Ion association and dipolar dumbbells: Solutions of the HNC and HNC/MS approximations at $L = \sigma/2$ and $\sigma/3$ for the sticky electrolyte model

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We extend an earlier analytic study of a sticky electrolyte model (SEM) to the case $L = \sigma/3$, where L is the distance at which positive and negative ions bind to each other, using the hypernetted chain (HNC) approximation within the spherical core and the mean spherical approximation (MSA) outside. We also present numerical solutions to the HNC approximation alone for $\sigma/3 < L < \sigma/2$. The average number of bonded pairs is found to be essentially the same for the two approximations but the ion–ion correlation functions are very different except at high concentrations when the shielding is large. Small amounts of tetramers are also observed in the HNC correlation functions for $\sigma/3 < L < \sigma/2$, and trimers are found when $L = \sigma/2$. An expression for the excess free energy of the SEM electrolyte is derived by turning on the stickiness between oppositely charged ions. The excess energy of the system of dipolar dumbbells with charges at a distance $L = \sigma/3$ is obtained in the MSA and the atom–atom correlation functions are compared with the HNC approximation and with recent Monte Carlo simulations. The asymptotic form of the direct correlation functions defined through the Ornstein–Zernike equation is given for dipolar dumbbells.

I. INTRODUCTION

In this study we extend an earlier analysis[1] of a sticky electrolyte model (SEM) to the case where the oppositely charged ions of diameter σ can bind at a distance $L = \sigma/3$. The equilibrium properties for this model, which are discussed in detail in this paper, are found to be strikingly different from those previously determined for $L = \sigma/2$, when the model parameters and approximations for the correlation functions are left unchanged. In addition, we extend our discussions of pairing at $L = \sigma/2$ and $\sigma/3$ to include the equilibrium properties in the limit of complete association when the system consists of dipolar dumbbells. Our earlier study of the SEM used the hypernetted chain (HNC) approximation within the spherical core and the mean spherical approximation (MSA) outside. This HNC/MSA combination allows a major part of the solution to be obtained analytically, but its accuracy is uncertain. We have therefore undertaken a numerical study of the same model in the HNC approximation alone using methods similar to those employed in earlier studies of the restricted primitive model.[2] The equilibrium constant for dimerization is found to be essentially unchanged, but the ion–ion correlation functions are significantly altered at low concentrations and show evidence of association beyond the formation of dimers when $L < \sigma/2$. This behavior is unexpected since it is implicitly excluded by the Hamiltonian for the SEM when $L < \sigma/2$, but our HNC computations indicate that an approximate solution may not necessarily obey this restriction. However, a less accurate theory like the HNC/MSA combination shows no evidence of association beyond dimerization when $L < \sigma/2$ for the systems reported in this paper. One advantage of the HNC/MS approximation is that its solution can be determined analytically. This also leads to an expression in closed form for the energy of dipolar dumbbells in the MSA which is given here for $L = \sigma/3$. The form of the energy for $L = \sigma/n$ is discussed in an Appendix. The correlation functions in the MS and HNC approximations are compared with each other and with recent Monte Carlo simulations.[3,4]

The association of ions to form extended dipoles modifies the asymptotic form of the direct correlation function defined through the Ornstein–Zernike (OZ) relation. We show in another Appendix to this paper that, in the absence of a solvent, the asymptotic form of the direct correlation function is given by

$$c_{ij}(r) = -\beta A e_i e_j / r \tag{1.1}$$

with $A = \epsilon/(\epsilon - 1)$ where ϵ is the dielectric constant of dipolar dumbbells. We find that the effect of this modification on the atom–atom correlation function in the MSA is to slightly improve agreement with computer simulations of the same system. However, in our studies of electrolytes in high dielectric solvents, A is taken to be unity and the asymptotic form of the direct correlation function is assumed to be

$$c_{ij}(r) = -\beta e_i e_j / (\epsilon_0 r), \tag{1.2}$$

in which ϵ_0 is the dielectric constant of the solvent.

It is convenient to summarize some features of the model before discussing the details of the solutions for $L = \sigma/3$ and $L = \sigma/2$. The equilibrium statistical mechanics of ions whose potential energy functions are drawn in Fig. 1 mimic ion association. The model, however, is difficult to solve analytically even in the MSA. A modification of the potential in which the well centered at $r = L$ is made infinitely deep ($\epsilon_2 \to \infty$) and infinitesimally narrow ($w \to 0$) such that the second virial coefficient is unchanged is easier to treat. This innovation was introduced by Cummings and Stell[5] in their study of chemical association following Baxter's work on adhesive hard species[6] and Høye and Olaussen's treatment

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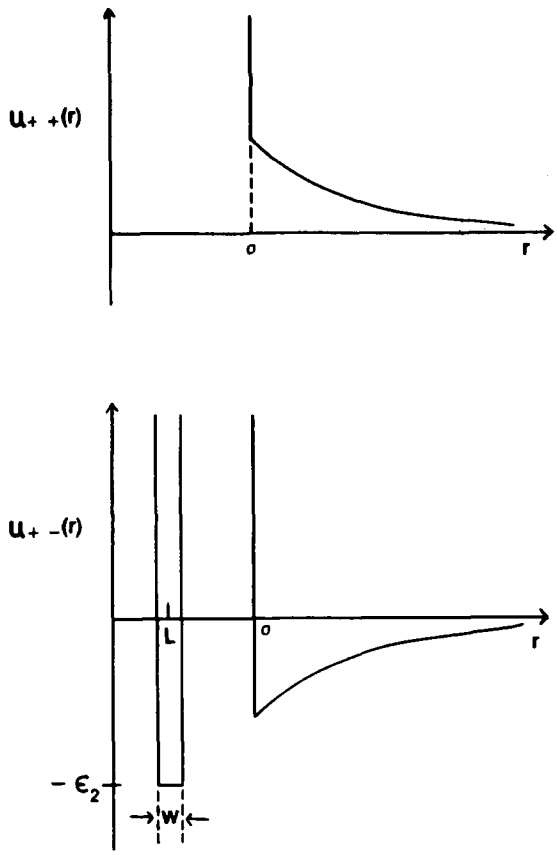

FIG. 1. The pair potential for the sticky electrolyte model (SEM) studied in this paper. The model parameters used are $w = 0.1\sigma$, $\epsilon_2/k = 4000$ K, and $L = \sigma/2$ and $\sigma/3$ for a 2–2 electrolyte ($e = 2$ esu) in a solvent of dielectric constant $\epsilon_0 = 78.358$.

of chemical association.[7] The Mayer f function for oppositely charged ions in the modified potential is defined by

$$f^*_{+-}(r) = -1 + L\delta(r-L)/12\tau, \quad 0<r<\sigma \tag{1.3a}$$

$$= -1 + \exp(e^2/\epsilon_0 k\,\mathrm{Tr}), \quad r>\sigma, \tag{1.3b}$$

where e is the magnitude of the charge in the ion, ϵ_0 is the dielectric constant of the continuum background solvent, k is Boltzmann constant, T is the absolute temperature, and τ is related to the parameters of the model depicted in Fig. 1 by the requirement that the second virial coefficient is unchanged:

$$\tau = \frac{L^3}{12L^2w + w^3}\exp(-\epsilon_2/kT). \tag{1.4}$$

The f functions for like ions are the same for both models but the presence of a delta function in $f_{+-}(r)$ induces a corresponding delta function term in the indirect correlation function for unlike ions:

$$h_{+-}(r) = -1 + \lambda L\delta(r-L)/12 \quad (0<r<\sigma). \tag{1.5}$$

The association parameter λ in Eq. (1.5) is related to the average number of ions $\langle N\rangle$ bound to a given ion by

$$\langle N\rangle = \lambda\eta(L/\sigma)^3, \tag{1.6}$$

where $\eta = \pi\rho\sigma^3/6$ and ρ is the total ion density. If $L<\sigma/2$, the Hamiltonian for this model implicitly excludes association beyond dimerization and the reduced association constant is given by[5]

$$K = \frac{\pi\lambda(L/\sigma)^3}{3(1-\langle N\rangle)^2}. \tag{1.7}$$

The parameters λ and τ are related by

$$\lambda\tau = y_{+-}(L), \tag{1.8}$$

where $y_{+-}(r) = [1 + h_{+-}(r)]\exp[u_{+-}(r)/kT]$ is determined by the approximation used for the ion–ion correlation functions inside the hard cores. The interpretation of λ as an association parameter remains sensible only if it is never negative. The use of the HNC approximation within the hard core ensures this. We also expect, $0\leq\langle N\rangle\leq 1$ when $L<\sigma/2$ in the SEM. When $\lambda = 0$, $\langle N\rangle = 0$ and the electrolyte is completely dissociated while $\lambda = \eta^{-1}(\sigma/L)^3$ corresponds to complete association when $\langle N\rangle = 1$.

The thermodynamic properties are conveniently determined through the energy equation. A simple extension of derivation of the excess energy E^{ex} given in Ref. 1 to take account of the temperature dependence of the dielectric constant of the solvent background leads to the relation

$$\frac{\beta E^{ex}}{N} = -\frac{\langle N\rangle\beta\epsilon_2}{2} - (1 + d\ln\epsilon_0/d\ln T)\kappa\frac{H}{2}, \tag{1.9}$$

where $\beta = 1/kT$, κ is the inverse Debye length defined by

$$\kappa^2 = \frac{4\pi}{\epsilon_0 kT}\sum_i e_i^2\rho_i \tag{1.10}$$

and

$$H = \kappa\int_\sigma^\infty sh_D(s)\,ds. \tag{1.11}$$

In Eq. (1.11), $h_D(r) = [h_{+-}(r) - h_{++}(r)]/2$. The first term in Eq. (1.9) is the binding energy for pair formation, while the second term (also a function of λ) is determined by the remaining ion–ion interactions, which can be determined analytically in the MSA. When λ is zero, the binding energy is zero and the energy and other equilibrium properties of the SEM reduce to those of the restricted primitive model (RPM). The temperature coefficient of the dielectric constant of the solvent background appears as a constant factor in the second term of Eq. (1.9). It is assumed to be zero in all of our computations since we have not specified the solvent except when we are dealing with a vacuum background when the temperature coefficient is zero. However, for water, at room temperature (25 °C), $d\ln\epsilon_0/d\ln T = -1.3679$ which changes the sign of the second term in Eq. (1.9).[2] Other routes to the thermodynamic properties such as the virial and compressibility equations are discussed in connection with the HNC computations.

We conclude this introduction by deriving an expression for the Helmholtz free energy of the SEM electrolyte by turning on the stickiness between oppositely charged ions in an RPM electrolyte. The Mayer f functions are written as

$$f_{ij}(r;\xi) = f^0_{ij}(r) + (1-\delta_{ij})\xi L\delta(r-L)/12, \tag{1.12}$$

where $f^0_{ij}(r)$ is the f function for an RPM electrolyte $\xi = 1/\tau$ and we use the notation $i,j = 1,2$ to represent $+,-$ ions, respectively. The functional derivative of the Helmholtz free energy per unit volume with respect to $f_{ij}(r;\xi)$ is given by

$$\delta(\beta A/V)/\delta f(r;\xi) = -\tfrac{1}{2}\rho_i \rho_j y_{ij}(r;\xi). \tag{1.13}$$

We consider the variation $\delta f_{ij}(r;\xi)$ due to a change in ξ;

$$\delta f_{ij}(r;\xi) = (1-\delta_{ij})L\delta(r-L)\delta\xi/12. \tag{1.14}$$

Using Eq. (1.14) in Eq. (1.13), integrating over r and ξ, and summing over i and j we find

$$\beta[A(\text{SEM}) - A(\text{RPM})]/N = -\tfrac{1}{2}\eta(L/\sigma)^3 \int_0^{\xi} y_{+-}(L;\xi')\,d\xi', \tag{1.15}$$

where we have used the fact that $\rho_+ = \rho_- = \rho/2$ and $\eta = \pi\rho\sigma^3/6$. The function $y_{+-}(L;\xi)$ is determined by the parameters of the SEM and by the concentration and temperature. As $\rho \to 0$, $y_{+-}(L;\xi) \to 1$, and Eq. (1.15) can be integrated trivially to obtain the contribution of the change in the second virial coefficient to the free energy when the stickiness is turned on. This can be confirmed by direct calculation.[1] The application of Eq. (1.15) to uncharged sticky molecules is equivalent to integration over the inverse temperature.[9] It follows from Eqs. (1.8) and (1.4) that the integral in Eq. (1.15) can also be written as

$$\int_{-\infty}^{\ln\xi} \lambda(\xi')\,d\ln\xi' = \beta\int_{-\infty}^{\epsilon_2} \lambda(\epsilon_2')\,d\epsilon_2'. \tag{1.16}$$

The lower limit of integration in the last integral corresponds to the well in Fig. 1 filling up to the infinite height characteristic of the RPM. The first integral in Eq. (1.16) is determined by the way in which the association parameter $\lambda(\xi)$ changes with the sticking coefficient ξ which is the origin of the ion association discussed in this paper. It should be emphasized however that although the narrow square well potential (Fig. 1) provides an attractive way to estimate the sticking coefficient ξ it is not an essential part of the theory and may be discarded or replaced by other criteria for determining the sticking coefficient. Differentiating Eq. (1.15) with respect to the concentration we obtain the osmotic coefficient ϕ_s and the mean activity coefficient $\gamma_{\pm,s}$ for the SEM:

$$\phi_s(\text{SEM}) - \phi(\text{RPM}) = -\tfrac{1}{2}\eta(L/\sigma)^3 \times \int_0^{\xi} [y_{+-}(L;\xi') + \rho\partial y_{+-}(L;\xi')/\partial\rho]\,d\xi' \tag{1.17}$$

$$\ln\gamma_{\pm,s}(\text{SEM}) - \ln\gamma_{\pm}(\text{RPM}) = -\tfrac{1}{2}\eta(L//\sigma)^3 \times \int_0^{\xi} [\rho\partial y_{+-}(L;\xi')/\partial\rho + 2y_{+-}(L,\xi')]\,d\xi'. \tag{1.18}$$

The subscript s characterizes the stickiness which is turned on to obtain the excess thermodynamics of the SEM.

This paper is organized as follows: Section II contains the HNC/MSA solution for electrolytes and the MSA solution for dipolar dumbbells when $L = \sigma/3$. The HNC approximation for these systems with $\sigma/3 < L < \sigma/2$ is discussed in Sec. III. The results for the two approximations are compared and analyzed in Sec. IV. The Appendices discuss the asymptotic form of the direct correlation function for dipolar dumbbells and the general form of the energy in the MS approximation for $L = \sigma/n$.

II. HNC/MSA SOLUTION FOR A SYMMETRICAL ELECTROLYTE AND THE MSA SOLUTION FOR DIPOLAR DUMBBELLS WITH $L = \sigma/3$

As discussed in Ref. 1, a simple strategy for dealing with a symmetrical electrolyte that associates is to consider the sum (S) and difference (D) correlation functions

$$h_s(r) = [h_{+-}(r) + h_{++}(r)]/2, \quad c_s(r) = [c_{+-}(r) + c_{++}(r)]/2, \tag{2.1}$$

$$h_D(r) = [h_{+-}(r) - h_{++}(r)]/2, \quad c_D(r) = [c_{+-}(r) - c_{++}(r)]/2. \tag{2.2}$$

This enables the Ornstein–Zernike (OZ) equations for the mixture of ions to be decoupled into two equations, one for the sum and the other for the difference correlation functions:

$$h_s(r) = c_s(r) + \rho\int c_s(s)h_s(|\mathbf{r}-\mathbf{s}|)\,d\mathbf{s}, \tag{2.3}$$

$$h_D(r) = c_D(r) - \rho\int c_D(s)h_D(|\mathbf{r}-\mathbf{s}|)\,d\mathbf{s}, \tag{2.4}$$

where

$$h_s(r) = -1 + \lambda L\delta(r-L)/24, \quad r<\sigma, \tag{2.5}$$

$$h_D(r) = \lambda L\delta(r-L)/24, \quad r<\sigma \tag{2.6}$$

are exact relations. In the MSA for electrolytes

$$c_s(r) = 0, \quad r>\sigma, \tag{2.7}$$

$$c_D(r) = Ae^2/(\epsilon_0 rkT), \quad r>\sigma, \tag{2.8}$$

where ϵ_0 is the dielectric constant of the solvent and we assume, for the present, that A is unity. The correct form of A in the limit of complete association is discussed in Appendix A.

The sum OZ equation and closure are identical to the corresponding equations for the dimerization of uncharged sticky hard spheres, which has been solved for $L = \sigma/2$ and $L = \sigma/3$ by Cummings and Stell.[5] We are thus left with finding the solutions to the difference equations for $L = \sigma/3$. Factorization of the difference OZ equation yields[1]

$$rh_D(r) = q_D^{0\prime}(r) + 2\pi\rho\int_0^{\infty} dt\,[M + q_D^0(t)](r-t)h_D(|r-t|), \tag{2.9a}$$

$$rc_D^0(r) = q_D^{0\prime}(r) + 2\pi\rho\left[Mq_D^0(r) - \int_0^{\infty} dt\,q_D^{0\prime}(t)q_D^0(t-r)\right], \tag{2.9b}$$

where

$$q_D^0(r) = q_D(r) - M, \tag{2.10a}$$

$$M = -\kappa/2\pi\rho, \tag{2.10b}$$

and $q_D^{0\prime}(r)$ is the derivative with respect to r of $q_D^0(r)$. Also ρ is the total density of ions, and $c_D^0(r)$ is the short range part of the direct correlation function.[1] The function $q_D^0(r)$ is related to the direct correlation function $c_D(r)$ by

$$[1 + \rho\tilde{c}_D(k)] = \tilde{q}_D(k)\,\tilde{q}_D(-k), \tag{2.11}$$

where $\tilde{c}_D(k)$ and $1 - \tilde{q}_D(k)$ are the Fourier transforms of $c_D(r)$ and $2\pi\rho q_D(r)$, respectively. Thus the solution to the problem hinges on determining $q_D^0(r)$ for all r. It follows from

Eqs. (2.6) and (2.9a) that $q_D^0(r)$, in the domain $0<r<\sigma$, is the solution to

$$q_D^{0\prime}(r) - pq_D^0(r+\sigma/3) = pM - H, \quad 0<r<\sigma/3, \tag{2.12a}$$

$$q_D^{0\prime}(r) - p[q_D^0(r+\sigma/3) - q_D^0(r-\sigma/3)] = -H, \quad \sigma/3<r<2\sigma/3, \tag{2.12b}$$

$$q_D^{0\prime}(r) + pq_D^0(r-\sigma/3) = -H, \quad 2\sigma/3<r<\sigma, \tag{2.12c}$$

where H is defined in Eq. (1.11), and $p\sigma = \nu = \eta\lambda/18$. We also know from Eqs. (2.8) and (2.9b) that $q_D^0(r) = 0$ for $r>\sigma$. Solving Eqs. (2.12), we find

$$q_D^0(r) = (pM/2 - H)r + D + E\cos(\sqrt{2}\,pr) + F\sin(\sqrt{2}\,pr), \quad 0<r<\sigma/3 \tag{2.13a}$$

$$= -M/2 + \sqrt{2}\,F\cos[\sqrt{2}\,p(r-\sigma/3)] - \sqrt{2}\,E\sin[\sqrt{2}\,p(r-\sigma/3)], \quad \sigma/3<r<2\sigma/3 \tag{2.13b}$$

$$= (pM/2 - H)r + D + H/p + 2\sigma H/3 - \nu M/3 - E\cos[\sqrt{2}\,p(r-2\sigma/3)] - F\sin[\sqrt{2}\,p(r-2\sigma/3)], \quad 2\sigma/3<r<\sigma, \tag{2.13c}$$

where the constants D, E, and F are determined by the boundary conditions

$$q_D^0(\sigma^+/3) = q_D^0(\sigma^-/3) + p/2\pi\rho, \tag{2.14a}$$

$$q_D^0(2\sigma^+/3) = q_D^0(2\sigma^-/3), \tag{2.14b}$$

$$q_D^0(\sigma^+) = 0. \tag{2.14c}$$

We thus obtain

$$D' = \frac{D}{\sigma^2} = \frac{H'/(3\nu)[3\sqrt{2}(\nu-2) + (9-4\nu)s + 3\sqrt{2}\,c] + M'/6[-3\sqrt{2}(1+\nu) + (3+4\nu)s + 3\sqrt{2}\,c] + \nu(s-\sqrt{2})/(12\eta)}{3\sqrt{2} - 4s - \sqrt{2}\,c}, \tag{2.15a}$$

$$E' = \frac{E}{\sigma^2} = \frac{H'/(3\nu)[\nu\sqrt{2} - (3+2\nu)s + 3\sqrt{2}\,c] + M'/6[(3-\nu)\sqrt{2} + (2\nu-3)s - 3\sqrt{2}\,c] + \nu(s-\sqrt{2}\,c)/12\eta}{3\sqrt{2} - 4s - \sqrt{2}\,c}, \tag{2.15b}$$

$$F' = \frac{F}{\sigma^2} = \frac{H'/(3\nu)[-3 + 3\sqrt{2}\,s + (2\nu+3)c] + M'/6[3 - 3\sqrt{2}\,s + (3-2\nu)c] + \nu(1-c-\sqrt{2}\,s)/12\eta}{3\sqrt{2} - 4s - \sqrt{2}\,c}, \tag{2.15c}$$

where $s = \sin(\sqrt{2}\nu/3)$, $c = \cos(\sqrt{2}\nu/3)$, $H' = H/\sigma$, and $M' = M/\sigma^2$. Note that $q(r)$ has three distinct domains in the region $0<r<\sigma$ when $L = \sigma/3$ in contrast to two regions when $L = \sigma/2$.[1] For $L = \sigma/n$ there are n such domains and n constants to be determined which makes it difficult to obtain a solution for arbitrary n. However, the general form of the energy is discussed in Appendix B.

The parameter H is determined from the electroneutrality condition

$$\int_0^\infty J(t)\,dt = 1/(4\pi\rho), \tag{2.16}$$

where $J(r)$ is defined by

$$J(r) = \int_r^\infty sh_D(s)\,ds. \tag{2.17}$$

It follows from Eq. (1.11) that

$$H = \kappa J(\sigma), \tag{2.18}$$

and Eq. (2.6) implies that

$$J(r) = J(0), \quad 0<r<\sigma^-/3 \tag{2.19a}$$

$$= J(\sigma) = J(0) - p/2\pi\rho, \quad \sigma^+/3<r<\sigma. \tag{2.19b}$$

Integration of Eq. (2.9a) provides an expression for $J(r)$:

$$J(r) = -q_D(r) + 2\pi\rho\int_0^\infty dt\,q_D(t)J(|r-t|), \tag{2.20a}$$

which on evaluation at $r = 0^+$ leads to a quadratic equation for H:

$$12a_1\eta H'^2 + (a_2 + 12a_3\eta M')H' + (a_4\nu + 6a_5\eta M')M' = 0, \tag{2.20b}$$

where

$$a_1 = \frac{(3\sqrt{2} - 4s + \sqrt{2}\,c)\nu^2 + 6(-\sqrt{2} + 2s + \sqrt{2}\,c)\nu + 9\sqrt{2}(1-c)}{9\nu^2(3\sqrt{2} - 4s - \sqrt{2}\,c)},$$

$$a_2 = \frac{2(-\sqrt{2} + s)\nu - 6(2\sqrt{2} - 2s - \sqrt{2}\,c)}{3(3\sqrt{2} - 4s - \sqrt{2}\,c)},$$

$$a_3=\frac{(-3\sqrt{2}+4s-\sqrt{2}\,c)\nu^2+3(5\sqrt{2}-8s-\sqrt{2}\,c)\nu+18(-\sqrt{2}+s+\sqrt{2}\,c)}{9\nu(3\sqrt{2}-4s-\sqrt{2}\,c)},$$

$$a_4=\frac{(\sqrt{2}-s)\nu+3(\sqrt{2}-s-\sqrt{2}\,c)}{3(3\sqrt{2}-4s-\sqrt{2}\,c)},$$

$$a_5=\frac{(3\sqrt{2}-4s+\sqrt{2}\,c)\nu^2+12(-2\sqrt{2}+3s)\nu+18(3\sqrt{2}-4s-\sqrt{2}\,c)}{18(3\sqrt{2}-4s-\sqrt{2}\,c)},$$

whose solution (determined by the requirement that $H\to 0$ as $\rho^{1/2}M\to 0$) is

$$H=\frac{2/3[(\sqrt{2}-s)\nu+3(2\sqrt{2}-2s-\sqrt{2}\,c)]+\kappa\sigma/9\nu[(-3\sqrt{2}+4s-\sqrt{2}\,c)\nu^2+3(5\sqrt{2}-8s-\sqrt{2}\,c)\nu+18(-\sqrt{2}+s+\sqrt{2}\,c)]}{8\eta/3\nu^2[(3\sqrt{2}-4s+\sqrt{2}\,c)\nu^2+6(-\sqrt{2}+2s+\sqrt{2}\,c)\nu+9\sqrt{2}(1-c)]}$$
$$-\frac{\{4/9[(\sqrt{2}-s)\nu+3(2\sqrt{2}-2s-\sqrt{2}c)]^2+4\kappa\sigma/3\nu[(12-17\sqrt{2}s+3\sqrt{2}cs-4c+12s^2)\nu+3(-8+7\sqrt{2}s-5\sqrt{2}cs+8c-2s^2)]\}^{1/2}}{8\eta/3\nu^2[(3\sqrt{2}-4s+\sqrt{2}c)\nu^2+6(-\sqrt{2}+2s+\sqrt{2}c)\nu+9\sqrt{2}(1-c)]} \tag{2.21}$$

Equation (2.21) is the principal result of this section for the thermodynamic properties of sticky electrolytes with $L=\sigma/3$. When $\lambda\to 0$ we recover the MSA solution for H in the RPM:

$$H(\text{RPM})=\frac{(1+x)-(1+2x)^{1/2}}{2\pi\rho\sigma^2}, \tag{2.22}$$

while $\lambda=27/\eta$ corresponds to complete dimerization and yields

$$H(\text{dipoles})=\frac{(c_1+c_2x)-(c_1^2+c_3x)^{1/2}}{4c_4\pi\rho\sigma^2/3}, \tag{2.23}$$

where

$$c_1=5\sqrt{2}-5\sin(1/\sqrt{2})-2\sqrt{2}\cos(1/\sqrt{2}),$$
$$c_2=[-\sqrt{2}-4\sin(1/\sqrt{2})+5\sqrt{2}\cos(1/\sqrt{2})]/6,$$
$$c_3=4[12\cos(1/\sqrt{2})-3\sqrt{2}\sin(1/\sqrt{2})$$
$$-3.5\sqrt{2}\sin(\sqrt{2})-4\cos(\sqrt{2})]/3,$$
$$c_4=[3\sqrt{2}+4\sin(1/\sqrt{2})+\sqrt{2}\cos(1/\sqrt{2})]/3, \tag{2.24}$$

and $x=\kappa\sigma$ may be also interpreted as a reduced dipole moment defined by the relation

$$x=6(\pi\rho/\epsilon_0 kT)^{1/2}\mu, \tag{2.25}$$

in which $\mu=e\sigma/3$ is the dipole moment. In the absence of a solvent we use the asymptotic form for the direct correlation function given by Eq. (1.1) with the dielectric constant of the background equal to unity. Instead of Eq. (2.8) $c_D(r)$ in the MSA is now defined by

$$c_D(r)=Ae^2/(rkT), \tag{2.26}$$

which leaves the analysis of this section unchanged except that κ has to be redefined and Eq. (2.25) modified to read

$$x=6(A\pi\rho/kT)^{1/2}\mu. \tag{2.27}$$

The excess energy (excluding the binding energy) of the system of extended dipoles is given, in the MSA, by

$$\frac{\beta E^{\text{ex}}}{N_D}=-\kappa H(\text{dipole})$$
$$=-x[c_1+c_2x-(c_1^2+c_3x)^{1/2}]/(8c_4\eta), \tag{2.28}$$

where N_D is the number of dipoles. This is of the same form as the equation for the excess energy of dipoles in MSA for $L=\sigma/2$, except that the constants c_1, c_2, c_3, and c_4 are different.[1] It is also remarkably similar to the expression for the reduced excess energy $\beta E^{\text{ex}}/N$ of the RPM electrolyte ($\lambda=0$) in the MSA, when $c_1=c_2=1$, $c_3=2$, and $c_4=3/2$.[8] We find that this general form obtains for all $L=\sigma/n$, where n is an integer (see Appendix B). Integration of the excess energy with respect to β, from 0 to some finite β, at constant ρ, leads to the excess Helmholtz free energy.[1] A difficulty with the MSA for dipoles is that the excess thermodynamic functions do not vanish in the limit of zero density. In this respect it is similar to the analog of the zero-pole approximation[10(a)] for the direct correlation function of dipolar dumbbells defined through the site–site Ornstein–Zernike equation.[10(b)] When $\lambda=0$, however, the system reverts to the RPM and all of the excess thermodynamic functions in the MSA vanish at zero density.

When there are free ions in the system ($0<\lambda<27/\eta$), the association parameter λ is determined from Eq. (1.8) and the HNC approximation, when

$$\lambda\tau=\exp[h_s(\sigma/3)-c_s(\sigma/3)+h_D(\sigma/3)-c_D(\sigma/3)], \tag{2.29}$$

where $h_s(\sigma/3)-c_s(\sigma/3)$ is derived in Ref. 5 and we find, from our analysis, that

$$h_D(\sigma/3)-c_D(\sigma/3)=6\nu E'-36\sqrt{2}\eta M'F'+36\eta S, \tag{2.30}$$

in which

$$S=-\sqrt{2}(\nu M'/2-H')[F'(1/3+s/\sqrt{2}-2c/3)$$
$$+E'(2s/3-(1-c)/\sqrt{2}\nu)]$$
$$-2(D'-\nu M'/6+H'/3)[E's+F'(1-c)]$$
$$-\nu M'^2/12+M'H'/6$$
$$+(H'/\nu-M')[E'(1-c)-F's]$$
$$-2\nu(E'^2+F'^2)/3. \tag{2.31}$$

The exponential function in Eq. (2.29) ensures that λ is always positive in the HNC approximation. The equilibrium constant is calculated from Eq. (1.7).

III. SOLUTION OF THE SEM IN THE HNC APPROXIMATION

The solution to the HNC approximation is of necessity obtained numerically by a simple modification of the numerical methods used in studies of electrolytes in the primitive model.[2] The correlation function for oppositely charged ions $h_{+-}(r)$ is separated into two terms, one of which contains the delta function inside the hard core, and the other the remainder. Thus,

$$h_{+-}(r) = h'_{+-}(r) + \Delta h_{+-}(r), \tag{3.1}$$

where

$$\Delta h_{+-}(r) = \lambda L \delta(r - L)/12, \quad r < \sigma, \tag{3.2a}$$

$$= 0, \quad r > \sigma, \tag{3.2b}$$

and $h'_{+-}(r)$ is the remainder. The HNC approximation[2,11] assumes that

$$\ln h_{ij}(r) = -\beta u^*_{ij}(r) + q_{ij}(r) + \tau_{ij}(r), \tag{3.3}$$

in which

$$q_{ij} = -e_i e_j \exp(-\kappa r)/(\epsilon_0 k \,\mathrm{Tr}). \tag{3.4}$$

$u^*_{ij}(r)$ is the short range part of the potential and $\tau_{ij}(r)$ is determined from the matrix equation

$$\tau = X * h + q * X + q * X * h, \tag{3.5}$$

where

$$X = h - q - \tau. \tag{3.6a}$$

and the convolution

$$(A * B)_{ij} = \sum_{i=1}^{2} \rho_i \int A_{ik} B_{kj}\, d\{k\}. \tag{3.6b}$$

Equation (3.5), which corresponds to the Ornstein–Zernike equation, is solved in Fourier space starting with a trial function which takes τ as zero or equal to the same function obtained previously at a neighboring concentration. The Fourier transforms are determined by adding the transform of the delta function term, determined analytically, to the rest calculated numerically. Thus the transform of $h_{+-}(r)$ is

$$\tilde{h}_{+-}(k) = \tilde{h}'_{+-}(k) + \pi\lambda L^2 \sin(kL)/(3k), \tag{3.7}$$

in which the first term $\tilde{h}'_{+-}(k)$ is computed using a fast Fourier transform (FFT) algorithm in each step of the iterative procedure and the second term is the transform of Eq. (3.2a). The inverse transforms of τ, which determine the correlation functions outside the spherical core, are obtained numerically using the FFT routine. When the solutions have converged, the association parameter λ is determined from Eq. (1.8) where $y_{+-}(L)$, is given, in the HNC approximation by

$$y_{+-}(L) = \exp\{\beta e_+ e_- [1 - \exp(-\kappa L)]/(\epsilon_0 L) + \tau_{+-}(L)\}. \tag{3.8}$$

Starting with the virial equation in the form[12]

$$\beta P^{ex} = \frac{-1}{6} \sum_i \sum_j \rho_i \rho_j \int_0^\sigma r \frac{d[1 + f_{ij}(r)]}{dr} y_{ij}(r) 4\pi r^2\, dr, \tag{3.9}$$

where $f_{ij}(r)$ is the Mayer f function, we find that for the electrolyte model,

$$\frac{\beta P^{ex}}{\rho} = \frac{2\pi\rho\sigma^3}{3}[1 + h_s(\sigma)] - \frac{\kappa H}{\sigma} - \frac{\langle N \rangle}{2}\{1 + L y'_{+-}(L)/[3 y_{+-}(L)]\}, \tag{3.10}$$

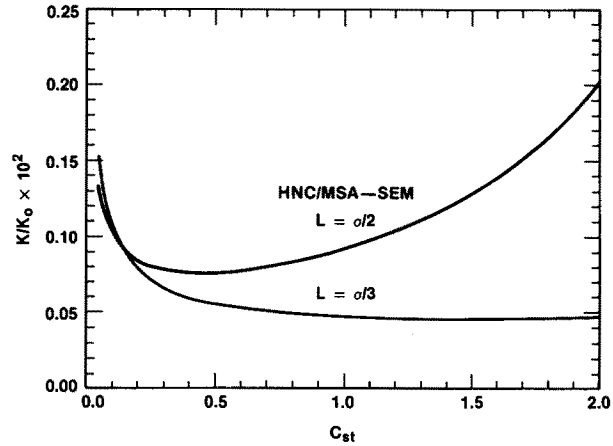

FIG. 3. The reduced mass action association constant K/K_c for a 2–2 electrolyte as a function of the electrolyte concentration c_{st} in the SEM with $L = \sigma/2$ and $\sigma/3$ ($T = 298$ K, $\epsilon_0 = 78.358$, and $\sigma = 4.2$ Å, $\epsilon_2/k = 4000$ K, $w = 0.1\sigma$).

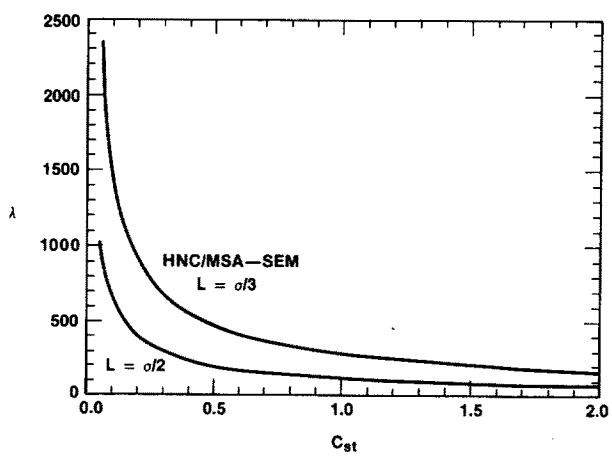

FIG. 2. The parameter λ as a function of the electrolyte concentration c_{st} for a 2–2 electrolyte using the SEM in HNC/MSA with $L = \sigma/2$ and $\sigma/3$ ($T = 298$ K, $\epsilon_0 = 78.358$, $\sigma = 4.2$ Å, $\epsilon_2/k = 4000$ K, $w = 0.1\sigma$).

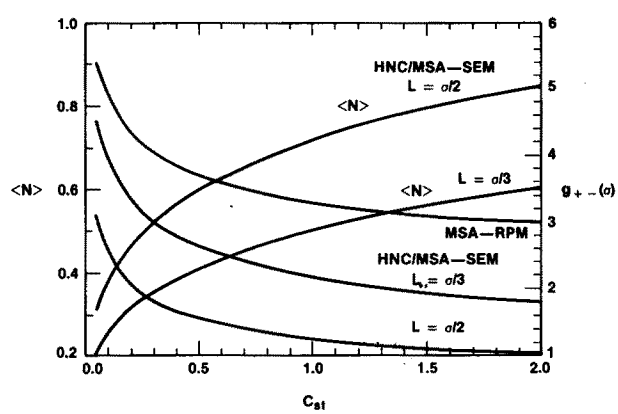

FIG. 4. The average number $\langle N \rangle$ of oppositely charged ions at $\sigma/2$ and $\sigma/3$ from the center of a given ion of a 2–2 electrolyte in the SEM. The distribution functions at contact for oppositely charged ions in the RPM and SEM with $L = \sigma/2$ and $\sigma/3$ are also shown ($T = 298$ K, $\epsilon_0 = 78.358$, $\sigma = 4.2$ Å, $\epsilon_2/k = 4000$ K, $w = 0.1\sigma$).

TABLE I. The contact values of the distribution functions $g_{+-}(r)$ at $r=\sigma$ and the cusp at $r=\sigma+L$ for a 2–2 electrolyte.[a]

	RPM	$L=\sigma/2$ (SEM)				$L=\sigma/3$ (SEM)	
	$g_{+-}(\sigma)$	$g_{+-}(\sigma)$		$g_{+-}(L+\sigma)$		$g_{+-}(\sigma)$	
c_{st}	MSA	HNC/MSA	HNC	HNC/MSA	HNC	HNC/MSA	HNC
0.1	4.87	2.60	5.93	...	2.62	3.93	15.4
0.5625	3.62	1.51	1.93	1.14	1.27	2.56	4.82
1.0	3.28	1.25	1.42	1.06	1.13	2.18	3.35
1.5	3.10	1.11	1.18	1.04	1.08	1.94	2.65
2.0	3.01	1.03	1.07	1.05	1.07	1.80	2.27

[a] $\epsilon_0=78.358$, $T=298$ K, $\epsilon_2=4000$ K, $w=0.1\sigma$, $\sigma=4.2$ Å.

where $y'_{+-}(L)$ is the derivative of $y_{+-}(r)$ with respect to r at $r=L$. The osmotic coefficient ϕ_v is defined by $P^{ex}/\rho kT=\phi_v-1$. The compressibility equation is given by Eq. (4.8) of Ref. 2 or alternatively Eq. (144) of Ref. 13 with

$$G_{+-}=4\pi\int_0^\infty h_{+-}(r)r^2\,dr$$

$$=2\langle N\rangle/\rho+4\pi\int_\sigma^\infty h_{+-}(r)r^2\,dr. \tag{3.11}$$

We also define the deviations[14(a),14(b)] from the electro-neutrality and second moment conditions[15,16] by

$$\Delta_0=(1-S_0) \tag{3.12}$$

and

$$\Delta_2=(1-S_2), \tag{3.13}$$

where for the SEM,

$$S_0=\langle N\rangle+\rho\int_\sigma^\infty h_D(r)4\pi r^2\,dr, \tag{3.14}$$

$$S_2=\kappa^2\left[\langle N\rangle L^2+\rho\int_\sigma^\infty h_D(r)4\pi r^4\,dr\right]\Big/6. \tag{3.15}$$

IV. RESULTS AND DISCUSSION

Except as noted below, the model parameters used in our calculation of the equilibrium properties of the SEM with $L=\sigma/3$ are the same as those used previously with $L=\sigma/2$. The width w and the depth ϵ_2/k of the sticky well are assumed to be 0.1σ and 4000 K, respectively, and the ions are assumed to have a diameter of 4.2 Å and a charge $2e$, where e is the electronic charge. The temperature is taken as 25 °C and the dielectric constant ϵ_0 of the continuum background is 78.358. In viewing our results for the two electrolytes, it should be borne in mind that the dipole moments of the ion pairs are in the ratio 3:2. When we compare our MSA results for dipolar dumbbells with the Monte Carlo simulations[3,4] however, the parameters correspond naturally to those for which the simulations have been carried out. The model parameters are now adjusted in both cases ($L=\sigma/2$ and $\sigma/3$) to give the reduced dipole moments[3,4] $\mu^*=(\beta\mu^2/\sigma^3)^{1/2}$ of 1.52 and 1.42, respectively. The reduced densities $\rho_D\sigma^3$ are 0.462 and 0.526, respectively, where ρ_D is the density of the dipolar dumbbells, and the direct correlation function in the MSA is assumed to be given by Eqs. (2.26) and (2.7). Since the dipoles are formed by allowing two oppositely charged ions to stick together, the total density of the ions which associate to form dipoles is twice that of the dipoles.

The association parameters λ, the reduced association constant K/K_0,[1] and the average number $\langle N\rangle$ of ions bound to a given ion are plotted against the electrolyte concentration in Figs. 2, 3, and 4, respectively, for $L=\sigma/3$ and $\sigma/2$. In the concentration range shown (0.05–2.0 molar) the values of λ, K/K_0, and $\langle N\rangle$ are essentially the same in the HNC/MS

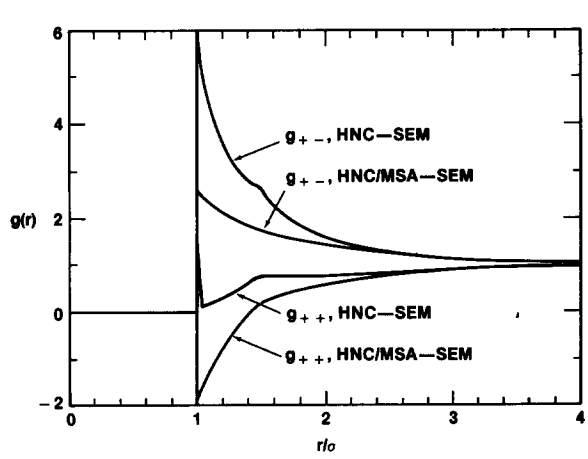

FIG. 5. The pair distribution functions $g_{+-}(r)$ and $g_{++}(r)$ of a 2–2 electrolyte at a concentration $c_{st}=0.1$ M according to the HNC/MS and HNC approximations for the SEM with $L=\sigma/2$ ($T=298$ K, $\epsilon_0=78.358$, $\sigma=4.2$ Å, $\epsilon_2/k=4000$ K, $w=0.1\sigma$). The peak in the HNC $g_{++}(r)$ at $r=\sigma$ (Table II) corresponds to triplet formation. The cusp is discussed in the text.

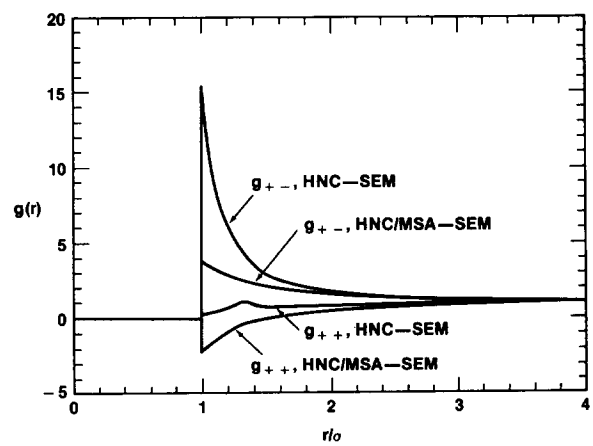

FIG. 6. The pair distribution functions $g_{+-}(r)$ and $g_{++}(r)$ for the system at $c_{st}=0.1$ M depicted in Fig. 5 except that $L=\sigma/3$.

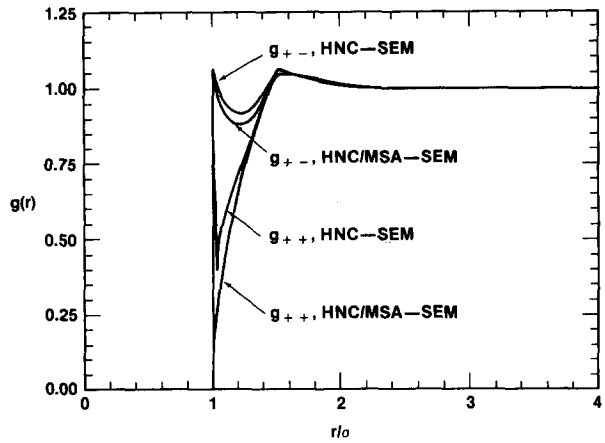

FIG. 7. The pair distribution functions $g_{+-}(r)$ and $g_{++}(r)$ for the system depicted in Fig. 5 ($L = \sigma/2$) except that $c_{st} = 2.0$ M. The peak in the HNC $g_{++}(r)$ at $r = \sigma$ (Table II) corresponds to triplet formation.

and HNC approximations. The magnitudes of distribution functions at contact $g_{+-}(\sigma)$ for oppositely charged ions, also plotted as a function of the concentration in Fig. 4, are however quite different for these two approximations. Table I provides a more detailed comparison. Although the association parameter λ is larger for $L = \sigma/3$ than for $L = \sigma/2$ (see Fig. 2), the average number of ion pairs $\langle N \rangle$ is smaller because $\langle N \rangle$ is determined by the product of λ and $(L/\sigma)^3$ [see Eq. (1.6)] and an increase in λ is compensated for by a decrease in $(L/\sigma)^3$ when L is changed from $\sigma/2$ to $\sigma/3$. These studies confirm our earlier conclusion[1] that an increase in the number of bonded pairs is accompanied by a decrease in the distribution functions at contact for unlike ions (see Fig. 4). Thus, the smaller values of $\langle N \rangle$ for $L = \sigma/3$ are accompanied by a smaller reduction in the distribution functions at contact $g(\sigma)$ below those for the RPM (see Table I).

The atom–atom correlation functions for + + and + − ions in the HNC/MS and HNC approximations are shown in Figs. 5 to 8 at 0.1 and 2.0 M, respectively, for $L = \sigma/2$ and $\sigma/3$. The correlation functions for the two approximations become more nearly alike as the concentration

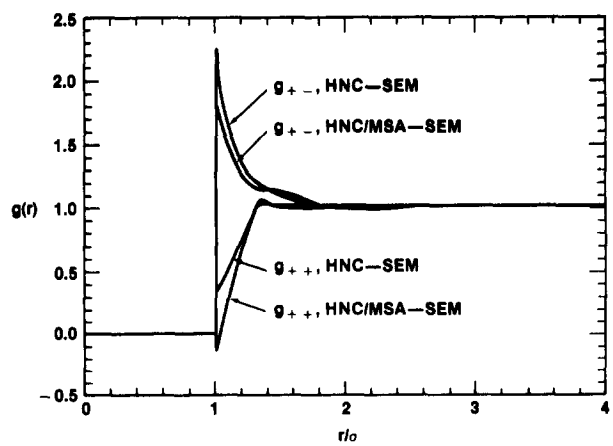

FIG. 8. The pair distribution function $g_{+-}(r)$ and $g_{++}(r)$ for the system at $c_{st} = 2.0$ M depicted in Fig. 7 except that $L = \sigma/3$.

increases. The HNC/MSA predicts negative correlation functions near contact between ions of like charge at low concentrations which is, of course, unrealistic. The appearance of a cusp at $L + \sigma$ in the HNC and HNC/MS correlation functions, when $L = \sigma/2$, suggests that it is not an artifact of the approximations used but a real phenomenon related to what is observed for uncharged systems. The increased prominence of the cusps at higher concentrations may be aided by greater shielding, as suggested in Ref. 1. The cusps become less pronounced as L decreases and are hardly visible when $L = \sigma/3$. Additional features of the correlation functions are discussed below.

Thermodynamic properties and other data for the SEM in the HNC approximation are given in Table II. The excess energies of the SEM and the RPM are drawn in Fig. 9 from which we note that they are nearly the same for the two approximations considered. A large part of the excess energy comes from the binding energy of dimerization. Figure 10 shows the osmotic coefficients ϕ of the SEM and RPM according to the HNC approximation. Dimerization apparently causes a decrease in the pressure. The changes in the free energy and the osmotic coefficient of the electrolyte when stickiness is introduced are tabulated in Table III. Since the association parameter λ is essentially the same for the HNC/MS and HNC approximations, the agreement between the changes in ϕ computed by two different routes is a reflection of the accuracy with which these differences can be predicted by either of these two approximations.

The + + (or − −) correlation functions in the HNC approximation show a peak at $r = \sigma +$ and $L = \sigma/2$ implying the existence of triplets. This is consistent with the Hamiltonian, when L is interpreted as $\sigma + /2$. As expected, the peak disappears when $L < \sigma/2$ but a small blip (see Fig. 11) indicating quadruplet formation at $r = 3L$ appears in the correlation functions for oppositely charged ions, when L lies between $\sigma/2$ and $\sigma/3$. This is quite distinct from the cusp at $L + \sigma$, but the two reinforce each other in the special case that $L = \sigma/2$. These unexpected features, which are absent in the HNC/MSA, show that the HNC theory does not necessarily obey the restriction to dimers implied by the Hamiltonian when $L < \sigma/2$. This can be understood by examining the leading terms[17] in the graphical f-bond expansion of the indirect correlation functions for + − ions. The diagrams, to lowest order in the density, which contribute to $h_{+-}(r)$ for a linear configuration of four alternating positive and negative ions with each adjacent pair bonded at a distance L, are shown below.

A dark line denotes a delta function bonding two oppositely charged ions separated by a distance L and a dotted line represents an f bond of − 1 between two charges at a distance less than the hard core diameter but not equal to L when the charges are of opposite sign. The root points, denoted by open circles, are at a distance $3L$ apart. If the magnitude of the first diagram is I, the magnitudes of the others

TABLE II.[a] Thermodynamic properties and zeroth- and second-moment tests of HNC results for the SEM of a 2–2 electrolyte.[b]

	$-E^{ex}/NkT$		ϕ_v		$-\partial \ln \gamma \pm / \partial \ln c$		$g_{++}(\sigma)$		$\Delta_0(\%)$		$\Delta_2(\%)$	
c_{st}	$L=\sigma/2$	$L=\sigma/3$	$L=\sigma/2$	$L=\sigma/3$	$L=\sigma/2$	$L=\sigma/3$	$L=\sigma/2$	$L=\sigma/3$	$L=\sigma/2$	$L=\sigma/3$	$L=\sigma/2$	$L=\sigma/3$
0.1	3.45	2.94	0.391	0.483	0.348	0.359	1.26	0.199	0.140	0.210	4.43	3.44
0.5625	5.01	4.26	0.274	0.395	0.294	0.302	0.673	0.196	0.155	0.070	5.17	1.20
1.0	5.54	4.73	0.288	0.417	0.218	0.225	0.699	0.237	0.239	0.101	10.4	2.62
1.5	5.92	5.06	0.330	0.467	0.117	0.124	0.741	0.282	0.324	0.134	17.0	4.53
2.0	6.18	5.30	0.387	0.529	0.0023	0.011	0.789	0.325	0.396	0.164	23.9	6.67

[a] $g_{+-}(\sigma)$ is given in Table I.
[b] $\epsilon_0 = 78.358$, $T = 298$ K, $\epsilon_2 = 4000$ K, $w = 0.10\sigma$, $\sigma = 4.2$ Å.

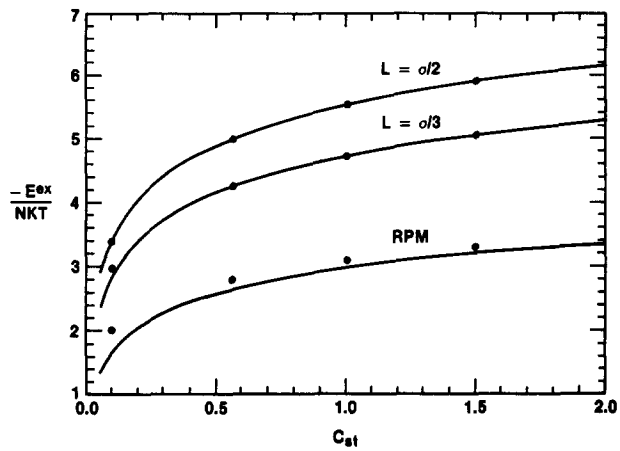

FIG. 9. The excess energy E^{ex} in dimensionless units of NkT as a function of the electrolyte concentration c_{st} for a 2–2 electrolyte according to two different models—RPM and SEM. The lines and points are the results of the HNC/MS and HNC approximations for the SEM or the MS and HNC approximation for the RPM, respectively. The other parameters are the same as for the preceding figures. In addition, $\partial\epsilon_0/\partial T$ is assumed to be zero.

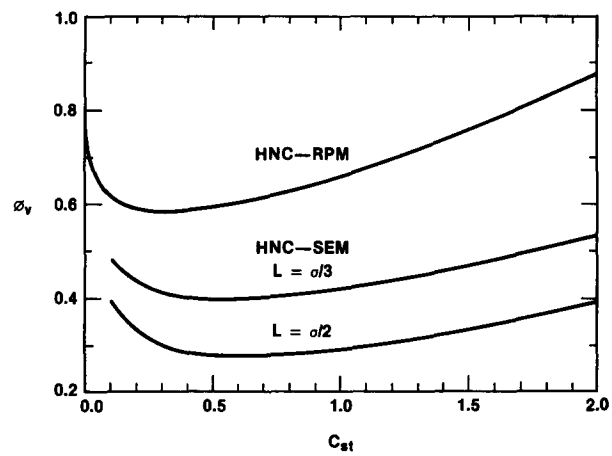

FIG. 10. The osmotic coefficient ϕ_v calculated from the virial equation as a function of the electrolyte concentration c_{st} for a 2–2 electrolyte according to two different models—RPM and SEM in the HNC approximations. The parameters are the same as for Fig. 8.

TABLE III. Changes in the excess Helmholtz free energy and the osmotic coefficient of a model 2–2 electrolyte[a] when the stickiness is turned on.

	$\Delta \equiv$ SEM–RPM		
c_{st}	$-\Delta A^{ex}NkT$ (HNC/MSA)	$-\Delta\phi_z$ (HNC/MSA)	$-\Delta\phi_v$ (HNC)
0.1	0.835	0.21	0.22
0.5625	1.25	0.30	0.32
1.0	1.46	0.36	0.37
1.5	1.63	0.44	0.42
2.0	1.68	0.50	0.49

[a] $\epsilon_0 = 78.358$, $T = 298$ K, $\sigma = 4.2$ Å, $L = \sigma/2$, $\epsilon_2 = 4000$ K, $w = 0.1\sigma$.

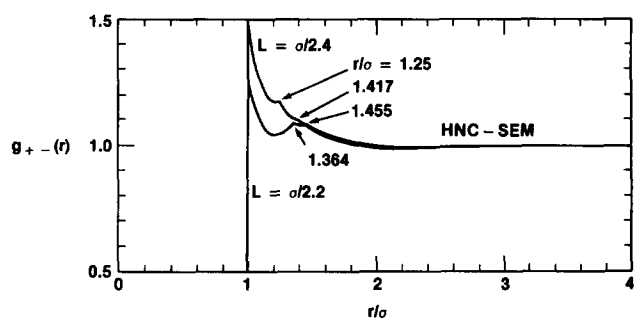

FIG. 11. The pair distribution functions $g_{+-}(r)$ for oppositely charged ions of a 2–2 SEM electrolyte with $L = \sigma/2.2$ and $\sigma/2.4$ at a concentration $c_{st} = 2.0$ M in the HNC approximation ($T = 298$ K, $\epsilon_0 = 78.358$, $\sigma = 4.2$ Å, $\epsilon_2/k = 4000$ K, $w = 0.1\sigma$). The arrows point to small peaks at $r = 3L$ (tetramers) and $r = L + \sigma$ (cusp).

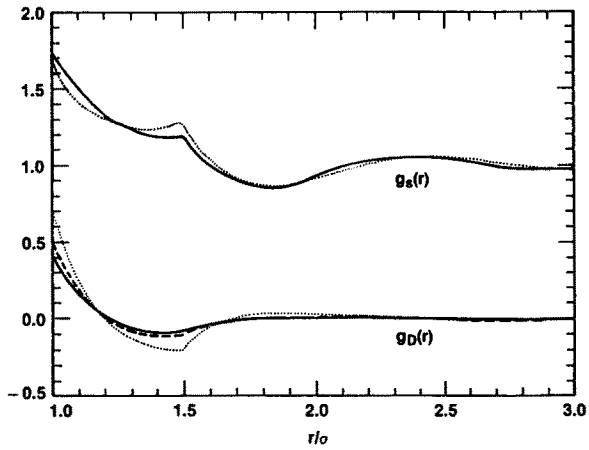

FIG. 12. The sum and difference distribution functions $g_s(r)$ and $g_D(r)$ for dipolar dumbbells with $L = \sigma/2$. The dotted, solid, and broken lines show the Monte Carlo results, MSA results for the SEM with $A = 1.0$ and $A = 1.25$, respectively. The model parameters are $T = 253$ K, $\sigma = 3.5$ Å, $\rho_D\sigma^3 = 0.462$, and $\mu = 6.2\times10^{-30}$ C m, where ρ_D is the density of dipolar dumbbells. $\mu^* = (\mu^2/kT\sigma^3)^{1/2} = 1.52$.

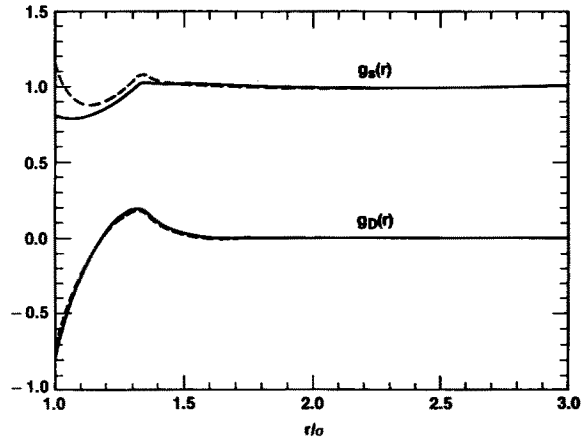

FIG. 14. Comparison of the sum and difference distribution functions for dipolar dumbbells with $L = \sigma/3$ calculated according to the MS and HNC approximations for the SEM with $A = 1.0$. The other parameters are $T = 253$ K, $\sigma = 3.5$ Å, $\rho_D\sigma^3 = 0.0517$ (or $c_{st} = 2.0$ M), $\mu = 6.2\times10^{-30}$ C m. $\mu^* = (\mu^2/kT\sigma^3)^{1/2} = 1.52$. The broken and solid lines show the HNC and MS approximations, respectively.

are $-I$, $-I$, and I, respectively. The last diagram (a bridge function) is absent in the HNC approximation, and cancellation is incomplete when they are summed, leaving a small probability for the formation of quadruplets at $r = 3L$ in the HNC approximation. It is easily verified that trimers, with the end atoms separated by $2L$ cannot occur if $L < \sigma/2$. In the limit of complete dimerization the calculated atom–atom correlation functions show no evidence of the formation of distinct polymeric forms when $L < \sigma/2$.

In Figs. 12 and 13 we compare our MSA correlation functions with Monte Carlo calculations for dipolar dumbbells.[3,4] To compute the MSA correlation functions in a self-consistent way one needs to determine λ and A in each step of an iterative procedure beginning with an appropriate trial function, until the correlation functions and the dielectric constants, calculated from these functions[18] converge. This is beyond the scope of this paper, but since the effects are small, we determine the MSA correlation functions with values of A determined from the dielectric constant estimated by computer simulation.[3,4] We assume $\epsilon = 5.0$ and 9.5, respectively, for $L = \sigma/2$ and $\sigma/3$. This corresponds to A values of 1.25 and 1.12 respectively. Figures 12 and 13 show that there is a small improvement in the $h_D(r)$ correlation functions near contact over calculations assuming A to be unity. The sum functions are unaffected by the choice of A since they reflect the properties of the corresponding uncharged system. The correlation functions for a fully associated 2.0 M electrolyte are also shown in Fig. 14 assuming A and the dielectric constant ϵ_0 of the background equal to unity, and $L = \sigma/3$. The agreement between the MS and HNC approximations for the difference correlation functions at this concentration is good. It is the sum function in the MSA, which refers to an uncharged system [see Eq. (2.7)], that requires improvement.

Fries and Patey[19] have solved the HNC approximation applied to the molecular correlation functions of spheres with point dipoles, while Morris and Perram[20] and Morris and Isbister[9] have treated dipolar dumbbells in the interaction site approximation and in the analog of the zero pole approximation respectively using the site–site Ornstein–Zernike equation. The methods discussed here and in Ref. 1 illustrate an alternative approach to the study of ions and dipoles using a single theoretical framework. Its application to other chemically interesting systems, e.g., the dissociation of weak acids, would be of great interest.

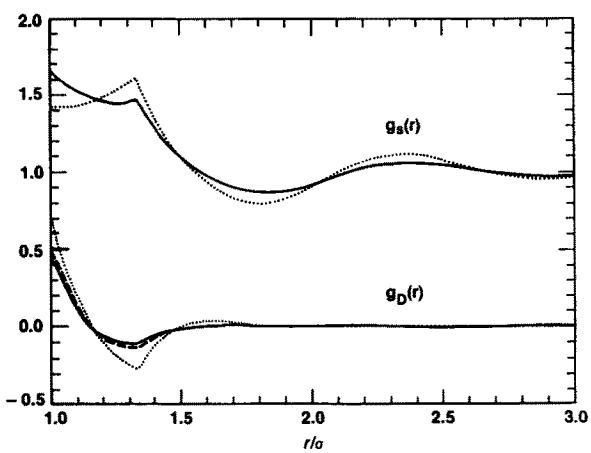

FIG. 13. The sum and difference distribution functions $g_s(r)$ and $g_D(r)$ for the dipolar dumbbell system $L = \sigma/3$ with $A = 1.0$ and $A = 1.12$. The model parameters are $T = 253$ K, $\sigma = 3.5$ Å, $\rho_D\sigma^3 = 0.526$, $\mu = 5.792\times10^{-30}$ C m, where ρ_D is the density of the dipolar dumbbells. $\mu^* = (\mu^2/kT\sigma^3)^{1/2} = 1.42$. See caption of Fig. 12 for explanation of graph.

ACKNOWLEDGMENTS

We thank Gary Morris for the details of the simulations for dipoles at $L = \sigma/2$ and Dennis Isbister (RMC) for new simulations at $L = \sigma/3$. The hospitality and computing facilities at the National Bureau of Standards, where this research was done, are most gratefully acknowledged. This research was supported by a grant from the National Science Foundation No. CHE-8305747.

APPENDIX A: THE ASYMPTOTIC FORM OF THE DIRECT CORRELATION FUNCTION FOR DIPOLAR DUMBBELLS

The OZ equation (2.4) for the difference functions can be written in Fourier space as

$$[1-\rho\tilde{h}_D(k)][1+\rho\tilde{c}_D(k)]=1, \tag{A1}$$

where $\tilde{h}_D(k)$ and $\tilde{c}_D(k)$ are the Fourier transforms of $h_D(r)$ and $c_D(r)$, respectively. From Eq. (2.6) it follows that

$$h_D(r)=\lambda L\delta(r-L)/24+h'_D(r), \tag{A2}$$

where $h'_D(r)$ is the contribution to $h_D(r)$ from the intramolecular part of the indirect correlation functions when association is complete [$\lambda\eta=(\sigma/L)^3$]. For this case Fourier transformation of Eq. (A2) gives

$$\tilde{h}_D(k)=\frac{\pi\lambda L^3}{6}w(k)+\tilde{h}'_D(k), \tag{A3}$$

where

$$w(k)=\sin(kL)/(kL)=1-k^2L^2/6+\cdots. \tag{A4}$$

For sufficiently large r we assume that the direct correlation functions $c_D(r)$ may be written as

$$c_D(r)=c_D^0(r)+\beta e^2A\exp(-zr)/r, \tag{A5}$$

where the short range part $c_D^0(r)$ contains a delta function reflecting the delta function in $h_D(r)$. Taking the Fourier transform of Eq. (A5) followed by the limit $z\to 0$, we have for the completely associated electrolyte,

$$\rho\tilde{c}_D(k)=\rho\tilde{c}_D^0(k)+\kappa^2A/k^2$$
$$=1-k^2L^2/6+\kappa^2A/k^2+\cdots, \tag{A6}$$

where we assume no singularities in $c_D^0(r)$ other than the delta function. Inserting Eqs. (A3) and (A6) in Eq. (A1), and collecting terms to order k^2 in $\rho\tilde{h}'_D(k)$ we find

$$\rho\tilde{h}'_D(k)=k^2[L^2/6-1/(\kappa^2A)]+O(k^4). \tag{A7}$$

Comparing this with the expression for the dielectric constant of dipolar diatomics,[18]

$$\rho\tilde{h}'_D(k)=k^2L^2[1/6-(\epsilon-1)/(18y\epsilon)]+O(k^4), \tag{A8}$$

where $18y=(\kappa L)^2=4\pi\beta\rho(eL)^2$, it follows that

$$A=\epsilon/(\epsilon-1). \tag{A9}$$

The assumption $A=1$ implies $\epsilon=\infty$. In contrast to Eq. (A9) the asymptotic form of the direct correlation function defined through the site–site Ornstein–Zernike equation is given by Eq. (1.1) but with a different state dependent coefficient[21] $A=[1+\epsilon(3y-1)]/[3y(\epsilon-1)]$. For nonlinear triatomic molecules the SSOZ direct correlation function diverges.[21] Chandler *et al.*[22,23] have discussed improvements to the SSOZ for which the SSOZ direct correlation functions are well behaved at infinity. We have been informed recently that Eq. (A9) has been derived independently by Stell and Cummings.[24]

APPENDIX B: THE EXCESS ENERGY OF THE SEM WHEN $L=\sigma/n$ IN THE MSA WHERE n IS AN INTEGER

Equation (2.9a) for the function $h_D(r)$ can be written in the form

$$rh_D(r)=q_D^{0\prime}(r)+2\pi\rho\int_0^\sigma dt\,q_D^0(t)(r-t)h_D(|r-t|)$$
$$-2\pi\rho MJ(r), \tag{B1}$$

where

$$2\pi\rho M=-\kappa, \tag{B2}$$

and $J(r)$ is defined in Eq. (2.17). It follows that

$$J(r)=J(0),\quad 0<r<\sigma/n \tag{B3}$$
$$=J(\sigma)=J(0)-p/(2\pi\rho),\quad \sigma/n<r<\sigma, \tag{B4}$$

where p is redefined here as $2\pi\rho\lambda L^2/24$. As discussed in Sec. II the MSA closure implies that $q_D^0(r)=0$ for $r>\sigma$. Combining Eqs. (2.4) and (B1) we find that

$$q_D^{0\prime}(r)-pq_D^0(r+\sigma/n)=pM-H,\quad 0<r<\sigma/n, \tag{B5}$$
$$q_D^{0\prime}(r)-p[q_D^0(r+\sigma/n)$$
$$-q_D^0(r-\sigma/n)]=-H,\quad \sigma/n<r<(n-1)\sigma/n, \tag{B6}$$
$$q_D^{0\prime}(r)+pq_D^0(r-\sigma/n)=-H,\quad (n-1)\sigma/n<r<\sigma, \tag{B7}$$

where the constant $H=-2\pi\rho MJ(\sigma)=\kappa J(\sigma)$. The solution $q_D^0(r)$ has n distinct domains and n constants to be determined by n boundary conditions. The details of the solutions are determined by whether n is odd or even. However the essential point in our derivation of the general form for the energy is that M, H, and $\nu=\eta\lambda/(2n^2)=\langle N\rangle n/2$ appear linearly as coefficients of functions of r in the solutions. This is a simple consequence of the fact that Eqs. (B4) to (B6) are linear differential equations. It follows immediately that the integrals of the solutions are also linear combinations of M, H, and ν. To see why this is relevant consider the integrated form of Eq. (B1) which is

$$J(r)=-q_D^0(r)-M/2+2\pi\rho\int_0^\sigma dt\,q_D^0(t)J(|r-t|)$$
$$-\kappa\int_0^r J(t)\,dt. \tag{B8}$$

When $r=0+$,

$$J(0)=-q_D^0(0)-M/2+2\pi\rho\left[J(0)\int_0^{\sigma/n}dt\,q_D^0(t)\right.$$
$$\left.+J(\sigma)\int_{\sigma/n}^\sigma dt\,q_D^0(t)\right]. \tag{B9}$$

Equation (B9) is equivalent to

$$H=pM+\pi\rho M^2+2\pi\rho H\int_0^\sigma dt\,q_D^0(t)$$
$$+2\pi\rho M\left[q_D^0(0)-p\int_0^{\sigma/n}dt\,q_D^0(t)\right]. \tag{B10}$$

Since the integrals are linear combinations of H, M, and ν, Eq. (B10) can be written in dimensionless units as

$$H'=\nu M'+6\eta M'^2+12\eta H'[bH'+cM'+d\nu/(12\eta)]$$
$$-12\eta M'[eH'+fM'+g\nu/(12\eta)], \tag{B11}$$

where b, c, d, e, f, and g are coefficients and $H'=H/\sigma$, $M'=M/\sigma^2$. Rearrangement of Eq. (B10) leads to a quadratic equation for H':

$$12b\eta H'^2+H'[(\nu d-1)+12\eta M'(c-e)]$$
$$+M'[\nu(1-g)+6\eta M'(1-2f)]=0 \tag{B12}$$

whose solution, taking note of Eq. (B2), is

$$H' = \frac{(1-\nu d) + x(c-e) - \{(1-\nu d)^2 + 2x[(1-\nu d)(c-e) + 2b\nu(1-g)] + X\}^{1/2}}{24b\eta}, \tag{B13}$$

where $x = \kappa\sigma$ and

$$X = 144\eta^2 M'^2[(c-e)^2 - 2b(1-2f)]. \tag{B14}$$

The requirement that $H' \to H'$ (RPM) when $\lambda = 0$ determines the negative sign in front of the square root in Eq. (B13). Comparing Eqs. (B13) and (2.22) we find

$$c - e = 1 + f_{1,n}(\nu), \quad b = \tfrac{1}{2} + f_{2,n}(\nu), \quad X = f_{3,n}(\nu), \tag{B15}$$

where $f_{i,n}(\nu) = 0$ when $\nu = 0$. For $n = 1$ to 4 we find, from the detailed solutions, that $X = 0$, but we do not have a general proof that this holds for arbitrary n. In the saturation limit $\nu = n/2$ and Eq. (2.28) for the excess energy (excluding the binding energy) follows from Eqs. (B13), (B15), and (1.9) with $d \ln \epsilon_0 / d \ln T = 0$.

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