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Analytic solution of the mean spherical approximation for a dipolar hard-sphere fluid with intracore anisotropic sticky interactions

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A model of associating multipolar fluid is introduced. It is a one-component fluid with dipole-dipole and anisotropic intracore sticky interaction. The Mayer function of associative sticky interaction consists of the spherically symmetric part and the terms of dipolar and spin-spin symmetry. This model of anisotropic penetrable dipolar hard spheres permits the formation of dimer and higher-order n-mer species. Specific orientation-dependent correlations which result from the association of the monomers influence the structural, dielectric, and thermodynamic properties. The model is analytically solved within the mean spherical approximation. It is shown that the solution reduces to a linear combination of the solutions for the model of overlapping hard spheres of Cummings and Stell. This mapping is similar to that obtained by Wertheim for the dipolar hard-sphere model [M. S. Wertheim, J. Chem. Phys. **55**, 4291 (1971)].

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I. INTRODUCTION

The theory of associating fluids is of much interest to those in chemistry and chemical engineering. Its applications include a description of phase equilibria, chemical reactions, solvation, catalysis, and other areas. During the past two decades the theory has been developed rapidly, using the method of integral equations [1–13]. The most common approaches used to study associating fluids are those of Stell and co-workers [4–10] and of Wertheim [11–13]. The objective is to provide an adequate theoretical treatment of the strong short-range attractive term of the interparticle interaction that provides association.

The models of associating fluids can be classified according to the symmetry and range of this interaction [10]. Although the phenomenon of association in an ionic fluid was first considered by Bjerrum [14], the model of sticky interaction of Baxter [15] is perhaps the first attempt to discuss association in a proper statistical mechanic formulation.

However, a serious difficulty arises with the Baxter model of an equal size isotropic sticky hard-sphere model, which was pointed out by Stell [16]. This model is thermodynamically unstable, and every particle of the system will bond to form a gel. The problem is that, normally, the statistical mechanics of fluids is based on expansions of interactions that will not exclude the interaction of an unlimited number of particles in a given cluster. The chemical bonds, however, will not allow more than a few particles in a cluster. Typically, dimerization

$$A + A \rightleftharpoons A_2$$

allows only one bond per atom. In other words, the bonds saturate. Traditional statistical mechanics do not include the saturation of bonds. An early discussion of this problem was put forth by Chandler, Pratt, Høye, and Olaussen [1–3]. The proper formulation of the saturating forces requires a reformulation of the cluster expansions and a new Ornstein-Zernike (OZ) equation, the Wertheim OZ equation [11–13].

At the same time Cummings and Stell [4,5] developed a simpler scheme, which is analytically tractable and which is based on the fact that the sticky shell can be placed inside the hard sphere: in this case the hard core will limit the number of participants in a given cluster. For example, if the sticky shell is placed at a distance $L \leq \sigma/2$, where σ is the hard-core diameter of the particles A, then not more than two monomers can be bonded at once. As was shown by Stell and Zhou [6,7], the thermodynamic perturbation theory of Wertheim [11–13] and the simple interpolation scheme of these authors are equivalent and very accurate, at least for small penetrations.

Highly directional attractive forces are treated as the interaction between the off-center sticky sites in the Wertheim theory [11–13]. It is based on a novel fugacity expansion to include explicitly the presence of bounded particles. Analytic solutions of the off-center site models are derived from the Wertheim OZ integral equation and relevant closure relations. Both of the theories refer to the correlation functions of bounded and unbounded particles in opposition to the standard OZ equation and closures.

Originally proposed for models with no electrostatic interactions, both of the theories were extended for fluids

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with charged particles [17–22]. The association of ions leads to the formation of extended dipoles or complexes possessing dipole, quadrupole, and higher-order multipole moments in these fluids. The screening of Coulomb interactions and the ordering of ions are strongly affected by association.

There are clearly questions on when we want a formalism of sticky points, which characterize highly directional forces, like those of the sticky points of Wertheim, and when can we get away with a simpler model like that of the sticky shell of Stell *et al.* A case in point is water: if we are going to build water from oxygen and hydrogen atoms, like in the Stillinger-Lemberg model [23], then quite clearly the interactions should be highly directional. Surprisingly, though, it has been recently found [24] that the structural and thermodynamic properties of a hydrogen bonded fluid can be explained by a (dipolar plus octupolar) potential that is not very directional.

It is therefore of interest to develop a theory that is, in a certain sense, intermediate between the sticky point association of Wertheim and the sticky inner-shell association of Stell; namely, the inner shell with dipolar symmetry. Then, only properly oriented spheres will associate. Clearly a more sophisticated system (tetrahedral or octahedral) can be addressed. Analytical models with anisotropic surface adhesion were discussed in the past [25,26], but only surface adhesion was treated. Anisotropic dipole-dipole interactions with surface stickiness were also used to account for directional forces in the computation of the dielectric constant ε of a number of solvents. Multipolar expansions in conjunction with Wertheim's thermodynamic perturbation theory were applied to study chemical association for a number of fluids [27].

In this paper we introduce a class of models for associating multipolar fluids. The models are characterized by interparticle electrostatic multipolar interaction and intracore anisotropic sticky interaction. Therefore the particles can overlap and form dimers, trimers, and higher-order *n*-mers made of overlapping monomers. The simplest member of this family is the anisotropic penetrable dipolar (APD) hard-sphere model. We also discuss briefly the anisotropic penetrable quadrupolar (APQ) hard-sphere fluid. The species resulting from the association of monomers in the APD or APQ model will evidently possess dipole, quadrupole, and higher-order multipole moments.

As was mentioned above, in charged associating fluids the screening radius is essentially affected by the association. In dipolar fluids the effect of the medium results in a decay of correlations by a factor $1/\varepsilon$. Therefore it is of interest to estimate the effect of the association on the dielectric constant for the APD model. The dependence of the thermodynamic properties on the degree of association is of relevance to the phase behavior of the system.

The model also lends itself to a number of other interesting applications, such as ionic solvation, since nonassociated dipolar hard-sphere (DHS's) and associated (APD) solvents will have different effects on the potential of mean force. Moreover, the APD model can be used to construct an ion-dipole model of ionic solutions, where all species can be penetrable. The technical aspects of this problem will be discussed in a future work.

Our main objective here is to obtain the analytical solution of the APD model. The model will be solved by using the mean spherical approximation (MSA). We show that the problem can be mapped onto that for a chemically reacting simple fluid. The solution obtained has the form of a linear combination of the solutions for the model of overlapping hard spheres of Cummings and Stell [4,5].

II. MODEL AND BASIC FORMALISM

Consider a one-component fluid consisting of "hard-core" particles with intracore square wells and with embedded pointlike dipoles in their centers. The depth of the wells depends on the orientations of the dipole moments. The diameter of particles is denoted by σ and without loss of generality is assumed to be equal to 1. The density of the fluid is ρ_s. The potential energy of the system can be written as follows:

$$U_{\text{pot}}=\sum_{i<j}\left[U_{dd}(ij)+U_{\text{assoc}}(ij)\right], \tag{1}$$

where i symbolizes both the position $\mathbf{r}_i$ of the center of mass of particle i and orientation of its dipole moment Ω_i. The first term corresponds to the energy of the dipole-dipole interactions and the second denotes the associative interaction energy. In what follows we shall use the orientation-invariant expansions of Blum and Torruella [28–30],

$$F(ij)=\sum_{m,n,l,\mu,\nu}F^{mnl}_{\mu\nu}(r_{ij})\Phi^{mnl}_{\mu\nu}(\Omega_i,\Omega_j,\Omega_{\mathbf{r}_{ij}}), \tag{2}$$

where $\Phi^{mnl}(\Omega_i,\Omega_j,\Omega_{\mathbf{r}_{ij}})$ are the rotational invariants. For linear molecules the indices $\mu,\nu=0$ and we shall omit them. Consider the Boltzmann factor that corresponds to the pair interactions in the potential energy given by Eq. (1), $e(12)=1+f(12)=\exp\{-\beta[U_{dd}(ij)+U_{\text{assoc}}(ij)]\}$, where $f(12)$ is the Mayer function, and let us introduce another Boltzmann factor $\tilde{e}(12)$, which is defined as

$$\tilde{e}(12)\begin{cases}0, & 0<r_{12}<L-w/2,\\ D_0\Phi^{000}(\Omega_1,\Omega_2,\Omega_{r_{12}})+D_1\Phi^{110}(\Omega_1,\Omega_2,\Omega_{r_{12}})+D_2\Phi^{112}(\Omega_1,\Omega_2,\Omega_{r_{12}}), & L-w/2<r_{12}<L+w/2\ ,\\ \exp(-\beta\varepsilon^*), & L+w/2<r_{12}<1,\\ \exp[-\beta U_{dd}(12)], & r_{12}>1,\end{cases} \tag{3}$$

where $r_{12}=|\mathbf{r}_{12}|$, w is the width of the attractive wells, and D_k $(k=0,1,2)$ are their depths. The wells are centered at bonding distance L. The parameter ε^* denotes the height of the square mound and is chosen sufficiently large to assure $\exp(-\beta\varepsilon^*)\approx 0$. The parameters D_k describe the energetic aspects of associative interactions, whereas L and w give their geometry.

Let us analyze an assumption (3) in more detail. We consider a model that contains an orientation-dependent square well inside a hard core of particles. The transition from $e(12)$ to $\tilde{e}(12)$ in the form of Eq. (3) has been thoroughly investigated by Blum and Torruella for arbitrary potentials (see [30] for a detailed description). It reads

$$e(12)=\exp\sum_{m'n'l'}U^{m'n'l'}(r_{12})\Phi^{m'n'l'}(\Omega_1,\Omega_2,\Omega_{r_{12}})$$
$$=\sum_{mnl}\tilde{e}^{mnl}(r_{12})\Phi^{mnl}(\Omega_1,\Omega_2,\Omega_{r_{12}})\ . \tag{4}$$

Truncation of the series on the right-hand side of Eq. (4) is certainly an approximation. Therefore, the form for $\tilde{e}(12)$ given by Eq. (3) can be considered as corresponding to a certain approximate "effective" Hamiltonian, i.e., with the effective interparticle interactions. It is evident then that each of the parameters D_k $(k=0,1,2)$ depends on the contributions from all of the types of anisotropy contained in the initial Hamiltonian, and will also depend on the geometric characteristics (L,w) of the initial associative interaction.

With respect to the steric constraints the model behaves similarly to its isotropic counterpart of Cummings and Stell [4]. We shall restrict ourselves to the case $L+w/2\le 1/2$, i.e., to a practically dimerization case [4]. However, at given L and w the steric constraints for our model are more restrictive due to the anisotropy of the intracore square well. If one demands that $U_{\rm assoc}(12)$ for $L-w/2<r_{12}<L+w/2$ be attractive for arbitrary orientations of the dipole moments, then D_0 has to be sufficiently larger if compared with D_1 and D_2. Otherwise, the dimers will be formed only for specific mutual orientations of dipoles.

The form of the Boltzmann factor given by Eq. (3) does not permit one to obtain the analytic solution. Let us now develop a limiting process to get an analytically tractable problem. It is similar to that proposed by Baxter [15] for the isotropic square well fluid. We take the sticky limit ($w\to 0$; $D_0,D_1,D_2\to\infty$) in such a way that

$$\int d\mathbf{r}\,\tilde{e}^{000}(r),\ \int d\mathbf{r}\,\tilde{e}^{110}(r),\ \text{and}\ \int d\mathbf{r}\,\tilde{e}^{112}(r)\ ,$$

remain fixed, where $\tilde{e}^{mnl}(r)$ are the expansion coefficients of $\tilde{e}(12)$ in the orientation-invariant expansion [28–30]. This implies that the sticky representation of the Mayer function $f(12)$ becomes

$$f_{(\tau)}(12)=\begin{cases}-1+\dfrac{L}{12\tau^{000}}\delta(r_{12}-L)\Phi^{000}(\Omega_1,\Omega_2,\Omega_{r_{12}})+\dfrac{L}{12\tau^{110}}\delta(r_{12}-L)\Phi^{110}(\Omega_1,\Omega_2,\Omega_{r_{12}})\\ +\dfrac{L_{r_{12}}}{12\tau^{112}}\delta'(r_{12}-L)\Phi^{112}(\Omega_1,\Omega_2,\Omega_{r_{12}}),\quad 0<r_{12}<1\\ -1+\exp[-\beta U_{dd}(12)],\quad r_{12}>1,\end{cases} \tag{5}$$

where τ^{000}, τ^{110}, and τ^{112} are sticky parameters dependent on the magnitude of the spherically symmetric and anisotropic terms of attractive associative interaction and temperature. Notice that the (112) term contains the derivative of the δ function in opposition to the Mayer function for the model with spherically symmetric associative interaction. This is a feature of the sticky representation that is necessary in order to obtain a simple sticky parameter equation at the level of irreducible representation of the OZ equation [25,26].

To relate a set of parameters τ to the energetic parameters of interparticle effective interaction we apply the so-called "second virial coefficient device" proposed by Baxter [15] and used already for the models of overlapping hard spheres [3,4]. It implies that the second virial coefficient for the model with initial interaction is equal to the one that follows from the Mayer function given within the sticky representation. Here we assume this equality for the contributions from each of the anisotropies, i.e.,

$$\int_0^1\tilde{e}^{mnl}(r)r^2dr=\int_0^1[1+f_{(\tau)}^{mnl}(r)]r^2dr\ , \tag{6}$$

where $(mnl)=(000),(110),(112)$, and $f_{(\tau)}^{mnl}(r)$ are the coefficients in the orientation-invariant expansion of the Mayer function $f_{(\tau)}(12)$ given by Eq. (5). It follows then from Eq. (6) that

$$\tau^{000}=\frac{L^3}{[12L^2w+w^3]D_0}\ ,$$
$$\tau^{110}=\frac{L^3}{[12L^2w+w^3]D_1}\ , \tag{7}$$
$$\tau^{112}=\frac{3L^2}{[12L^2w+w^3]D_2}\ .$$

It could be seen from Eq. (7) that a specific form of the (112) term in the Mayer function given by Eq. (5) leads to another dependence of the parameter τ^{112} on the parameters of the associative interaction. In the limit D_0, D_1, and $D_2\to\infty$ the model reduces to a system of nonoverlapping hard spheres, whereas at $D_1, D_2 \to \infty$ it reduces to the one-component hard-sphere fluid with possible overlap, i.e., to the model of Cummings and Stell [4]. Two other limits, i.e., $D_0, D_1 \to \infty$ and $D_0, D_2 \to \infty$ lead to the models in which the dimers with the specific configurations of dipole moments of monomers are able to form.

The Mayer function $f(12)$ represents a low density limit of the pair correlation function $h(12)=g(12)-1$, where $g(12)$ is the pair distribution function. It is evident that the function $h(12)$ will contain δ-type discontinuities in the same harmonic coefficients as $f(12)$. In order to obtain the closure relations for the correlation functions we shall use the anisotropic truncated Percus-Yevick (PY) approximation, i.e., we assume that the only nonzero harmonics in $h(12)$ and $c(12)$ are those contained in $f(12)$ and those that can be obtained from that set by repeated convolution. Thus, the intracore closure that follows from the form of $f_{(\tau)}(12)$ is

$$\begin{aligned} h(12) = &-1 + \frac{L\lambda^{000}}{12}\delta(r_{12}-L)\Phi^{000}(\Omega_1,\Omega_2,\Omega_{\mathbf{r}_{12}}) \\ &+ \frac{L\lambda^{110}}{12}\delta(r_{12}-L)\Phi^{110}(\Omega_1,\Omega_2,\Omega_{\mathbf{r}_{12}}) \\ &+ \frac{L_{r_{12}}\lambda^{112}}{12}\delta'(r_{12}-L)\Phi^{112}(\Omega_1,\Omega_2,\Omega_{\mathbf{r}_{12}}) \\ &\text{for } r_{12}<1\,, \end{aligned} \tag{8}$$

where λ^{mnl} are the mean association parameters. The long-range dipole-dipole interaction is treated by using the mean spherical approximation (MSA) for the direct correlation function $c(12)$, which implies [31]

$$c(12) = -\beta U_{dd}(12) \quad \text{for } r_{12}>1\ . \tag{9}$$

The closure given by Eqs. (8) and (9) are the anisotropic truncated PY-MSA approximation for anisotropic penetrable dipolar hard spheres. This approximation is used to solve the OZ integral equation. As in the method developed for chemically reacting simple fluids, we have to relate the set of τ^{mnl} parameters to the set of λ^{mnl}, which are not independent of each other. Relevant equations will be obtained in the following sections.

III. SOLUTION OF THE ORNSTEIN-ZERNIKE INTEGRAL EQUATION AND THE DIFFERENTIAL-DIFFERENCE EQUATIONS

We need to solve the Ornstein-Zernike integral equation for the correlation functions. It has the following form:

$$h(12) = c(12) + \rho_s \int d3\, h(13)c(32)\ . \tag{10}$$

A detailed description of the Baxter-Wertheim factorization technique to solve Eq. (10) for the models with angular-dependent interparticle interaction has been given in previous papers on the subject (see, for example, [25,26]). The factored OZ integral equation reduces to a pair of integral equations for the functions $J_\chi^{mn}(r)$, $S_\chi^{mn}(r)$, which are defined as follows [25]:

$$J_\chi^{mn}(r) = 2\pi\rho_s(-1)^\chi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \times \int_r^\infty dt\, tP_l\left(\frac{r}{t}\right) h^{mnl}(t) \tag{11}$$

and

$$S_\chi^{mn}(r) = 2\pi\rho_s(-1)^\chi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \times \int_r^\infty dt\, tP_l\left(\frac{r}{t}\right) c^{mnl}(t)\ , \tag{12}$$

where $h^{mnl}(r)$, $c^{mnl}(r)$ are the projections of the corresponding correlation functions and where the values for χ are restricted by the condition $|\chi| \le m,n$, in accordance with the properties of the $3j$ Wigner symbols. The factored OZ equation contains the unknown factor functions $q_\chi^{mn}(r)$, which are related to the functions $J_\chi^{mn}(r)$ and $S_\chi^{mn}(r)$ by convolution-type equations

$$J_\chi^{mn}(r) = q_\chi^{mn}(r) + \sum_{n_1} \int_0^1 dt\, J_\chi^{mn_1}(|r-t|)q_\chi^{n_1 m}(t)\ , \tag{13}$$

and

$$S_\chi^{mn}(r) = -q_\chi^{mn}(r) + \sum_{n_1} \int_r^1 dt\, q_\chi^{mn_1}(t)q_\chi^{n_1 m}(t-r)\ . \tag{14}$$

For the dipolar fluid under consideration the indices m,n take the values 0,1. From the definition (11) and closure relation (8) it follows that, for $r<1$,

$$J_0^{00}(r) = J_0^{00} + \pi\rho_s r^2 + \nu\theta(L-r)\ , \tag{15}$$

where $\nu = \pi\rho_s L^2\lambda^{000}/6$ and

$$J_0^{00} = 2\pi\rho_s \int_1^\infty dt\, th^{000}(t) - \pi\rho_s\ . \tag{16}$$

In a similar way, for $m,n=1$ and $\chi=0,1$ we obtain

$$J_0^{11}(r) = J_0^{11(0)} + J_0^{11(2)}r^2 + \nu_0\theta(L-r)\ , \tag{17}$$

where $\nu_0 = \pi\rho_s L^2\lambda_0^{11}/6$, $\lambda_0^{11} = -\lambda^{110}/\sqrt{3} + 2(\lambda^{112}/\sqrt{30})$ and

$$J_0^{11(0)} = -2\pi\rho_s \left[\frac{1}{\sqrt{3}}\int_1^\infty dt\, th^{110}(t) - \frac{1}{\sqrt{30}}\int_1^\infty dt\, th^{112}(t)\right], \tag{18}$$

$$J_0^{11(2)} = b_2 = 2\pi\rho_s \frac{3}{\sqrt{30}} \int_1^\infty dt\, t^{-1}h^{112}(t)\ .$$

Finally,

$$J_1^{11}(r) = J_1^{11(0)} - b_2 r^2 + \nu_1\theta(L-r)\ , \tag{19}$$

where $\nu_1 = \pi\rho_s L^2\lambda_1^{11}/6$, $\lambda_1^{11} = -\lambda^{110}/\sqrt{3} - \lambda^{112}/\sqrt{30}$, and

$$J_0^{11(0)}=-2\pi\rho_s\left[\frac{1}{\sqrt{3}}\int_1^\infty dt\, th^{110}(t)-\frac{1}{2\sqrt{30}}\int_1^\infty dt\, th^{112}(t)\right]. \qquad (20)$$

Consider Eq. (13) at $r<1$: substitute (15)–(20) and then differentiate once the result by r. We then obtain three differential-difference equations for the Baxter functions,

$$q_0^{00\prime}(r)+\nu[q_0^{00}(r+L)-q_0^{00}(r-L)]+\nu\delta(r-L)=M_0^{(0)}r+M_0^{(1)}, \qquad (21)$$

$$q_0^{11\prime}(r)+\nu_0[q_0^{11}(r+L)-q_0^{11}(r-L)]+\nu_0\delta(r-L)=\mu_0^{(0)}r+\mu_0^{(1)}, \qquad (22)$$

$$q_1^{11\prime}(r)+\nu_1[q_1^{11}(r+L)-q_1^{11}(r-L)]+\nu_1\delta(r-L)=\mu_1^{(0)}r+\mu_1^{(1)}, \qquad (23)$$

where

$$M_0^{(0)}=2\pi\rho_s(1-K_0^{00(0)}),\quad M_0^{(1)}=2\pi\rho_s K_0^{00(1)}, \qquad (24)$$

$$\mu_0^{(0)}=2b_2(1-K_0^{11(0)}),\mu_0^{(1)}=2b_2K_0^{11(1)}, \qquad (25)$$

$$K_\chi^{mn(i)}=\int_0^1 dt\, t^i q_\chi^{mn}(t). \qquad (26)$$

The moments $\mu_1^{(i)}$ are similar to (25), but with $-b_2/2$ instead of b_2, and they contain the corresponding moments $K_1^{11(i)}$ of the factor functions $q_1^{11}(r)$. It is evident from Eqs. (21)–(23) that our problem has been mapped onto the one-component chemically reacting fluid of the penetrable hard spheres of Cummings and Stell [4,5]. The difference is that here we deal with a set of sticky parameters ν,ν_0,ν_1 and have to replace $\pi\rho$ in the solution of Cummings and Stell [4] by b_2 or $-b_2/2$ to obtain the solution for $(m,n)=1$. Equation (21)–(23) are easy to solve; we can just use the solution for different L from [4,5,9]. Let us consider the simplest case with $L=\frac{1}{2}$ and pay the most attention to the solution of Eq. (22). Making modifications needed for our model we have

$$q_0^{11}(r)=\begin{cases} A_0\cos(\nu_0 r)+B_0\sin(\nu_0 r)-\dfrac{\mu_0^{(0)}}{\nu_0}r+\mu_0^{(0)}\left[1-\dfrac{\nu_0}{2}\right]-\dfrac{\mu_0^{(1)}}{\nu_0} & \text{for } 0<r<\frac{1}{2}, \\ A_0\sin[\nu_0(r-\frac{1}{2})]-B_0\cos[\nu_0(r-\frac{1}{2})]+\dfrac{\mu_0^{(0)}}{\nu_0}r+\mu_0^{(0)}\left[1-\dfrac{\nu_0}{2}\right]+\dfrac{\mu_0^{(1)}}{\nu_0} & \text{for } \frac{1}{2}<r<1, \end{cases} \qquad (27)$$

where the coefficients A_0, B_0 and the moments $\mu_{(0)}^{(i)}$ are

$$\begin{aligned} A_0&=\frac{1}{\Delta_0}(-\nu_0T_{13}+2b_2T_{33}), \\ B_0&=\frac{1}{\Delta_0}(-\nu_0T_{14}+2b_2T_{34}), \\ \mu_0^{(0)}&=\frac{1}{\Delta_0}(-\nu_0T_{11}+2b_2T_{31}), \\ \mu_0^{(1)}&=\frac{1}{\Delta_0}(-\nu_0T_{12}+2b_2T_{32}). \end{aligned} \qquad (28)$$

The determinant Δ_0 and all necessary cofactors T_{ij} were calculated in [4] (see Appendix B of [4]); one only has to replace the multiplier 6η by b_2. For the convenience of the reader we present the cofactors in the Appendix. At $\nu_0\to 0$, $\Delta_0\to(1-b_2/6)^2=\beta_6^2$ for $L=\frac{1}{2}$ as well as for $L=\frac{1}{3}$. The solution of Eq. (23) is similar to (27); we just have to make the following substitutions: $A_0,B_0\to A_1,B_1$; $T_{ij}\to T_{ij}^*$, $\Delta_0\to\Delta_1$, $\mu_0^{(i)}\to\mu_1^{(i)}$, $\nu_0\to\nu_1$. For $\chi=1$, $\Delta_1\to(1+b_2/12)^2=\beta_{12}^2$. The parameters β_6 and β_{12} are the key ingredients of the MSA solution for dipolar hard spheres [31], and now we have their equivalents for the APD model. The general case of different L can be handled similarly. In Ref. [9] a general form for $\frac{1}{3}<L<\frac{1}{2}$ and $\frac{1}{2}<L<1$ can be found.

We would like to note that the closure given by Eq. (8) with the derivative of the δ function replaced by the δ function does not provide mapping onto the PY solution for overlapping hard spheres. It leads to an integro-differential equation, since the right-hand sides of Eqs. (21)–(23) contain additional integrals of $q_\chi^{mn}(r)$ and moments $K_\chi^{mn(i)}$. It is therefore impossible to solve analytically the general dipolar and higher-order anisotropy problem with this closure.

According to the MSA closure given by Eq. (9), the direct correlation function outside the hard core is given as

$$\begin{aligned} c^{112}(r)&=-\beta U_{dd}^{112}(r)=\beta\frac{\sqrt{30}}{3}\frac{Q_1^{(0)^2}}{r^3},\quad r>1, \\ c^{mnl}(r)&=0,\quad r>1,\ \{mnl\}\neq\{112\}, \end{aligned} \qquad (29)$$

since we assumed no long-range interactions other than dipole-dipole ($Q_1^{(0)}$ is the dipole moment). It follows then from the definition (12) and boundary condition (29) that

$$S_\chi^{mn}(r)=0 \text{ for } r>1. \qquad (30)$$

The direct correlation function $c^{mnl}(r)$, as well as $h^{mnl}(r)$, are obtained by the inverse transformation of Eqs. (11) and (12) [25,26],

$$\frac{2\pi\rho_s}{2l+1}f^{mnl}(r)=-\sum_{\chi=-\inf(m,n)}^{\inf(m,n)}(-1)^{\chi}\begin{pmatrix} m & n & l \\ \chi & -\chi & 0\end{pmatrix}\int_0^{\infty}dt\,F_{\chi}^{mn}(t)\left[\frac{1}{r}\delta'(r-t)-P_l'(1)\frac{1}{r^2}\delta(r-t)+P_l''\left[\frac{r}{t}\right]\frac{1}{r^3}\theta(r-t)\right], \tag{31}$$

where $(f,F)=(h,J)$ or (c,S). Substituting Eq. (29) for $c^{112}(r)$ and (30) in (31), we obtain

$$\tfrac{4}{3}\pi\rho_s\beta Q_1^{(0)^2}=\int_0^1 dt\,S_1^{11}(t)-\int_0^1 dt\,S_0^{11}(t)\ . \tag{32}$$

Now, it is necessary to determine the moments of $S_{\chi}^{mn}(r)$ in terms of the corresponding Baxter functions. At first glance it looks cumbersome, because one has to substitute (27) in (14) and then calculate the moments of S_{χ}^{mn}. However, it was shown in [26] [see Eqs. (61)–(64)] that there exists a simple relation between the moments of S_{χ}^{mn} and the moments of $K_{\chi}^{mn(i)}$. Using the result given by Eq. (64) of [26], rewrite Eq. (32) in the form

$$3y=\left[\frac{\mu_0^{(0)}}{2b_2}\right]^2-\left[\frac{\mu_1^{(0)}}{b_2}\right]^2, \tag{33}$$

where $y=\frac{4}{9}\pi\rho_s\beta Q_1^{(0)^2}$ and $\mu_0^{(0)},\mu_1^{(0)}$ are determined by Eq. (25). This equation has a form similar to its equivalent for DHS [31], as well as for the case of anisotropic surface adhesion [see Eq. (82) of [26] and its corrected form in the notes of [24]]. The dielectric constant of the APD model is, in the MSA,

$$\varepsilon=\left[\frac{\mu_0^{(0)^2}}{4\mu_1^{(0)^2}}\right]=\left[\frac{\Delta_1^2}{4\Delta_0^2}\right]\left[\frac{-\nu_0T_{11}+2b_2T_{31}}{-\nu_1T_{11}^{*}-b_2T_{31}^{*}}\right]^2, \tag{34}$$

where for $L=\frac{1}{2}$,

$$\begin{aligned} T_{11}&=-\frac{2b_2}{\nu_0}\left[1-\frac{b_2}{2\nu_0}\right](1-s-c)\\ &\quad-\frac{4b_2^2}{\nu_0^4}[4-\nu_0+(\nu_0-4)c-\nu_0s]\ ,\\ T_{31}&=\left[1-\frac{b_2}{2\nu_0}\right](1+s)+\frac{2b_2}{\nu_0^2}(1+s-c)\\ &\quad+\frac{2b_2}{\nu_0^3}[2\nu_0-2+(2-\nu_0)c-2s]\ , \end{aligned} \tag{35}$$

and where $s=\sin(\nu_0/2)$, $c=\cos(\nu_0/2)$. The cofactors T_{11}^{*} and T_{31}^{*} are also given by (35); one has to make the substitutions $b_2\to-b_2/2$ and $\nu_0\to\nu_1$.

Equations (33) and (34) are our main results. In a future work we will investigate numerically the dependence of the dielectric constant on the density ρ_s, dipole moment $Q_1^{(0)}$, and association parameters λ^{mnl}.

IV. STICKY AND ASSOCIATION PARAMETERS

To derive the necessary equations that relate the sticky τ^{mnl} and the mean association parameters λ^{mnl}, we use the definition of the cavity function $y(12)$,

$$g(12)=[1+f_{(\tau)}(12)]y(12)\ . \tag{36}$$

We are working within a truncated PY-MSA closure [25,26], so that only a restricted set of angular invariants are included. Expanding (36) in rotational invariants, we obtain

$$\begin{aligned}\lambda^{000}\tau^{000}&=y^{000}(L)+y^{110}(L)\frac{\tau^{000}}{\tau^{110}}\\ &\quad+[y^{112}(L)+Ly^{112'}(L)]\frac{\tau^{000}}{\sqrt{3}\tau^{112}}\ ,\end{aligned} \tag{37}$$

$$\lambda^{110}\tau^{000}=y^{110}(L)+y^{000}(L)\frac{\tau^{000}}{\tau^{110}}\ , \tag{38}$$

$$\lambda^{112}\tau^{000}=y^{112}(L)+[y^{000}(L)+Ly^{112'}(L)]\frac{\tau^{000}}{\tau^{112}}\ , \tag{39}$$

where $y^{mnl'}(r)$ is the derivative of the cavity function. To derive Eqs. (37)–(39) we used Eqs. (5) and (8) and the multiplicative properties of rotational invariants [28–30]. It is necessary to note also that Eqs. (37)–(39) result from the integration of (36) with respect to r from L^- to L^+. The main approximation in (37)–(39) is the truncation of the set of rotational invariants that arises. What kind of approximation for $y^{mnl}(r)$ inside a hard core does one have to utilize? This issue has to be studied in more detail. For spherically symmetric intracore stickiness, Stell and Zhou [6,7] and later Rasaiah and Zhu [32] studied approximations that satisfy the mass action law. For the model under study the equilibrium association constant

$$\mathcal{K}=\frac{[A_2]}{[A]^2} \tag{40}$$

is determined within the MSA by the parameter λ^{000} only, due to the orthogonality of rotational invariants. So one can, in principle, use the schemes proposed in [6,7] for our model. However, the peculiarity of the APD model is that three parameters λ^{mnl} are determined as a solution of the system of equations (37)–(39). More precisely, we have to solve the system of equations (37)–(39) together with Eq. (33), which contains three unknown λ^{mnl} and b_2, which depend on the dipole moment. It is clear then, that this issue is quite delicate and will be investigated in more detail in a future work.

V. COMMENTS ON THE SOLUTION FOR QUADRUPOLAR-TYPE INTRACORE STICKINESS

Quadrupolar-type surface adhesion has been utilized in [25] to generate specific angular correlations between the particles. We would like to demonstrate here that the procedure presented in the previous sections for the APD model can be transferred to the case of quadrupolar-type intracore stickiness or higher-order anisotropy. It can also be combined with dipolar or quadrupolar electrostatic interactions, in a manner similar to the ion-dipole-quadrupole model of electrolyte solutions [33]. To deal with the problem, assume that the Mayer function in the sticky (τ) representation has the form

$$f^{000}_{(\tau)00}(r)=-1+\frac{L}{12\tau^{000}}\delta(r-L), \quad r<1 \tag{41}$$

$$f^{224}_{(\tau)\mu\nu}(r)=\frac{Lr^3}{12\tau^{224}}\delta'''(r-L), \quad r<1 \tag{42}$$

$$f^{mnl}_{(\tau)\mu\nu}(r)=0, \quad r<1, \ \{mnl\}\neq\{000,224\} \ . \tag{43}$$

It follows then, that the appropriate closure for the pair correlation function is

$$h^{000}_{00}(r)=-1+\frac{\lambda^{000}L}{12}\delta(r-L), r<1 \tag{44}$$

$$h^{220}(r)=\frac{\lambda^{220}L}{12}\delta(r-L), \quad r<1 \tag{45}$$

$$h^{222}(r)=\frac{\lambda^{222}Lr}{12}\delta'(r-L), \quad r<1 \tag{46}$$

$$h^{224}(r)=\frac{\lambda^{224}Lr^3}{12}\delta'''(r-L), \quad r<1 \tag{47}$$

$$h^{mnl}_{\mu\nu}(r)=0, \quad r<1, \quad \{mnl\}\neq\{000,220,222,224\} \ . \tag{48}$$

Using the closures (44)–(48) in Eq. (11) we can write the function $J^{mn}_{\chi}(r)$ for $r<1$ in the form of a polynomial and a sticky term as follows:

$$J^{22}_{\chi}(r)=\alpha_\chi+\beta_\chi r^2+\gamma_\chi r^4+\zeta_\chi\theta(L-r), \quad r<1 \ , \tag{49}$$

which leads to the following differential-difference equation:

$$\begin{aligned} q'_\chi(r)&+\zeta_\chi\rho_s[q_\chi(r+L)-q_\chi(r-L)]+\zeta_\chi\delta(r-L)\\ &=4\gamma_\chi(1-K^{(0)}_\chi)r^3+12\gamma_\chi K^{(1)}_\chi r^2\\ &\quad+[2\beta_\chi(1-K^{(0)}_\chi)-12\gamma_\chi K^{(2)}_\chi]r+2\beta_\chi K^{(0)}_\chi+K^{(3)}_\chi \ . \end{aligned} \tag{50}$$

The complication in the solution of the quadrupolar problem is the presence of higher-order moments ($K^{(2)}_\chi$ and $K^{(3)}_\chi$). The function $q_\chi(r)$ will possess an intramolecular part and a polynomial of the fourth order in r. Then, the matrix necessary to find the coefficients of $q_\chi(r)$ and the moments will be of the size 8×8 in comparison with 4×4 for the dipolar problem. Finally, the set of equations relating λ^{mnl} and τ^{mnl} will contain the third derivative of the cavity function. This brief formal description is, we believe, sufficient to solve the problem for quadrupolar type intracore stickiness.

VI. CONCLUSIONS

We have presented an analytically solvable model of anisotropic penetrable dipolar hard spheres. The solution is given in terms of the corresponding problem for the overlapping hard spheres. It is shown that for the models with an anisotropic shielded sticky shell, the intracore closure for the pair correlation function must be of a special form containing the derivatives of the δ function. We have demonstrated the solution for the algebraically simplest case, i.e., $L=\frac{1}{2}$. Some other cases can be treated analytically, but for arbitrary L it is more convenient to solve the problem numerically. Implementation of the closures other than PY-MSA requires a numerical solution, too.

Along with the properties of the APD model that deserve to be studied in detail, it is necessary to list the dielectric, thermodynamic, and dynamic properties. Possible extensions of the model are of interest. In particular, the ionic solvation with the APD model used as a solvent, and adsorption of associating polar fluid on surfaces, are the phenomena in which the association of polar species can lead to interesting effects. These issues will become a subject of our future studies.

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APPENDIX

For the case $L=\frac{1}{2}$ the cofactors T_{ij} are

$$\begin{aligned} T_{12}=&-\frac{2b_2}{\nu_0^2}\left[1-\nu_0-\left(1-\frac{\nu_0}{2}\right)c+s\right]\\ &-\frac{b_2^2}{\nu_0^3}\left[1+\nu_0-\left(1+\frac{\nu_0}{2}\right)c-3s\right]\\ &+\frac{4b_2^2}{\nu_0^4}\left[1+\frac{\nu_0}{2}-\left(1+\frac{\nu_0}{2}\right)s-c\right]\\ &+\frac{4b_2^2}{\nu_0^5}[4-\nu_0+(\nu_0-4)c-s\nu_0] \ , \end{aligned} \tag{A1}$$

$$\begin{aligned} T_{13}=&-\left(1-\frac{b_2}{2\nu_0}\right)^2c-\frac{b_2}{\nu_0^2}\left(1-\frac{b_2}{2\nu_0}\right)(1+c-s)\\ &+\frac{b_2}{\nu_0^3}[-\nu_0c+(4-2\nu_0)s]\\ &+\frac{b_2^2}{\nu_0^4}\left[-2+\left(2+\frac{\nu_0}{2}\right)c+\nu_0s\right]\\ &+\frac{4b_2^2}{\nu_0^5}\left[1-\left(1+\frac{\nu_0}{2}\right)c+(1-\nu_0)s\right] \ , \end{aligned} \tag{A2}$$

$$T_{14}=-\left[1-\frac{b_2}{2\nu_0}\right]^2 s+\frac{b_2}{\nu_0^2}\left[1-\frac{b_2}{2\nu_0}\right](1-c-s)$$

$$+\frac{b_2}{\nu_0^3}[4-\nu_0-(4-2\nu_0)c-s\nu_0]$$

$$-\frac{b_2^2}{2\nu_0^4}[-\nu_0+2\nu_0 c-(4+\nu_0)s]$$

$$+\frac{4b_2^2}{\nu_0^5}\left[1-\frac{\nu_0}{2}-(1-\nu_0)c-\left[1+\frac{\nu_0}{2}\right]s\right], \tag{A3}$$

$$T_{32}=-\frac{2b_2}{\nu_0^2}(1-c), \tag{A4}$$

$$T_{33}=-\frac{1}{\nu_0^2}(1+s)-\frac{1}{2\nu_0}\left[1-\frac{b_2}{2\nu_0}\right](1+s-2c)$$

$$-\frac{b_2}{2\nu_0^3}(1+s-4c)$$

$$+\frac{4b_2^2}{\nu_0^5}\left[1+(1-\nu_0)s-\left[1+\frac{\nu_0}{2}\right]c\right], \tag{A5}$$

$$T_{34}=\frac{c}{\nu_0^2}+\frac{1}{2\nu_0}\left[1-\frac{b_2}{2\nu_0}\right](2s+c)+\frac{b_2}{2\nu_0^3}(4s+c)$$

$$+\frac{4b_2^2}{\nu_0^5}\left[1-\nu_0-(1-\nu_0)c\left[1+\frac{\nu_0}{2}\right]s\right]. \tag{A6}$$

These expressions can be used to obtain the explicit expression for the dielectric constant.

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