Calculation of orientational pair correlation factors with the interaction site formalism

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The arrangement of the interaction site cluster series provided by the proper integral equation theory for polyatomic fluids is applied in a perturbative fashion, using solutions to the RISM equation as input, to obtain \( g_2 \) factors for liquid carbon disulfide. The theoretical calculations are in good accord with experiment and simulation. The methodology appears to be rather general in its applicability and possible extensions to polar systems are described.

I. INTRODUCTION

This paper is devoted to the calculation of the orientational pair correlation factor \( g_2 \) from a new theory based upon the proper integral equation\(^{1}\) for site–site distributions in molecular fluids. The proper integral equation is a formally exact writing of the interaction site cluster series\(^{2,3}\) in the form of a Dyson equation. Therefore it is analogous to the Ornstein–Zernike equation of simple fluids.\(^{4}\) An approximation to this exact proper integral equation yields the RISM equation.\(^{2,5-7}\) While it has provided a useful theorem for local pair correlations in molecular liquids,\(^{7,8}\) the RISM approximation demolishes all but the most trivial facets of long wavelength orientational pair correlations.\(^{8-11}\) Fortunately, with the proper integral equation theory,\(^{1\text{b}}\) it is not difficult to improve upon the approximation. The ability to make these improvements has already been sketched in two earlier papers: the first\(^{1\text{b}}\) was devoted to the dielectric constant and the second\(^{1\text{c}}\) was concerned with the \( g_2 \) factor relevant to depolarized light scattering.

In this, the third paper of the series, we perform an explicit calculation of \( g_2 \) for liquid carbon disulfide. Along with the numerical results which should be of interest, the present paper emphasizes a perturbative methodology with which one may compute long wavelength properties such as dielectric constants and \( g_2 \) by employing the RISM theory as a reference.

The proper integral equation for site–site correlations is\(^{1\text{c}}\)

\[
\omega + \rho \beta = (1 - \rho \epsilon) (\omega + \rho \epsilon) + \omega \Omega, \tag{1.1}
\]

where we employ the notation defined in Ref. 1, and for notational simplicity confine ourselves to one component uniform fluids. (Generalizations are straightforward.) The elements of the matrices \( \omega \) and \( \beta \) are the intramolecular and intermolecular site–site correlation functions, respectively. The matrix \( \epsilon \) has elements \( \epsilon_{\alpha\beta}(r - r') \) which are direct correlation functions of a certain type. In particular, employing \( f \) bonds and \( s \) vertices,\(^{2,3}\) they sum all nodeless contributions to \( \beta \) for which the roots are not associated with any intramolecular bonds (i.e., the roots are not "s circles").

The hypervertex functions which comprise the elements of \( \Omega \) are given by

\[
\Omega = \omega + \Delta \Omega = (1 - \rho \epsilon) (\omega + \rho \epsilon) (1 - \rho \epsilon)^{-1}, \tag{1.2}
\]

where the elements of \( \epsilon_\alpha, \epsilon_s \), and \( \epsilon_0 \) are direct correlation functions too. In this case, \( \epsilon_{\alpha}(r - r') \) sums all nodeless graphs for which the root point \( \alpha \) is an \( s \) circle and the root point \( \beta \) is not; \( \epsilon_s = \epsilon_s \); and \( \epsilon_{\alpha\beta}(r - r') \) sums all nodeless graphs for which both roots are \( s \) circles.

In the RISM approximation, one neglects \( \Delta \Omega \) and assumes that \( \epsilon_\alpha = \epsilon_0 \) with \( \epsilon_0 \) being short ranged, or that \( \epsilon \) is asymptotic to \(-\beta \eta \) where \( \beta^{-1} \) is Boltzmann's constant times temperature and \( \eta \) is the matrix of site–site potentials. However, by assuming \( \epsilon_0 + \beta \eta \) is not long ranged, it is easily shown that the deviations from ideal gas behavior for the dielectric constant\(^{10}\) and the \( g_2 \) factor\(^{11}\) are determined entirely by \( \Delta \Omega \). For example, as reported in Ref. 11 and derived in the Appendix to this paper, one finds that for a linear molecule

\[
g_2 = 1 - \text{Tr} \Psi \Delta \Omega - (5/4) \Delta \Omega, \tag{1.3}
\]

Here, \( \Delta \Omega \) is the coefficient of the \( k^n \) term in the small wave vector expansion of \( \Delta \Omega \). \( \Delta \Omega \) is independent of matrix index and therefore called \( \Delta \Omega \) and

\[
\Psi = (45/14) \begin{bmatrix}
1 & -1 & 0 \\
-1 & 1 & 0 \\
0 & 0 & 0 \\
\end{bmatrix}, \tag{1.4}
\]

where sites 1 and 2 are nonequivalent sites lying on the principal axis of the molecule and separated by a distance \( l \). This formula can be further reduced to

\[
g_2 = 1 - \rho \text{Tr} \Psi \epsilon_0 - (5/4) \rho \epsilon_0. \tag{1.5}
\]

Here, \( \epsilon_0 \) refers to \( \epsilon_0(k) \) evaluated at \( k = 0 \) where the matrix elements are independent of index. To obtain a nontrivial prediction for \( g_2 \), one must make a nontrivial statement about \( \Delta \Omega \) unlike the RISM approximation which simply sets \( \Delta \Omega \) to zero. A procedure for developing such statements is the subject of the next section.

II. TOPOLOGICAL REDUCTION AND CLUSTER EXPANSIONS FOR \( \epsilon_0, \epsilon_s \), AND \( \epsilon_0 \)

In Ref. 1, we introduced the graphical representations of the direct correlation functions \( \epsilon_0, \epsilon_s \), and \( \epsilon_0 \) as functionals of the site–site Mayer cluster functions \( f \) and the intramolecular distributions \( s \). These representations are described
in the previous section and illustrated in Fig. 1. In Ref. 10 we advocated the idea of removing the dependence upon \( f \) in favor of the correlation function \( h_0 \) since any low order truncation of the cluster series structured with \( h_0 \) bonds will guarantee that the dielectric constant will be proportional to the molecular dipole moment squared in both the limits of high and low values for the dipole moment. In these limits, this proportionality is believed to be the correct behavior and truncations of the series employing \( f \) bonds will not obey the proportionality for high values of the dipole. We are motivated by this observation to employ the series with \( h_0 \) bonds rather than \( f \) bonds for any calculation of long wavelength orientational properties. The \( g_2 \) factor is one such property.

To deduce the greater rearrangement from \( f \) to \( h_0 \), consider the graphical representation of \( h_0 \) in terms of \( f \) bonds. This cluster series is illustrated in Fig. 2. It is the sum of all those graphs contributing to \( h \) for which the roots are not \( s \) circles. As a result, the element \( h_{0,0}(r) \), has the physical interpretation of the pair correlation function between two free atoms \( \alpha \) and \( \gamma \) dissolved at infinite dilution in the molecular fluid of interest. Notice that the topology of the graphs is such that except for the leading term, the removal of the roots produces a graph which may be disconnected and at least one part has one or more black circles, and the dangling bonds (those that had been connected to the roots) are not intramolecular \( s \) functions. In analogy with the notational conventions employed in the theory of simple fluids, we shall describe the roots in \( h_0 \) as an articulation pair of circles. Such a pair is defined by the topology of what remains after the pair is removed. Thus, they need not be white root circles. For example, the last graph in Fig. 2 contains an articulation pair of black field point circles. The second to last graph has one black circle and one white circle which together form an articulation pair.

With this notational convention, it is clear that one can generate all the graphs in \( e_1 \), \( e_2 \), and \( e_3 \) by considering only those graphs without articulation pairs and replacing the \( f \) bonds with \( h_0 \) bonds. This is true since \( h_0 - f \) is the sum of all those connected graphs with \( f \) bonds for which the two roots are an articulation pair. Hence,

\[
e_{0,0}(r) = \text{the sum of all connected simple nodeless graphs with two white one circles, labeled } \alpha \text{ and } \gamma, \text{ one or more black circles, } h_0 \text{ bonds, } s \text{ vertices, root } \alpha \text{ is an } s \text{ circle, root } \gamma \text{ is not an } s \text{ circle, there are no articulation vertices, and there are no articulation pairs.}
\]

(2.1)

If the solid line bonds in Fig. 1(a) were to refer to \( h_0 \) bonds, then all but the last pictured graph would be contained in Eq. (2.1). The topologically reduced series for \( e_1 \) is the same as that for \( e_3 \) except that in \( e_3 \), it is the right root which is the \( s \) circle. For \( e_3 \), both roots are \( s \) circles.

The \( h_0 \) bonds already contain many effects due to the finite density of a fluid environment. Therefore, it might be reasonable, even at liquid densities, to organize the series described in Eq. (2.1) by ordering them in terms of the number of molecules explicitly considered in the graphs. We shall call such an arrangement molecular ordering. To lowest order, only two molecules are involved, those associated with the roots. These graphs are shown in Fig. 3 for the case in which molecules contain only two sites. In the more general multisite case, the lowest order approximations to \( e_1 \), \( e_2 \), and \( e_3 \) in the molecular ordering scheme with \( h_0 \) bonds can be expressed as

\[
e_{1,0}(r) = \int d\mathbf{u} \left[ \prod_{\alpha = 1}^{m} \left[ 1 + h_{0,0}(r) \right] - 1 \right] - \sum_{\gamma} h_{0,0}(r)
\]

(2.2a)

\[
e_{2,0}(r) = \int d\mathbf{u} \left[ \prod_{\alpha = 1}^{m} \left[ 1 + h_{0,0}(r) \right] - 1 - (\alpha h_0 \delta_{0,0})(r) \right]
\]

(2.2b)

\[
e_{3,0}(r) = \int d\mathbf{u} \left[ \prod_{\alpha = 1}^{m} \left[ 1 + h_{0,0}(r) \right] - 1 \right] - (\alpha h_0 \delta_{0,0})(r) - (\alpha h_0 \delta_{0,0})(r) - (\alpha h_0 \delta_{0,0})(r)
\]

(2.2c)

\[
\]

FIG. 2. Graphs in \( h_0 \).

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where the \( \int d \theta \) stands for the (normalized) integration over orientations of molecules 1 and 2 with \( |\mathbf{r}^{(1)} - \mathbf{r}^{(2)}| \) fixed at the distance \( r \). \( \chi_{\text{atom}} \) stands for

\[
\chi_{\text{atom}}(\mathbf{r}_{12}) = \chi_{\text{atom}}(\mathbf{r}_{12}^{(1)} - \mathbf{r}_{12}^{(2)}),
\]

and in the last equality it is to be understood that \( \chi_{\text{atom}} \) are taken from the previous two equalities. In deriving these equations, the reader may find it useful to refer to Ref. 2.

Equations (2.2) are the primary approximations we will use for the calculations presented in the next section. To apply this theory, one must have expressions for the \( h_{\text{atom}} \) functions. While in principal these functions can be obtained from a self-consistent application of the proper integral equation, the use of a low order truncation of the molecular ordering scheme suggests a simpler alternative. In particular, we will obtain the \( h_{\text{atom}} \) functions from the RISM theory\(^\text{5-7} \) for pairs of free atoms at infinite dilution in the molecular fluid. These functions together with the straightforward numerical quadrature involved in evaluating the angle integrations in Eqs. (2.2) produce the direct correlation functions.

The appropriate combinations of moments with Eq. (1.5) yield \( g_{\text{c}} \). Note the disappearance of \( c_{\text{c}} \) and \( c_{\text{cc}} \) from the final expression for \( g_{\text{c}} \). This result is a general one not confined to the simple molecular ordering scheme employed herein. The dependence on only \( g_{\text{c}} \) makes physical sense in light of the fact that when cast into the form of orientational integrations, as in Eqs. (2.2), the graphs of \( c_{\text{c}} \) and \( c_{\text{cc}} \) are independent of the orientations of one of the two root molecules.

It is interesting to note that an alternative though equivalent representation of Eqs. (1.5) and (2.2) for rigid molecules is\(^\text{10} \)

\[
g_{\text{c}} - 1 = V^{-1} \int d \mathbf{r} \int d \mathbf{r}' P_{\text{c}}(\mathbf{r}, \mathbf{r}') \rho H(1,2),
\]

where \( V \) is the volume, \( d \mathbf{r} \) indicates integrations over all positions and orientations of molecule 1, and

\[
H(1,2) = \prod_{\alpha \beta} \left[ 1 + h_{\text{atom}}(\mathbf{r}_{12}^{(1)} - \mathbf{r}_{12}^{(2)}) \right].
\]

If the product over sites in \( H(1,2) \) is expanded, it is seen that all terms that are not at least doubly connected contribute nothing to the integrations and hence the correspondence with \( g_{\text{c}} \). There is a striking similarity between Eq. (2.3) and the result one would write down as a site superposition approximation (SSA). Along with differences associated with possible choices of normalization, however, Eq. (2.3) differs from the \textit{ad hoc} SSA through the use of \( h_{\text{b}} \) bonds rather than \( h \) bonds.

An analogous calculation of the dielectric constant \( \varepsilon \) could be carried out too. In that case, some further care must be taken since, as discussed in Ref. 10, the \( h_{\text{b}} \) functions which are used should have the correct \( -1/\varepsilon r \) behavior for large \( r \). To construct that type of theory, the recent extensions of the RISM theory due to Rossky and coworkers\(^\text{8} \) could be very useful. If carried out, the procedure will yield \( c_{\text{c}}, c_{\text{cc}}, \) and \( c_{\text{cc}} \) functions which depend upon \( \varepsilon \) and the theory will therefore produce self-consistent equations for the dielectric constant.

III. IMPLEMENTATION AND RESULTS FOR LIQUID CARBON DISULFIDE

The first step in applying the theory is the evaluation of the \( h_{\text{b}} \) functions. These are the pair correlation functions between free atoms at infinite dilution in the fluid. They are determined from the RISM theory by applying the usual Ornstein-Zernike-like equations for this mixture problem.\(^\text{7} \)

For hard core interactions, the equations are

\[
h_{\text{atom}}(r) = -1, \quad r < d_{\text{atom}},
\]

\[
= (c_{\text{c}} + c_{\text{cc}} + c_{\text{ccc}})(r), \quad r > d_{\text{atom}},
\]

\[
(3.1)
\]

where \( d_{\text{atom}} \) is the distance of closest approach for atoms \( a \) and \( b \).

\[
\chi_{\text{atom}}(r) = \rho \omega_{\text{atom}}(r) + \rho^{2} h_{\text{atom}}(r)
\]

\[
(3.2)
\]

is the site density pair correlation function for the pure molecular fluid, the stars denote convolutions, and the free atom to molecular site direct correlation function \( c_{\text{c}}(r) \) is zero for \( r > d_{\text{atom}} \) and is determined for \( r < d_{\text{atom}} \) by enforcing the condition

\[
0 = 1 + c_{\text{c}}(r) + (c_{\text{c}} + c_{\text{cc}} + c_{\text{ccc}})(r), \quad r < d_{\text{atom}}.
\]

\[
(3.3)
\]

Finally, \( \chi_{\text{atom}}(r) \) is determined by solving the familiar RISM equations for the pure fluid

\[
\chi(r) = \rho \omega_{\text{atom}}^{-1} \rho_{\text{atom}}(r),
\]

\[
(3.4)
\]

\[
h_{\text{atom}}(r) = -1, \quad r < d_{\text{atom}},
\]

\[
c_{\text{atom}}(r) = 0, \quad r > d_{\text{atom}}.
\]

\[
(3.5)
\]

These are the RISM equations as first proposed by Chandler and Andersen\(^\text{9} \) and subsequently applied to various systems.\(^\text{7} \)

Equations (3.3) and (3.4) are the closure relations to Eq. (3.4) (and its extension to mixtures) that are appropriate for hard core systems. Generalizations for continuous force systems have been derived by Chandler,\(^\text{a} \) by Rossky and coworkers,\(^\text{b} \) and by others.\(^\text{12} \)

The generalizations to continuous force systems are perhaps most appropriate for the application given below since we compare with results of computer simulations\(^\text{13} \) which employ continuous Lennard-Jones interactions for the site-site potentials. We, however, use a simpler and more approximate approach. First, we employ only the repulsive portion (in the WCA sense)\(^\text{14} \) of the Lennard-Jones potentials. Second, the continuous nature of the repulsions is accounted for with the bjp function procedure of Ladanyi and Chandler\(^\text{2} \) which expands about a hard core reference. Hence, \( h_{\text{b}} \) is obtained perturbatively from the \( h_{\text{b}} \) given by the integral Eqs. (3.1)-(3.5). The solutions to those equations are obtained conveniently and to sufficient accuracy by applying Lowden's variational procedure\(^\text{15} \) [modified slightly to exploit the fact that Eq. (3.3) is linear].

Having obtained the \( h_{\text{b}} \) functions, the next step requires the evaluation of the \( c_{\text{c}} \) functions and their fourth moments through the application of Eq. (2.2). The linear combination of moments in Eq. (1.5) can be cast into the evaluation of a single four dimensional integral.\(^\text{16} \) This integral, Eq. (2.3), is efficiently performed with the Haselgrove method.\(^\text{16} \) The grid size was adjusted to assure an overall accuracy of \( \pm 0.01 \) in the evaluation of \( g_{\text{c}} \).

The results shown in Fig. 4 and Table I were determined as described above for the same model of liquid CS\(_2\) studied by Impey et al.\(^\text{17} \) The comparison shows that the interaction site formalism is indeed capable of making reasonable predictions of orientational pair correlation factors. It would not be difficult to apply the same theory to a variety

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of liquids. It should also not be difficult to extend the theory to polar fluids along the lines sketched in the previous section. Finally, the principal approximations—retaining only the first term in the molecular ordering scheme, the neglect of attractive site-site interactions and the use of the RISM equation for hard core systems—are all features which can be improved upon in practice. 

APPENDIX

We sketch here the derivation of Eq. (1.3). The starting point is our rewriting of the Sullivan–Gray result for linear molecules as given in Eq. (4.5) of Ref. 11

\[ g_2 = - \frac{1}{\rho} \text{Tr} \chi^{-1} (\chi - 1) \]

where \( \chi = \rho \alpha + \rho \mathbf{n} \). With Eq. (1.1), we have

\[ \frac{1}{\rho} \text{Tr} \chi^{-1} = \text{Tr} \Psi^{-1} \Psi^{-1} \]

\[ + \rho \text{Tr} \Psi^{-1} \left[ 1 - \rho \hat{e}_0(0) \hat{\mathbf{n}}(0) - \hat{e}_0(0) \right] \]

where this result follows from the fact that \( \Omega \) is independent of index at \( k = 0 \), and therefore \( \text{Tr} \Psi \mathbf{n}(0) = 0 \). Furthermore, from Eq. (1.1) at \( k = 0 \), we find

\[ \sum_{n} \left[ \frac{[1 - \rho \hat{e}_0(0) \hat{\mathbf{n}}(0)] - \hat{e}_0(0)}{\alpha_{n}} \right] = \left( k(0) - \Delta(0)/\rho \right) \Omega \]

where the quantities on the right all refer to matrices evaluated at \( k = 0 \) where these matrices are independent of matrix index. With this last result one may show that since for any matrix \( A \),

\[ \sum_{n} A_{n} \left[ \Omega_{n}^{(2)} - \Omega_{n}^{(2)} \right] = \left( \Omega^{2}/\rho \right) \sum_{n} A_{n}, \]

we have

\[ \rho \text{Tr} \Psi^{(2)} \left[ 1 - \rho \hat{e}_0(0) \right] - \hat{e}_0(0) \Omega^{(2)} = \left( 5/4 \right) \left[ k(0) - \Delta(0)/\rho \right]. \]

Equation (1.3) follows straightforwardly from Eqs. (1.1), (2.2), (A5), and (1.1). Similar manipulations lead to Eq. (1.5).

16. L. J. Lowden and D. Chandler, J. Chem. Phys. 64, 5228 (1976); L. J. Lowden, RISM, RISMGR, RIM, Program QCPE 306, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47401.