Chemical ion association and dipolar dumbbells in the mean spherical approximation

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(Received 25 August 1986; accepted 26 September 1986)

The sticky electrolyte model (SEM) is solved analytically in the mean spherical approximation (MSA) for binding between oppositely charged ions of a symmetrical electrolyte at a distance $L = \sigma/4$ and $\sigma/5$, where σ is the atomic diameter, extending earlier analytic studies for $L = \sigma$, $\sigma/2$, and $\sigma/3$. The excess energy of a fluid of dipolar dumbbells of elongation $L < \sigma/2$ is calculated in this approximation by considering the saturation limit when all the ions are associated to form dimers and steric hindrance prevents polymerization. The results are in good agreement with Monte Carlo simulations for dipolar dumbbells and compare favorably with the solutions to the MSA and the HNC approximation using the site–site Ornstein–Zernike equation.

I. INTRODUCTION

The sticky electrolyte model (SEM), in which stickiness or bonding exists between oppositely charged ions, has been introduced recently[1–3] in the study of electrolytes. It is related to Baxter's model[4] for surface adhesion and to the model for chemical association investigated by Cummings and Stell.[5] An important feature of this model is that it enables a dipolar fluid, under appropriate circumstances, to be considered as the limit of complete chemical association of ions into dipoles so that the same theory may be used for both species. Between the extremes of complete dissociation and complete association we have an equilibrium mixture of ions and dipoles similar to the behavior of a weak acid.

In this paper we use the SEM to undertake an investigation of dipolar dumbbells for several values of the charge (and atom) separation L ranging from $L = 1$ to $0.2\,\sigma$, where σ is the diameter of the atoms. We employ the mean spherical approximation (MSA) for the direct correlation functions defined through the Ornstein–Zernike (OZ) equation and compare our analytic results for the energy in this approximation with Monte Carlo (MC) simulations[6] of this property. We also compare our results for dipolar dumbbells with the solutions obtained by others[7] to the MSA and the hypernetted chain (HNC) approximations for the direct correlation functions defined through the site–site Ornstein–Zernike equation (SSOZ). The direct correlation functions for the atoms in dipolar dumbbells have different asymptotic forms when they are defined through the OZ[2] and SSOZ[8] equations, respectively. Our study shows that the energy obtained from the MSA associated with the OZ equation is sensitive to the details of the asymptotic form of the direct correlation function used in the formulation of this approximation. The usual assumption is, that, away from the critical point, the asymptotic form of the direct correlation function $c_{ij}(r)$ is given by

$$c_{ij}(r) = -Ae_ie_j/(kTr), \quad (1.1)$$

where $A = 1$, e_i and e_j are the charges, separated by a distance r, on the atoms of two distinct dipoles, T is the absolute temperature, k is Boltzmann's constant, and the dielectric constant of the continuum background is taken as unity. However, the exact value[2] of A for a dipolar dumbbells is $\epsilon/(\epsilon - 1)$, where ϵ is the dielectric constant of the dipolar system. We find that the use of $A = 1$ instead of $\epsilon/(\epsilon-1)$ in the MSA leads to an error in the energy of the order of 15% for a typical dipolar fluid at liquid densities. The effect of the analogous correction[8] to the energies calculated with approximations associated with the SSOZ[7] equation has not been determined.

The SEM seeks to model chemical association between ions A and B to form a dipole AB or chemically associated ion pair according to the equation

$$A^+ + B^- \rightleftharpoons AB. \quad (1.2)$$

We assume a symmetrically charged electrolyte containing ions of equal size for which the Mayer f functions are defined by

$$f_{ij}(r) = -1 + L\xi(1-\delta_{ij})\delta(r-L)/12, \quad 0<r<\sigma \quad (1.3a)$$

$$= \exp(-\beta e_ie_j/\epsilon_0 r) - 1, \quad r>\sigma, \quad (1.3b)$$

where e_i is the charge on ion i, σ is the diameter of the ions, ϵ_0 is the dielectric constant of the solvent, δ_{ij} is a Kronecker delta, $\delta(r-L)$ is a delta function, and $\beta = 1/(kT)$. The parameter ξ is the sticking coefficient which measures the strength of the bonding or adhesiveness between unlike ions $(+, -)$; it is the inverse of the parameter τ used by Baxter[4] in his study of adhesive hard spheres.

The correlation function $h_{ij}(r)$ for $r<\sigma$ has the form

$$h_{ij}(r) = -1 + \lambda(1-\delta_{ij})L\delta(r-L)/12, \quad r<\sigma, \quad (1.4)$$

where the association parameter λ is related to the average number $\langle N \rangle$ of ion pairs by[1–3]

$$\langle N \rangle = \eta\lambda(L/\sigma)^3, \quad (1.5)$$

where $\eta = \pi\rho\sigma^3/6$ and ρ is the total concentration of the ions. The reduced association constant is given by[2]

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$$K = k'/\sigma^3 = \frac{\pi\lambda(L/\sigma)^3}{3(1-\langle N\rangle)^2} \quad (1.6)$$

When $\lambda = 0$ the system is identical to the RPM electrolyte, and when $\langle N\rangle = 1$ or $\lambda = (\sigma/L)^3/\eta$ every ion is on the average bonded to another ion of opposite sign. If $L < \sigma/2$, steric hindrance inhibits polymerization and the system should only contain dipolar dumbells when $\langle N\rangle = 1$.

The sticking coefficient ξ and the association parameter λ are related by

$$\lambda(\xi) = \xi y_{+-}(L, \xi) \quad (1.7)$$

which follows from Eqs. (1.3) and (1.4) and the cavity function $y_{ij}(r)$ in Eq. (1.7) is related to the distribution function $g_{ij}(r) = 1 + h_{ij}(r)$ by

$$g_{ij}(r,\xi) = [1 + f_{ij}(r,\xi)]y_{ij}(r,\xi). \quad (1.8)$$

When $0 < \lambda < (\sigma/L)^3/\eta$ the function $y_{+-}(L,\xi)$ is determined by the approximation (e.g., HNC or PY) used for the adhesiveness at contact.[1–3]

The Helmholtz free energy of the system is given by[2,3]

$$\beta[A(\text{SEM}) - A(\text{RPM})]$$
$$= -\tfrac{1}{2}\eta(L/\sigma)^3\int_0^{\xi} y_{+-}(L,\xi')d\xi' \quad (1.9a)$$
$$= -(v/n)[1 - \ln y_{+-}(L,\lambda)] - v/(2\lambda n) \times \int_0^{\lambda} \ln y_{+-}(L,\lambda')\,d\lambda', \quad (1.9b)$$

where $v = \eta\lambda(L/\sigma)^2/2 = n\langle N\rangle/2$ and $n = \sigma/L$, and the excess internal energy E is given by[2,3]

$$\beta E^{\text{ex}}/N = \langle N\rangle(d\ln\xi/d\ln\beta)/2 - (1 + d\ln\epsilon_0/d\ln T)\kappa H/2, \quad (1.10)$$

where κ is the inverse Debye length and $H = \kappa J(\sigma+)$ where $J(\sigma+)$ is defined by Eq. (2.18). The first term in Eq. (1.10) is the binding energy for pair formation, while the second term (also a function of λ) is determined by the remaining electrical interactions, which we determine 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) electrolyte. The virial equation for the pressure of the SEM[3] system is

$$\beta P^{\text{ex}}/\rho = 2\pi\rho\sigma^3[1 + h_S(L)]/3 - \kappa H/6 - \langle N\rangle\{1 + Ly'_{+-}(L)/[3y_{+-}(L)]\}/2, \quad (1.11)$$

where $y'_{+-}(L)$ is the derivative of $y_{+-}(r)$ with respect to r at $r = L$ and $h_S(L) = [h_{+-}(L) + h_{++}(L)]/2$.

The solutions to the MSA for the SEM with $L = \sigma, \sigma/2$, and $\sigma/3$ have been given elsewhere[1–3] and the new results presented here are for $L = \sigma/4$ and $\sigma/5$. This covers nearly the whole range of values for which Monte Carlo simulations of the energy[6] dipolar dumbbells are available. When the charges are turned off we have the corresponding solutions for association between neutral atoms at $L = \sigma/4$ and $\sigma/5$ supplementing those obtained earlier by Cummings and Stell[5] for $L = \sigma/2$ and $\sigma/3$.

This paper is organized as follows. In Sec. II the solutions to the MSA for the SEM with $L = \sigma/4$ and $\sigma/5$ are presented together with comments on the solutions for $L = \sigma/n$ where n is an integer. Our results for dipolar dumbbells are discussed in Sec. III where comparison is made with Monte Carlo simulations and other approximations for these systems associated with the SSOZ equation.

II. MSA SOLUTION OF THE SEM WITH $L=\sigma/4$ AND $\sigma/5$ WITH PARTIAL SOLUTIONS FOR $L=\sigma/n$

For the model considered here we have the exact relations

$$h_S(r) = -1 + \lambda L\delta(r-L)/24, \quad 0<r<\sigma, \quad (2.1a)$$
$$h_D(r) = \lambda L\delta(r-L)/24, \quad 0<r<\sigma, \quad (2.1b)$$

where $h_S(r)$ and $h_D(s)$ are the sum and difference correlation functions defined by $h_S(r) = [h_{+-}(r) + h_{++}(r)]/2$ and $h_D(r) = [h_{+-}(r) - h_{++}(r)]/2$. For the corresponding sum and difference direct correlation functions we have in the mean spherical approximation

$$c_S(r) = 0, \quad r>\sigma, \quad (2.2a)$$
$$c_D(r) = A\beta e^2/(\epsilon_0 r), \quad r>\sigma, \quad (2.2b)$$

where ϵ_0 is the dielectric constant of the solvent and we set A equal to unity for convenience in our mathematical analysis. A correction for this is made later in our treatment of dipolar dumbbells in a vacuum background. The short range part of the direct correlation function $c_D^0(r)$ is defined by

$$c_D^0(r) = c_D(r) - A\beta e^2/(\epsilon_0 r). \quad (2.2c)$$

As discussed elsewhere,[1–3] the OZ equation for this model system can be discussed in terms of a pair of equations for the sum correlation functions, $h_S(r)$ and $c_S(r)$, and a pair for the difference correlation functions, $h_D(r)$ and $c_D(r)$. As far as possible we keep our analysis general by taking $L = \sigma/n$. Consider first the sum OZ equations for $r>0$,

$$rc_S(r) = -q'_S(r) + 2\pi\rho\int_0^{\infty} q'_S(t)q_S(t-r)dt, \quad (2.3)$$

$$rh_S(r) = -q'_S(r) + 2\pi\rho\int_r^{\infty} q_S(t)(r-t)h_S(|r-t|)dt. \quad (2.4)$$

When the closure equation (2.2a) is inserted in Eq. (2.3), we find that

$$q_S(r) = 0 \quad \text{for} \quad r>\sigma. \quad (2.5)$$

From the integrated form of Eq. (2.4),

$$J_S(r) = q_S(r) + 2\pi\rho\int_0^{\sigma} dt\, q_S(t)J_S(|r-t|), \quad r>0, \quad (2.6)$$

where $J_s(r)$ is defined by

$$J_s(r) = \int_r^{\infty} th_S(t)dt \quad (2.7)$$

we find

$$q_S(\sigma-/n) - q_S(\sigma+/n) = \lambda\sigma^2/(24n^2) \quad (2.8)$$

since $J_S(\sigma-) = J_S(\sigma+) + \lambda\sigma^2/(24n^2)$. When $0<r<\sigma$, the solution to Eq. (2.4) is

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$$q_s'(r) = ar + b - \lambda\sigma^2(r - \sigma/n)/(24n^2) + (\pi\rho\lambda\sigma/12\eta)\int_0^\sigma (r-t)q_S(t) \times \delta(|r-t| - \sigma/n)dt, \quad (2.9)$$

where

$$a = 1 - 2\pi\rho\int_0^\sigma q_s(t)dt \quad (2.10)$$

and

$$b = 2\pi\rho\int_0^\sigma tq_S(t)dt. \quad (2.11)$$

The detailed expressions for $q_S'(s)$ are different for three separate regions of r:

$$q_S'(r) + pq_S(r+\sigma/n) = ar + b \ (0<r<\sigma/n) \quad (2.12a)$$

$$q_S'(r) + p[q_S(r+\sigma/n) - q_S(r-\sigma/n)] = ar + b \ [\sigma/n<r<(n-1)\sigma/n], \quad (2.12b)$$

$$q_S'(r) + p\,q_S(r-\sigma/n) = ar + b \ [(n-1)\sigma/n<r<\sigma], \quad (2.12c)$$

where $p = \pi\rho\lambda\sigma^2/(12n^2)$. These are a set of coupled differential equations whose solutions for $n = 2$ and 3 have already been given by Cummings and Stell.[5] The solutions become more complicated as n increases in magnitude. For a given integral n, it is necessary to split the interval $[\sigma/n, (n-1)\sigma/n]$ into subintervals of width σ/n with $q_S(r)$ continuous in this range. Thus

$$q_S(m\sigma - /n) = q_S(m\sigma + /n) \quad [m = 2,3,...(n-1)] \quad (2.13)$$

and Eq. (2.5) applies at $r = \sigma/n$. The general form of the solution depends on whether n is even or odd. The solutions for $n = 4$ and 5 are given below:

(a) $n = 4$:

$$q_S(r) = -2ar/p + a(3-v)/p^2 - 2b/p + A\cos(xpr) + B\sin(xpr) + E\cos(ypr) + F\sin(ypr) \quad (0<r<\sigma/4) \quad (2.14a)$$

$$= ar/p + a(2-v/4)/p^2 + b/p - Bx\cos[xp(r-\sigma/4)] + Ax\sin[xp(r-\sigma/4)] - Fy\cos[yp(r-\sigma/4)] + Ey\sin[yp(r-\sigma/4)] \quad (\sigma/4<r<\sigma/2) \quad (2.14b)$$

$$= -ar/p + a(2-v/4)/p^2 - b/p + Ax\cos[xp(r-\sigma/2)] + Bx\sin[xp(r-\sigma/2)] - Ey\cos[yp(r-\sigma/2)] - Fy\sin[yp(r-\sigma/2)] \quad (\sigma/2<r<3\sigma/4) \quad (2.14c)$$

$$= 2ar/p + a(3-v)/p^2 + 2b/p - B\cos[xp(r-3\sigma/4)] + A\sin[xp(r-3\sigma/4)] + F\cos[yp(r-3\sigma/4)] - E\sin[yp(r-3\sigma/4)] \quad (3\sigma/4<r<\sigma), \quad (2.14d)$$

where $x = (\sqrt{5}-1)/2$ and $y = (\sqrt{5}+1)/2$. Substitution in Eqs. (2.5), (2.8), (2.10), (2.11), and (2.13) with $m = 2, 3$ provides six equations which can be solved to give the coefficients a, b, A, B, E, and F which are given in Appendix A.

(b) $n = 5$:

The solution for $q_S(r)$ in the range $(0, \sigma)$ is

$$q_S(r) = ar^2/2 + (-a/p + 2a\sigma/5 + b)r + D + A\cos(pr) + B\sin(pr) + E\cos(\sqrt{3}pr) + F\sin(\sqrt{3}pr) \quad (0<r<\sigma/5) \quad (2.15a)$$

$$= a/p^2 - 2a\sigma/5p - B\cos[p(r-\sigma/5)] + A\sin[p(r-\sigma/5)] - \sqrt{3}F\cos[\sqrt{3}p(r-\sigma/5)] + \sqrt{3}E\sin[\sqrt{3}p(r-\sigma/5)] \quad (\sigma/5<r<2\sigma/5) \quad (2.15b)$$

$$= ar^2/2 + br + a\sigma(1-2v/5)/5p + b(1-2v/5) + D - 2E\cos[\sqrt{3}p(r-2\sigma/5)] - 2F\sin[\sqrt{3}p(r-2\sigma/5)] \quad (2\sigma/5<r<3\sigma/5) \quad (2.15c)$$

$$= a/p^2 - 2a\sigma/5p - B\cos[p(r-3\sigma/5)] + A\sin[p(r-3\sigma/5)] + \sqrt{3}F\cos[\sqrt{3}p(r-3\sigma/5)] - \sqrt{3}E\sin[\sqrt{3}p(r-3\sigma/5)] \quad (3\sigma/5<r<4\sigma/5) \quad (2.15d)$$

$$= ar^2/2 + (a/p - 2a\sigma/5 + b)r + 2b(1-2v/5)/p + D - A\cos[p(r-4\sigma/5)] - B\sin[p(r-4\sigma/5)] + E\cos[\sqrt{3}p(r-4\sigma/5)] + F\sin[\sqrt{3}p(r-4\sigma/5)] \quad (4\sigma/5<r<\sigma). \quad (2.15e)$$

The constants a, b, A, B, D, E, and F are determined from Eqs. (2.8), (2.10), (2.11), and (2.13) (with $m = 2,3,4$) and are given in Appendix A. The $q_S(r)$ functions for $n = 2,3,4$, and 5 are plotted in Fig. 1 together with the corresponding $q_D^0(r)$ functions discussed below.

As shown elsewhere[1–3] the difference OZ equation for electrolytes leads to the following pair of equations:

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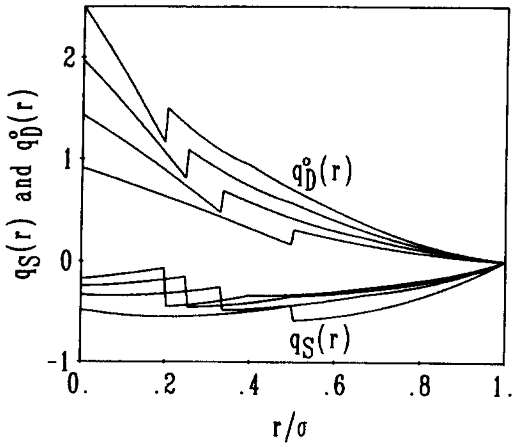

FIG. 1. The $q_S(r)$ and $q_D^0(r)$ functions inside the hard core for dipolar dumbbells. The different elongations $L = \sigma/n$ with $n = 2,3,4$, and 5 are identified by the discontinuities in these functions at $r = 0.5$, 0.333, 0.25, and 0.2σ, respectively.

$$rc_D^0(r) = q_D^{0\prime}(r) + 2\pi\rho\left[Mq_D^0(r) - \int_0^\infty q_D^0(s)q_D^{0\prime}(r+s)ds\right] \tag{2.16}$$

and

$$rh_D(r) = q_D^{0\prime}(r) + 2\pi\rho\left[\int_0^\infty q_D^0(s)(r-s)\,h_D(|r-s|)ds\right] - 2\pi\rho MJ_D(r). \tag{2.17}$$

$q_D^0(r) = 0$ for $r<0, M$ is related to the inverse Debye length κ by $-2\pi\rho M = \kappa$ and $J_D(r)$ is defined by

$$J_D(r) = \int_r^\infty sh_D(s)ds. \tag{2.18}$$

In the MSA,

$$c_D^0(r) = 0 \quad (r>\sigma), \tag{2.19}$$

and it follows from Eq. (2.16) that

$$q_D^0(r) = 0 \quad (r>\sigma). \tag{2.20}$$

The integrated form of Eq. (2.17) is

$$J_D(r) = -q_D^0(r) - M/2 + 2\pi\rho\int_0^\sigma ds\, q_D^0(s)J_D(|r-s|) - \kappa\int_0^r J_D(s)ds. \tag{2.21}$$

The presence of a delta function in $h_D(r)$ distinguishes $J_D(\sigma+)$ from $J_D(\sigma-)$:

$$J = J_D(\sigma-) = J_D(\sigma+) + \lambda\sigma^2/(24n^2) \tag{2.22}$$

and it follows from Eq. (2.19) that

$$q_D^0(\sigma+/n) = q_D^0(\sigma-/n) + \lambda\sigma^2/(24n^2). \tag{2.23}$$

When $0<r<\sigma$, the solution to Eq. (2.17) is

$$q_D^{0\prime}(r) = 2\pi\rho MJ_D(r) - (\pi\rho\lambda\sigma/12n)\int_0^\sigma q_D^0(t)(r-t)\delta(|r-t|-\sigma/n)dt + \lambda\sigma^2\delta(r-\sigma/n)/(24n^2) \tag{2.24}$$

and the detailed expressions for $q_D^{0\prime}(r)$ are

$$q_D^{0\prime}(r) - pq_D^0(r+\sigma/n) = pM - H \quad (0<r<\sigma/n), \tag{2.25a}$$

$$q_D^{0\prime}(r) - p[q_D^0(r+\sigma/n) - q_D^0(r-\sigma/n)] = -H \quad [\sigma/n<r<(n-1)\sigma/n\,], \tag{2.25b}$$

$$q_D^{0\prime}(r) + pq_D^0(r-\sigma/n) = -H \quad [(n-1)\sigma/n<r<\sigma\,], \tag{2.25c}$$

where $H = -2\pi\rho MJ(\sigma+) = \kappa J(\sigma+)$. Like the corresponding relations for $q_S'(r)$, this set of coupled differential equations is solved by similar methods which include splitting the interval $[\sigma/n, (n-1)\sigma/n]$ into subintervals of width σ/n in which $q_D^0(r)$ is continuous and Eq. (2.20) applies at $r=\sigma/n$. Thus we have the additional boundary conditions

$$q_D^0(m\sigma+/n) = q_D^0(m\sigma-/n) \quad [m=2,3,..(n-1)] \tag{2.26}$$

for integral $n>1$. The solutions for $n = 1, 2$, and 3 have been obtained earlier in a series of papers[1-3] and the solutions for $n=4$ and 5 are given below.

(c) $n=4$:

$$q_D^0(r) = -2H/p + A\cos(xpr) + B\sin(xpr) + E\cos(ypr) + F\sin(ypr) \quad (0<r<\sigma/4) \tag{2.27a}$$

$$= -M + H/p + xB\cos[xp(r-\sigma/4)] - xA\sin[xp(r-\sigma/4)] + yF\cos[yp(r-\sigma/4)] - yE\sin[yp(r-\sigma/4)] \quad (\sigma/4<r<\sigma/2) \tag{2.27b}$$

$$= -H/p + xA\cos[xp(r-\sigma/2)] + xB\sin[xp(r-\sigma/2)] - yE\cos[yp(r-\sigma/2)] - yF\sin[yp(r-\sigma/2)] \quad (\sigma/2<r<3\sigma/4) \tag{2.27c}$$

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$$= -M + 2H/p + B\cos[xp(r-3\sigma/4)] - A\sin[xp(r-3\sigma/4)]$$
$$- F\cos[yp(r-3\sigma/4)] + E\sin[yp(r-3\sigma/4)] \quad (3\sigma/4 < r < \sigma), \tag{2.27d}$$

where $x = (\sqrt{5}-1)/2$, $y = (\sqrt{5}+1)/2$, and $H = \kappa J(\sigma+)$. Applying the boundary conditions given in Eqs. (2.20), (2.23), and (2.26) we find the coefficients A, B, E, and F as linear combinations of M, H, and p. The results are given in the Appendix B.

(d) $n = 5$:

$$q_D^0(r) = (pM/3 - M)r + D + A\cos(pr) + B\sin(pr) + E\cos(\sqrt{3}pr)$$
$$+ F\sin(\sqrt{3}pr) \quad (0 < r < \sigma/5) \tag{2.28a}$$
$$= -2M/3 + B\cos[p(r-\sigma/5)] - A\sin[p(r-\sigma/5)] + \sqrt{3}F\cos[\sqrt{3}p(r-\sigma/5)]$$
$$- \sqrt{3}E\sin[\sqrt{3}p(r-\sigma/5)] \quad (\sigma/5 < r < 2\sigma/5) \tag{2.28b}$$
$$= (pM/3 - H)r + D + (H/p - 2vM/15 + 2\sigma H/5) - 2E\cos[\sqrt{3}p(r-2\sigma/5)]$$
$$- 2F\sin[\sqrt{3}p(r-2\sigma/5)] \quad (2\sigma/5 < r < 3\sigma/5) \tag{2.28c}$$
$$= -M/3 + B\cos[p(r-3\sigma/5)] - A\sin[p(r-3\sigma/5)] - \sqrt{3}F\cos[\sqrt{3}p(r-3\sigma/5)]$$
$$+ \sqrt{3}E\sin[\sqrt{3}p(r-3\sigma/5)] \quad (3\sigma/5 < r < 4\sigma/5) \tag{2.28d}$$
$$= (PM/3 - H)r + D + 2(H/p - 2vM/15 + 2\sigma H/5) - A\cos[p(r-4\sigma/5)]$$
$$- B\sin[p(r-4\sigma/5)] + E\cos[\sqrt{3}p(r-4\sigma/5)] + F\sin[\sqrt{3}p(r-4\sigma/5)] \quad (4\sigma/5 < r < \sigma). \tag{2.28e}$$

The constants A, B, D, E, and F are obtained from the boundary conditions, Eqs. (2.20), (2.23), and (2.26) (with $m = 2, 3, 4$), as linear combinations of H, M, and p. The results are given in Appendix B. We will next comment on the solutions for arbitrary n.

The forms of the functions $q_D^0(r)$ and $q_S(r)$ which determine the correlation functions and the equilibrium properties depend on whether n is odd or even. We restrict our remarks to the $q_D^0(r)$ functions, since they determine the energy of the system which is of particular interest to us, but analogous remarks also apply to the corresponding sum functions $q_S(r)$. For even $n = 2m$ the solution has the form

$$q_D^0(r) = -mH/p + \sum_{i=1}^{m} [A_{i1}\cos(x_i pr) + B_{i1}\sin(x_i pr)], \quad 0 < r < \sigma/n$$
$$= -M + H/p + \sum_{i=1}^{m} \{A_{i2}\cos[x_i p(r-\sigma/n)] + B_{i2}\sin[x_i p(r-\sigma/n)]\}, \quad \sigma/n < r < 2\sigma/n$$
$$= -(m-1)H/p + \sum_{i=1}^{m} \{A_{i3}\cos[x_i p(r-2\sigma/n)] + B_{i3}\sin[x_i p(r-2\sigma/n)]\}, \quad 2\sigma/n < r < 3\sigma/n$$
$$= -M + 2H/p + \sum_{i=1}^{m} \{A_{i4}\cos[x_i p(r-3\sigma/n)] + B_{i4}\sin[x_i p(r-3\sigma/n)]\}, \quad 3\sigma/n < r < 4\sigma/n$$
$$\vdots \quad \vdots \quad \vdots$$
$$= -H/p + \sum_{i=1}^{m} \{A_{in-1}\cos[x_i p(r-(n-2)\sigma/n)] + B_{in-1}\sin[x_i p(r-(n-2)\sigma/n)]\}, \quad \frac{n-2}{n}\sigma < r < \frac{n-1}{n}\sigma$$
$$= -M + mH/p + \sum_{i=1}^{m} \{A_{in}\cos[x_i p(r-(n-1)\sigma/n)] + B_{in}\sin[x_i p(r-(n-1)\sigma/n)]\}, \quad \frac{n-1}{n}\sigma < r < \sigma \tag{2.29}$$

and for odd $n = 2m+1$ we have

$$q_D^0(r) = [pM/(m+1) - H]r + A_0 + \sum_{i=1}^{m} [A_{i1}\cos(x_i pr) + B_{i1}\sin(x_i pr)], \quad 0 < r < \sigma/n$$
$$= -mM/(m+1) + A_0 + \sum_{i=1}^{m} \{A_{i2}\cos[x_i p(r-\sigma/n)] + B_{i2}\sin[x_i p(r-\sigma/n)]\}, \quad \sigma/n < r < 2\sigma/n$$
$$= [pM/(m+1) - H]r + A_0 + \{H/p - 2[pM/(m+1) - H]\sigma/n\}$$
$$+ \sum_{i=1}^{m} \{A_{i3}\cos[x_i p(r-2\sigma/n)] + B_{i3}\sin[x_i p(r-2\sigma/n)]\}, \quad 2\sigma/n < r < 3\sigma/n$$

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$$= -(m-1)M/(m+1) + A_0 + \sum_{i=1}^{m} \{A_{i4}\cos[x_i p(r-3\sigma/n)] + B_{i4}\sin[x_i p(r-3\sigma/n)]\}, \quad 3\sigma/n < r < 4\sigma/n$$

$$\vdots \quad \vdots \quad \vdots$$

$$= -M/(m+1) + A_0 + \sum_{i=1}^{m} \{A_{in-1}\cos[x_i p(r-(n-2)\sigma/n)]$$

$$+ B_{in-1}\sin[x_i p(r-(n-2)\sigma/n)]\}, \quad \frac{n-2}{n}\sigma < r < \frac{n-1}{n}\sigma$$

$$= [pM/(m+1) - H]r + A_0 + m\{H/p - 2[pM/(m+1) - H]\sigma/n\}$$

$$+ \sum_{i=1}^{m} \{A_{in}\cos[x_i p(r-(n-1)\sigma/n)] + B_{in}\sin[x_i p(r-(n-1)\sigma/n)]\}, \quad \frac{n-1}{n}\sigma < r < \sigma. \tag{2.30}$$

The solutions contain similar trigonometric forms but the remaining terms, which are functions of H, M, and p, are different for odd and even n. A term involving r is also present in alternate intervals of width σ/n for odd n. The coefficients A_{in}, B_{in}, and A_0 (for n odd), obtained by applying the boundary conditions given in Eqs. (2.20), (2.23), and (2.26), are functions of H'/v, M', and $v/(12\eta)$ where $H' = H/\sigma$, $M' = M/\sigma^2$, and $v = p\sigma = \eta\lambda/(2n^2) = n\langle N\rangle/2$.

The function H' is related to the energy of the system through Eq. (1.11). We have shown elsewhere[2] that H' in the MSA is given quite generally for $L = \sigma/n$ (where n is an integer) by

$$H' = \frac{(1-vd) + x(c-e) - \{(1-vd)^2 + 2x[(1-vd)(c-e)] + 2bv(1-g) + X\}^{1/2}}{24b\eta}, \tag{2.31}$$

where $x = \kappa\sigma$,

$$X = x^2[(c-e)^2 - 2b(1-2f)] \tag{2.32}$$

and $b, c, d, e, f,$ and g (which are trignometric functions of v for $n > 1$) are the coefficients of H', M', or $v/(12\eta)$ in the relations

$$\int_0^\sigma dt\, q_D^0(t) = [bH' + cM' + dv/(12\eta)], \tag{2.33}$$

$$q_D^0(0) - p\int_0^{\sigma/n} dt\, q_D^0(t) = -[eH' + fM' + gv/(12\eta)]. \tag{2.34}$$

We find that $X = 0$ from the detailed solutions of $n = 1$ to 5. Defining

$$a_1 = (1 - vd), \tag{2.35}$$

$$a_2 = (c - e), \tag{2.36}$$

$$a_3 = a_1 a_2 + 2bv(1-g), \tag{2.37}$$

$$a_4 = b\eta, \tag{2.38}$$

we have the remarkably simple form

$$H' = \frac{a_1 + a_2 x - [a_1^2 + 2xa_3]^{1/2}}{24\, a_4 \eta} \tag{2.39}$$

for the sticky electrolyte model. The solutions for $n = 4$ and 5 are given below together with those for $n = 1$, 2, and 3 for comparison.

(i) $n = 1$, $v = \eta\lambda/2$:

$$a_1 = (1 + v), \tag{2.40a}$$

$$a_2 = (1 - v), \tag{2.40b}$$

$$a_3 = 1 = 2a_4. \tag{2.40c}$$

(ii) $n = 2$, $v = \eta\lambda/8$, $c = \cos(v/2)$, $s = \sin(v/2)$:

$$a_1 = 2 - c, \tag{2.41a}$$

$$a_2 = 2(-3 + 3c + s)/v, \tag{2.41b}$$

$$a_3 = 2(c^2 + c - 2 + 2s - cs)/v, \tag{2.41c}$$

$$a_4 = 4(1-c)/v^2. \tag{2.41d}$$

(iii) $n = 3$, $v = \eta\lambda/18$, $c = \cos(\sqrt{2}v/3)$, $s = \sin(\sqrt{2}v/3)$:

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$$a_1 = 2(\sqrt{2} - s)v + 6(2\sqrt{2} - 2s - \sqrt{2}c), \tag{2.42a}$$

$$a_2 = (-3\sqrt{2} + 4s - \sqrt{2}c)v/3 + (5\sqrt{2} - 8s - \sqrt{2}c) + 6(-\sqrt{2} + s + \sqrt{2}c)/v, \tag{2.42b}$$

$$a_3 = 6(12 - 17\sqrt{2}s + 3\sqrt{2}cs - 4c + 12s^2) + 18(-8 + 7\sqrt{2}s - 5\sqrt{2}cs + 8c - 2s^2)/v, \tag{2.42c}$$

$$a_4 = (3\sqrt{2} - 4s + \sqrt{2}c)/3 + 2(-\sqrt{2} + 2s + 2c)/v + 3\sqrt{2}(1 - c)/v^2. \tag{2.42d}$$

(iv) $n = 4$, $v = \eta\lambda/32$, $c_1 = \cos(vx/4)$, $s_1 = \sin(vx/4)$, $c_2 = \cos(vy/4)$, $s_2 = \sin(vy/4)$, $x = (\sqrt{5} - 1)/2$, and $y = (\sqrt{5} + 1)/2$:

$$\begin{aligned} a_1 = {} & \sqrt{5}(2c_2s_1 + 5c_2 + 2c_1s_2 - 5c_1 - 3s_1 - 3s_2) \\ & - 9c_1c_2 - 10c_2s_1 - 5c_2 + 10c_1s_2 - 5c_1 - 6s_1s_2 + 15s_1 - 15s_2 + 24, \end{aligned} \tag{2.43a}$$

$$\begin{aligned} a_2 = {} & [7\sqrt{5}(-5c_2s_1 - 5c_2 - 5c_1s_2 + 5c_1 + 6s_1 + 6s_2) \\ & + 4c_1c_2 + 75c_2s_1 + 75c_2 - 75c_1s_2 + 75c_1 - 34s_1s_2 - 60s_1 + 60s_2 - 154]/v, \end{aligned} \tag{2.43b}$$

$$\begin{aligned} a_3 = {} & [-\sqrt{5}(50c_1c_2s_1 + 50c_1c_2s_2 + 81c_2s_1^2s_2 + 27c_2s_1^2 + 108c_2s_1s_2 + 108c_2s_1 \\ & + 27c_2s_2 + 81c_2 + 81c_1s_1s_2^2 - 108c_1s_1s_2 + 27c_1s_1 - 27c_1s_2^2 + 108c_1s_2 \\ & - 81c_1 - 220s_1^2s_2 - 220s_1s_2^2 - 220s_1 - 220s_2) \\ & + 3(38c_1c_2s_1s_2 + 38c_1c_2 + 25c_2s_1^2s_2 + 55c_2s_1^2 + 80c_2s_1s_2 + 80c_2s_1 \\ & + 55c_2s_2 + 25c_2 - 25c_1s_1s_2^2 + 80c_1s_1s_2 - 55c_1s_1 + 55c_1s_2^2 - 80c_1s_2 \\ & + 25c_1 - 88s_1^2s_2^2 - 76s_1^2 - 328s_1s_2 - 76s_2^2 - 88)]/v, \end{aligned} \tag{2.43c}$$

$$\begin{aligned} a_4 = {} & [42\sqrt{5}(c_2s_1 + c_2 + c_1s_2 - c_1 - s_1 - s_2) - 2(2c_1c_2 + 45c_2s_1 + 45c_2 - 45c_1s_2 \\ & + 45c_1 - 2s_1s_2 - 45s_1 + 45s_2 - 92)]/v. \end{aligned} \tag{2.43d}$$

(v) $n = 5$, $v = \eta\lambda/50$, $c_1 = \cos(v/5)$, $s_1 = \sin(v/5)$, $c_2 = \cos(\sqrt{3}v/5)$, $_2 = \sin(\sqrt{3}v/5)$:

$$\begin{aligned} a_1 = {} & -3\sqrt{3}v(c_1c_2 + s_1 - 3) - 5\sqrt{3}(3c_1c_2 + 2c_2s_1 - 2c_2 + 18c_1 + 10s_1 - 25) \\ & - 3s_2v(5 - 2s_1) - 30s_2(7 - 5c_1 - 3s_1), \end{aligned} \tag{2.44a}$$

$$\begin{aligned} a_2 = {} & -\sqrt{3}v(-2c_1c_2 - c_2 + 7c_1 - 12s_1 + 14)/5 \\ & - \sqrt{3}(2c_1c_2 - 4c_2s_1 + c_2 + 9c_1 + 40s_1 - 30) \\ & - 10\sqrt{3}(4c_1c_2 + 3c_2s_1 - 4c_2 - 40c_1 - 21s_1 + 40)/3v - 3s_2v(7s_1 - 4c_1 - 8)/5 \\ & - s_2(-16c_1 - 69s_1 + 52) - 10s_2(23c_1 + 12s_1 - 23)/v, \end{aligned} \tag{2.44b}$$

$$\begin{aligned} a_3 = {} & 15\sqrt{3}s_2(-49c_1c_2s_1 + 48c_1c_2 + 12c_2s_1^2 + 14c_2s_1 - 24c_2 - 194c_1s_1 + 168c_1 \\ & - 336s_1^2 + 679s_1 - 336) \\ & + 150\sqrt{3}s_2(4c_1c_2s_1 - 21c_1c_2 - 21c_2s_1^2 + 4c_2s_1 + 21c_2 + 224c_1s_1 - 291c_1 - 280s_1 \\ & + 291)/v \\ & + 45(28c_1c_2s_1 - 28c_1c_2 - 7c_2s_1^2 - 8c_2s_1 + 14c_2 + 56c_1s_1s_2^2 + 56c_1s_1 - 47c_1s_2^2 \\ & - 50c_1 + 100s_1^2s_2^2 + 94s_1^2 - 196s_1s_2^2 - 196s_1 + 94s_2^2 + 100) \\ & + 150(-7c_1c_2s_1 + 36c_1c_2 + 36c_2s_1^2 - 7c_2s_1 - 36c_2 - 197c_1s_1s_2^2 - 191c_1s_1 \\ & + 252c_1s_2^2 + 252c_1 + 244s_1s_2^2 + 241s_1 - 252s_2^2 - 252)/v, \end{aligned} \tag{2.44c}$$

$$\begin{aligned} a_4 = {} & -3\sqrt{3}(2c_1c_2 + c_2 - 7c_1 + 12s_1 - 14)/10 - 6\sqrt{3}(c_2s_1 - 4c_1 - 7s_1 + 4)/v \\ & - 20\sqrt{3}(-c_1c_2 + c_2 + 7c_1 - 7)/v^2 - 9s_2(4c_1 - 7s_1 + 8)/10 \\ & - 6s_2(7c_1 + 12s_1 - 7)/v - 240s_2(1 - c_1)/v^2. \end{aligned} \tag{2.44d}$$

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TABLE I. Numerical values of the constants c_1, c_2, and c_3 in Eq. (2.47) for the energy of dipolar dumbbell fluids of different elongations $L = \sigma/n$ in the MSA.

n	c_1	c_2	c_3
1[a]	3.0	1.0	4.0
2	2.292 192 7	0.458 158 68	1.550 187 9
3	1.901 546 2	0.258 259 56	0.735 694 4
4	1.616 220 0	0.164 874 27	0.399 644 61
5	1.398 506 9	0.114 156 34	0.239 451 56

[a] When $n<2$ trimers and more complex association products may be formed in addition to dipoles, see Refs. 2 and 3.

A check on these expressions is provided by the recovery of H' in the MSA for the RPM in the limit $v \to 0$ when we confirm that

$$H'(\mathrm{RPM}) = \frac{(1+x)-(1+2x)^{1/2}}{12\eta}. \qquad (2.45)$$

In the saturation limit when $\langle N \rangle = 1$ and $v = n/2$ we reinterpret x as the reduced dipole moment defined by

$$x' = 2n(A\pi\rho/kT)^{1/2}\mu, \qquad (2.46)$$

where the dipole moment $\mu = e\sigma/n$. Here the dielectric constant of the vacuum background has been taken to be unity and $A = \epsilon/(\epsilon - 1)$ where ϵ is the dielectric constant of the system which depends on the elongation of the molecules.[6]

It follows from Eq. (1.31) that the electrical energy of the dipoles is given by

$$\beta E^{\mathrm{ex}}/N_D = \frac{-x[(c_1 + c_2 x') - (c_1^2 + c_3 x')^{1/2}]}{24\,\eta}, \qquad (2.47)$$

where x is the unmodified κ and c_1, c_2, and c_3 are obtained from the corresponding a_1, a_2, a_3, and a_4 by setting $v = n/2$ and $N_D = N/2$ is the number of dipoles. Numerical values for the coefficients with $n = 1$, 2, 3, 4, and 5 are given in Table I.

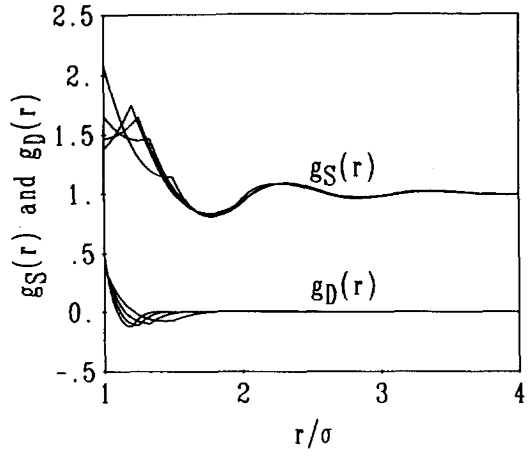

FIG. 2. The sum and difference distribution functions $g_S(r)$ and $g_D(r)$ for dipolar dumbbells at a reduced density $\rho_D\sigma^3 = 0.526$ and reduced dipole moment $\mu^* = (\mu^2/kT\sigma^3)^{1/2} = 1.42$. The different elongations $L = \sigma/n$ with $n = 2$, 3, 4, and 5 are identified by the cusps in $g_S(r)$ at $r = 1.5$, 1.333, 1.25, and 1.2σ and discontinuities in the slopes of $g_D(r)$ at these distances.

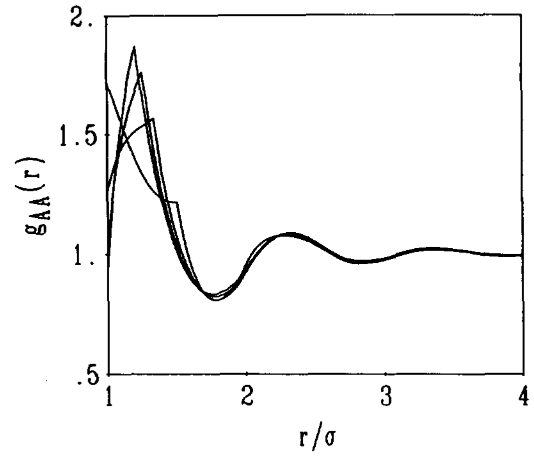

FIG. 3. The atom–atom distribution functions of like charges (+ + or − −) on different dipoles for the systems shown in Fig. 2.

III. RESULTS AND DISCUSSION

In Fig. 2 we plot the sum and difference correlation functions $g_S(r)$ and $g_D(r)$ for $n = 2$, 3, 4, and 5 in the saturation limit $\lambda = n^3/\eta$ for dipole formation and in Figs. 3 and 4 we have the corresponding atom–atom correlation functions. The reduced dipole moment $\mu^* = (\mu^2/kT\sigma^3)^{1/2} = 1.42$ and reduced density $\rho_D\sigma^3 = 0.526$ for all of the dipolar systems shown in these figures. Here ρ_D is the density of dipoles. Comparisons with Monte Carlo simulations for elongations corresponding to $n = 2$ and 3 have been made by us in Ref. 2. The energy of these dipoles is plotted as a function of the elongation in Fig. 5 at constant reduced density and dipole moment. We see that it becomes less negative as the elongation increases which is the opposite of what one might expect from the multipole expansions.

These states however have different molecular and excluded volumes, which suggests[5] examining the equilibrium properties at constant molecular volume, when the radius d of the equivalent hard sphere is related to the atomic diameter σ by

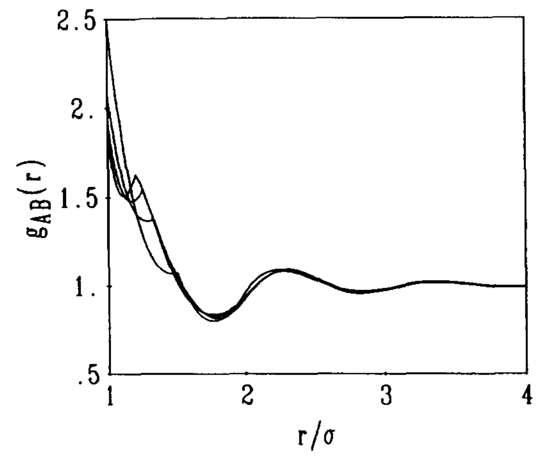

FIG. 4. The atom–atom distribution functions of unlike charges (+ − or − +) on different dipoles for the systems shown in Fig. 2.

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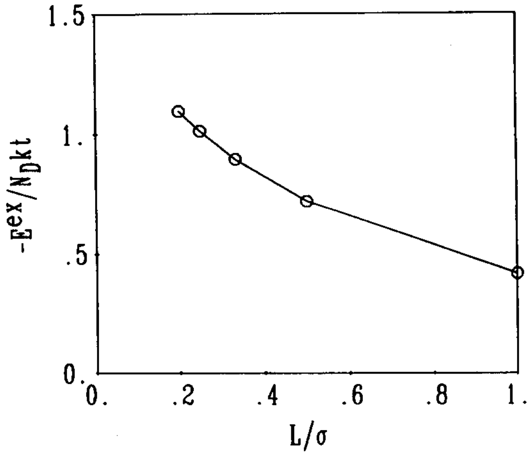

FIG. 5. The excess energy as a function of elongation L for the dipolar systems whose distribution functions are shown in Figs. 2–4. The dipoles moments and densities are the same in all systems. $[\mu^* = (\mu^2/kT\sigma^3)^{1/2} = 1.42, \rho_D^* = \rho_D\sigma^3 = 0.526]$.

$$d^3 = [1 + 3/(2n) - 1/(2n^3)]\sigma^3 . \quad (3.1)$$

We choose states defined by a reduced density $\rho_D^* = \rho_D d^3 = 0.78$ and reduced dipole moment $\mu^* = [\mu^2/(kTd^3)]^{1/2} = 1.37$ for n ranging from 1 to 5 to overlap with those studied by Morriss[5] in his Monte Carlo simulations. Note the use of d instead of σ in the definitions of μ^* and ρ_D^*. Our calculations of the energy of dipolar dumbbells in MSA are compared with Monte Carlo results in Table II. The dielectric constant ϵ used in the calculation of A [see Eqs. (1.1) and (2.46)] is listed in the second column of this table as a function of the elongation L as determined by Morriss in his MC simulation.[6] The error in these estimates of ϵ[9] is reflected in the uncertainties in our MSA energies in column 4. The energies in column 5 are from the MSA assuming $A = 1$. The results show that the factor $A = \epsilon/(\epsilon - 1)$ in the asymptotic form of the direct correlation function[2] makes nearly a 15% contribution to the excess energy of a typical dipolar fluid at liquid densities bringing it into closer agreement with the simulations. In columns 6 and 7 we list the energies calculated by Morriss and MacGowan[7] using the MSA and the HNC approximation for the direct correlation function defined by the SSOZ equation without further explicit consideration of the asymptotic form of the direct correlation function associated with this equation.[8] Their results were obtained numerically. Figure 6 shows a plot of the energies as a function of the dipole elongation; it is clear that the overall agreement of all of the approximations with the Monte Carlo (MC) simulations is satisfactory, reproducing the trend in the change in energy with elongation as well. Uncertainties in the dielectric constant[9] and energy determined by MC simulations make it difficult to discuss the relative accuracies of the different approximations except to note that the approximations based on the SSOZ equation appear to deteriorate as L becomes large while the opposite is true of the MSA associated with the OZ equation. Although the MSA offers the advantage of an analytic solution it suffers from the defect[2] that the excess energy tends to a small but finite constant in the limit of zero density. However, the energy at zero charge is given correctly as zero. An approximation which bears a close resemblence to this is the analog of the zero-pole approximation[10,11] derived from the SSOZ equation. The two are however quite distinct since they are based on two different OZ equations and have different asymptotic forms for the direct correlation functions. It is also known that the excess energy in the analog of the zero-pole approximation applied to dipolar dumbbells is not equal to zero in the limit of zero density or zero charge.[11]

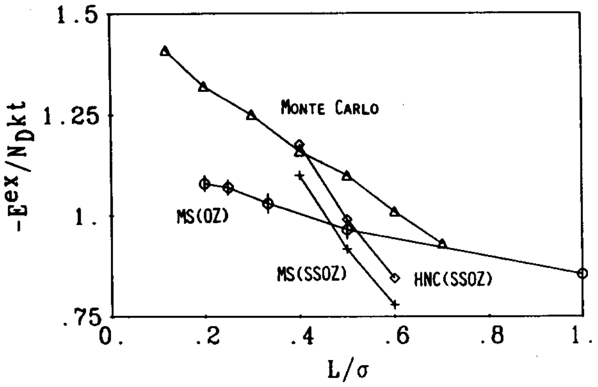

FIG. 6. The excess energy as a function of elongation L for the dipolar systems shown in Table IV. The molecular volumes are the same in all of these systems. $[\mu^* = (\mu^2/kTd^3)^{1/2} = 1.37, \rho_D^* = \rho_D d^3 = 0.78.]$

TABLE II. The excess energy $E^{ex}/N_D\,kT$ of dipolar dumbbells of the same molecular volume but different elongations. $\mu^* = (\mu^2/kTd^3)^{1/2} = 1.37$, $\rho_D d^3 = 0.78$, $d^3 = [1 + 3/(2n) - 1/(2n^3)]\sigma^3$.

			E^{ex}/N_DkT(OZ)		E^{ex}/N_DkT(SSOZ)	
$1/n$	ϵ(M.C)[a]	E^{ex}/N_DkT(M.C.)	MS($A = \epsilon)/(\epsilon - 1$)	MS($A = 1$)	MS	HNC
0.12		− 1.41				
0.2	10.9 ± 1.7	− 1.32	− 1.08 ± 0.02	− 0.971		
0.25	(10.2 ± 1.7)		− 1.07 ± 0.02	− 0.947		
0.3		− 1.25				
0.3333	(9.5 ± 1.7)		− 1.03 ± 0.025	− 0.905		
0.4		− 1.16			− 1.10	− 1.17
0.5	7.7 ± 1.2	− 1.10	− 0.965 ± 0.025	− 0.827	− 0.917	− 0.990
0.6		− 1.01			− 0.779	− 0.846
0.7		− 0.93				
1.0	(3.0 ± 0.6)		− 0.855 ± 0.018	− 0.571		

[a] Values in parentheses interpolated from Fig. 1 of Ref. 9.

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Solutions to the HNC approximation for the SEM have been discussed by us earlier[2] and it should be possible to use the same methods to determine the equilibrium properties of dipolar dumbbells in the saturation limit of complete association. We have not pursued that here to keep this report from getting too long but hope to study this in the future.

ACKNOWLEDGMENTS

The computing and other facilities made available to us as guests at the National Bureau of Standards are most gratefully acknowledged. This work was supported by a grant from the National Science Foundation No. CHE-8305747.

APPENDIX A: THE COEFFICIENTS IN THE EXPRESSIONS FOR $q_S(r)$ for $n=4$ and 5

These are obtained as solutions to the following equations which follow from the boundary conditions to $q_S(r)$ and the definitions of a and b given in the text.

(a) $n=4$:

$$(2-3v)a/(2v^2) - 3b'/v + c_1A' + (\sqrt{5}+2s_1-1)B'/2 + c_2E' + (\sqrt{5}+2s_2+1)F'/2 = \lambda/384,$$

$$a/v + 2b'/v + (\sqrt{5}-1)(s_1-1)A'/2 + c_1(1-\sqrt{5})B'/2 + (\sqrt{5}+1)(1+s_2)E' - c_2(\sqrt{5}+1)F'/2 = 0,$$

$$-(2+3v)a/(2v^2) - 3b'/v + c_1(\sqrt{5}-1)A'/2 + (\sqrt{5}s_1 - s_1 + 2)B'/2 - c_2(\sqrt{5}+1)E'/2 - (\sqrt{5}s_2 + s_2 + 2)F'/2 = 0,$$

$$(-15\eta v + 120\eta + 4v^2)a/(4v^2) + 6\eta(\sqrt{5}+3)(1-c_1+s_1)A'/v + 6\eta(\sqrt{5}+3)(1-c_1-s_1)B'/v$$
$$+ 6\eta(\sqrt{5}-3)(c_2+s_2-1)E'/v + 6\eta(\sqrt{5}-3)(1-c_2+s_2)F'/v = 1,$$

$$-15\eta a/v^2 + (4v-15\eta)b'/(4v) + 3\eta[\sqrt{5}(4vc_1 - vs_1 - 3v - 8c_1 - 8s_1 + 8)$$
$$+ 8vc_1 - 7vs_1 - 5v - 16c_1 - 16s_1 + 16]A'/(2v^2)$$
$$+ 3\eta[\sqrt{5}(vc_1 + 4vs_1 + 8c_1 - 8s_1 - 8) + 7vc_1 + 8vs_1 - 4v - 16c_1 - 16s_1 - 16]B'/(2v^2)$$
$$+ 3\eta[\sqrt{5}(-4vc_2 - vs_2 + 3v + 8c_2 - 8s_2 - 8) + 8vc_2 + 7vs_2 - 5v - 16c_2 + 16s_2 + 16]E'/(2v^2)$$
$$+ 3\eta[\sqrt{5}(vc_2 - 4vs_2 + 8c_2 + 8s_2 - 8) - 7vc_2 + 8vs_2 + 4v - 16c_2 - 16s_2 + 16]F'/(2v^2) = 0,$$

$$(v+3)a/v^2 + 2b'/v + s_1A' - c_1B' - s_2E' + c_2F' = 0.$$

(b) $n=5$:

$$(v^2+2v-10)a/(10v^2) + b'/5 + c_1A' + (s_1+1)B' + D' + c_2E' + (\sqrt{3}+s_2)F' = \lambda/600,$$

$$(5-3v)a/(5v^2) - b'/v + s_1A' - c_1B' - D' + (\sqrt{3}s_2+2)E' - \sqrt{3}c_2F' = 0,$$

$$(v^2+6v-10)a/(10v^2) + (v+5)b'/(5v) + B' + D' - 2c_2E' - (\sqrt{3}+2s_2)F' = 0,$$

$$(5-6v)a/(5v^2) - 2b'/v + (s_1+1)A' - c_1B' - D' - (1+\sqrt{3}s_2)E' + \sqrt{3}c_2F' = 0,$$

$$(42\eta v^2 + 60\eta v + 600\eta + 125v^2)a/(125v^2) + 18\eta(v+10)b'/(25v) + 24\eta(1-c_1)A'/v - 24\eta s_1B'/v + 36\eta D'/5 = 1,$$

$$-3\eta(3v^2+20v+40)a/(50v^2) - (48\eta v + 690\eta - 125v)b'/(125v)$$
$$+ 24\eta(3vc_1 + 2vs_1 - 2v - 5s_1)A'/(5v^2) + 24\eta(-2vc_1 + 3vs_1 + 2v + 5c_1 - 5)B'/(5v^2)$$
$$-18\eta D'/5 + 24\eta(1-c_2)E'/(5v) - 24\eta s_2F'/(5v) = 0,$$

$$(v+10)a/(10v) + (v+10)b'/(5v) - c_1A' - s_1B' + D' + c_2E' + s_2F' = 0,$$

where $b' = b/\sigma$, $A' = A/\sigma^2$, $B' = B/\sigma^2$, $D' = D/\sigma^2$, $E' = E/\sigma^2$, and $F' = F/\sigma^2$.

APPENDIX B: THE COEFFICIENTS IN THE EXPRESSIONS FOR $q_D^0(r)$ for $n=4$ and 5

(a) $n=4$:

$$A' = [a_1H' + a_2M' + a_3v/(12\eta)]/(\mathrm{Det}\,4),$$

$$a_1 = [\sqrt{5}(6s_1s_2 + 15s_2c_1 - 10s_2 + 3c_2s_1 + 2c_1c_2 + 3c_2 - 10s_1 - 15c_1 + 6)$$
$$+ (22s_1s_2 + 27s_2c_1 - 14s_2 - 3c_2s_1 - 2c_1c_2 - 3c_2 - 14s_1 - 27c_1 + 22)]/v,$$

$$a_2 = \sqrt{5}(-3s_1s_2 - 5s_2c_1 + 5s_2 - c_2s_1 - c_1c_2 - c_2 + 5s_1 + 5c_1 - 3)$$
$$+ (-11s_1s_2 - 9s_2c_1 + 7s_2 + c_2s_1 + c_1c_2 + c_2 + 7s_1 + 9c_1 - 11),$$

$$a_3 = 5(-3s_2c_1 - c_2 + 2c_1) + (-3s_2c_1 + 2c_2s_1 - c_2 + 6c_1),$$

$$B' = [b_1H' + b_2M' + b_3v/(12\eta)]/(\mathrm{Det}\,4),$$

$$b_1 = [\sqrt{5}(15s_1s_2 - 6s_2c_1 + 3s_2 + 2c_2s_1 - 3c_1c_2 - 15s_1 + 10c_1 - 3)$$

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$$+ (27s_1s_2 - 22s_2c_1 + 3s_2 - 2c_2s_1 + 3c_1c_2 - 4c_2 - 27s_1 + 14c_1 - 3)]/v,$$

$$b_2 = \sqrt{5}(-5s_1s_2 + 3s_2c_1 - s_2 - c_2s_1 + c_1c_2 - 5s_1 - 5c_1 + 1)$$

$$+ (-9s_1s_2 + 11s_2c_1 - s_2 + c_2s_1 - c_1c_2 + 2c_2 + 9s_1 - 7c_1 + 1),$$

$$b_3 = \sqrt{5}(-3s_1s_2 - s_2 + 2s_1) + (-3s_1s_2 + s_2 - 2c_1c_2 + 6s_1 + 2),$$

$$E' = [e_1H' + e_2M' + e_3v/(12\eta)]/(\text{Det } 4),$$

$$e_1 = [\sqrt{5}(-6s_1s_2 + 3s_2c_1 - 10s_2 + 15c_2s_1 - 2c_1c_2 + 15c_2 - 10s_1 - 3c_1 - 6)$$

$$+ (22s_1s_2 + 3s_2c_1 + 14s_2 - 27c_2s_1 - 2c_1c_2 - 27c_2 + 14s_1 - 3c_1 + 22)]/v,$$

$$e_2 = \sqrt{5}(3s_1s_2 - s_2c_1 + 5s_2 - 5c_2s_1 + c_1c_2 - 5c_2 + 5s_1 + c_1 + 3)$$

$$+ (-11s_1s_2 - s_2c_1 - 7s_2 + 9c_2s_1 + c_1c_2 + 9c_2 - 7s_1 + c_1 - 11),$$

$$e_3 = \sqrt{5}(-3s_1c_2 - 2c_2 + c_1) + (-2s_2c_1 + 3c_2s_1 + 6c_2 - c_1),$$

$$F' = [f_1H' + f_2M' + f_3v/(12\eta)]/(\text{Det } 4),$$

$$f_1 = [\sqrt{5}(15s_1s_2 - 2s_2c_1 + 15s_2 + 6c_2s_1 - 3c_1c_2 + 10c_2 - 3s_1 - 3)$$

$$+ (-27s_1s_2 - 2s_2c_1 - 27s_2 - 22c_2s_1 - 3c_1c_2 - 14c_2 + 3s_1 + 4c_1 + 3)]/v,$$

$$f_2 = \sqrt{5}(-5s_1s_2 + s_2c_1 - 5s_2 - 3c_2s_1 + c_1c_2 - 5c_2 + s_1 + 1)$$

$$+ (9s_1s_2 + s_2c_1 + 9s_2 + 11c_2s_1 + c_1c_2 + 7c_2 - s_1 - 2c_1 - 1),$$

$$f_3 = \sqrt{5}(-3s_1s_2 - 2s_2 + s_1) + (3s_1s_2 + 6s_2 + 2c_1c_2 + s_1 - 2),$$

$$\text{Det } 4 = 6\sqrt{5}(s_1 + s_2) + 2(-7s_1s_2 + 2c_1c_2 - 7).$$

(b) $n = 5$:

$$A' = [a_1H' + a_2M' + a_3v/(12\eta)]/\text{Det } 5),$$

$$a_1 = 3[3(7\sqrt{3}s_1 - 4\sqrt{3} - 12s_1s_2 + 7s_2)$$

$$+ 5(3\sqrt{3}c_1c_2 - \sqrt{3}c_2 + 12\sqrt{3}s_1 - 21\sqrt{3}c_1 + 7\sqrt{3} - 21s_1s_2 + 36s_2c_1 - 12_2s)/v],$$

$$a_2 = 3v(-7\sqrt{3}s_1 + 4\sqrt{3} + 12s_1s_2 - 7s_2) + 5(-3\sqrt{3}c_1c_2 + \sqrt{3}c_2 + 9\sqrt{3}s_1$$

$$+ 21\sqrt{3}c_1 - 19\sqrt{3} - 15s_1s_2 - 36s_2c_1 + 33s_2),$$

$$a_3 = 15(\sqrt{3}c_2s_1 - \sqrt{3}c_2 - 7\sqrt{3}s_1 + 9\sqrt{3}c_1 - 2\sqrt{3} + 12s_1s_2 - 15s_2c_1 + 3s_2),$$

$$B' = [b_1H' + b_2M' + b_3v/(12\eta)]/(\text{Det } 5),$$

$$b_1 = 9[(\sqrt{3}c_2 - 7\sqrt{3}c_1 + 12s_2c_1)$$

$$+ 5(\sqrt{3}c_2s_1 - 7\sqrt{3}s_1 - 4\sqrt{3}c_1 + 4\sqrt{3} + 12s_1s_2 - 7s_2c_1 - 7s_2)/v],$$

$$b_2 = 3v(-\sqrt{3}c_2 + 7\sqrt{3}c_1 + 12s_2c_1)$$

$$+ 15(-\sqrt{3}c_2s_1 + \sqrt{3}c_2 + 7\sqrt{3}s_1 - 3\sqrt{3}c_1 - 4\sqrt{3} - 12s_1s_2 + 5s_2c_1 + 7s_2),$$

$$b_3 = 15(-\sqrt{3}c_1c_2 - \sqrt{3}c_2 + 9\sqrt{3}s_1 + 7\sqrt{3}c_1 - 5\sqrt{3} - 15s_1s_2 - 12s_2c_1 + 9s_2).$$

$$D' = [d_1H' + d_2M' + d_3v/(12\eta)]/(\text{Det } 5),$$

$$d_1 = 6[(2\sqrt{3}c_1c_2 + 12\sqrt{3}s_1 - 14\sqrt{3} - 21s_1s_2 + 24s_2) + 5(\sqrt{3}c_2s_1 - 2\sqrt{3}c_1c_2$$

$$+ \sqrt{3}c_2 - 19\sqrt{3}s_1 - 11\sqrt{3}c_1 + 18\sqrt{3} + 33s_1s_2 + 19s_2c_1 - 31)/v],$$

$$d_2 = 2v(-2\sqrt{3}c_1c_2 - 12\sqrt{3}s_1 + 14\sqrt{3} + 21s_1s_2 - 24s_2) + 5(-\sqrt{3}c_2s_1 - 2\sqrt{3}c_1c_2$$

$$+ 2\sqrt{3}c_2 - 5\sqrt{3}s_1 - 10\sqrt{3}c_1 + 10\sqrt{3} + 9s_1s_2 + 17s_2c_1 - 17),$$

$$d_3 = 30(-\sqrt{3}c_1c_2 - \sqrt{3}s_1 + 3\sqrt{3} + 2s_1s_2 - 5s_2),$$

$$E' = [e_1H' + e_2M' + e_3v/(12\eta)]/(\text{Det } 5),$$

$$e_1 = 3[(2\sqrt{3}c_1c_2 + 3\sqrt{3}s_1 - 2\sqrt{3} - 6s_1s_2 + 3s_2) + 5(2\sqrt{3}c_2s_1$$

$$+ \sqrt{3}c_1c_2 - \sqrt{3}c_2 - 2\sqrt{3}s_1 - 5\sqrt{3}c_1 + 5\sqrt{3} + 3s_1s_2 + 10s_2c_1 - 10s_2)/v],$$

$$e_2 = v(-2\sqrt{3}c_1c_2 - 3\sqrt{3}s_1 + 2\sqrt{3} + 6s_1s_2 - 3s_2) + 5(-2\sqrt{3}c_2s_1$$

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$$+\sqrt{3}c_1c_2+\sqrt{3}c_2+5\sqrt{3}s_1+5\sqrt{3}c_1-7\sqrt{3}-9s_1s_2-10s_2c_1+13s_2),$$

$$e_3=15(-3\sqrt{3}c_2s_1-2\sqrt{3}c_1c_2+3\sqrt{3}c_2-\sqrt{3}s_1+\sqrt{3}c_1+2s_1s_2-3s_2c_1+s_2),$$

$$F'=[f_1H'+f_2M'+f_3v/(12\eta)]/(\text{Det } 5),$$

$$f_1=3[(2\sqrt{3}s_2c_1+6c_2s_1-3c_2-3c_1)+5(2\sqrt{3}s_1s_2+\sqrt{3}s_2c_1-\sqrt{3}s_2$$

$$-3c_2s_1-10c_1c_2+10c_2-3s_1-2c_1+2)/v],$$

$$f_2=v(-2\sqrt{3}s_2c_1-6c_2s_1+3c_2+3c_1)+5(-2\sqrt{3}s_1s_2+\sqrt{3}s_2c_1+\sqrt{3}s_2$$

$$+9c_2s_1+10c_1c_2-13c_2+3s_1-c_1-2),$$

$$f_3=15(-3\sqrt{3}s_1s_2-2\sqrt{3}s_2c_1+3\sqrt{3}s_2-2c_2s_1+3c_1c_2-c_2+5s_1+3c_1-5),$$

$$\text{Det } 5=30(2\sqrt{3}c_1c_2-\sqrt{3}c_2+12\sqrt{3}s_1+7\sqrt{3}c_1-14\sqrt{3}-21s_1s_2-12s_2c_1+24s_2),$$

where $A'=A/\sigma^2$, $B'=B/\sigma^2$, $D'=D/\sigma^2$, $E'=E/\sigma^2$, and $F'=F/\sigma^2$.

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[3]J. C. Rasaiah and S. H. Lee, J. Chem. Phys. **83**, 6396 (1985). (Errata: Eqs. (1.9) and (2.42) of Ref. 3 have transcription errors. Equation (1.9) is given correctly in Eq. (1.9b) of the present paper with $n = 1$. Equation (2.42) has a misplaced bracket and should be $c = -24\tau + (-14\eta + 2)/(1-\eta)$. Also near the end of Sec. I of this reference read "The phase diagrams were determined from an analysis of μ vs P and P vs η."

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