

SOLUTION OF THE SITE-SITE ORNSTEIN-ZERNIKE
EQUATION FOR NON-IDEAL DIPOLAR SPHERES

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ABSTRACT

An interaction-site model for molecular fluids (non-ideal dipolar hard spheres) is introduced, and solved analytically for a family of approximate closures. We find that there is a distinguished closure, the precise form of which can be determined by considering the dielectric constant of the fluid. Our analysis shows that this quantity appears in the large- r behavior of the site-site direct correlation function.

I.. INTRODUCTION

The Interaction Site Model (ISM) for molecular fluids was introduced by Chandler and Andersen¹ as a computationally convenient means for calculating the structural properties of molecular fluids. The key assumption in ISM is that the molecular pair potential, $u(\vec{r}_{12}^{\omega_1\omega_2})$, which depends on the orientations ω_i of molecules 1 and 2 and the vector \vec{r}_{12} between the molecular centers, can be expressed as a sum of site-site potentials, viz.

$$u(\vec{r}_{12}^{\omega_1\omega_2}) = \sum_{\alpha,\gamma=1}^m u_{\alpha\gamma}(r_{\alpha\gamma}) . \quad (1)$$

In Eq. (1), $u_{\alpha\gamma}(r)$ is the interaction potential and $r_{\alpha\gamma}$ the distance between sites α and γ in distinct molecules; the molecules each have m sites. The key quantity of theoretical interest in an ISM is the site-site total correlation function $h_{\alpha\gamma}(r)$, which is related to the site-site distribution function $g_{\alpha\gamma}(r)$ by

$$h_{\alpha\gamma}(r) = g_{\alpha\gamma}(r) - 1 . \quad (2)$$

The function $g_{\alpha\gamma}(r)$ is related to the probability of finding sites α and γ , in distinct molecules, separated by distance r , and can be formally defined in terms of the molecular pair distribution function $g(\vec{r}_{12}^{\omega_1\omega_2})$.²

Andersen and Chandler,¹ however, suggested an alternative method based on analogy with the Ornstein-Zernike (OZ) equation³ for simple fluids. They defined an auxiliary function, the site-site direct correlation function $c_{\alpha\gamma}(r)$, via the Site-Site Ornstein-Zernike equation (SSOZ)

which is a matrix equation in Fourier k-space given by

$$h(k) = \omega(k)c(k)h(k) + \rho\omega(k)c(k)h(k) . \quad (3)$$

Here ρ is the number density of molecules and the elements of the $h(k)$ and $c(k)$ matrices, $h_{\alpha\gamma}(k)$ and $c_{\alpha\gamma}(k)$, are the three-dimensional Fourier transforms of $h_{\alpha\gamma}(r)$ and $c_{\alpha\gamma}(r)$ respectively; the elements of the $\omega(k)$ matrix are given by

$$\omega_{\alpha\gamma}(k) = \delta_{\alpha\gamma} + (1 - \delta_{\alpha\gamma}) \frac{\sin k\ell_{\alpha\gamma}}{k\ell_{\alpha\gamma}} \quad (4)$$

where $\ell_{\alpha\gamma}$ is the fixed distance between sites α and γ within the same molecule; $\omega_{\alpha\gamma}(k)$ is the Fourier transform of the real space function $\omega_{\alpha\gamma}(r)$ which may be identified as the intramolecular site-site correlation function. Recently, Stell, et al.⁴ have demonstrated that Eq. (3), rather than being simply analogous to the OZ equation for molecule-molecule correlations, can be derived easily from the OZ equation for mixtures.

Andersen and Chandler¹ considered in detail two ISMs. In the case where the $u_{\alpha\gamma}(r)$ in Eq. (1) are hard sphere potentials only, i.e.,

$$u_{\alpha\gamma}(r) = \begin{cases} \infty & r < \sigma_{\alpha\gamma} \\ 0 & r > \sigma_{\alpha\gamma} \end{cases} , \quad (5)$$

Andersen and Chandler referred to this model as a Reference Interaction Site Model (RISM) due to its expected role as the reference system in perturbation theories. For RISMs, Andersen and Chandler proposed the closure

$$h_{\alpha\gamma}(r) = -1 \quad r < \sigma_{\alpha\gamma} \quad (6a)$$

$$c_{\alpha\gamma}(r) = 0 \quad r > \sigma_{\alpha\gamma} \quad (6b)$$

which we shall refer to as the Reference Interaction Site Approximation (RISA) to distinguish the integral equation approximation for obtaining $h_{\alpha\gamma}(r)$ from the Hamiltonian model (RISM) under study.⁵ For the ISMs in which the $u_{\alpha\gamma}(r)$ have hard cores of diameter $\sigma_{\alpha\gamma}$ but are non-zero for $r > \sigma_{\alpha\gamma}$, Andersen and Chandler suggest the approximation

$$h_{\alpha\gamma}(r) = -1 \quad r < \sigma_{\alpha\gamma} \quad (7a)$$

$$c_{\alpha\gamma}(r) = -\beta u_{\alpha\gamma}(r) \quad r > \sigma_{\alpha\gamma} \quad (7b)$$

where $\beta = 1/kT$, k is Boltzmann's constant, T is absolute temperature. We will refer to this approximation as the Interaction Site Approximation (ISA). In both the RISA and ISA, the hard core condition [Eqs. (7a) and (7b)] are exact; the approximation is in the assumed form for $c_{\alpha\gamma}(r)$.

Both the RISA and ISA are strongly suggested by analogy to the Percus-Yevick (PY)⁷ approximation for hard spheres and the Mean Spherical Approximation (MSA)⁸ for hard core systems in the theory of simple fluids. The MSA can be derived from a number of viewpoints,⁶ one of which begins with the observation that for simple fluids (e.g., Lennard-Jones fluids), the direct correlation function satisfies the following relation (valid off critical points)

$$c(r) \rightarrow -\beta u(r) \quad r \rightarrow \infty \quad (8)$$

where $u(r)$ is the interatomic potential; the MSA can then be viewed as the extrapolation of the asymptotic statement (8) to all separations r greater than the hard core distance. We will contrast this behavior of the MSA with that of the ISA in the discussion in Section III of this paper.

One of the surprising aspects of the SSOZ equation, given its complexity, is that it has been shown to be factorizable analytically for a number of special RISMs and ISMs when the corresponding RISA or ISA closure is used. For the cases reported previously,⁹⁻¹⁴ the particular simplifying feature of the SSOZ equations involved were that they reduced to one or more disjoint scalar SSOZ equations. For example, for symmetric n -atomics (i.e., for $n = 3$, 3 equal diameter triangularly-co-ordinated hard spheres; for $n = 4$, 4 equal diameter hard-spheres tetrahedrally-co-ordinated, etc.) the SSOZ equation reduces to the scalar equation

$$h(k) = [1 + (n-1)\omega(k)]^2 c(k) + n\rho[1 + (n-1)\omega(k)]c(k)h(k) . \quad (9)$$

Morriss, et al.⁹⁻¹¹ exhibited a Baxter Weiner-Hopf factorization¹⁵ of this problem for $n = 2$ (symmetric diatomics). Morriss and Perram¹² have also reported the solution of the ISA for two rigid polar molecules -- polar hard dumbbells (two charged, equal diameter, fused hard spheres) and four charged, equal diameter, tetrahedrally co-ordinated charged hard spheres. In each of these cases, use of sum and difference correlation functions, as is used in the solution of the Restricted

Primitive Model (RPM) of electrolytes in the MSA,¹⁶ yields (again as in the RPM in the MSA) two decoupled scalar SSOZ equations.

In this paper we begin an exploration of a further class of analytically solvable rigid polar molecule ISMs. We restrict our attention in this paper to a model of non-ideal dipolar hard spheres, although the reader will note that our method is sufficiently general to admit a wide class of models as analytically solvable cases. The particular model we have in mind is depicted in Figure 1: it consists of a hard sphere of diameter σ with two point charges at sites 2 and 3 of $+q$ and $-q$, respectively. The center of the sphere is at site 1; all three sites lie on one straight line; sites 2 and 3 are located at distance $\ell/2$ from site 1 (i.e., $\ell_{12} = \ell_{13} = \ell/2$; $\ell_{23} = \ell$).

The molecular model proposed is thus hard spheres with a non-ideal dipole, the dipole moment being $\mu = q\ell$. In Section II we give the analytic solution of this model with the following quite general closure:

$$h_{\alpha\gamma}(r) = -1 \quad r < \sigma_{\alpha\gamma} \quad (10)$$

where

$$\begin{aligned} \sigma_{11} &= \sigma, & \sigma_{12} &= \sigma_{21} = \sigma_{13} = \sigma_{31} = \sigma - \ell/2 \\ \sigma_{22} &= \sigma_{23} = \sigma_{32} = \sigma_{33} = \sigma - \ell \end{aligned} \quad (11)$$

$$\begin{aligned} c_{\alpha\gamma}(r) &= c_{\alpha\gamma}^{(0)}(r) \quad r > \sigma_{\alpha\gamma} \\ \text{for } \alpha\gamma &= 11, 12, 21, 13, 31 \end{aligned} \quad (12a)$$

$$\begin{aligned} c_{\alpha\gamma}(r) &= c_{\alpha\gamma}^{(0)}(r) + (-)^{\alpha+\gamma+1} \frac{A}{r} \quad r > \sigma - \ell \\ \text{for } \alpha\gamma &= 22, 23, 32, 33 \end{aligned} \quad (12b)$$

The quantities with superscript 0 refer to quantities calculated for the RISM model corresponding to the ISM considered here -- i.e., $q = 0$ -- which corresponds to a hard sphere with two auxiliary sites. If $c_{\alpha\gamma}^{(0)}(r)$ is assumed to be zero for $r > \sigma_{\alpha\gamma}$, then this corresponds to calculating $c_{\alpha\gamma}^{(0)}(r)$ in the RISA; here we are allowing for the possibility that $c_{\alpha\gamma}^{(0)}(r)$ may be calculated exactly.

It should also be noted that we have not made any identification of the parameter A . With the identification $A = \beta q^2$ and $c_{\alpha\gamma}^{(0)}(r)$ calculated in the RISA, Eqs. (12) correspond to the ISA approximation. In Section III we shall discuss an identification for A which, in the spirit of the MSA, would appear to be more appropriate than the ISA value.

II. METHOD OF SOLUTION

The SSOZ equation for the non-ideal dipolar hard sphere fluid under study in this paper involves four distinct site-site total correlation functions -- $h_0 \equiv h_{11}$, $h_1 \equiv h_{12} = h_{21} = h_{13} = h_{31}$, $h_2 \equiv h_{22} = h_{33}$, and $h_3 \equiv h_{23} = h_{32}$; c_i , $i = 0, 1, 2, 3$ are defined similarly. The h_i and c_i ($i = 0, 1, 2, 3$) satisfy the closures given in Eqs. (10) - (12). It is also useful to define four new functions: the sum (S) and difference (D) site-site total and direct correlation functions given by

$$h_S(r) = \frac{1}{2} [h_2(r) + h_3(r)] , \quad h_D(r) = \frac{1}{2} [h_2(r) - h_3(r)] \quad (13a)$$

$$c_S(r) = \frac{1}{2} [c_2(r) + c_3(r)] , \quad c_D(r) = \frac{1}{2} [c_2(r) - c_3(r)] . \quad (13b)$$

The SSOZ equation for the non-ideal dipolar hard sphere fluid can be written as

$$h'(k) = \omega(k)c'(k)\omega(k) + \rho\omega(k)c'(k)h'(k) \quad (14)$$

where the matrices $h'(k)$, $c'(k)$ and $\omega(k)$ are given by

$$h'(k) = \begin{pmatrix} h_0(k) & h_1(k) & h_1(k) \\ h_1(k) & h_2(k) & h_3(k) \\ h_1(k) & h_3(k) & h_2(k) \end{pmatrix} ,$$

$$c'(k) = \begin{pmatrix} c_0(k) & c_1(k) & c_1(k) \\ c_1(k) & c_2(k) & c_3(k) \\ c_1(k) & c_3(k) & c_2(k) \end{pmatrix} \quad (15)$$

and

$$\omega(k) = \begin{pmatrix} 1 & \omega_1(k) & \omega_1(k) \\ \omega_1(k) & 1 & \omega_2(k) \\ \omega_1(k) & \omega_2(k) & 1 \end{pmatrix} \quad (16)$$

where

$$\omega_1(k) = \frac{\sin(k\ell/2)}{k\ell/2}, \quad \omega_2(k) = \frac{\sin k\ell}{k\ell}. \quad (17)$$

By writing [see Eq. (13)]

$$\begin{aligned} h_2(r) &= h_S(r) + h_D(r) & h_3(r) &= h_S(r) - h_D(r) \\ c_2(r) &= c_S(r) + c_D(r) & c_3(r) &= c_S(r) - c_D(r) \end{aligned} \quad (18)$$

and substituting into (14), the SSOZ equation is found to decouple into two SSOZ equations:

$$h(k) = \omega(k)c(k)\omega(k) + \rho\omega(k)c(k)h(k) \quad (19)$$

$$H(k) = \omega(k)C(k)\omega(k) + \rho\omega(k)C(k)H(k). \quad (20)$$

Here,

$$h(k) = \begin{pmatrix} h_0(k) & h_1(k) & h_1(k) \\ h_1(k) & h_S(k) & h_S(k) \\ h_1(k) & h_S(k) & h_S(k) \end{pmatrix} \quad (21)$$

and $c(k)$ has the analogous form; the matrix $H(k)$ [and likewise $C(k)$] is given by

$$H(k) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & h_D(k) & -h_D(k) \\ 0 & -h_D(k) & h_D(k) \end{pmatrix}. \quad (22)$$

Equation (22) further reduces to the scalar equation

$$h_D(k) = [1 - \omega_2(k)]^2 c_D(k) + 2\rho[1 - \omega_2(k)]c_D(k)h_D(k) . \quad (23)$$

Now from Eqs. (10) - (13) it can be seen that the closure for c_0 , c_1 and $c_S(r)$ imply that the solution of the SSOZ equation (19) subject to closures (10) - (12) is simply the solution of the SSOZ equation for a hard sphere with two uncharged auxiliary sites. The solution of this problem is known exactly (see, for example, Refs. 2, 17) and is given by

$$\begin{aligned} h_0(k) &= h^{HS}(k), & h_1(k) &= \omega_1(k)h^{HS}(k), \\ h_S(k) &= [\omega_1(k)]^2 h^{HS}(k) \end{aligned} \quad (24a)$$

$$c_0(k) = c^{HS}(k), \quad c_1(k) = c_S(k) = 0 \quad (24b)$$

where $h^{HS}(k)$, $c^{HS}(k)$ are the Fourier transforms of the exact hard sphere total and direct correlation functions at density ρ . (The RISA for this problem would replace h^{HS} , c^{HS} by their PY approximations -- see Ref. 2.)

The closure for Eq. (23) is easily seen to be

$$\begin{aligned} h_D(r) &= 0 & r &< \sigma - \ell \\ c_D(r) &= -\frac{A}{r} & r &> \sigma - \ell. \end{aligned} \quad (25)$$

This problem has already been solved analytically via a Weiner-Hopf factorization by Morriss and Perram.¹²

Thus we have derived an analytic solution for the SSOZ equation (14) with closures (10) - (12).

III. DISCUSSION

Of obvious interest in dipolar fluids is the calculation of the dielectric constant ϵ . For ISMs, Høye and Stell¹⁸ have shown that the dielectric constant may be written in terms of site-site total correlation functions as

$$\sum_{\alpha\gamma} q_{\alpha} q_{\gamma} h_{\alpha\gamma}^{(2)} = \frac{\mu^2}{9\rho} \left[\frac{\epsilon-1}{y\epsilon} - 3 \right] \quad (26)$$

where

$$y = \frac{4}{9} \pi \rho \beta \mu^2 \quad (27)$$

and $h_{\alpha\gamma}^{(2)}$ is the coefficient of k^2 in the low- k expansion of $h_{\alpha\gamma}(k)$.

For the model considered here, (26) becomes

$$4q^2 h_D^{(2)} = \frac{\mu^2}{9\rho} \left[\frac{\epsilon-1}{y\epsilon} - 3 \right]. \quad (28)$$

Thus the dielectric constant is determined solely by the low- k behavior of Eq. (23), and hence the calculation of ϵ given by Morriss and Perram¹² can be followed without change. If the parameter A is taken to be its ISA value (i.e., q^2/kT) then the ideal gas result

$$\epsilon = 1 + 3y \quad (29)$$

follows as shown by Morriss and Perram.¹² (In fact, this is just a special case of the more general analyses of Høye and Stell^{18,19} and Sullivan and Gray.²⁰) If we therefore write

$$A = \beta q^2 (1 - B) \quad (30)$$

we find (by simple adaptation of the Morriss-Perram method) that

$$\epsilon = 1 + \frac{3y}{1 - 3yB} \quad (31)$$

Equation (31) may be inverted, yielding

$$B = \frac{1}{3y} - \frac{1}{\epsilon - 1} \quad (32a)$$

or, after substitution into Eq. (30)

$$A = \beta q^2 \left[\frac{1 + \epsilon(3y-1)}{3y(\epsilon-1)} \right] \quad (32b)$$

Clearly, the ISA assumption ($A = \beta q^2$) leads to incorrect dielectric behavior for the model system under consideration in this problem. Although there are no simulation results available for the model studied in this paper -- non-ideal dipolar hard spheres -- the inadequacy of (29) is easily seen. It is moreover interesting to note that in the ISA, Eq. (29) remains true even in the ideal dipole limit ($\ell \rightarrow 0$, $q \rightarrow \infty$ such that $\mu = q\ell$ remains fixed) which leads to the following difficulty: the ISA for non-ideal dipolar spheres (which has been suggested by analogy with the MSA¹) does not yield the known MSA result²¹ for dipolar spheres in the ideal dipole limit.

One consequence of the above subtlety is that the ISA is not the natural extension of the MSA to site-site potentials. As was discussed in the Introduction, the spirit of the MSA for central potentials is that it is the extrapolation of the asymptotic form of $c(r)$ to the full range of r outside the hard core diameter. In this spirit, then, the true site-site analogue of the MSA is Eq. (10) - (12) with A given by Eq. (32b) rather than by unity. This improved analogue shares a

conceptual feature with the "generalized" mean spherical approximation previously introduced to treat dipolar spheres.^{22,23} The use of Eqs. (10) - (12) with closure given by (32b) requires a priori knowledge of the dielectric constant for the system under investigation -- i.e., it is not a predictive theory of the dielectric constant, unlike the MSA for central potentials. This loss of predictive capacity appears to be deeply rooted in the geometry of the site-site treatment;¹⁸ the very fact that the asymptotic form of the site-site $c_{\alpha\gamma}(r)$ depends explicitly on ϵ shows that no simple state-independent approximant to $c_{\alpha\gamma}(r)$ can yield a dielectrically adequate theory. We note that taking the ideal dipole limit in the analysis presented in this section, while avoiding the trivial result (29), will not yield the MSA result for ideal-dipolar hard spheres unless the exact ϵ implicitly used in (32b) is replaced by an approximate dielectric constant, ϵ' , which in the ideal dipole limit has the property

$$\epsilon' \rightarrow \epsilon_W$$

where ϵ_W is the Wertheim expression for the dielectric constant of ideal dipolar hard spheres solved in the MSA.²¹ The simplest choice of ϵ' is clearly ϵ_W .

Some impression of the behavior of the parameter B (which amounts to a dimensionless correction to the ISA) can be gained for near-ideal dipolar hard spheres by evaluating (32a) with ϵ replaced by ϵ_W : this is shown in Figure 2. In particular, the limiting behavior

$$\lim_{y \rightarrow 0} B = \frac{1}{3}$$

is exact, and follows generally from the low- y expansion of ϵ ²⁴

$$\epsilon = 1 + 3y + 3y^2 + O(y^3) .$$

In this paper, we have solved analytically a useful model for molecular fluids -- the non-ideal dipolar hard sphere model -- using a quite general closure within the framework of the ISM formalism. It is intended that numerical work on this model will be reported when Monte Carlo simulation results for this model become available.²⁵

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FIGURE CAPTIONS

Figure 1. The non-ideal dipolar hard sphere model considered in this paper. The diameter of the sphere is σ ; point charges of $+q$ and $-q$ are located at sites 2 and 3 respectively, each a distance $\ell/2$ from the center of the sphere, identified as site 1.

Figure 2. Behavior of the parameter B defined in Eqs. (30) and (32a), with the true dielectric constant ϵ replaced by ϵ_W , the dielectric constant obtained by Wertheim for ideal dipolar hard spheres solved in the MSA.²¹



Figure 1.

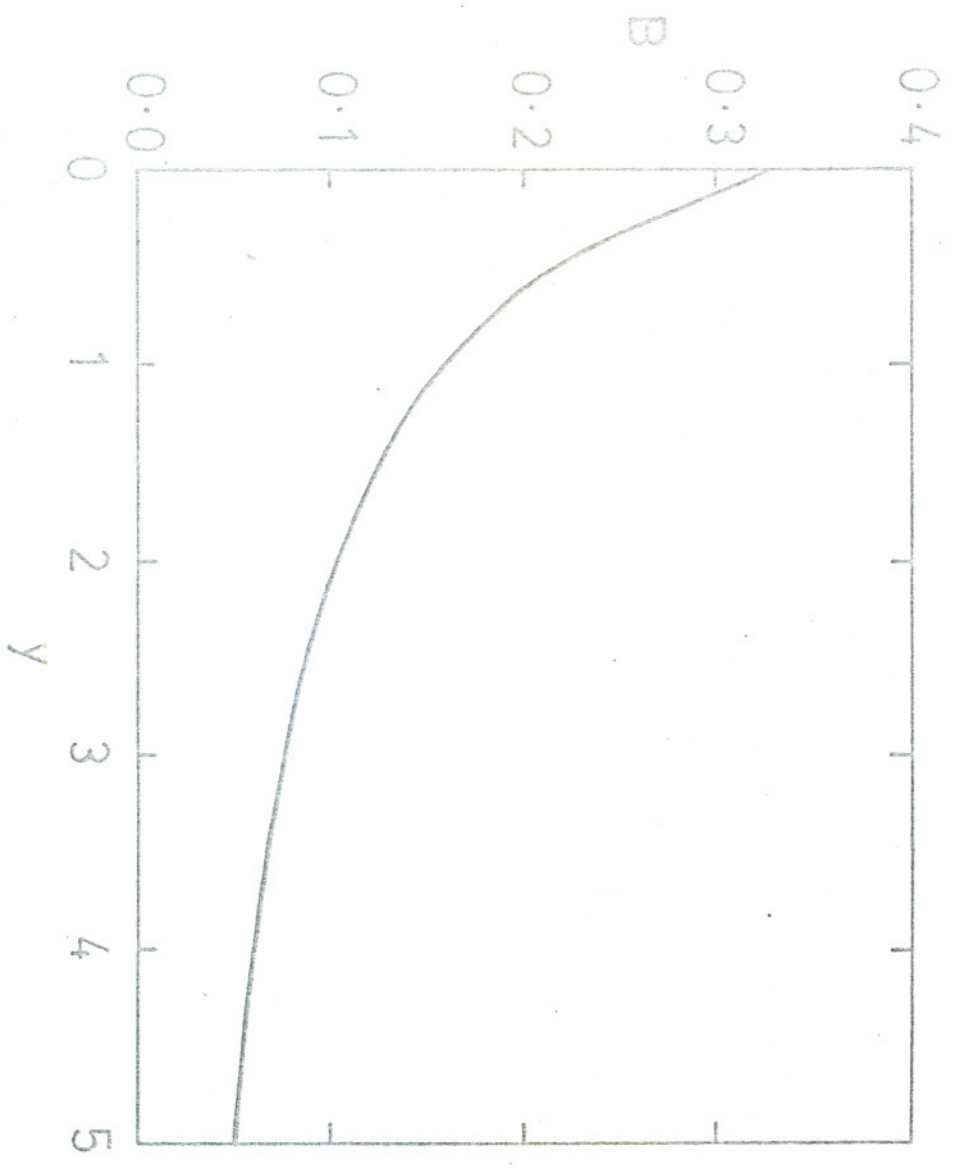


Figure 2.