SEM), which mimics bonding between oppositely charged ions in an electrolyte, are sufficiently interesting to justify
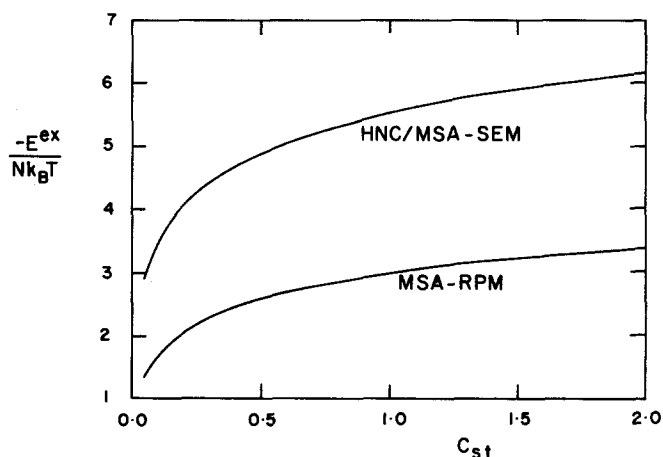

FIG. 7. The pair distribution function $g_{+-}(r)$ for the system depicted in Fig. 5 except that $c_{st} = 1.0$ M.

FIG. 9. The excess energy E^{ex} in dimensionless units of $Nk_B T$ as a function of the electrolyte concentration c_{st} for a 2–2 electrolyte according to two different models—SEM and RPM. All the parameters are the same as for the preceding figures. In addition, $\partial\epsilon/\partial T$ is assumed to be zero.

applications to other systems (molten salts, molecular solvents) especially if better approximations (e.g., HNC) can be employed for the ion–ion interactions. The atom–atom correlation functions for the fully associated system of extended dipoles, although not discussed in detail here, follow from our analysis in Sec. II on setting $\nu = p\sigma = 1$.

ACKNOWLEDGMENTS

[1]P. T. Cummings and G. Stell, Mol. Phys. 51, 253 (1984).
[2]P. T. Cummings and G. Stell, Mol. Phys. (submitted).
[3]H. C. Andersen, J. Chem. Phys. 59, 4714 (1973).
[4]J. S. Høye and K. Olaussen, Physica A 104, 435 (1980).
[5]J. S. Høye and G. Stell, S. U. N. Y. at Stony Brook College of Engineering and Applied Sciences Report No. 307 (1977).
[6]J. K. Percus and G. J. Yevick, Phys. Rev. 110, 10 (1958).
[7]H. L. Friedman, Annu. Rev. Phys. Chem. 32, 179 (1981).
[8]H. L. Friedman and W. D. T. Dale, in Modern Theoretical Chemistry. Vol. 5. Statistical Mechanics, edited by B. J. Berne (Plenum, New York, 1976).
[9]J. C. Rasaiah, J. Solut. Chem. 2, 310 (1973).

[10]G. Stell and B. Hajksfold, in The Liquid State of Matter: Fluids Simple and Complex, edited by E. W. Montroll and J. L. Lebowitz (North–Holland, Amsterdam, 1982).
[11]J. C. Rasaiah and H. L. Friedman, J. Chem. Phys. 48, 2742 (1968).
[12]J. C. Rasaiah and H. L. Friedman, J. Chem. Phys. 50, 3965 (1969).
[13]J. C. Rasaiah, J. Chem. Phys. 52, 704 (1970).
[14]J. C. Rasaiah, Chem. Phys. Lett. 1, 260 (1970).
[15]J. C. Rasaiah, D. N. Card, and J. D. Valleau, J. Chem. Phys. 56, 248 (1972).
[16]J. C. Rasaiah, J. Chem. Phys. 56, 3071 (1972).
[17]J. L. Lebowitz and J. K. Percus, Phys. Rev. 144, 251 (1966).
[18]E. Waisman and J. L. Lebowitz, J. Chem. Phys. 52, 430 (1970); 56, 3086, 3093 (1972).
[19]L. Blum, Mol. Phys. 30, 1529 (1975).
[20]L. Blum, in Theoretical Chemistry: Advances and Perspectives, edited by H. Eyring and D. Henderson (Academic, New York, 1980), Vol. 5.
[21]G. Stell, K. C. Wu, and B. Larsen, Phys. Rev. Lett. 37, 1369 (1976).
[22]H. L. Friedman and B. Larsen, J. Chem. Phys. 70, 92 (1979).
[23]W. Ebeling and N. Grigo, Ann. Phys. (Leipzig) 37, 21 (1980).
[24]N. Bjerrum, K. Dan. Vidensk. Selsk. 7, 1 (1926).
[25]R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd revised ed. (Butterworths, London, 1980).
[26]R. Bacquet and P. Rossky, J. Chem. Phys. 79, 1419 (1983).
[27]R. J. Baxter, Aust. J. Phys. 21, 563 (1968).
[28]An equivalent set of factorized equations were derived by M. S. Wertheim, J. Math. Phys. 5, 643 (1964) using Laplace transform techniques.
[29]N. Thompson, University of Maine, Chemistry Department Report No. 2001 (1978).
[30]R. J. Baxter, J. Chem. Phys. 49, 2770 (1968).
[31]L. S. Ornstein and F. Zernike, Proc. Akad. Sci. (Amsterdam) 17, 793 (1914).
[32]F. J. Stillinger and R. Lovett, J. Chem. Phys. 48, 3858 (1968); 49, 1991 (1968).
[33]B. Barboy and R. Tenne, Chem. Phys. 38, 369 (1979).
[34]This approximation for the fully associated electrolyte is similar to the analog of zero pole approximation (ZPA) for hard dumbbell fluids (HDF)—see Morris and Cummings [Mol. Phys. 49, 1103 (1983)] and Morris and Isbister [ibid. 52, 57 (1984)]. The related interacting site approximation (ISA) for polar hard dumbbells (PHD) has been discussed by Morris and Perram [Mol. Phys. 43, 669 (1981)]. See also Cummings and Stell [Mol. Phys. 44, 529 (1981); 46, 383 (1982)] for discussions of the dielectric constant in the ISA.