Derivation of an integral equation for pair correlation functions in molecular fluids

David Chandler

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801
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A new integral equation for equilibrium pair correlation functions in molecular fluids is derived from a systematic functional Taylor expansion. The derivation employs a new Ornstein-Zernike-like equation and a generalization of the functional Taylor expansion techniques frequently employed to derive integral equations for radial distribution functions in simple atomic liquids.

I. INTRODUCTION

In a recent publication, Andersen and this author proposed a new theory to describe the equilibrium pair correlations in classical molecular fluids. The foundation of the theory is an integral equation for the correlation functions of a fluid in which the molecules are composed of fused hard spheres. The equation, which we called the reference interaction site model (RISM) equation, was formulated from heuristic arguments. However, the validity of the arguments was not clear.

More recently the equation has been solved numerically for a few nontrivial molecular models. A report of this work will be published soon. On the basis of consistency tests (i.e., comparing results obtained from different routes to the thermodynamics) it was concluded that the theory is fairly accurate. This success motivated the development of a more systematic derivation of the RISM equation which is the subject of this article.

Section II is used to present definitions of the class of systems under consideration and of the correlation functions that can be used to describe these systems. Some pertinent functional derivative relations are derived in Sec. III. Then the functional Taylor expansion procedure employed to obtain equations for the correlation functions is presented in Sec. IV. The derivation of a new integral equation is given in Sec. V along with a discussion of its relation to the RISM equation of Ref. 1. The paper is concluded in Sec. VI.

II. MOLECULAR MODELS AND STATISTICAL MECHANICAL FUNCTIONS

Throughout this paper we consider a classical one-component fluid, with $N$ molecules in a volume $V$, for which the total potential energy (in the absence of applied fields) can be written as a sum of pair potentials $\omega(i,j)$. Here, $i$ and $j$ denote the positions and orientations of molecules $i$ and $j$, respectively. In particular, let $i$ stand for $\mathbf{R}_i$ (the position of the center of the $i$th molecule) and $\mathbf{N}_i$ (the Euler angles necessary to specify the orientation of the $i$th molecule).

Each molecule contains $m$ interaction sites.

The location of the $s$th site on molecule $j$ is denoted by

$$ r_j^s = \mathbf{R}_j + \mathbf{l}_j^s. \tag{2.1} $$

For simplicity (though not necessity), it will be assumed that a molecule is rigid. Thus, $\mathbf{l}_j^s$ depends on the phase space variable $\mathbf{N}_j$ only, and the magnitude $l^s$ is a constant as are the angles between different $\mathbf{l}_j^s$ vectors within the same molecule.

In the reference interaction site model (RISM), $\omega(1,2)$ is a sum of site-site interactions,

$$ \omega(1,2) = \sum_{\alpha=1}^{m} \sum_{\beta=1}^{m} \omega_{\alpha\beta}(|r_1^\alpha - r_2^\beta|), \tag{2.2} $$

where the $\omega_{\alpha\beta}(r)$ functions are hard sphere interactions,

$$ \omega_{\alpha\beta}(r) = \infty, \quad r < \sigma_{\alpha\beta}, $$

$$ = 0, \quad r \geq \sigma_{\alpha\beta}. \tag{2.3} $$

If the sphere diameters are additive [i.e., $\sigma_{\alpha\beta} = \sigma_\alpha$ and $\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$], then a RISM molecule is composed on $m$ hard spheres with diameters $\sigma_1, \sigma_2, \ldots, \sigma_m$. Since there is no restriction on $l^s$, the spheres may (or may not) overlap. An example of a RISM molecule is depicted in Fig. 1.

When discussing molecular systems with angular dependent forces, it seems natural to describe the intermolecular correlations with the full two-particle distribution function $g(1,2) = g(\mathbf{R}_1, \mathbf{R}_2, \mathbf{N}_1, \mathbf{N}_2)$. However, there is a simpler class of functions, which are averages of $g(1,2)$, that describe all the measurable structural and thermodynamic properties in a molecular fluid; and it is these functions which are treated in this paper. In particular, consider the site-site radial distribution functions defined by
\[ g_{\alpha\beta}(r) = \rho^2 \left\langle \sum_{i \neq j}^N \sum_{i \neq j}^N \delta(r_i^\alpha) \delta(r_j^\beta - r) \right\rangle, \]

(2.4)

where \( \delta(\cdot) \) is the Dirac delta function, the brackets \( \langle \cdots \rangle \) denote the equilibrium ensemble average, and \( \rho = \langle N / V \rangle \) is the average molecular density. The quantity \( 4\pi r^2 g_{\alpha\alpha}(r) \) is the probability distribution for finding a site \( \alpha \) at a distance \( r \) away from the origin, given that a site \( \alpha \) (on another molecule) is located at the origin.

There are three functions related to \( g_{\alpha\alpha}(r) \) that are important in our analysis. First, there is the site-site correlation function, \( h_{\alpha\alpha}(r) \), defined as \( h_{\alpha\alpha}(r) = g_{\alpha\alpha}(r) - 1 \). The Fourier transform of it is

\[ \hat{h}_{\alpha\alpha}(k) = \int dr \, h_{\alpha\alpha}(r) e^{-i\mathbf{k}\cdot\mathbf{r}}. \]

(2.5)

Next, there is the internal structure factor \( \hat{\omega}_{\alpha\alpha}(k) \), defined as

\[ \hat{\omega}_{\alpha\alpha}(k) = \Omega^{-1} \int \, d\Omega \exp[i\mathbf{k} \cdot (\mathbf{l}^\alpha - \mathbf{l}^\beta)] = \sin[k|\mathbf{l}^\alpha - \mathbf{l}^\beta|] / k |\mathbf{l}^\alpha - \mathbf{l}^\beta|. \]

(2.6)

Here, \( \Omega \) is the unweighted integral over Euler angles for one molecule, \( \int d\Omega = \Omega \). The inverse Fourier transform of \( \hat{\omega}_{\alpha\alpha}(k) \) is denoted by \( \omega_{\alpha\alpha}(r) \).

Finally, we define the site-site direct correlation function \( c_{\alpha\alpha}(r) \) by an Ornstein–Zernike-like equation:

\[ h(r) = \omega * c * \omega(r) + \rho \omega * c * h(r). \]

(2.7)

Here, * denotes a convolution and the matrices \( h(r), \omega(r), \), and \( c(r) \) have elements \( h_{\alpha\alpha}(r), \omega_{\alpha\alpha}(r) \), and \( c_{\alpha\alpha}(r) \), respectively. Thus, for example, the first term on the right-hand side of Eq. (2.7) is a matrix with the \( \alpha \beta \) element given by

\[ \sum_{n=1}^m \int dr' \int d\mathbf{r}' \omega_{\alpha\alpha}(r') c_{\alpha\alpha}(|r - r'|) \omega_{\alpha\alpha}(|r' - r'|). \]

The iterative expansion of Eq. (2.7) shows that

\[ h_{\alpha\alpha}(r) = \int d1 \, d2 \, H(1, 2) \delta(r_i^\alpha) \delta(r_j^\beta - r), \]

where \( d1 = \Omega^{-1} \int d\Omega_i d\Omega_i \) and

\[ H(1, 2) = T(1, 2) + \sum_{n=1}^N \rho \int d3 \cdots d(n+2) \]

\[ \times T(1, 3) T(3, 4) \cdots T(n+2, 2), \]

with \( T(1, 2) = \sum_{\alpha, \beta} c_{\alpha\beta} \delta(r_i^\alpha - r_j^\beta) \). The \( c_{\alpha\beta}(r) \) function should not be confused with the full two-particle direct correlation function that is related to \( g(1, 2) \) through the usual Ornstein–Zernike equation. However, it should be noticed that \( c_{\alpha\alpha}(r) \) represents a generalization of the direct correlation function utilized in the theory of simple liquids.

The Fourier transform representation of Eq. (2.7) is

\[ \hat{h}(k) = \hat{\omega}(k) \hat{c}(k) [1 - \hat{\rho} \hat{\omega}(k) \hat{c}(k)]^{-1} \hat{\omega}(k), \]

(2.8)

where \( \hat{A}^{-1} \) denotes the matrix inverse of a matrix \( \hat{A} \), and \( 1 \) is the identity matrix.

The reader is referred to Ref. 1 for alternative discussions of Eqs. (2.7) and (2.8).

III. SOME FUNCTIONAL DERIVATIVE RELATIONS

The density of sites of type \( \alpha \) located at position \( r \) is

\[ \rho_{\alpha}(r) = \sum_{j=1}^N \delta(r - r_j^\alpha). \]

(3.1)

In an isotropic system, \( \langle \rho_{\alpha}(r) \rangle = \rho \). However, the application of a field alters the average of \( \rho_{\alpha}(r) \). Consider a set of potential fields \( \phi_{\gamma}(r) \) which contributes to the potential energy as

\[ \sum_{\gamma} \int dr \rho_{\gamma}(r) \phi_{\gamma}(r). \]

The linear response of \( \langle \rho_{\alpha}(r) \rangle \) to these fields is calculated straightforwardly to give

\[ \delta \langle \rho_{\alpha}(r) / \beta \phi_{\gamma}(r') \rangle_{\beta} = \langle \rho_{\alpha}(r) \rho_{\gamma}(r') \rangle - \rho^2. \]

(3.2)

Here, the derivative on the left-hand side is a functional derivative, \( \beta = (\hbar^2 T)^{-1} \), and subscript 0 denotes that the derivative is evaluated at zero field [i.e., \( \phi_{\gamma}(r) = 0 \)].

By combining Eqs. (3.1) and (3.2) and comparing with Eq. (2.4), one finds that

\[ \delta \langle \rho_{\alpha}(r) / \beta \phi_{\gamma}(r') \rangle_{\beta} = -\rho^2 h_{\alpha\alpha}(|r - r'|) \]

\[ + \rho \omega_{\alpha\alpha}(|r - r'|). \]

(3.3)

The inverse of Eq. (3.3) is calculated from the definition of the inverse, namely,

\[ \delta_{\alpha\beta} \delta(r - r') = \sum_{\gamma} \int dr'' \{ \delta - \beta \phi_{\alpha}(r') / \beta \phi_{\gamma}(r''') \}

\times \{ \delta(r''') / \beta - \beta \phi_{\gamma}(r''') \}, \]

where \( \delta_{\alpha\beta} \) is the Kronecker delta. One finds

FIG. 1. An example of a RISM molecule composed of fused hard spheres. The \( \gamma \)th interaction site is an auxiliary site. (See discussion at the end of Sec. V; since \( |1\beta - 1\gamma| \neq 1\beta / 2 \neq 1\gamma / 2 \), its inclusion does not alter the intermolecular interactions.)
\[
\delta - \beta \phi_\alpha(r')/\delta \langle \rho_\alpha(r) \rangle_\beta = I_{\beta \alpha}(r - r'),
\]
where \(I_{\beta \alpha}(r)\) is the \(\alpha \gamma\) matrix element of
\[
I(r) = (2\pi)^3 \rho^{-1} \int \! dk \left\{ [\omega^{-1}(k) - 1 - \rho \omega(k) \bar{c}(k)] \right\} e^{ik \cdot r}.
\]  

(3.5)

IV. EXPANSION PROCEDURE

In this section, a generalization of a method derived by Percus\(^3\) is introduced as a technique to generate integral equations for \(g_{\alpha \gamma}(r)\).

Focusing attention on molecule \(1\) located at \(R_1\) with orientation \(\Omega_1\), replace the site-site interactions originating from molecule 1 with the arbitrary site-site functions \(\phi_{\alpha \gamma}(r)\). Then the total potential energy for \(N\) molecules is
\[
\sum_{\alpha \gamma} \sum_{i \in N} \phi_{\alpha \gamma}(|r_i - r_i'|) + \sum_{\alpha \gamma} \sum_{i \in N} \epsilon_{\alpha \gamma}(|r_i - r_i'|).
\]

With molecule 1 held fixed, one can regard the potential energy as that of a fluid with \(N - 1\) particles under the influence of the applied fields
\[
\phi_\gamma(r) = \sum_{\alpha} \phi_{\alpha \gamma}(|r - r_i'|).
\]

(4.1)

Let \(\langle \rho_\gamma(r) \rangle_\epsilon\) denote the average density of \(\gamma\) sites at \(r\) for the \(N - 1\) particle system under the influence of the applied fields given by Eq. (4.1). When the \(\phi_{\alpha \gamma}(r)\) functions are set equal to \(\epsilon_{\alpha \gamma}(r)\), one has
\[
\int \! d1 \delta(r_i^\alpha) \langle \rho_\gamma(r) \rangle_{\epsilon \omega_\alpha} = \rho \epsilon_{\alpha \gamma}(r) + 1.
\]

(4.2)

On the other hand, when molecule 1 is “turned off” \(\{\text{i.e., } \phi_{\alpha \gamma}(r) = 0\}\), one has the isotropic fluid result:
\[
\int \! d1 \delta(r_i^\alpha) \langle \rho_\gamma(r) \rangle_{\epsilon \omega_\alpha} = \rho \epsilon_{\alpha \gamma}(r).
\]

(4.3)

Equations (4.2) and (4.3) provide limiting conditions that can be used to calculate \(g_{\alpha \gamma}(r)\) from functional Taylor expansions. As a simple example of the method, assume \(\epsilon_{\alpha \gamma}(r)\) is a weak interaction \(\{\text{rather than a singular one}\}\). Then we can expand
\[
\rho \epsilon_{\alpha \gamma}(r) = \int \! d1 \delta(r_i^\alpha) \langle \rho_\gamma(r) \rangle_{\epsilon \omega_\alpha} = \rho
\]

in a Taylor expansion which is ordered in powers of \(\rho \epsilon_{\alpha \gamma}(r)\):
\[
\rho \epsilon_{\alpha \gamma}(r) = \int \! d1 \delta(r_i^\alpha) \int \! dr' \sum_\eta \left\{ \delta(\rho_\gamma(r'))/\delta \phi_\alpha(r') \right\}_0 \times \left\{ \sum_\nu \epsilon_{\alpha \gamma}(r' - r_\nu) \right\} + \cdots.
\]

The truncation at linear order gives, with Eq. (3.3),
\[
\rho \epsilon_{\alpha \gamma}(r) = \int \! d1 \delta(r_i^\alpha) \int \! dr' \sum_\eta \left\{ \rho \omega_\gamma(r' - r') \right\}_0 \times \left\{ \sum_\nu \epsilon_{\alpha \gamma}(r' - r_\nu) \right\} + \rho^2 \omega_\gamma(r' - r') \left\{ \sum_\nu \epsilon_{\alpha \gamma}(r' - r_\nu) \right\}_0
\]

With the notation defined in Sec. II, this equation can be written as
\[
h(r) = \omega * (-\beta u(r)) + \rho \omega * (-\beta u(r)) * h(r),
\]
which, when compared with Eq. (2.7), gives
\[
c_{\alpha \gamma}(r) = -\beta u_{\alpha \gamma}(r).
\]

This result, of course, is valid only when \(-\beta u_{\alpha \gamma}(r)\) is small. It is derived here simply to demonstrate a general expansion technique. We now turn to the problem of considering physically interesting systems—in particular, fluids composed of RISM molecules in which \(u_{\alpha \gamma}(r)\) is a hard sphere interaction.

V. DERIVATION OF THE REFERENCE INTERACTION SITE MODEL EQUATION

There are a large number of possible expansions (and thus integral equations) that can be generated with the method outlined in the previous section. The one used below is motivated by the expansion used by Percus to derive the Percus–Yevick equation.\(^3\)

Consider the quantity
\[
Q_{\alpha \gamma}(r, \psi) = \langle \rho_\gamma(r) \rangle_{\epsilon \omega_\alpha} \int \! d1 \! d2 \! d3 \delta(r_i^\alpha) \delta(r_i^\beta - r)
\]
\[
\times \exp \left\{ -\beta \sum_\gamma \phi_\gamma(r_i^\alpha - r_i^\gamma) \right\} \right|_{\psi = 1}.
\]

(5.1)

At the end points
\[
\int \! d1 \delta(r_i^\alpha) Q_{\alpha \gamma}(r, \psi = 0) = \rho,
\]
and
\[
\int \! d1 \delta(r_i^\alpha) Q_{\alpha \gamma}(r, \psi = \psi_0) = \rho g_{\alpha \gamma}(r) \left[ \tilde{f}_{\alpha \gamma}(r) + 1 \right]^{-1},
\]

(5.3)

where
\[
\tilde{f}_{\alpha \gamma}(r) = \int \! d1 \! d2 \delta(r_i^\alpha) \delta(r_i^\beta - r)
\]
\[
\times \left\{ \exp \left\{ -\beta \sum_\gamma u_{\alpha \gamma}(r_i^\alpha - r_i^\gamma) \right\} - 1 \right\}
\]

(5.4)

is the average Mayer cluster function when site \(\alpha\) on molecule 1 and site \(\gamma\) on molecule 2 are held fixed a distance \(r\) away from each other.

Rather than expand \(Q_{\alpha \gamma}(r, \psi)\) in powers of the stimulus, we follow Percus\(^3\) and anticipate more rapid convergence if we expand in powers of the response \(\langle \rho_\gamma(r) \rangle_{\psi = 0} - \rho\):
\[
\rho g_{\alpha \gamma}(r) \left[ \tilde{f}_{\alpha \gamma}(r) + 1 \right]^{-1} - \rho
\]
PAIR CORRELATION FUNCTIONS IN FLUIDS

\[ = \int \delta(\mathbf{r}) \left\{ \int d\mathbf{r}' \sum_q [\delta Q_{\alpha \beta}(\mathbf{r}, \mathbf{r}')/\delta \rho_\alpha(\mathbf{r}')] \right\} \times (\rho_\alpha(\mathbf{r}')) - \rho \right\} + \cdots \right\} \]  \tag{5.5}

Truncation at linear order and the application of Eq. (3.4) and (3.5) give

\[ \rho g_{\alpha \beta}(r) [\bar{f}^{\alpha \beta}(r) + 1]^{-1} = \rho 2g_{\alpha \beta}(r) \left[ c_{\alpha \beta}(r) \bar{f}^{\alpha \beta}(r) \right] \]  \tag{5.6}

By comparing Eq. (5.6) with (2.7), one concludes that

\[ \omega \ast c \ast \omega(r) = y_{\alpha \beta}(r) \bar{f}^{\alpha \beta}(r) \]  \tag{5.7}

where

\[ y_{\alpha \beta}(r) = g_{\alpha \beta}(r) \left[ \bar{f}^{\alpha \beta}(r) + 1 \right]^{-1} \]  \tag{5.8}

is a noninfinite function for all \( r \).

Equation (5.7) is the principal result of this article. When combined with Eq. (2.7), it forms a closed integral equation for \( g_{\alpha \beta}(r) \) once the site-site interactions \( u_{\alpha \beta}(r) \) are specified. We are particularly interested in the case in which \( u_{\alpha \beta}(r) \) is a hard sphere potential. In that case, \( \bar{f}^{\alpha \beta}(r) = -1 \) for \( r < \sigma_{\alpha \beta} \). This means that \( h_{\alpha \beta}(r) = -1 \) for \( r < \sigma_{\alpha \beta} \).

Further \( \bar{f}^{\alpha \beta}(r) = 0 \) for \( r > R_{\alpha \beta} \), where \( R_{\alpha \beta} \) is determined from the geometry of the RISM molecules. (For example, for a molecule composed of two hard spheres separated by a distance \( L \), \( R_{\alpha \beta} = \sigma_{\alpha \beta} + 2L \).) As a result, Eq. (5.7) gives [\( \omega \ast c \ast \omega(r) \) at all \( r > R_{\alpha \beta} \). It is straightforward to show that one way of satisfying this condition is to have \( c_{\alpha \beta}(r) = 0 \) for all \( r > R_{\alpha \beta} \). If it is assumed that \( c_{\alpha \beta}(r) \) does vanish for \( r > R_{\alpha \beta} \), we then have the closure relations

\[ c_{\alpha \beta}(r) = 0 \quad r > R_{\alpha \beta} \]  \tag{5.9a}

and

\[ h_{\alpha \beta}(r) = -1 \quad r < \sigma_{\alpha \beta} \]  \tag{5.9b}

Equations (5.9) together with Eq. (2.7) form the RISM equation originally presented in Ref. 1. It is emphasized that Eqs. (5.9) are an approximation to Eq. (5.7). The reason is as follows: It is true that Eq. (5.9a) satisfies the requirement [imposed by (5.7)] that \( \omega \ast c \ast \omega(r) \) vanish for \( r > R_{\alpha \beta} \); however, it is not true that the requirement implies Eq. (5.9a).

There are four important features of Eq. (5.7). First, in the low density limit, the equation states that

\[ \lim_{\rho \to 0} h_{\alpha \beta}(r) = \bar{f}^{\alpha \beta}(r) \]

which is the exact low density form.

Second, the equation can be used to calculate the pair correlation function between any point within one molecule and any point within another molecule. This is done by using auxiliary sites. An auxiliary site is an interaction site whose removal does not change the total pair potential \( \omega(1, 2) \). (For example, consider a RISM molecule composed of fused hard spheres; i.e., the hard core diameters are additive. If one of the spheres is entirely enveloped by another, the interaction site associated with the enveloped sphere is an auxiliary site. See Fig. 1.) By definition, the presence of an auxiliary site does not alter \( \bar{f}^{\alpha \beta}(r) \); thus it does not alter \( c_{\alpha \beta}(r) \). As a result, if the RISM equation is used as an approximation to Eqs. (5.7) and (2.7) one may solve the RISM equation in the absence of auxiliary sites. Then, the correlation function between auxiliary sites can be computed from Eq. (2.8) with \( \tilde{c}_{\alpha \beta}(k) = 0 \) (where \( k \) and/or \( \nu \) are auxiliary sites) and with \( \tilde{c}_{\alpha \beta}(k) \) remaining unchanged (where neither \( k \) nor \( \nu \) is an auxiliary site). Third, the simplicity of Eq. (5.7) is striking. It provides a means of calculating properties of complicated molecular models in terms of a one-dimensional integral equation. An interesting aspect of the RISM approximation [Eqs. (5.9) and (2.7)] to the integral equation is that it can be cast into the form of a nonlinear variational problem. The variational formulation is presented in Eqs. (4.13) and (4.15) of Ref. 1 and will not be duplicated here. It might be worthwhile, however, for the reader to know that the variational problem can be solved extremely rapidly. (For a molecule composed of two fused hard spheres, an IBM 360/75 computer can solve the RISM equation in 20 sec—even at very high densities.)

Finally, it should be noted that Eq. (5.7) reduces to the Percus–Yevick equation when the interaction sites within a molecule become concentric and/or all but one interaction site become auxiliary sites. In that same limit, the RISM equation becomes the Percus–Yevick equation for hard spheres.

VI. CONCLUSION

In summary, this paper presents (1) a generalization of the Ornstein–Zernike equation [Eqs. (2.7) and (2.8)]? (2) a generalization of Percus’ functional Taylor expansion method in Sec. IV; and (3) a systematic derivation of a computationally convenient integral equation in Sec. V.

There are a few generalizations of the developments given here that can be briefly described. Real molecules differ from a RISM molecule in at least three ways. First, real molecules are not rigid. The feature of rigidity can be removed by generalizing the definition of the internal structure factor so that the right-hand side of Eq. (2.8) becomes \( \exp[i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')] \). In general, the single particle average includes an average over vibrational states as well as an average over \( \Omega \).
Second, real molecules contain attractive forces. These can be added to $u_\alpha(r)$. One way of including their effects in a theory for $h_\alpha(r)$ is to use the weak interaction form for $c_\alpha(r')$ outside the hard cores (see end of Sec. III). Within the context of the RISM equation, this perturbation-like approach leads to the closure relations $c_\alpha(r) = -\beta u_\alpha(r)$ for $r > \sigma_\alpha$ and $g_\alpha(r) = 0$ for $r < \sigma_\alpha$. When combined with Eq. (2.7), they form an integral equation (which was also presented in Ref. 1) that is analogous to the mean spherical model equations.  

Third, real molecules contain harsh repulsive forces that are only approximately hard core interactions. The inclusion of realistic repulsions into the present theory can be done with the aid of a simple generalization of the blip function expansion, which provides a means to generate the properties of fluids with realistic repulsive forces once the properties of hard core molecules are known.

It is hoped that all of these generalizations as well as applications to liquid crystals will be pursued in future publications.

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3 L. Lowden and D. Chandler (unpublished).