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L. Blum, P. T. Cummings, and D. Bratko

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A general solution of the molecular Ornstein–Zernike equation for spheres with anisotropic adhesion and electric multipoles

L. Blum
Department of Physics, P.O. Box 23343, University of Puerto Rico, Rio Piedras, Puerto Rico 00931-3343

P. T. Cummings
Department of Chemical Engineering, Thornton Hall, University of Virginia, Charlottesville, Virginia 22903-2442

D. Bratko
Department of Chemistry, Faculty of Natural Sciences and Technology, University of Ljubljana, Ljubljana, Yugoslavia

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We present the analytic solution of the molecular Ornstein–Zernike equation for a very general closure in which the direct correlation function is of the form suggested by the mean-spherical approximation for arbitrary multipolar interactions and the total correlation function contains terms that arise in the Percus–Yevick approximation for spheres with anisotropic surface adhesion. In addition to generalizing several earlier analyses of special cases of this closure, the solution presented here contains new simplifying insights that reduce the complexity of the resulting algebraic equations. A special case of the analysis is described to illustrate the method of solution.

I. INTRODUCTION

While modern computer simulations have provided a wealth of information about the structure of molecular fluids, there are many applications (chemical process design, for example) where computer simulations are not a practical tool for computing the thermodynamic properties of the system of interest. In such circumstances, analytic models with explicit, closed form expressions for thermodynamic and structural properties can be very useful in understanding the nature of some important processes.

In particular, due to its important role in many physical, chemical and biological processes, water has been the subject of many computer simulation studies and a number of acceptable effective intermolecular potential models exist.[1–11] In most of these models, the water molecule is represented as a sphere with Lennard-Jones interaction containing a number of charges or force centers, not necessarily at the center of the sphere, and which create directional forces to emulate the hydrogen bonding of water. These models have been studied by computer simulation, and yield good results for many of the properties of pure water. However, when one wants to look at the hydration of an ion, or better, at the hydrated ion near an interface, then even a large computer is not sufficient. This is because the normal concentrations used in many electrochemical experiments are so low that the number of molecules required to give statistically meaningful results far exceeds the capacity of existing computers. This explains the continued interest in the rather crude model of aqueous ionic solutions in which the water molecule is depicted by a hard sphere with a point dipole. This model has been solved analytically in the mean-spherical approximation[12–14] and has been extensively studied.[15,16] Clearly, one wants a more realistic model that still can be solved analytically, if possible, or numerically in the simplest possible way, and which can be used to study homogeneous and inhomogeneous solutions, as well as some properties relevant to chemical kinetics, such as the electric microfield.[17]

Such is the model that was proposed recently by us[18,19]: It consists of a hard sphere with an embedded electrical dipole (higher multipoles are also possible and tractable) and a sticky interaction that is angular dependent, to emulate the strongly directional hydrogen bonds. This model has several attractive features: It is able to reproduce the dielectric behavior of water, it has the required structure, as was tested by computer simulation, and in principle, is able to yield explicit algebraic expressions for the thermodynamic properties and the direct correlation function. However, the formalism as it was discussed in previous work[20,21] is implicit and requires the solution of a complicated system of algebraic equations, which is special for each case. For example, the quadrupolar model of water[22] can still be solved analytically, but the more realistic octupole model could not be handled with that method.

In the present work we present a new way to solve the factored Ornstein–Zernike equation which is explicit for the sticky multipole model, in the sense that the generalization of the Wertheim solution of spheres with point dipoles[23] appears as a set of coupled nonlinear equations in which there are matrix inverses to be computed. The matrix size depends on the order of the highest multipole of the correlation function. The formalism lends itself to a form which can be solved efficiently by iteration.

II. BASIC FORMALISM

We study the Ornstein–Zernike (OZ) equation for a molecular fluid

$$h(12) = c(12) + \rho \int d3\, h(13)c(32), \tag{1}$$

where $h(12)$ is the molecular total correlation function and

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$c(12)$ is the molecular direct correlation function, ρ is the number density of the molecules, and $i = 1,2$ symbolizes the position $\mathbf{r}_i$ and orientation $\Omega_i = (\theta_i,\phi_i,\chi_i)$ of molecule $i = 1,2$. The approximations that will be discussed here are based on Baxter's sticky potential,[24] in which the pair correlation function is of the form

$$h(12) = \bar{h}(12) + \Lambda(12)\delta(r_{12} - \sigma^-), \tag{2}$$

where $\bar{h}(12)$ and $\Lambda(12)$ are functions of the orientation of molecules 1 and 2, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and σ is the distance of closest approach of the two molecules. The function $\bar{h}(12)$ is nonsingular: that is, it has no delta functions and at worst has step discontinuities. While the discussion of the relation of the function $\Lambda(12)$ to actual intermolecular sticky potentials has been dealt with in a brilliant series of papers by Wertheim,[25–31] in this paper we will not be concerned with this point in detail. We will regard the quantities in $\Lambda(12)$ as parameters only whose physical significance will be discussed briefly at the conclusion of the paper. Since the inclusion of the solution of the arbitrary multipole mean-spherical approximation (MSA) does not require much additional work we will do so. In the MSA the direct correlation function is

$$c(12) = -\beta u(12), \quad r > \sigma, \tag{3}$$

where $\beta = 1/k_B T$ is the Boltzmann thermal factor and $u(12)$ is the electrostatic interaction between the molecules.

One key ingredient of the analytical solution process is the invariant expansion of the correlaton functions.[32] The invariant expansion of the functions $h(12)$ and $c(12)$ in terms of the rotational invariants $\hat{\Phi}^{mnl}_{\mu\nu}(\Omega_1\Omega_2\Omega_r)$ is

$$h(12) = \sum_{\substack{mnl \\ \mu\nu}} \hat{h}^{mnl}_{\mu\nu}(r_{12})\hat{\Phi}^{mnl}_{\mu\nu}(\Omega_1\Omega_2\Omega_r), \tag{4}$$

$$c(12) = \sum_{\substack{mnl \\ \mu\nu}} \hat{c}^{mnl}_{\mu\nu}(r_{12})\hat{\Phi}^{mnl}_{\mu\nu}(\Omega_1\Omega_2\Omega_r), \tag{5}$$

where

$$\hat{\Phi}^{mnl}_{\mu\nu}(\Omega_1\Omega_2\Omega_r) = [(2m+1)(2n+1)]^{1/2} \sum_{\mu'\nu'\lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} \times D^m_{\mu\mu'}(\Omega_1) D^n_{\nu\nu'}(\Omega_2) D^l_{0\lambda'}(\Omega_r). \tag{6}$$

In this equation, $D^m_{\mu\mu'}(\Omega)$ is the Wigner rotation matrix and

$$\begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix}$$

is the usual notation for the 3-j symbol,[33,34] Ω_1, Ω_2 are the Euler angles that give the orientation of molecules 1 and 2, respectively, and Ω_r gives the orientation of the vector $\mathbf{r}_{12}$ joining the centers of mass of molecules 1 and 2. The expansions will be truncated at a given value of the multipole index n_m (i.e., we will assume that $h^{mnl}_{\mu\nu}(r_{12}) = 0$ and $c^{mnl}_{\mu\nu}(r_{12}) = 0$ for $m > n_m$ and $n > n_m$). This requires that

$$m \leqslant n_m, \quad n \leqslant n_m, \quad l \leqslant l_m = 2n_m. \tag{7}$$

The hard-core exclusion condition and the sticky interactions lead to the following conditions for the invariant coefficients of

$$\bar{h}^{mnl}_{\mu\nu}(r) = \hat{h}^{mnl}_{\mu\nu}(r), \quad r > \sigma, \tag{8}$$

$$\bar{h}^{mnl}_{\mu\nu}(r) = \hat{h}^{mnl}_{\mu\nu}(r) = 0, \quad r < \sigma, \quad m,n,l > 0, \tag{9}$$

$$\bar{h}^{000}_{00}(r) = \hat{h}^{000}_{00}(r) = -1, \quad r < \sigma, \tag{10}$$

$$\Lambda(12) = \Lambda(21) = \sum_{\substack{mnl \\ \mu\nu}} \lambda^{mnl}_{\mu\nu} \hat{\Phi}^{mnl}_{\mu\nu}(\Omega_1\Omega_2\Omega_r). \tag{11}$$

For the direct correlation function the explicit form of the boundary condition is

$$\hat{c}^{mnl}_{\mu\nu}(r) = -\beta \frac{1}{r^{l+1}} Q^m_\mu Q^n_\nu \left[\frac{(2l+1)!}{(2m+1)!(2n+1)!}\right]^{1/2} = -\frac{1}{r^{l+1}} \mu^{mnl}_{\mu\nu}. \tag{12}$$

To solve the OZ equation we need the Fourier transform of the pair correlation functions. If we let $f(12)$ stand for either $c(12)$ or $h(12)$, then the Fourier transform of $f(12)$, $\tilde{f}(12)$, is defined by

$$\tilde{f}(12) = \int d\mathbf{r}_{12} \exp(i\mathbf{k}\cdot\mathbf{r}_{12}) f(12). \tag{13}$$

After straightforward algebraic operations we obtain

$$\tilde{f}(12) = \sum_{\substack{mnl \\ \mu\nu}} \tilde{f}^{mnl}_{\mu\nu}(k) \hat{\Phi}^{mnl}_{\mu\nu}(\Omega_1\Omega_2\Omega_k), \tag{14}$$

where k is the absolute value of $\mathbf{k}$ and Ω_k its orientation. Here,

$$\tilde{f}^{mnl}_{\mu\nu}(k) = 4\pi i^l \int_0^\infty dr r^2 \hat{f}^{mnl}_{\mu\nu}(r) j_l(kr). \tag{15}$$

The expansions (4) and (5) are the so-called invariant representations of the correlation functions and are independent of the choice of the reference frame. A very convenient choice of this reference frame is to take the z axis along the intermolecular axis, the vector $\mathbf{r}_{12}$. This yields the irreducible representation in which the OZ equation is decomposed in a set of matrix equations.[20,21] Now we get from Eqs. (4)–(6)

$$\tilde{f}(12) = (-)^\chi \sum_{\substack{mn \\ \mu\nu\chi}} \tilde{f}^{mn}_{\mu\nu\chi}(k) \bar{\Phi}^{mn}_{\mu\nu\chi}(\Omega_1\Omega_2), \tag{16}$$

where

$$\bar{\Phi}^{mn}_{\mu\nu\chi}(\Omega_1\Omega_2) = [(2m+1)(2n+1)]^{1/2} D^m_{\mu\chi}(\Omega_1) D^n_{\nu-\chi}(\Omega_2) \tag{17}$$

and

$$\tilde{f}^{mn}_{\mu\nu\chi}(k) = (-)^\chi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \tilde{f}^{mnl}_{\mu\nu}(k). \tag{18}$$

Substitution of these definitions and expansions into the OZ Eq. (1) yields the desired irreducible matrix form of the OZ equation[20,21]

$$\tilde{\mathbf{H}}_\chi - \tilde{\mathbf{C}}_\chi = \tilde{\mathbf{H}}_\chi \tilde{\mathbf{C}}_\chi, \tag{19}$$

where the matrix elements of $\tilde{\mathbf{F}}_\chi = \tilde{\mathbf{H}}_\chi, \tilde{\mathbf{C}}_\chi$ are given by

$$\tilde{\mathbf{F}}_\chi = \rho \tilde{f}^{mn}_{\mu\nu\chi}(k). \tag{20}$$

We still need to convert the Fourier Bessel transform of Eq. (15) into a one-dimensional Fourier transform. This is done using the integral representation of the spherical Bessel function

$$j_l(kr) = \frac{1}{2} i^{-l} \int_0^1 dt\, P_l(t)[e^{ikrt} - (-)^l e^{-ikrt}], \tag{21}$$

where $P_l(t)$ is the Legendre polynomial of order l.

Substituting into Eq. (15) and also using the transforms (18) and (20), we obtain for the pair correlation function $h(12)$

$$\tilde{H}^{mn}_{\mu\nu\chi}(k) = \int_0^\infty [e^{ikr} J^{mn}_{\mu\nu\chi}(r) + e^{-ikr} J^{nm}_{\nu\mu\chi}(r)]\, dr, \tag{22}$$

where the matrix $\mathbf{J}$ has elements

$$J^{mn}_{\mu\nu\chi}(r) = (-)^\chi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} 2\pi\rho \times \int_r^\infty dr_1 r_1 P_l(r/r_1) \hat{h}^{mnl}_{\mu\nu}(r_1). \tag{23}$$

Explicitly, we get for $r < \sigma$

$$J^{mn}_{\mu\nu\chi}(r) = (-)^\chi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \times \sum_{i=0} a_i^l b^{mnl}_{\mu\nu,i} r^i - 2\pi\rho \Lambda^{mn}_{\mu\nu\chi} \theta(r - \sigma^-), \tag{24}$$

where a_i^l is the coefficient of the Legendre polynomial which is nonzero and given by

$$a_i^l = (-)^{(l-i)/2} \frac{(l+i)!}{2^l i![(l-i)/2]![(l+i)/2]!} \tag{25}$$

for $l - i \geqslant 0$ and even. For other values of l and i, $a_i^l = 0$. The parameters $b^{mnl}_{\mu\nu,i}$ are defined by

$$b^{mnl}_{\mu\nu,i} = 2\pi\rho \int_\sigma^\infty dr_1\, r_1^{l-i} \hat{h}^{mnl}_{\mu\nu}(r_1). \tag{26}$$

Equation (24) can be rearranged into the form

$$J^{mn}_{\mu\nu\chi}(r) = \sum_{i=0} B^{mn;i}_{\mu\nu,\chi} r^i - 2\pi\rho \Lambda^{mn}_{\mu\nu\chi} \theta(r - \sigma^-) \tag{27}$$

with

$$B^{mn;i}_{\mu\nu,\chi} = (-)^\chi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} a_i^l b^{mnl}_{\mu\nu,i} \tag{28}$$

The elements of the matrix Λ_χ are given by

$$\Lambda^{mn}_{\mu\nu\chi} = (-)^\chi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \lambda^{mnl}_{\mu\nu}. \tag{29}$$

Similarly manipulation of the direct correlation function yields

$$\tilde{C}^{mn}_{\mu\nu\chi}(k) = \int_0^\infty [e^{ikr} S^{mn}_{\mu\nu\chi}(r) + e^{-ikr} S^{nm}_{\nu\mu\chi}(r)]\, dr, \tag{30}$$

where the matrix $\mathbf{S}$ has elements

$$S^{mn}_{\mu\nu\chi}(r) = (-)^\chi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} 2\pi\rho \times \int_r^\infty dr_1\, r_1 P_l(r/r_1) \hat{c}^{mnl}_{\mu\nu}(r_1). \tag{31}$$

For neutral spheres with arbitrary multipolar interactions, the MSA condition on the direct correlation function, Eq. (3), yields

$$S^{mn}_{\mu\nu\chi}(r) = 0 \quad \text{for } r > \sigma. \tag{32}$$

From the orthogonality properties of the Legendre polynomials we invert the integral equations (22) and (30). Using the generic notation $\hat{f}^{mnl}_{\mu\nu}(r)$ to represent either $\hat{h}^{mnl}_{\mu\nu}(r)$ or $\hat{c}^{mnl}_{\mu\nu}(r)$ and $\mathcal{F}^{mn}_{\mu\nu\chi}(r)$ to represent $J^{mn}_{\mu\nu\chi}(r)$ or $S^{mn}_{\mu\nu\chi}(r)$, we have

$$2\pi\rho \hat{f}^{mnl}_{\mu\nu}(r) = -(2l+1) \sum_{\chi=-\inf(m,n)}^{\inf(m,n)} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} (-)^\chi \int_0^\infty \mathcal{F}^{mn}_{\mu\nu\chi}(r_1) \left\{ \frac{1}{r} \delta'(r - r_1) - \frac{1}{r^2} P_l'(1) \delta(r - r_1) + \frac{1}{r^3} P_l''\left(\frac{r_1}{r}\right) \theta(r - r_1) \right\} dr_1. \tag{33}$$

We must now find explicit expressions for the coefficients $b^{mnl}_{\mu\nu,i}$ as functions of the parameters $\mu^{mnl}_{\mu\nu}$ and $\lambda^{mnl}_{\mu\nu}$.

III. BAXTER–WERTHEIM FACTORIZATION OF THE OZ EQUATION

In Sec. III, we describe the Baxter–Wertheim[35,36] (BW) factorization of the OZ equation following the method of Blum.[19–21] The OZ equation (19) can be rewritten in the form[20,21]

$$[\mathbf{I} + \tilde{\mathbf{H}}_\chi(k)][\mathbf{I} - \tilde{\mathbf{C}}_\chi(k)] = \mathbf{I}, \tag{34}$$

where $\mathbf{I}$ is the identity matrix. The second term in this equation can be factorized using the Blum extension of the BW factorization as

$$[\mathbf{I} - \tilde{\mathbf{C}}_\chi(k)] = [\mathbf{I} - \tilde{\mathbf{Q}}_\chi(k)][\mathbf{I} - \tilde{\mathbf{Q}}_\chi^T(k)], \tag{35}$$

where $\tilde{\mathbf{Q}}_\chi^T(-k)$ is the complex conjugate and transpose of $\tilde{\mathbf{Q}}_\chi(k)$. In essence, it is because the matrix $\mathbf{I} - \tilde{\mathbf{C}}_\chi(k)$ is even and symmetric as a function of k that it can be factorized into the two matrices $\mathbf{I} - \tilde{\mathbf{Q}}_\chi(k)$ and $\mathbf{I} - \tilde{\mathbf{Q}}_\chi^T(-k)$.

The first matrix is nonsingular in the upper half complex k plane, while the second is nonsingular in the lower half complex k plane.

From Eq. (32) and several applications of Cauchy's theorem, it can be shown[20,21,19] that the factored correlation functions must be of the form

$$\tilde{\mathbf{Q}}_\chi(k) = \int_0^\sigma dr\, e^{ikr}\mathbf{Q}_\chi(r). \tag{36}$$

Fourier inversion of Eq. (35) leads to

$$\mathbf{S}_\chi(r) = \mathbf{Q}_\chi(r) - \int_0^\sigma dr_1\, \mathbf{Q}_\chi(r_1)\mathbf{Q}_\chi^T(r_1 - r), \tag{37}$$

where $\mathbf{Q}_\chi^T(r)$ is the transpose of $\mathbf{Q}_\chi(r)$. Considering Eq. (37) at $r = \sigma$ leads to the condition

$$\mathbf{Q}_\chi(\sigma) = 0. \tag{38}$$

A key step in the BW factorization is the Fourier inversion of

$$[\mathbf{I} - \tilde{\mathbf{H}}_\chi(k)][\mathbf{I} - \tilde{\mathbf{Q}}_\chi(k)] = [\mathbf{I} - \tilde{\mathbf{Q}}_\chi^T(k)]^{-1}. \tag{39}$$

In this version, by Cauchy's theorem the right-hand side makes no contribution, leading to

$$\mathbf{J}_\chi(r) = \mathbf{Q}_\chi(r) + \int_0^\sigma dr\, \mathbf{J}_\chi(r - r_1)\mathbf{Q}_\chi(r_1). \tag{40}$$

This equation must be used to determine the functions $\mathbf{Q}_\chi(r)$. Taking the l_m successive derivatives of Eq. (40) and using Eqs. (24) and (38), we find that $\mathbf{Q}_\chi(r)$ must be of the form

$$\mathbf{Q}_\chi(r) = \sum_{i=1}^{l_m} \frac{1}{i!}\mathbf{q}_{i,\chi}(r^i - \sigma^i) + 2\pi\mathbf{\Lambda}_\chi[1 - \theta(r - \sigma^-)], \quad 0 \leqslant r \leqslant \sigma. \tag{41}$$

The equations for the coefficient matrices $\mathbf{q}_{i,\chi}$ are obtained by, for example, setting $r = 0$ in all the derivatives. We have

$$\mathbf{J}_\chi^{(n)}(r) = \mathbf{Q}_\chi^{(n)}(r) + \int_0^\sigma dr_1\, \mathbf{J}_\chi^{(n)}(-r_1)\mathbf{Q}_\chi(r_1) \tag{42}$$

which gives

$$n\mathbf{B}_{n,\chi} = \frac{1}{(n-1)!}\mathbf{q}_{n,\chi} + \sum_{i=n}^{l_m}(-)^{i-n}\mathbf{B}_{n,\chi}\frac{i!}{(i-n+1)!(n-1)!} \times [(i-n+1)\mathbf{K}_{(i-n),\chi} + \sigma^{i-n+1}\mathbf{\Lambda}_\chi], \tag{43}$$

where we have defined the moments of the factor distribution function

$$K_{j,\chi} = \int_0^\sigma dr\, r^j \sum_{i=1}^{l_m}\frac{1}{i!}\mathbf{q}_{i,\chi}(r^i - \sigma^i), \quad j = 0,\ldots,l_m \tag{44}$$

$$K_{j,\chi} = -\frac{\sigma^{j+1}}{j+1}\sum_{i=1}^{l_m}\frac{1}{(i-1)!}\mathbf{q}_{i,\chi}\frac{1}{(i+j)}. \tag{45}$$

This can be written in matrix notation as

$$\mathcal{S}\mathbf{n}[\mathbf{K}_\chi] = -\mathcal{H}\mathcal{S}\mathbf{n}[\mathbf{q}_\chi], \tag{46}$$

where we have defined

$$\mathcal{S} = \begin{bmatrix} 1 & 0 & . & . \\ 0 & \sigma & 0 & . \\ . & 0 & \sigma^2 & . \\ . & . & . & . \end{bmatrix}, \tag{47}$$

$$\mathbf{n} = \begin{bmatrix} 1 & 0 & . & . \\ 0 & 2 & 0 & . \\ . & 0 & 3 & . \\ . & . & . & . \end{bmatrix}, \tag{48}$$

$$[\mathbf{K}_\chi] = \begin{bmatrix} K_{0,\chi} \\ K_{1,\chi} \\ . \\ . \\ K_{(l_m-1),\chi} \end{bmatrix}, \tag{49}$$

$$[\mathbf{q}_\chi] = \begin{bmatrix} q_{1,\chi} \\ q_{2,\chi}/1! \\ . \\ . \\ q_{l_m\chi}/(lm-1)! \end{bmatrix}, \tag{50}$$

and $\mathcal{H}_\chi$ is a Hilbert matrix. That is,

$$\mathcal{H}_{ij,\chi} = \frac{1}{i+j} \tag{51}$$

and the size of $\mathcal{H}_\chi$ depends on the index χ of the irreducible representation.

We can now write Eq. (43) in a condensed matrix form. To do so, we need to define a supermatrix $\mathcal{B}_\chi$ with submatrix elements:

$$\mathcal{B}_{ni,\chi} = (-)^{i-n}\frac{i!}{(i-n+1)!(n-1)!}B_{i,\chi} \quad i \geqslant n$$
$$\mathcal{B}_{ni,\chi} = 0 \quad i < n.$$

For $l_m = 4$ (for example, the case of the linear quadrupole), for all χ's we get

$$\mathcal{B}_\chi = \begin{bmatrix} \mathbf{B}_{1,\chi} & -\mathbf{B}_{2,\chi} & \mathbf{B}_{3,\chi} & -\mathbf{B}_{4,\chi} \\ 2\mathbf{B}_{2,\chi} & -3\mathbf{B}_{3,\chi} & 4\mathbf{B}_{4,\chi} & 0 \\ 3\mathbf{B}_{3,\chi} & -6\mathbf{B}_{4,\chi} & 0 & 0 \\ 4\mathbf{B}_{4,\chi} & 0 & 0 & 0 \end{bmatrix}. \tag{52}$$

The dimensions of the submatrices $\mathbf{B}_{i,\chi}$ are different for each value of χ. Using this quantity, Eq. (43) can be rewritten as

$$\mathcal{S}\mathcal{B}_\chi[\mathbf{I}_0] = \mathbf{n}\mathcal{S}[\mathbf{q}_\chi] + \mathcal{S}\mathcal{B}_\chi\mathcal{S}\{\mathbf{n}\mathcal{S}[\mathbf{K}_\chi] + \mathcal{S}[\mathbf{\Lambda}_\chi]\}, \tag{53}$$

where we have used the definitions

$$[\mathbf{I}_0] = \begin{bmatrix} I_\chi \\ 0 \\ . \\ . \\ 0 \end{bmatrix}, \tag{54}$$

$$[\Lambda_\chi] = \begin{bmatrix} \Lambda_\chi \\ \Lambda_\chi \\ \cdot \\ \cdot \\ \Lambda_\chi \end{bmatrix}. \tag{55}$$

Multiplying Eq. (53) on the left by the Hilbert matrix $\mathscr{H}$ and using Eq. (46), we obtain the remarkably simple equation

$$\{[\mathbf{I}\eta] - \mathbf{n}\mathscr{S}^{-1}[\mathbf{K}_\chi] - [\Lambda_\chi]\} = [\mathbf{I}_0 - \mathscr{H}\mathscr{S}\mathscr{B}_\chi]^{-1}\{[\mathbf{I}_0] - [\Lambda_\chi]\}. \tag{56}$$

Equation (56) is a new result. Together with Eq. (46), this equation explicitly yields the coefficients of the factor correlation functions $\mathbf{Q}_\chi(r)$ as a function of the moments $\mathbf{B}_{i,\chi}$ of the distribution function $h(12)$ for any arbitrary multipole. The problem is reduced to finding the inverse of the expanded matrix in Eq. (56). In general, this cannot be done analytically, but it is straightforward numerically.

IV. RESOLUTION OF BOUNDARY CONDITIONS

To derive the algebraic equations that determine the coefficients $b^{mnl}_{\mu\nu,i}$, we use the inverse of Eq. (31). For $r > \sigma$, this yields

$$\hat{c}^{mnl}_{\mu\nu}(r) = -\frac{(2l+1)}{2\pi\rho}\sum_{\chi=-\inf(m,n)}^{\inf(m,n)}\begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix}(-)^\chi \times\left\{-\frac{1}{r}\frac{\partial S^{mn}_{\mu\nu\chi}(r)}{\partial r} + \frac{1}{r^2}P_l'(0)S^{mn}_{\mu\nu\chi}(0) + \frac{1}{r^3}\int_0^r S^{mn}_{\mu\nu\chi}(r_1)P_l''\left(\frac{r_1}{r}\right)dr_1\right\}. \tag{57}$$

Using the boundary condition given in Eq. (32) that $\mathscr{S}_\chi(r) = 0, r > \sigma$ and the explicit form of the Legendre polynomial,

$$P_l(x) = \sum_{i=0}^{l} a_i^l x^i \tag{58}$$

so that

$$P_l''(x) = \sum_{i=2}^{l} i(i-1)a_i^l x^{i-2}. \tag{59}$$

Equation (57) simplifies to

$$\hat{c}^{mnl}_{\mu\nu}(r) = -\sum_{i=2}^{l}\frac{1}{r^{i+1}}i(i-1)a_i^l\frac{(2l+1)}{2\pi\rho} \times\sum_{\chi=-\inf(m,n)}^{\inf(m,n)}\begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix}(-)^\chi \times\int_0^r r_1^{i-2}S^{mn}_{\mu\nu\chi}(r_1)dr_1. \tag{60}$$

Now consider the definition of the factor correlation functions in Fourier space obtained by Fourier transformation of Eq. (37):

$$S^{mn}_{\mu\nu\chi}(k) = Q^{mn}_{\mu\nu\chi}(k) + Q^{nm}_{\nu\mu\chi}(-k) - \sum_{n_1,\nu_1} Q^{nn_1}_{\nu\nu_1\chi}(k)Q^{mn_1}_{\mu\nu_1\chi}(-k). \tag{61}$$

Note that, by definition,

$$S^{mn}_{\mu\nu\chi}(k) = \int_0^\sigma dr\, e^{ikr}S^{mn}_{\mu\nu\chi}(r), \tag{62}$$

$$Q^{mn}_{\mu\nu\chi}(k) = \int_0^\sigma dr\, e^{ikr}Q^{mn}_{\mu\nu\chi}(r). \tag{63}$$

Therefore, differentiating with respect to ik at $ik = 0$ yields, in matrix form

$$\mathbf{S}^j_\chi = \int_0^\sigma dr\, r^j\mathbf{S}_\chi(r) = \left(\frac{\partial}{\partial(ik)}\right)^j\mathbf{S}_\chi(k)\Big|_{ik=0} = \mathbf{K}^j_\chi + (-)^j(\mathbf{K}^j_\chi)^T - \sum_{s=0}^{j}(-)^s\frac{j!}{s!(j-s)!}\mathbf{K}^{j-s}_\chi(\mathbf{K}^s_\chi)^T, \tag{64}$$

where we recall that

$$\mathbf{K}^j_\chi = \int_0^\sigma dr\, r^j\mathbf{Q}_\chi(r) \tag{65}$$

and the matrix $\mathbf{S}^j_\chi$ has elements $S^{mnj}_{\mu\nu\chi}$.

These expressions can be written in a more compact form by using the super matrices $\mathbf{D}^j_\chi$ defined by

$$\mathbf{D}^0_\chi = \begin{bmatrix} \mathbf{1} & \mathbf{0} & . & . \\ \mathbf{0} & \mathbf{0} & . & . \\ . & . & . & . \\ . & . & . & . \end{bmatrix},$$

$$\mathbf{D}^1_\chi = \begin{bmatrix} \mathbf{0} & -\mathbf{1} & . & . \\ \mathbf{1} & \mathbf{0} & . & . \\ . & . & . & . \\ . & . & . & . \end{bmatrix},$$

$$\mathbf{D}^2_\chi = \begin{bmatrix} \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} & . \\ \mathbf{0} & -\mathbf{21} & \mathbf{0} & \mathbf{0} & . \\ \mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} & . \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & . \\ . & . & . & . & . \end{bmatrix},$$

$$\mathbf{D}^2_\chi = \begin{bmatrix} \mathbf{0} & . & \mathbf{0} & (-)^j & \mathbf{1} & \mathbf{0} & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & \\ . & . & (-)^s\binom{j}{s}\mathbf{1} & . & . & . & . \\ . & . & . & . & . & . & . \\ \mathbf{1} & . & . & . & . & . & . \end{bmatrix},$$

where $\mathbf{1}$ and $\mathbf{0}$ are unit matrices and matrices composed of zeros whose size depends on the index χ, and

$$\binom{j}{s} = j!/s!(j-s)!.$$

In terms of these quantities, Eq. (64) becomes

$$\mathbf{S}_\chi^j = [\mathbf{I}_\chi^0]^T \mathbf{D}_\chi^j [\mathbf{K}_\chi] + [\mathbf{K}_\chi]^T \mathbf{D}_\chi^j [\mathbf{I}_\chi^0] - [\mathbf{K}_\chi]^T \mathbf{D}_\chi^j [\mathbf{K}_\chi]. \tag{66}$$

By requiring that the invariant expansion coefficients of $c(12)$, Eq. (12), for $r>\sigma$ be equal to those from Eq. (60) leads to the equations

$$\mu_{\mu\nu}^{mnl}\delta_{jl} = j(j-1)a_j^l \frac{(2l+1)}{2\pi\rho} \times \sum_{\chi=-\inf(m,n)}^{\inf(m,n)} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} (-)^\chi S_{\mu\nu\chi}^{mnj}, \quad m,n\geqslant 1. \tag{67}$$

For $m=0$, $n\geqslant 1$, the supplementary condition $S_{\mu\nu\chi}^{0nj}=0$ is needed.[37] This equation, together with Eqs. (66) and (56), constitute a set of coupled nonlinear algebraic equations for the parameters $b_{\mu\nu,i}^{mnl}$. This represents the complete, formal analytic factorization of the molecular OZ equation subject to the closures 8–10 and 12. In the following section, we illustrate the formalism by considering a restricted form of the analysis.

V. MOLECULES WITH SURFACE ADHESION OF DIPOLAR SYMMETRY

As an illustration of the formalism developed in the preceding sections, consider now a fluid composed of molecules which have surface adhesion with dipolar symmetry and at most dipole–dipole multipolar interactions. The closures on the correlation functions are given by

$$h(12) = -1 + [\lambda^{000} + \lambda^{110}\hat{\Phi}^{110} + \lambda^{112}\hat{\Phi}^{112}]\sigma\delta(\mathbf{r}-\sigma^-), \quad r<\sigma \tag{68}$$

and

$$c(12) = -\beta\frac{\sqrt{30}}{r^3}(Q_0^1)^2\hat{\Phi}^{112}(\Omega_1\Omega_2\Omega_r), \quad r>\sigma. \tag{69}$$

For notational simplicity, we are omitting all the μ, ν and other irrelevant indices. The OZ equation, Eq. (19), has two components, $\chi=0$ and $\chi=\pm 1$, given by

$$\begin{bmatrix} H_0^{00} & 0 \\ 0 & H_0^{11} \end{bmatrix} = \left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} H_0^{00} & 0 \\ 0 & \mathbf{H}_0^{11} \end{bmatrix} \right\} \times \begin{bmatrix} C_0^{00} & 0 \\ 0 & C_0^{11} \end{bmatrix} \tag{70}$$

$$H_1^{11} = [1+H_1^{11}]C_1^{11}. \tag{71}$$

Consider now the form of $J_\chi(r)$ given by Eq. (23) and following. We have

$$J_0^{00}(r) = B_0^{00,0} + B_0^{00,2}r^2 - 2\pi\rho\sigma^2\lambda^{000}\theta(r-\sigma), \tag{72}$$

$$B_0^{00,0} = b_0^{000} = 2\pi\rho\int_0^\infty dr_1\, r_1\hat{h}^{000}(r_1), \tag{73}$$

$$B_0^{00,2} = \pi, \tag{74}$$

$$J_0^{11}(r) = B_0^{11,0} + B_0^{11,2}r^2 - 2\pi\rho\sigma^2\theta(r-\sigma) \times \left\{ \begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}\lambda^{110} + (3/2-1/2) \times \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix}\lambda^{112} \right\}, \tag{75}$$

$$B_0^{00,2} = \frac{3}{2}\begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} b_2^{112} = \frac{3}{\sqrt{30}}\, b_2^{112} \equiv b_2 \tag{76}$$

while $B_0^{11,0}$ turns out to be irrelevant. Also, from Eq. (75),

$$\lambda_0^{11} = -\frac{1}{\sqrt{3}}\lambda^{110} + \sqrt{\frac{2}{15}}\lambda^{112} \equiv \lambda. \tag{77}$$

Similarly,

$$B_1^{11,2} = -\frac{3}{2}\frac{1}{\sqrt{30}}\, b_2^{112} = -\frac{b_2}{2} \tag{78}$$

and

$$\lambda_1^{11} = -\frac{1}{\sqrt{3}}\lambda^{110} - \frac{1}{\sqrt{30}}\lambda^{112}. \tag{79}$$

Consider now the J equations, Eq. (40) and following. For $\chi=0$, we have

$$\mathbf{B} = \begin{bmatrix} 0 & -b_2 \\ 2b_2 & 0 \end{bmatrix},$$

$$\mathscr{H} = \begin{bmatrix} 1/2 & 1/3 \\ 1/3 & 1/4 \end{bmatrix},$$

$$\mathbf{I} - \mathscr{H}\mathbf{B} = \begin{bmatrix} 1-2b_2/3 & -b_2 \\ b_2/2 & 1+b_2/3 \end{bmatrix}.$$

The solution of the compact form of Eq. (56) yields

$$\begin{bmatrix} 1-K_0^0 \\ -K_0^1 \end{bmatrix} - \begin{bmatrix} \lambda \\ \lambda \end{bmatrix} = [\mathbf{I}-\mathscr{H}\mathbf{B}]^{-1}\begin{bmatrix} 1-\lambda \\ -\lambda \end{bmatrix} \tag{80}$$

with

$$[\mathbf{I}-\mathscr{H}\mathbf{B}]^{-1} = \frac{1}{\Delta^2}\begin{bmatrix} 1+b_2/3 & -b_2/2 \\ b_2/2 & 1-2b_2/3 \end{bmatrix}$$

and $\Delta = 1-b_2/6$. Thus,

$$\begin{bmatrix} 1-K_0^0 \\ -K_0^1 \end{bmatrix} = \frac{1}{\Delta^2}\begin{bmatrix} 1+b_2/3-\lambda\Delta \\ -b_2/2-\lambda\Delta \end{bmatrix}. \tag{81}$$

The equations for $\chi=1$ are identical, but with the exchange $b_2\rightarrow -b_2/2$.

We now substitute the boundary condition (67), which in this case reads

$$\frac{4\pi\rho}{9}(Q_0^1)^2 = (1-K_0^0-\lambda_0^{11})^2 - (1-K_1^0-\lambda_1^{11})^2. \tag{82}$$

This equation is, in essence, a single nonlinear equation for the unknown quantity b_2. An especially interesting case arises when the dipole moment is zero (i.e., $Q_0^1=0$). Then from Eq. (81) we obtain

$$\frac{1+b_2/3-\lambda_0(1-b_2/6)}{(1-b_2/6)^2} = \frac{1-b_2/6-\lambda_1(1+b_2/12)}{(1+b_2/12)^2} \tag{83}$$

which turns out to be a cubic equation for b_2,

$$(12+2\lambda_0+4\lambda_1)(b_2/12)^3 + (-3+3\lambda_0)(b_2/12)^2 + (12-3\lambda_1)b_2/12 + \lambda_1 - \lambda_0 = 0 \tag{84}$$

and we recall that

$$\lambda_0 = 2\pi\rho\left[-\frac{1}{\sqrt{3}}\lambda^{110} + \sqrt{\frac{2}{15}}\lambda^{112}\right],$$

$$\lambda_1 = 2\pi\rho\left[-\frac{1}{\sqrt{3}}\lambda^{110} - \sqrt{\frac{1}{30}}\lambda^{112}\right].$$

VI. CONCLUSION

In this paper, we have presented the analytic solution of the molecular Ornstein–Zernike equation for the general closure, Eqs. (8)–(12). The closure on the direct correlation function is of the form suggested by the mean-spherical approximation for arbitrary multipolar interactions. The closure on the total correlation function contains terms that arise in the Percus–Yevick approximation for spheres with anisotropic surface adhesion.[19] This analysis generalizes several earlier analyses of special cases of this closure.[19–21] The solution presented here is simpler than any of the earlier analyses, particularly in view of the explicit form in Eq. (56). A special case of the analysis—that of molecules with dipolar symmetry—was described to illustrate the method of solution. Numerical studies will be the subject of a future publication.

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