ANALYTICAL APPROACH TO MOLECULAR LIQUIDS: V. SYMMETRIC DISSOCIATIVE DIPOLAR DUMBBELLS WITH THE BONDING LENGTH $\sigma/3 \le L \le \sigma/2$ AND RELATED SYSTEMS

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ABSTRACT

The exact asymptotic behavior of the particle-particle direct correlation function for dissociative dipolar dumbbells is discussed and used to motivate an extended mean spherical approximation (EMSA). The structure of a model liquid of symmetric dissociative dipolar dumbbells with two centers (each bearing a point charge of opposite sign) a distance L apart is investigated analytically for $\sigma/3 \le L \le \sigma/2$ under the EMSA, where σ is the diameter of the spheres that consistute the dumbbells. This study extends earlier analytical work for $L = \sigma/n, n = 1,2,3,4,5$ for the same model. The analytical expressions for the Born solvation free energy of a symmetric dipolar dumbbell in a symmetric dipolar

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dumbbell solvent and in a dipolar hard-sphere solvent are also obtained. Such expressions can be expected to be useful in investigating intramolecular electron-transfer reactions. Results for $\sigma/2 \leq L \leq \sigma$ that have a somewhat different conceptual status are obtained as well. They suggest a new interpretation of the Percus-Yevick solution to the sticky-sphere model considered by Baxter.

I. INTRODUCTION

In an earlier paper,[1] an extended mean-spherical approximation (EMSA) was developed for obtaining the site-site (or atom-atom) pair correlation function in interaction-site models of liquids such as the hard-dumbbell and the dipolar-dumbbell liquid. Our analytical solution given there was restricted to the case $L = \sigma/n, n = 1, 2, 3, 4, 5$. Here and below, L denotes the bond length of a dumbbell and σ is hard-core diameter. The results were used as input to investigate ionic solvation,[2] the Born solvation free energy for two ions at a fixed distance apart,[3,4] and solvation dynamics.[5] The purpose of this paper is twofold: to illuminate the conceptual status of the approximation off the full-association limit by noting a number of exact asymptotic results and also to extend the earlier analytical work under the EMSA for a dissociating dumbbell fluid and for a dipolar dumbbell in a dipolar solvent. Our discussion of the first point extends the results that we have already given in our series of papers on simple models of association[6]; this paper can be regarded as our latest contribution to that series as well as to the series on our analytic approach to molecular liquids.[1–4]

In Section II, the model is given and discussed. In Section III the general equations are reviewed. Then, the analytical solution for $\sigma/3 \leq L \leq \sigma/2$ is given in Section IV for a dipolar dumbbell fluid consisting of pairs of fused oppositely charged hard-sphere atoms. In Section V we use the same set of integral equations to obtain a solution for $\sigma/2 \leq L \leq \sigma$. As we discuss at the end of Section II, the conceptual status of the equations is different when $L \geq \sigma/2$. In particular, they no longer represent our EMSA for dipolar dumbbells. If one consider a single "solute" dipolar dumbbell in a dipolar dumbbell (or dipolar hard-sphere) solvent, however, one can consider $L \geq \sigma/2$ for the solute dumbbell without conceptual difficulties in our approximation scheme, even in the case of an "extended" dipole,[3,4] i.e., a pair of oppositely charged hard spheres a fixed distance apart with a gap between them (i.e. $L > \sigma$). Analytical expressions for the Born solvation free energy for a "solute" symmetric dipolar dumbbell in a symmetric dipolar dumbbell solvent or a dipolar hard-sphere solvent are obtained in Section VI. Further discussion and a summary are given in Section VII.

II. THE MODEL

In the dissociative dipolar dumbbell model described in detail in an earlier paper by us[1], a particle-particle pair correlation $H_{ij}(r)$ between a charged hard-sphere of species i and a charged hard-sphere of species j is given inside a core region by[1-9]

$$H_{ij}(r) = -1 + \lambda(1 - \delta_{ij})L\delta(r - L)/12, \quad r < \sigma, \tag{2.1}$$

where λ is the mean dissociation parameter, δ_{ij} is a Kronecker delta, $\delta(r - L)$ is a delta function and σ is the hard-core diameter. We have two species, indexed by 1 and 2, which can be identified as positively and negatively charged respectively. [When the charge is zero, equation (2.1) still differentiates between two species—like species do not have the associating term $\delta(r - L)$ as part of $H_{ii}(r)$)]. For completely associated dumbbell $\lambda = 1/[\eta(L/\sigma)^3]$. For a system of partly dissociated dumbbells $\lambda < 1/[\eta(L/\sigma)^3]$. The dependence of λ upon ρ and β has been discussed in our earlier work on chemical association[6] and we shall not repeat it here, where it will not be explicitly needed in our analysis. Here and below, $\eta = \pi\rho\sigma^3/3$ with 2ρ the total number density of particles and $T(= 1/k_B\beta)$ the temperature.

The Ornstein-Zernike (OZ) equation defines the particle-particle direct correlation function $C_{ij}(r)$

$$H_{ij} = C_{ij} + \sum_k \rho_k H_{ik} * C_{kj} \tag{2.2}$$

where $*$ denotes a convolution and ρ_k is the number density for species k. Here, we have $\rho_1 = \rho_2 = \rho$. For $\lambda = 1/[\eta(L/\sigma)^3]$, the extended MSA closes this OZ equation with the large-r form of C_{ij} used for all $r \geq \sigma$, to give[1]

$$C_{ij} = (-1)^{i+j+1}\frac{\Gamma}{r}, \quad r \geq \sigma \;, \tag{2.3a}$$

where

$$\Gamma = \frac{\epsilon \beta q^2}{\epsilon - 1} \tag{2.3b}$$

for a pure dipolar dumbbell fluid with the dielectric constant ϵ.

One knows (2.3) to give the correct large-r form for C_{ij} in the complete-association limit. That is, one has

$$C_{ij} \to (-1)^{i+j+1}\frac{\Gamma}{r} \quad \text{for } r \to \infty \tag{2.4}$$

Moreover, we concluded in ref [1] that one can expect (2.3) to be an adequate liquid-state approximation for all r greater than $2L$, i.e., when $L \leq \sigma/2$.

As one leaves the complete-association limit, $\lambda = 1/[\eta(L/\sigma)^3]$, one expects (for the reason discussed below) the functional form of C_{ij} to be different for $\kappa r << 1$ and $\kappa r >> 1$, where κ is a characteristic correlation length related to the dissociation parameter λ,

$$\kappa^2 = \frac{3[1-(\lambda')^2]}{(\lambda')^2 L^2}, \quad \lambda' = \lambda\eta(L/\sigma)^3 \,. \tag{2.5}$$

For $\kappa r >> 1$, one expects

$$C_{ij} \approx (-1)^{i+j+1}\frac{(\beta q^2)}{r} \tag{2.6}$$

while for $r > \sigma$, $\kappa r << 1$, one expects (2.3) to provide a good approximation. The source of these expectations is the change in the functional form, as one leaves the complete-association limit, of ω_{ij}, the "intramolecular" part of the H_{ij} of (2.1),

$$\omega_{ij}(r) = \rho\lambda(1-\delta_{ij})L\delta(r-L)/12 \tag{2.7}$$

The ω matrix with elements $\omega_{ij}(r)$ is reflected in the direct-correlation matrix via the OZ equation through $[\omega^{-1}]_{ij}$, the inverse-matrix elements, which, from (2.7), can easily be shown to have the large-r form

$$[\omega^{-1}(r)]_{ii} \rightarrow \frac{3e^{-\kappa r}}{4\pi L^2 r} \quad \text{for } r \rightarrow \infty \tag{2.8a}$$

$$[\omega^{-1}(r)]_{12} \rightarrow \frac{-3\lambda' e^{-\kappa r}}{4\pi L^2 r} \quad \text{for } r \rightarrow \infty \tag{2.8b}$$

At the complete-association limit $\lambda = 1/[\eta(L/\sigma)^3]$, at which $\lambda' = 1$ and $n = 0$, we already know that for $r >> \sigma$, we can expect

$$\rho C_{ij} \approx -\rho\beta q^2/r - B[\omega^{-1}(r)]_{ij}, \tag{2.9}$$

with $B = 3y/(\epsilon - 1)$ and $y = 4\pi\beta\rho(qL)^2/9$. [This is simply another way of writing (2.4).]

For $\lambda << 1/[\eta(L/\sigma)^3]$, the ω^{-1} terms in (2.9) are negligible for $\kappa r >> 1$, yielding, for $r \rightarrow \infty$,

$$C_{ij} \rightarrow (-1)^{i+j+1}\frac{\beta q^2}{r} \tag{2.10}$$

which is what one expects (off singular states such as a critical point) as a special case of the relation

$$C_{ij} \rightarrow -\beta u_{ij}(r) \tag{2.11}$$

where u_{ij} is the pair potential. We see then that the complete-association limit, in which (2.11) does *not* hold, represents a singular state in much the same sense that a liquid-gas critical point does, with a correlation length κ^{-1} that goes to infinity as one approaches the singular state, just as in the case of a critical point.

For $r >> \sigma$, but $\kappa r << 1$, (2.8) and (2.9) suggest a $C_{ij}(r)$ that differs little from the $\lambda = 1/[\eta(L/\sigma)^3]$ case. The precise form hinges upon the value of the coefficient B of (2.9). A plausible form is

$$B = \frac{3y_v}{\epsilon(\rho_v, \beta) - 1} \tag{2.12}$$

where $y_v = 4\pi\beta\rho_v(qL)^2/9$, with ρ_v the number density of the fully associated dipolar dumbbells, which can be thought of as the dipolar solvent for the dissociated ions. Here $\epsilon(\rho_v, \beta)$ is the dielectric constant of that (pure) solvent at density ρ_v and temperature) given by β.

Issues such as the precise form of B require further investigation. There is one case in which one can already proceed with some confidence, however, and that is when one is at ρ and β such that $\epsilon(\rho,\beta) >> 1$. Then the difference between $\epsilon/(\epsilon-1)$ and 1 is small enough so that the difference between the two asymptotic forms (2.4) and (2.10) is small. One can then continue to use (2.3b) with little error or, alternatively, replace it with $\Gamma = \beta q^2$.

In the complete-association limit, our EMSA, eq.(2.3) was obtained in ref [1] for the case $2L \le \sigma$ by using (2.9) for all $r \ge \sigma$ along with the observation that at full association, the asymptotic form (2.8) gives $\omega^{-1}(r)$ with good quantitative accuracy for all $r \ge 2L$. At $r = 2L$, ω_{ii}^{-1} has a jump discontinuity of magnitude $(16\pi L^3)^{-1}$, so that $\omega^{-1}(r)$ is no longer well approximated by (2.3) for all $r > \sigma$ when $2L > \sigma$. For this reason, as soon as $2L > \sigma$, we no longer regard (2.3) as a likely candidate for the role of an approximation that embodies the MSA idea of using a large-r result that stands a good chance of being adequate all the way down to $r = \sigma$. The approxmation

$$\rho C_{ij} = -\rho\beta q^2/r - B[\omega^{-1}(r)]_{ij}, \quad r > \sigma \tag{2.13}$$

does still embody this idea (at least in the full-association limit) but loses the useful property of yielding equations that have solutions expressible in terms of elementary functions. We intend to investigate (2.13) numerically, but will not do so in this paper.

An interesting question that remains is what meaning, if any, can be given to the equations that result from retaining (2.3) when $2L > \sigma$. This is an especially intriguing question in light of the fact that when $q = 0$ (which leads to $B = 1$) and $L = \sigma$ the equations have exactly the structure of the Percus-Yevick (PY) approximation as applied to the model of a hard-sphere mixture of species 1 and 2 with a "sticky" attraction only between unlike species. (This is a mixture version of Baxter's "sticky sphere" model[10]).

For $q \neq 0$ and $L = \sigma$ our equations have the same form as the hybrid PY/MSA equations considered by Rasaiah and Lee[8] in their investigation of the ionic version of the same mixture model. We note however that our treatment of the ρ and β dependence of λ appearing in Eq. (2.1) is in general different from that which comes out of a PY/MSA treatment.

In order to help illuminate the meaning of (2.3) for $2L > \sigma$, it is worthwhile considering briefly the expected behavior for $L > \sigma/2$ of the ionic "shielded sticky-shell" model that defines our dissociative dipolar dumbbell fluid when $L \leq \sigma/2$. For $L > \sigma/2$ the model remains well defined but no longer describes particles that can only associate into dumbbells.

For all L, the model is defined by the pair potential

$$u_{ij}(r) = \begin{cases} kT\ln[1 + f_{ij}(r)] & ,r \leq \sigma \\ (-1)^{(i+j+1)}q^2/r & ,r > \sigma \end{cases} \tag{2.14}$$

where

$$f_{ij}(r) = f^{HS}(r) + \delta(r - L)\delta_{ij}/12\pi L^2\tau \tag{2.15}$$

with

$$f^{HS}(r) = \begin{cases} -1 & \text{for } r \leq \sigma \\ 0 & \text{for } r > 0 \end{cases} \tag{2.16}$$

Here $f^{HS}(r)$ is the hard-sphere Mayer f-function that describes the repulsive core of the interaction, the δ-function term of strength $1/\tau$ describes the attractive "shielded sticky shell" and the q^2/r term describes the Coulombic interaction.

For $L \leq \sigma/2$ the shielding of the repulsive core prevents any association except dimerization between particles of species 1 and 2. In this regime, the "simple interpolation scheme" of ref. [6] appears to give a satisfactory description of the relation between the λ of Eq. (2.1) and the τ of Eq. (2.15). From the earlier work of refs. [11] and [7] it is clear that this is not true of the PY closure (for $q = 0$) or the PY/MSA closure (for $q \neq 0$). In particular, those closures violate the law of mass action at low densities. However, the "simple interpolation scheme" developed in ref. 6 appears to give a satisfactory description of the relation between λ and τ in this regime. For L slightly larger than $\sigma/2$, the model describes particles that can associate into chains of alternating species 1 and 2. As L/σ further increases, a greater variety of branched chain configurations becomes possible. In this regime spatial decay of $[\omega^{-1}(r)]_{ij}$ is no longer well approximated for small r by an inverse $-r$ falloff so that (2.3a) can no longer be expected to be a reasonable approximation to (2.13). Moreover the relation between λ and τ has not been investigated in this regime. For L still larger, so that L/σ is slightly less than 1, the system describes particles that can freely vulcanize into a wide variety of clusters. Here (2.1) - (2.3a) may offer a useful approximate description of the model.

When considering the general case of (2.14) in which $q \neq 0$ it is natural to take

$$\Gamma = \beta q^2, \tag{2.17}$$

instead of (2.3b) for $L > \sigma/2$, since the factor $\epsilon/(\epsilon - 1)$ of (2.3b) loses its relevance when one loses the steric constraint that assures that association only produces dipolar dimers for $L \leq \sigma/2$, while (2.3a) with (2.17) is consistent with (2.11).

With (2.17) and (2.3a) instead of (2.3b), one is back to the simple MSA closure for $r > \sigma$. One must continue to choose a closure condition for $r \leq \sigma$ to determine the λ of (2.1) as a function of the τ of (2.14). For L/σ less than (and close to) unity, the PY closure

$$c_{ij}(r) = f_{ij}(r)[h_{ij}(r) + 1]/[f_{ij}(r) + 1] \tag{2.18}$$

appears to remain sensible for $r \leq \sigma$.

On the mathematical side, we can continue to solve the set of equations (2.1), (2.2), and (2.3a) for all $\sigma/2 \leq L \leq \sigma$ and for this range we give the solution in Section V. In light of our discussion here, the solution appears likely to offer a useful approximate description of the system defined by the pair potential of (2.14) only when L/σ is a bit less than 1, although further work will be necessary to elucidate this question.

As L increases from $\sigma/2$, when it reaches the value σ, a new complication arises, since all steric shielding effects of the hard core relative to the sticky shell at $r = L$ are lost. This permits unbridled clustering or vulcanization of such an extent that the system will lose thermodynamic stability, as one of us has already discussed in detail elsewhere.[12] We have two remarks in this connection. First, the PY/MSA approximation defined by (2.1) - (2.3a) with (2.17) and (2.18) may remain a reasonable description of a system in which the $\delta(r-L)$ of (2.14) is replaced by a narrow sharply peaked function of finite height, reflecting a narrow well in the pair potential of finite depth. (This is the sense in which the Baxter sticky-sphere model and its extensions are typically used.) Second, a novel alternative way of giving thermodynamic meaning to the PY/MSA solution of the model for $L = \sigma$ is to regard it as an approximation to the solution for L slightly less than σ (given in Section V) where the model is free of the instability that sets in at $L = \sigma$.

III. GENERAL EQUATIONS

Eqs.(2.1), (2.2) and (2.3) can be decoupled into the sum and difference equations

$$h_s \doteq c_s + 2\rho c_s * h_s, \tag{3.1}$$

$$h_s(r) = -1 + \frac{\lambda L}{24}\delta(r-L), \quad r < \sigma, \tag{3.2a}$$

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

$$h_d = c_d - 2\rho c_d * h_d, \tag{3.3}$$

$$h_d(r) = \frac{\lambda L}{24}\delta(r-L), \quad r < \sigma, \tag{3.4a}$$

$$c_d(r) = \frac{\Gamma}{r}, \quad r > \sigma, \tag{3.4b}$$

with

$$h_s = \frac{H_{12}+H_{11}}{2}, \quad c_s = \frac{C_{12}+C_{11}}{2}, \tag{3.5a}$$

$$h_d = \frac{H_{12}-H_{11}}{2}, \quad c_d = \frac{C_{12}-C_{11}}{2}. \tag{3.5b}$$

Applying Baxter factorization[13], we have[1,7-9]

$$rh_s(r) = -q_s'(r) + 4\pi\rho\int_0^\sigma dt q_s(t)(r-t)h_s(|r-t|) \tag{3.6a}$$

$$rc_s(r) = -q_s'(r) + 4\pi\rho\int_r^\sigma dt q_s(t-r)q_s'(t) \tag{3.6b}$$

$$rh_d(r) = [q_d^0(r)]' + 4\pi\rho\int_0^\infty dt[A_d + q_d^0(t)](r-t)h_d(|r-t|) \tag{3.7a}$$

$$rc_d^0(r) = [q_d^0(r)]' + 4\pi\rho A_d q_d^0(r) - 4\pi\rho\int_0^\sigma dt q_d^0(t)[q_d^0(t+r)]' \tag{3.7b}$$

where we have defined

$$c_d^0(r) \equiv c_d(r) - \frac{\Gamma}{r}e^{-zr}, \quad z \to 0, \tag{3.8a}$$

$$q_d^0(r) \equiv q_d(r) - A_d e^{-zr}, \quad z \to 0, \tag{3.8b}$$

and we also have[1,7-9]

$$q_d^0(r) = 0,\ q_s(r) = 0, \quad r \geq \sigma, \tag{3.8c}$$

$$A_d \equiv -(\frac{\Gamma}{2\pi\rho})^{1/2}. \tag{3.9}$$

Substituting eqs.(3.2a) and (3.4a) into eqs. (3.6a) and (3.7a) respectively, we have, for $0 \leq r \leq \sigma$,

$$[q_s(r)]' + \nu[q_s(r+L) - q_s(r-L)] = -\frac{\lambda L^2}{24}\delta(r-L) + ar + b \tag{3.10a}$$

$$[q_d^0(r)]' + \nu[q_d^0(r-L) - q_d^0(r+L)] = \frac{\lambda L^2}{24}\delta(r-L) + H + \nu A_d[1-\theta(r-L)] \tag{3.10b}$$

where

$$\nu = \frac{\pi\rho\lambda L^2}{6} , \tag{3.11}$$

$$a = 1 - 4\pi\rho \int_0^\sigma q_s(r)dr \tag{3.12}$$

$$b = 4\pi\rho \int_0^\sigma r q_s(r)dr \tag{3.13}$$

$$H = 4\pi\rho A_d J_d(\sigma) , \tag{3.14}$$

$$J_d(r) \equiv \int_r^\infty r h_d(r)dr , \tag{3.15}$$

and $\theta(r) = 0$, $r < 0; = 1$, $r > 0$. Both $q_s(r)$ and $q_d^0(r)$ are continueous anywhere except at $r = L$.

$$q_s(L+) = q_s(L-) - \frac{\lambda L^2}{24}. \tag{3.16a}$$

$$q_d^0(L+) = q_d^0(L-) + \frac{\lambda L^2}{24}. \tag{3.16b}$$

Integration of eq.(3.7a) yields

$$J_d(r) = -q_d(r) + 4\pi\rho \int_0^\sigma dt q_d^0(t) J_d(|r-t|) + 4\pi\rho A_d \int_0^r J_d(y)dy + A_d/2 \tag{3.17}$$

where the condition $8\pi\rho \int_0^\infty J_d(r)dr = 1$[1-3,5] is used. At $r = 0$, we have [cf.(3.15), (3.4a)]

$$J_d(\sigma) + \frac{\lambda L^2}{24} = -q_d^0(0) + \nu \int_0^L dt q_d^0(t) - \frac{A_d}{2} + [4\pi\rho \int_0^\sigma dt q_d^0(t)] J_d(\sigma) . \tag{3.18}$$

Eq. (2.14) has been analytically solved for $q_s(r)$ and $q_d(r)$ for the case $L = \sigma/n$, $n = 1, 2, 3, 4, 5$. Analytical solution for $\sigma/3 \leq L \leq \sigma$ is obtained in Sections IV and V below.

Before closing this section, we point out that the parameter ν is closely related to the average relative concentration of dumbbells (i.e. degree of dumbbell association), which in fact is given by λ' of our eq.(2.5):

$$\frac{\pi\rho\lambda L^3}{3} = 2\nu L = \lambda' \tag{3.19}$$

When $\nu = 0$, we have completely dissociated dumbbells (charged hard-sphere fluids). When $\nu = 1/(2L)$, so that $\lambda' = 1$, we have the complete-association limit (dipolar dumbbell fluids).

IV. SOLUTIONS FOR $\sigma/3 \leq L \leq \sigma/2$

A. The Difference Equation

The mathematical method for solving eq.(3.10) for arbitrary L can be found in ref. 13 and is similar to the one used for the case of $L = \sigma/n$. For $\sigma/3 \leq L \leq \sigma/2$, we needs to divide the hard-core region (0,1) into the five intervals (0,1-2L), (1-2L,L), (L,1-L), (1-L,2L), and (2L,1). Here and below, we shall use $\sigma = 1$ for convenience. Following the method in ref. 13, the solution of eq.(3.10b) is

$$\begin{aligned} q_d^0(r) &= A_1\sin(\sqrt{2}\nu r) + A_2\cos(\sqrt{2}\nu r) + (H + \frac{\nu}{2}A_d)r + A_3,\ 0 \leq r \leq 1-2L, \\ &= B_1\sin[\nu(r-1+2L)] + B_2\cos[\nu(r-1+2L)] + \frac{H}{\nu},\ 1-2L \leq r \leq L, \\ &= \sqrt{2}A_1\cos[\sqrt{2}\nu(r-L)] - \sqrt{2}A_2\sin[\sqrt{2}\nu(r-L)] - \frac{A_d}{2},\ L \leq r \leq 1-L, \\ &= B_1\cos[\nu(r-1+L)] - B_2\sin[\nu(r-1+L)] - \frac{H}{\nu} - A_d,\ 1-L \leq r \leq 2L, \\ &= -A_1\sin[\sqrt{2}\nu(r-2L)] - A_2\cos[\sqrt{2}\nu(r-2L)] + (H + \frac{\nu}{2}A_d)(r-2L) + A_3 - \frac{H}{\nu}, \\ &\qquad 2L \leq r \leq 1, \end{aligned} \tag{4.1}$$

Coefficients A_1, A_2, A_3, B_1, and B_2 can be obtained from eq.(3.16b) and the continuity condition of $q_d^0(r)$ at $r = 1-2L$, $1-L$, $2L$, and 1. After some algebra, we obtain

$$\begin{aligned} A_1 =& \frac{1}{\Delta}\{\frac{H}{\nu}[-1 + 3c_2 - s_1 + \sqrt{2}s_1s_2 + 3s_1c_2 + \sqrt{2}s_2c_1 - 2c_1c_2 - \nu(1-2L)(\sqrt{2}s_1s_2 - 2c_1c_2)] \\ &+ \frac{A_d}{2}[-1 + 3c_2 - s_1 + 3c_2s_1 + \sqrt{2}s_2c_1 + 2\sqrt{2}s_1s_2 - 4c_1c_2 - \nu(1-2L)(\sqrt{2}s_1s_2 - 2c_1c_2)] \\ &+ \frac{\nu}{12\eta}[-1 + c_2 + 2c_2s_1 + \sqrt{2}s_2c_1]\} \end{aligned} \tag{4.2}$$

$$A_2 = \frac{1}{\Delta}\{\frac{H}{\nu}[-\sqrt{2} - 3s_2 + \sqrt{2}c_1 + 2s_2c_1 + \sqrt{2}c_2s_1 - 3s_2s_1 + \sqrt{2}c_2c_1$$
$$+ \nu(1-2L)(\sqrt{2} - 2s_2c_1 - \sqrt{2}c_2s_1)]$$
$$+ \frac{A_d}{2}[-2\sqrt{2} + \sqrt{2}c_1 - 3s_2 + 4s_2c_1 + 2\sqrt{2}c_2s_1 - 3s_2s_1 + \sqrt{2}c_2c_1 \quad (4.3)$$
$$+ \nu(1-2L)(\sqrt{2} - 2s_2c_1 - \sqrt{2}c_2s_1)]$$
$$- \frac{\nu}{12\eta}[s_2 + 2s_2s_1 - \sqrt{2}c_2c_1]\}$$

$$A_3 = \frac{1}{\Delta}\{\frac{H}{\nu}[-3\sqrt{2} - s_2 + \sqrt{2}c_1 + \sqrt{2}c_1c_2 - s_1s_2 + 3\sqrt{2}c_2s_1 + 4s_2c_1$$
$$+ \nu(1-2L)(3\sqrt{2} - 3\sqrt{2}c_2s_1 - 4s_2c_1)]$$
$$+ \frac{A_d}{2}[-s_2 + \sqrt{2}c_1 - 2\sqrt{2}c_2 + 2\sqrt{2}s_1 - s_1s_2 + \sqrt{2}c_1c_2 + \nu(1-2L)(3\sqrt{2} - 3\sqrt{2}c_2s_1 - 4s_2c_1)]$$
$$+ \frac{\nu}{12\eta}(-s_2 + \sqrt{2}c_1)\}$$
$$(4.4)$$

$$B_1 = \frac{1}{\Delta}\{\frac{2H}{\nu}[s_2 + \sqrt{2}s_1 - \sqrt{2}c_1 + \sqrt{2}c_2s_1 + s_2c_1 - \nu(1-2L)(s_2 - \sqrt{2}c_1)]$$
$$+ A_d[2s_2 + \sqrt{2}s_1 - 2\sqrt{2}c_1 + \sqrt{2}c_2s_1 + s_2c_1 - \nu(1-2L)(s_2 - \sqrt{2}c_1)] \quad (4.5)$$
$$+ \frac{\sqrt{2}\nu}{12\eta}[1 - c_2 + 2s_1]\}$$

$$B_2 = \frac{1}{\Delta}\{\frac{2H}{\nu}[-s_2 - \sqrt{2}c_2 + \sqrt{2}s_1 + \sqrt{2}c_1 + \sqrt{2}c_1c_2 - s_1s_2 - \nu(1-2L)(\sqrt{2}s_1 - \sqrt{2}c_2)]$$
$$+ A_d[-s_2 + 2\sqrt{2}s_1 + \sqrt{2}c_1 - 2\sqrt{2}c_2 - s_1s_2 + \sqrt{2}c_1c_2 - \nu(1-2L)(\sqrt{2}s_1 - \sqrt{2}c_2)]$$
$$+ \frac{\nu}{6\eta}[-s_2 + \sqrt{2}c_1]\}$$
$$(4.6)$$

where

$$\Delta = -3\sqrt{2} + \sqrt{2}c_2 - \sqrt{2}s_1 + 3\sqrt{2}c_2s_1 + 4s_2c_1 \quad (4.7)$$

$$c_1 = \cos[\nu(3L-1)],\ s_1 = \sin[\nu(3L-1)] \quad (4.8)$$

$$c_2 = \cos[\sqrt{2}\nu(1-2L)],\ s_2 = \sin[\sqrt{2}\nu(1-2L)] \quad (4.9)$$

$$\eta = \frac{\pi\rho}{3} \quad (4.10)$$

Substituting eqs.(4.1), (4.2), (4.3), (4.4) (4.5) and (4.6) into eq.(3.18) we can solve for H [cf. (3.14)]

$$H = \frac{a_1 + \alpha a_2 + \sqrt{a_1^2 + 2\alpha a_3}}{24 a_4 \eta} \tag{4.11}$$

with $\alpha = -4\pi\rho A_d$ and

$$a_1 = -6\sqrt{2} - 2s_2 + 2\sqrt{2}c_2 - 4\sqrt{2}s_1 + 2\sqrt{2}c_1 + 6c_1s_2 + 4\sqrt{2}s_1c_2 + (2s_2 - 2\sqrt{2}c_1)Y \tag{4.12}$$

$$\begin{aligned} a_2 = -\frac{\sqrt{2}}{\nu}[&-8 + 6c_1 - 4c_2 - 3\sqrt{2}s_2 + 6c_1c_2 + 4s_1c_2 + 4\sqrt{2}c_1s_2 - 3\sqrt{2}s_1s_2 \\ &+ (9 - 4c_1 - 3s_1 + 3c_2 + 2\sqrt{2}s_2 - 4c_1c_2 - 9s_1c_2 - 6\sqrt{2}c_1s_2 + 2\sqrt{2}s_1s_2)Y \\ &+ (-3 + s_1 - c_2 + 3s_1c_2 + 2\sqrt{2}c_1s_2)Y^2] \end{aligned} \tag{4.13}$$

$$\begin{aligned} a_3 = -\frac{1}{\nu}\{&[(4s_1 - 24c_1^2)s_2^2 + (-24s_1^2 - 4s_1)c_2^2 - 34\sqrt{2}c_1s_2s_1c_2 - 6\sqrt{2}c_1c_2s_2 + 6\sqrt{2}c_1s_1s_2 \\ &+ 34\sqrt{2}c_1s_2 + 16s_1^2c_2 + 48s_1c_2 + 8c_1^2c_2 - 12s_1 - 24]Y \\ &+ [(-12c_1 - 4)s_1 + 24c_1^2 - 12c_1]s_2^2 + [24s_1^2 + 16c_1s_1 + 4s_1 + 8c_1]c_2^2 \\ &+ [(34\sqrt{2}c_1 - 16\sqrt{2})s_1 + 12\sqrt{2}c_1^2 - 8\sqrt{2}s_1^2 + 6\sqrt{2}c_1 - 8\sqrt{2}]c_2s_2 \\ &+ 8\sqrt{2}s_1^2s_2 + 16\sqrt{2}s_1s_2 - 6\sqrt{2}c_1s_1s_2 + 12\sqrt{2}c_1^2s_2 - 34\sqrt{2}c_1s_2 + 8\sqrt{2}s_2 \\ &- 16s_1^2c_2 + 8c_1s_1c_2 - 48s_1c_2 - 8c_1^2c_2 - 8c_1c_2 + 12s_1 - 8c_1s_1 - 16c_1 + 24\} \end{aligned} \tag{4.14}$$

$$\begin{aligned} a_4 = \frac{1}{\nu^2}\{&(3\sqrt{2} - \sqrt{2}s_1 + \sqrt{2}c_2 - 3\sqrt{2}s_1c_2 - 4c_1s_2)Y^2 \\ &[-6\sqrt{2} + 4\sqrt{2}c_1 + 2\sqrt{2}s_1 - 2\sqrt{2}c_2 - 4s_2 + 4\sqrt{2}c_1c_2 + 6\sqrt{2}s_1c_2 + 8c_1s_2 - 4s_1s_2]Y \\ &+ (4s_1 - 4c_1 + 4)s_2 + (-\sqrt{2}s_1 - 4\sqrt{2}c_1 + 3\sqrt{2})c_2 + \sqrt{2}s_1 - 4\sqrt{2}c_1 + 5\sqrt{2}\} \end{aligned} \tag{4.15}$$

where $Y = \nu(1 - 2L)$. It worth noting that the excess energy satisfies $\beta E^{ex} = \alpha H/2$.[7] ($H$ used here is equal to $-H$ used in refs.7-9).

B. The Sum Equation

The sum equation (3.10a) can be solved in a similar way. Results are shown below.

$$q_s(r) = \frac{1}{2}ar^2 + [b - \frac{a}{2\nu}(1-2\nu L)]r + c + v\sin(\sqrt{2}\nu r) + u\cos(\sqrt{2}\nu r),\ 0 \le r \le 1-2L,$$

$$= -\frac{1}{\nu}a(r-L) - \frac{b}{\nu} + \frac{a}{\nu^2}(1-2\nu L) + q\sin[\nu(r-1+2L)] + p\cos[\nu(r-1+2L)],$$

$$1-2L \le r \le L,$$

$$= \frac{a}{2\nu^2}(1-2\nu L) - \sqrt{2}v\cos[\sqrt{2}\nu(r-L)] + \sqrt{2}u\sin[\sqrt{2}\nu(r-L)],\ L \le r \le 1-L,$$

$$= \frac{a}{\nu}(r+L) + \frac{b}{\nu} + \frac{a}{\nu^2}(1-2\nu L) - q\cos[\nu(r-1+L)] + p\sin[\nu(r-1+L)],$$

$$1-L \le r \le 2L,$$

$$= \frac{1}{2}ar^2 + [b + \frac{a}{2\nu}(1-2\nu L)]r + (1-2\nu L)\frac{b}{\nu} + c - v\sin[\sqrt{2}\nu(r-2L)] - u\cos[\sqrt{2}\nu(r-2L)],$$

$$2L \le r \le 1, \tag{4.16}$$

The coefficients a, b, c, u, v, p, and q can be obtained from eq.(3.16a), the continuity condition of q(r) at $r = 1-L,\ 1-2L,\ 2L,\ 1$, and equations (3.12) and (3.13).

$$(\frac{1}{2} + \frac{1-2\nu L}{2\nu})a + (1 + \frac{1-2\nu L}{\nu})b + c - c_2u - s_2v = 0 \tag{4.17}$$

$$\frac{a}{\nu^2} - c + u + s_1p - c_1q = 0 \tag{4.18}$$

$$[\frac{1-2\nu L}{2\nu^2} + \frac{1}{\nu}]a + \frac{b}{\nu} - \sqrt{2}s_2u + \sqrt{2}c_2v - q = 0 \tag{4.19}$$

$$\frac{(1-2\nu L)}{2\nu^2}a - \frac{b}{\nu} + \sqrt{2}v + c_1p + s_1q = \frac{\lambda L^2}{24} \tag{4.20}$$

$$(\frac{1}{2} - L + \frac{1}{2\nu} - \frac{1}{\nu^2})a + (1 - 2L + \frac{1}{\nu})b + c + c_2u + s_2v - p = 0 \tag{4.21}$$

$$\begin{aligned}
&- \frac{3\eta^2}{\nu^2}[(2L-1)^2\nu^2 + 2L(1-2L)\nu + 10L - 3]a \\
&+ \{1 + \frac{2\eta}{\nu}[(8L^3 - 24L^2 + 18L - 4)\nu - 6L^2 + 6L - 3]\}b \\
&- 12\eta(1-2L)c - \frac{6\eta}{\nu^2}[-(2\sqrt{2}L\nu - \sqrt{2})s_2 + (2L-2)\nu c_2 + 2L\nu]u \\
&+ \frac{6\eta}{\nu^2}[-(2L-2)\nu s_2 + (-2\sqrt{2}L\nu + \sqrt{2})c_2 + 2\sqrt{2}L\nu - \sqrt{2}]v \\
&- \frac{12\eta}{\nu^2}[(1+L\nu)s_1 + (1-2L\nu)c_1 + (1-L)\nu - 1]p \\
&+ \frac{12\eta}{\nu^2}[(2L\nu - 1)s_1 + (L\nu + 1)c_1 + (2L-1)\nu - 1]q = 0
\end{aligned} \tag{4.22}$$

$$\{1+\frac{2\eta}{\nu^2}[(8L^3-6L+2)\nu^2+(-18L^2+6L)\nu+30L-9]\}a$$
$$+\frac{12\eta}{\nu}[2L-1][(2L-1)\nu-1]b+24\eta(1-2L)c+\frac{12\eta}{\nu}(1-c_2)u \qquad (4.23)$$
$$-\frac{12\eta}{\nu}s_2v+\frac{12\eta}{\nu}(1+s_1-c_1)p+\frac{12\eta}{\nu}(1-s_1-c_1)q=1$$

Theses seven linear equations can be solved by using matrix transformation.

When $L=1/2$, $c_2=1$ and $s_2=0$. When $L=1/3$, $c_1=1$, $s_1=0$. At these vaules of L, all results presented here reduce correctly to results obtained in earlier work.[7–9]

V. SOLUTIONS FOR $\sigma/2 \le L \le \sigma$

When $1/2 \le L \le 1$, the hard core region (0,1) is divided into (0,1-L), (1-L,L),and (L,1). Analytical solution is shown below.

$$\begin{aligned} q_d^0(r) &= \frac{H}{\nu}+B_1\sin(\nu r)+B_2\cos(\nu r),\ 0\le r\le 1-L, \\ &= (H+\nu A_d)(r-1+L)+A_1, \qquad 1-L\le r\le L, \\ &= -\frac{H}{\nu}-A_d+B_1\cos[\nu(r-L)]-B_2\sin[\nu(r-L)],\ L\le r\le 1, \end{aligned} \qquad (5.1)$$

$$B_1=\frac{1}{1-s_1}\{\frac{H}{\nu}[c_1-2s_1-\nu(2L-1)s_1]+A_d[c_1-s_1-\nu(2L-1)s_1]-\frac{\nu}{12\eta}s_1\} \qquad (5.2)$$

$$B_2=\frac{1}{1-s_1}\{\frac{H}{\nu}[1-s_1-2c_1-\nu(2L-1)c_1]+A_d[1-s_1-c_1-\nu(2L-1)c_1]-\frac{\nu}{12\eta}c_1\} \qquad (5.3)$$

$$A_1=\frac{1}{1-s_1}\{\frac{H}{\nu}[c_1-s_1-1-\nu(2L-1)]+A_d[c_1-1-\nu(2L-1)]-\frac{\nu}{12\eta}\} \qquad (5.4)$$

where $c_1=\cos[\nu(1-L)]$, $s_1=\sin[\nu(1-L)]$, and ν, A_d, and η satisfy equations (3.11), (3.9) and (4.10) respectively. Besides, H still satisfies eq.(4.11) but with

$$a_1=-2+c_1-Y \qquad (5.5)$$

$$a_2=\frac{1}{\nu}[(1+s_1)Y^2-(3s_1-4c_1+3)Y-2s_1-6c_1+6] \qquad (5.6)$$

$$a_3=-\frac{1}{\nu}[-(c_1s_1-c_1)Y+2c_1s_1-4s_1-2c_1^2-2c_1+4] \qquad (5.7)$$

$$a_4=\frac{1}{2\nu^2}[(1+s_1)Y^2-(4s_1-4c_1+4)Y-8c_1+8] \qquad (5.8)$$

where $Y = \nu(1-2L)$.

For the sum equation, we have

$$\begin{aligned} q_s(r) &= -\frac{a}{\nu}r + \frac{a}{\nu^2}[1-\nu L] - \frac{b}{\nu} + p\cos(\nu r) + q\sin(\nu r),\ 0 \le r \le 1-L, \\ &= \frac{1}{2}ar^2 + br + u,\ 1-L \le r \le L, \\ &= \frac{a}{\nu}r + \frac{a}{\nu^2}(1-\nu L) + \frac{b}{\nu} + p\sin[\nu(r-L)] - q\cos[\nu(r-L)],\ L \le r \le 1, \end{aligned} \tag{5.9}$$

where a, b, u, p, q satisfies 5 linear equations.

$$[\frac{1}{\nu} + \frac{1}{\nu^2}(1-\nu L)]a + \frac{1}{\nu}b + s_1 p - c_1 q = 0 \tag{5.10}$$

$$[\frac{1}{\nu^2} - \frac{L^2}{2}]a + (\frac{1}{\nu} - L)b - u - q = -\frac{\lambda L^2}{24} \tag{5.11}$$

$$[\frac{\nu-1}{\nu^2} + \frac{(1-L)^2}{2}]a + [(1-L) + \frac{1}{\nu}]b + u - c_1 p - s_1 q = 0 \tag{5.12}$$

$$\begin{aligned} &-\frac{3\eta}{2\nu^2}[(4L^3 - 6L^2 + 4L - 1)\nu^2 - 8L + 8]a \\ &+ \{1 - \frac{4\eta}{\nu}[(2L^3 - 3L^2 + 3L - 1)\nu - 3L^2 + 3L]\}b \\ &+ 6\eta[1-2L]u - \frac{12\eta}{\nu^2}\{-[(L-1)\nu - 1]s_1 + (1-\nu)c_1 + L\nu - 1\}p \\ &- \frac{12\eta}{\nu^2}\{[(L-1)\nu - 1]c_1 + (1-\nu)s_1 + 1\}q = 0 \end{aligned} \tag{5.13}$$

$$\begin{aligned} &\{1 + \frac{2\eta}{\nu^2}[(2L^3 - 3L^2 + 3L - 1)\nu^2 + 6L(L-1)\nu - 12L + 12]\}a + 6\eta(2L-1)b \\ &+ 12\eta[2L-1]u - \frac{12\eta}{\nu}[-s_1 + c_1 - 1]p + \frac{12\eta}{\nu}[-s_1 - c_1 + 1]q = 1 \end{aligned} \tag{5.14}$$

When $L = 1$, and $L = 1/2$, our results reduce to the results obtained in earlier work.[6,9,10]

VI. THE BORN SOLVATION FREE ENERGY OF A DIPOLAR DUMBBELL IN A DIPOLAR SOLVENT

In earlier papers[3,4], we obtained the Born solvation free energy (BSFE) of a symmetric[3] or an unsymmetric[4] "extended" dipolar dumbbell in a symmetric dipolar dumbbell solvent or a dipolar hard-sphere solvent. Here, the "extended" means that the bonding length of the du l L_i is larger than or equal to the contact distance of the constituent ions of the d bell (i.e. the fixed distance between the ion centers, L_i, is greater or equal to the i ic diameter). The BSFE has been very useful in furthering an understanding of molecular solvent effects on electron-transfer reactions and solvation dynamics.[4,5] In this section, we shall obtain the BSFE for the symmetric dipolar dumbbell in a dipolar solvent, which we hope will also prove be useful in understanding intramolecular electron-transfer reactions and in determining equilibrium liquid-junction potentials and the partitioning of the dumbbell species between two immiscible fluid phases.[13]

First, we consider the symmetric dipolar dumbbell in a dipolar dumbbell solvent. The method for obtaining the BSFE is presented in detail in ref.3. It turns out that the difference Baxter-q function between the solvent dumbbell and solute dumbbell satisfies a equation similar to eq.(3.10b) but without the δ-function term. The equation can be solved by dividing the region (S_{di}, R_{id}) into intervals $(S_{di}, R_{id} - L)$, $(R_{id} - L, S_{di} + L)$, and $(S_{di} + L, R_{id})$ for $R_i/2 \leq L_i \leq R_i$, and dividing (S_{di}, R_{id}) into $(S_{di}, R_{id} - 2L_i)$, $(R_{id} - 2L_i, S_{di} + L_i)$, $(S_{di} + L_i, R_{id} - L_i)$, $(R_{id} - L_i, S_{di} + 2L_i)$, and $(S_{di} + 2L_i, R_{id})$ for $R_i/3 \leq L_i \leq R_i/2$. where L_i is the bonding length of the solute dumbbell, $R_{id} = (R_i + R_d)/2$, $S_{di} = (R_d - R_i)/2$ with hard core diameters R_d for a solvent dumbbell and R_i for a solute dumbbell.

The final result gives

$$F_{Born} = -\frac{2q_i^2(1 - 1/\epsilon)\chi_1}{-2L_i\chi_2 + \Delta_d} \;, \tag{6.1}$$

with

$$\chi_1 = \frac{1}{1 - s_0}[(1 + s_0)(R_i^*)^2 + 4(c_0 - s_0 - 1)R_i^* - 8c_0 + 8] \tag{6.2}$$

$$\chi_2 = \frac{1}{1 - s_0}[(1 + s_0)(R_i^*)^2 + (-5s_0 + 4c_0 - 5)R_i^* + 2s_0 - 10c_0 + 10] \tag{6.3}$$

for $R_i/2 \le L_i \le R_i$, and

$$\chi_1 = \frac{1}{2\Delta}\{[4c_1s_2 + (3\sqrt{2}s_1 - \sqrt{2})c_2 + \sqrt{2}s_1 - 3\sqrt{2}](R_i^*)^2$$
$$+ [(4s_1 - 24c_1 + 4)s_2 + (-18\sqrt{2}s_1 - 4\sqrt{2}c_1 + 6\sqrt{2}]c_2 - 6\sqrt{2}s_1 - 4\sqrt{2}c_1 + 18\sqrt{2}]R_i^*$$
$$+ (-12s_1 + 36c_1 - 12)s_2 + (25\sqrt{2}s_1 + 12\sqrt{2}c_1 - 11\sqrt{2})c_2 + 7\sqrt{2}s_1 + 12\sqrt{2}c_1 - 29\sqrt{2}\} \quad (6.4)$$

$$\chi_2 = \frac{1}{\Delta}\{[4c_1s_2 + (3\sqrt{2}s_1 - \sqrt{2})c_2 + \sqrt{2}s_1 - 3\sqrt{2})(R_i^*)^2$$
$$+ [(4s_1 - 20c_1 + 4)s_2 + (-15\sqrt{2}s_1 - 4\sqrt{2}c_1 + 5\sqrt{2})c_2 - 5\sqrt{2}s_1 - 4\sqrt{2}c_1 + 15\sqrt{2}]R_i^*$$
$$+ (-10s_1 + 24c_1 - 10)s_2 + (16\sqrt{2}s_1 + 10\sqrt{2}c_1 - 8\sqrt{2})c_2 + 4\sqrt{2}s_1 + 10\sqrt{2}c_1 - 20\sqrt{2}\} \quad (6.5)$$

for $R_i/3 \le L_i \le R_i/2$, where $\Delta_d = R_d - [1 - 4\pi\rho\int_0^{R_d} dt q_{dd}^0(t)]/(2\pi\rho A_d)$, $R_i^* = R_i/2L_i$, $s_0 = \sin(R_i^* - 1/2)$, $c_0 = \cos(R_i^* - 1/2)$, $s_1 = \sin(3/2 - R_i^*)$, $c_1 = \cos(3/2 - R_i^*)$, $s_2 = \sin[\sqrt{2}(R_i^* - 1)]$, $c_2 = \cos[\sqrt{2}(R_i^* - 1)]$, $\Delta = -3\sqrt{2} + \sqrt{2}c_2 - \sqrt{2}s_1 + 3\sqrt{2}c_2s_1 + 4s_2c_1$, ϵ is the solvent dielectric constant, q_i is the charge of the ion of the solute dumbbells, and $q_{dd}^0(t)$ is the short-range part of the pure solvent-dumbbell difference Baxter-q function, which is known from the analytical solution in previous sections as $q_d^0(t)$. It is easy to show that for a dipolar hard-sphere solvent, the BSFE of the dipolar dumbbell also satisfies eq.(6.1) but with

$$\Delta_d = R_d \frac{(1 - 2\xi)}{(1 + 4\xi)} \quad (6.5)$$

The MSA solvent factor ξ is the solution of the equation[14]

$$\frac{(1 + 4\xi)^2}{(1 - 2\xi)^4} - \frac{(1 - 2\xi)^2}{(1 + \xi)^4} = \frac{4\pi}{3}\beta\rho_d\mu_d^2 \quad (6.6)$$

where μ_d is the dipole moment of the solvent. The solvent dielectric constant ϵ is related to ξ by the equation[14]

$$\epsilon = \frac{(1 + 4\xi)^2(1 + \xi)^4}{(1 - 2\xi)^6} \quad . \quad (6.7)$$

Fig.1 shows the Born solvation free energy of a dumbbell in a dipolar hard-sphere solvent as a function of the bonding length L_i at a constant dipole moment. For comparison, the result for an extended dumbbell, $L_i > R_i$, [3,4] and a dipolar hard-sphere, $L_i = 0$ [15] in a dipolar hard-sphere solvent under the MSA are also plotted.

Once the Born solvation free energy is known, we can investigate the solvation dynamics[5] of a single dumbbell in a dipolar solvent by following the method of Wolynes.[18] In particular, the average relaxation time can be easily obtained analytically.[4] The activation free energy and reorganization free energy for electron-transfer reactions, in which an electron jumps from one of the dumbbell-constituent ions to the other, can also easily be obtained.[5] We shall defer a discussion of these results to a future article.

VII. DISCUSSION AND SUMMARY

In this paper we have obtained analytical solution for the case of $\sigma/3 \leq L \leq \sigma$ for the dissociative dipolar dumbbell model under the MSA. Analytical solution to other regions $\sigma/(n+1) \leq L \leq \sigma/n$, $n \geq 3$ can also be obtained by dividing the interval (0,1) into $2n+1$ parts. This work provides solvent fluid structural properties over a continueous range of L, which can be used to investigate ionic solvation, the Born solvation free energy for two ions at a fixed distance apart, and solvation dynamics.[2–5] We have also obtained the BSFE of a dipolar dumbbell in a dipolar dumbbell solvent or a dipolar hard-sphere solvent.

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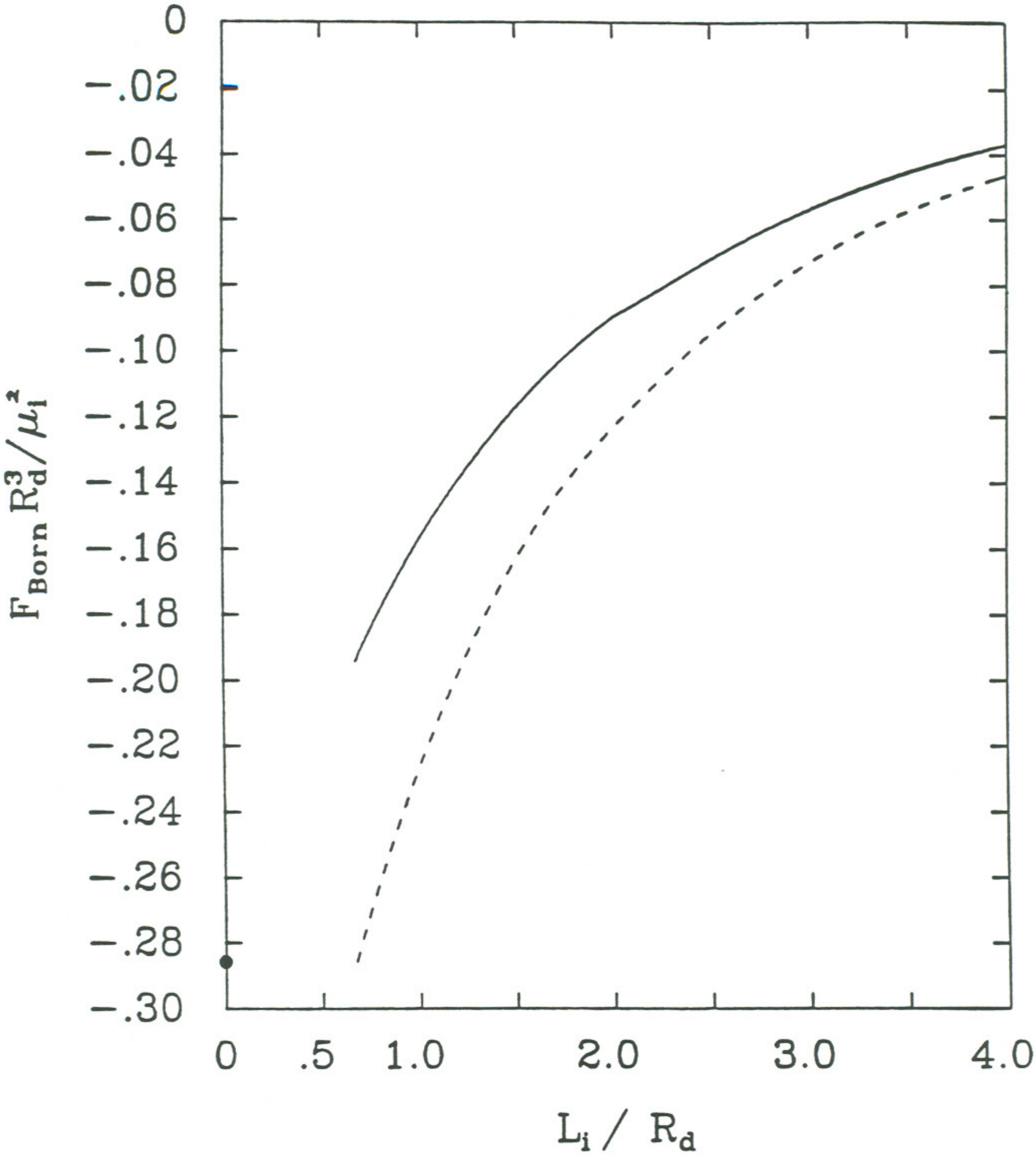
FIGURE CAPTION

Fig.1 The reduced BSFE, $F_{Born}R_d^3/\mu_i$, as a function of the reduced solute-dumbbell bonding length L_i/R_d. Here $\mu_i = q_iL_i$ is the dipole moment of a solute dumbbell. The dashed line denotes the BSFE of the same dumbbell in the continuum-solvent limit, $\Delta_d = 0$. The result of a dipolar hard-sphere in a dipolar hard-sphere solvent is also shown by the dot (•) in the lower left-hand corner.[15]



0
−.02
−.04
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−.08
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−.14
−.16
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−.24
−.26
−.28
−.30
$F_{Born} R_d^3/\mu_i^2$
0
.5
1.0
2.0
3.0
4.0
L_i / R_d