Optimized Cluster Expansions for Classical Fluids. II. Theory of Molecular Liquids*

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The optimized cluster expansion methods developed in the first article of this series (I) are generalized to apply to molecular fluids. These methods make use of summations of ring and chain cluster diagrams. The summations are performed explicitly for certain classes of molecular models. The molecules in these classes contain several "interaction sites," and the total interaction between two molecules is a sum of site-site potentials that depend on the scalar distances between sites on the two molecules. The principal results of this work are computationally simple techniques for calculating the thermodynamic properties and pair correlation functions of molecular fluids in which the intermolecular interactions are highly angular dependent. The techniques should be reliable since they arise from the same approximations that have been shown to be very accurate when applied to simple fluids.

I. INTRODUCTION

In the preceding paper (I), methods are presented for calculating the equilibrium properties of classical fluids. The methods are based on the procedure of summing ring and chain cluster diagrams, which was introduced by Mayer in his pioneering work on ionic solutions. As explicitly demonstrated in Paper I, these summations can be performed when the intermolecular interactions depend on intermolecular separations only. They can also be performed for some fluids in which the intermolecular forces are dependent also on the molecular orientations. The purposes of this paper are: (1) to demonstrate how the ring and chain summations can be calculated for certain classes of molecular models, and (2) to employ the ideas described in I to formulate theories for molecular fluids.

Ring and chain summations for molecules have already been used to investigate polar fluids. Except for Ref. 6, previous work of this type has been limited to models in which the potential energy between pairs of molecules can be accurately represented by a few terms in a general multipole expansion. But the models we study are of a more general form. We imagine that a molecule contains several sites, and the total interaction between two molecules is a sum of site-site interactions that depend on the distances between sites on the two molecules. Since molecules are composed of atoms, such models are probably good representations of reality for many polar and nonpolar molecules. Indeed, this is strongly indicated by the work of Steele and his co-workers.

There is another feature that distinguishes the present work from some earlier contributions. Ring and chain summations lead to approximations which are expressed in terms of a renormalized potential. As discussed in I, the usefulness and accuracy of these approximations is greatly dependent upon the choice of the renormalized potential. For simple liquids there is an optimal choice which leads to rapidly convergent cluster series and hence gives rise to accurate approximations when the series are truncated. In this paper we generalize the optimization procedure to molecular models. The ring and chain summations are usually used when it is felt that the long ranged forces make important contributions to the properties of fluids. These summations describe, rather conveniently, screening of the long ranged forces by the long ranged many-body behavior of the particles. But at moderate and high densities, the short ranged harshly repulsive forces also contribute to the screening, and the optimal renormalized potential can be used to take this effect into account. The resulting theories differ significantly from those obtained without optimization. This fact is illustrated by Wertheim's comparison of the results obtained from his solution of the mean spherical model equation for dipolar hard spheres (which utilizes a form of optimization) with the Jepsen-Friedman results (obtained without optimization).

Nienhuys and Deutch have used methods similar to those discussed in Sec. II of Paper I to discuss polar fluids. At this stage of their work, they have established a link between classical electrostatics and the statistical mechanics of dielectric liquids. They examine those effects in a dielectric fluid which are dependent on the size and shape of the sample (which we do not study herein since we confine our calculations to infinite systems). Further they present formal graphical expressions for properties such as the dielectric constant. Evaluation of these expressions requires a method for calculating the effect of excluded volumes, short ranged angular forces, and longer ranged electrostatic interactions upon the structure of a fluid. The techniques discussed in this paper can be used for such a calculation.

Section II presents definitions of the two models studied herein. The theories for the models are given in Secs. III and IV. Concluding remarks are contained in Sec. V.
II. DEFINITIONS OF MODELS AND STATISTICAL MECHANICAL FUNCTIONS

A. Models

Consider a one-component fluid, with \( N \) molecules in a volume \( V \), for which the total potential energy can be written as a sum of pair potentials \( w(i,j) \). 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 \( \Omega_i \) (the Euler angles required to specify the orientation of the \( i \)th molecule).

There are two classes of models for \( w(i,j) \) which are treated in this paper. We call them the embedded site and interaction site models. For both, it is convenient to consider sites in a molecule. The position of the \( \alpha \)th site on the \( j \)th molecule is denoted by

\[
\mathbf{r}_{\alpha}^j = \mathbf{R}_j + \mathbf{l}_\alpha^j.
\]

The molecules are assumed to be rigid. Thus, \( \mathbf{l}_\alpha^j \) depends on the phase space variables \( \Omega_j \) only. The magnitude \( |l_\alpha| \) is constant as are the angles between different \( \mathbf{l}_\alpha^j \) vectors within the same molecule. The interaction between two molecules is assumed to depend only on the distances between sites on the two molecules. Since some sites are located away from the molecular center, the forces are noncentral and may be highly anisotropic.

1. Embedded Site Model

In this model, each molecule is a hard sphere of diameter \( d \) with \( m \) embedded sites (i.e., \( l_\alpha < d/2 \) for \( \alpha = 1, \ldots, m \)). The site \( \alpha = 1 \) is taken to be the center of the molecule; that is, \( l_0 = 0, \mathbf{r}_1 = \mathbf{R}_1 \). The pair potential for the model is

\[
w_{\text{ES}}(1, 2) = u_d(|\mathbf{R}_1 - \mathbf{R}_2|) + \sum_{\alpha=1}^{m} \sum_{\gamma=1}^{m} u_{\text{av}}(|\mathbf{r}_\alpha^1 - \mathbf{r}_\gamma^2|),
\]

where

\[
u_d(R) = \begin{cases} \infty, & r \leq d, \\ 0, & r > d. \end{cases}
\]

The \( u_{\text{av}}(r) \) interactions are the perturbation interactions. The hard sphere potential \( u_d(R) \) is the reference potential. Figure 1 shows a schematic picture of an embedded site molecule.

2. Interaction Site Model

In this model, a molecule is composed of \( m \) rigidly connected hard spheres (the spheres within a molecule may overlap). The \( \alpha \)th sphere has diameter \( d_\alpha \) and is located at the \( \alpha \)th site. Further, perturbation interactions between sites on different molecules are also present. The pair potential for this model is

\[
w_{\text{IS}}(1, 2) = \sum_{\alpha=1}^{m} \sum_{\gamma=1}^{m} w_{\text{av}}(|\mathbf{r}_\alpha^1 - \mathbf{r}_\gamma^2|),
\]

where

\[
w_{\text{av}}(r) = u_{\text{av}}(r) + u_{\text{av}}(r).
\]

Here, \( u_{\text{av}}(r) \) is the hard sphere potential with diameter \( d_{\alpha \gamma} \), and \( u_{\text{av}}(r) \) is the perturbation. Figure 2 shows a schematic picture for an interaction site molecule.

B. Statistical Mechanical Functions

The Helmholtz free energy for these molecular systems can be obtained from the canonical ensemble partition function. In particular, employing the notation used in I, we write

\[
\mathcal{A} = -(k_B T)^{-1} \Delta A = V^{-1} \ln Q,
\]

\[
Q = \langle V \Omega \rangle^{-N} \int d\mathbf{R}^N d\Omega^N \exp \left[ - \sum_{i<j}^N w(i,j)/k_B T \right],
\]

where \( \Omega \) denotes the unweighted integral over Euler angles for one molecule, \( \int d\Omega_i = \Omega \).

When discussing molecular systems with angular dependent forces, it is natural to describe the intermolecular correlations with the full two-particle distribution function \( g(\mathbf{R}, \Omega, \Omega') \) defined by

\[
\langle \rho/\Omega \rangle^{N} g(\mathbf{R}, \Omega, \Omega')
\]

\[
= (\sum_{i=1}^N \sum_{j=1}^N \delta(\mathbf{R}_i - \mathbf{R}_j) \delta(\Omega_i - \Omega) \delta(\Omega_j - \Omega')), \tag{2.5}
\]

where \( \langle \cdots \rangle \) denotes ensemble average. For the embedded site and interaction site models, it is also convenient to consider the site-site radial distribution
function $g^{\alpha \gamma}(r)$,

$$
\rho^\alpha g^{\alpha \gamma}(r) = \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(r_{i}^{\alpha}) \delta(r_{j}^{\gamma} - r)
$$

$$
\times \rho^\gamma g^{\alpha \gamma}(R - R', \Omega, \Omega')
\times \delta(R + 1^\alpha(\Omega') - r). \tag{2.6}
$$

These distribution functions are related to the free energy by the following functional derivative relations:

$$
g(R, \Omega, \Omega') = - \left( \frac{2k_B T}{\rho^\alpha} \right)^{\gamma} \left[ \frac{\partial \omega}{\partial R} (R, \Omega, \Omega') \right],
$$

$$
g^{\alpha \gamma}(r) = - \left( \frac{2k_B T}{\rho^\alpha} \right)^{\gamma} \left[ \partial \omega / \partial u_{\alpha \gamma}(r) \right]. \tag{2.7}
$$

The cluster expansions employed to discuss simple fluids can be carried over to molecular fluids by making one, essentially notational, generalization. Whenever an integration over a particle position appears in the cluster expansion for simple fluids (i.e., whenever a black $\rho$ circle appears), the appropriate integral for a molecular fluid is $(\rho / \Omega) \int dR d\Omega$; that is,

$$
\rho^{\alpha} \int dR d\Omega \approx (\rho / \Omega) \int dR d\Omega. \tag{2.8}
$$

In the following two sections, the cluster expansions developed in I will be applied to the embedded site and interaction site models. The embedded site model is considered in Sec. III, and the interaction site model is treated in Sec. IV.

III. THEORY FOR EMBEDDED SITE MODEL

A. Generalized Ring and Chain Summations

In order to apply the methods developed in Paper I to the embedded site model, formulas for summing rings and chains must be derived. The reference system in this model is the hard sphere fluid. The ring diagrams discussed in I contain perturbation bonds and $h_\alpha$ bonds. All the ring diagrams involving $n$ perturbation bonds are conveniently written as one generalized ring by introducing $F_d(1, 2)$ which is defined as

$$
F_d(1, 2) = (\rho / \Omega) \delta(R_1 - R_2) \delta(\Omega_1 - \Omega_2)
$$

$$
+ (\rho / \Omega) \sum_{\lambda} h_{\lambda}(R_1 - R_2). \tag{3.1}
$$

This function is simply the generalization of the hyper-vertex function $F_d(r) = \rho^0(r) + \rho^0 h_{\alpha}(r)$ appearing in I. The generalized ring involving $n$ perturbation bonds is

$$
\rho^{(n)} = (2nV)^{-1} \int d\Omega(1) d(2) \cdots d(2n)
$$

$$
\times \sum_{\alpha, \gamma} \sum_{\lambda} \sum_{\tau} \Phi_{\alpha \gamma}(1, 2) F_d(2, 3)
$$

$$
\times F_d(3, 4) \cdots \Phi_{\alpha \gamma}(2n - 1, 2n) F_d(2n, 1), \tag{3.2}
$$

where

$$
\Phi_{\alpha \gamma}(1, 2) = - u_{\alpha \gamma}(|r_1^{\alpha} - r_2^{\gamma}|) / k_B T. \tag{3.3}
$$

It should be understood that the summations over Greek letters denote sums over embedded sites; thus each summation variable goes from 1 to $m$.

We assume the Fourier transform of $u_{\alpha \gamma}(r)$ exists, and hence $\phi_{\alpha \gamma}(1, 2)$ can be expressed as

$$
\phi_{\alpha \gamma}(1, 2) = (2\pi)^{-1} \int d\kappa \phi_{\alpha \gamma}(\kappa) \exp[i \kappa \cdot (r_1^{\alpha} - r_2^{\gamma})]. \tag{3.4}
$$

By inserting Eq. (3.4) into Eq. (3.2), one obtains, for example,

$$
\rho^{(n)} = (6V)^{-1} (2\pi)^{-1} \int d(1) \cdots d(6) \int d\kappa_0 d\kappa_1 d\kappa_2
$$

$$
\times \sum_{\alpha, \gamma} \sum_{\lambda} \sum_{\tau} \phi_{\alpha \gamma}(\kappa_0) \phi_{\lambda \alpha}(\kappa_1) \phi_{\gamma \lambda}(\kappa_2) F_d(2, 3) F_d(4, 5) F_d(6, 1)
$$

$$
\times \exp[i \kappa_0 \cdot (r_1^{\alpha} - r_2^{\gamma}) + i \kappa_1 \cdot (r_3^{\beta} - r_4^{\gamma}) + i \kappa_2 \cdot (r_5^{\alpha} - r_6^{\beta})].
$$

The integrals over configurations are performed by recalling that $r^\alpha = R^\alpha + \lambda r^\alpha$, and as a result

$$
(2\pi)^{-1} \int d(1) d(2) F_d(i, j) \exp[-i \mathbf{k} \cdot (r_i^\alpha + r_j^\beta)]
$$

$$
= \delta(\mathbf{k} + \mathbf{\Gamma}^\alpha) \left[ \rho_{\alpha \beta}(k) + \rho_{\alpha \beta}(\kappa) \sigma (\kappa) \right] \Gamma_{\alpha \beta}(k),
$$

$$
= \delta(\mathbf{k} + \mathbf{\Gamma}^\alpha) \Gamma_{\alpha \beta}(k), \tag{3.5}
$$

where

$$
\omega_{\alpha \beta}(k) = (\Omega - 1)^{-1} \int d\Omega \exp[i \mathbf{k} \cdot (1^\alpha - 1^\beta)]
$$

$$
= \sin(k |1^\alpha - 1^\beta|) / |1^\alpha - 1^\beta|, \tag{3.6}
$$

and

$$
\rho_{\alpha \beta}(k) = (\Omega - 1)^{-1} \int d\Omega \exp[i \mathbf{k} \cdot \mathbf{1}^\alpha]
$$

$$
= \sin(k \mathbf{1}^\alpha) / |1^\alpha| \mathbf{1}^\alpha. \tag{3.7}
$$

By using Eq. (3.5), $\rho^{(n)}$ reduces to

$$
\rho^{(n)} = [6(2\pi)^{-1} \int d\kappa \sum_{\alpha, \gamma} \sum_{\lambda} \sum_{\tau} \phi_{\alpha \gamma}(\kappa) \phi_{\lambda \alpha}(\kappa) \phi_{\gamma \lambda}(\kappa) \Gamma_{\alpha \beta}(k) \Gamma_{\alpha \beta}(k) \Gamma_{\alpha \beta}(k)]^n,
$$

$$
= [6(2\pi)^{-1} \int d\kappa \text{Tr}[\hat{\Phi}(\kappa) \Gamma(\kappa)]^n, \tag{3.8}
$$

where Tr denotes the trace of a matrix, and $\hat{\Phi}(\kappa)$ and $\Gamma(\kappa)$ are $m \times m$ matrices with elements $\phi_{\alpha \gamma}(\kappa)$ and $\Gamma_{\alpha \beta}(\kappa)$, respectively.

The evaluation of the general $\rho^{(n)}$ follows from the same procedure used above. The result is

$$
\rho^{(n)} = [2n(2\pi)^{-1} \int d\kappa \text{Tr}[\hat{\Phi}(\kappa) \Gamma(\kappa)]^n, \tag{3.9}
$$

The summation of all the generalized rings ($n \geq 2$) is now conveniently performed to give

$$
\rho_{\text{RING}} = \sum_{n=2}^{\infty} \rho^{(n)} = - \left[ 2 \right] (2\pi)^{-1} \int d\kappa \text{Tr}[\Gamma(\kappa) \hat{\Phi}(\kappa)]
$$

$$
+ \ln \det[1 - \Gamma(\kappa) \hat{\Phi}(\kappa)], \tag{3.9}
$$

where det denotes the determinant of a matrix, and 1 is the $m \times m$ identity matrix. When deriving Eq. (3.9), it is useful to note that $\text{Tr}(\kappa \kappa') = \ln \det(\kappa \kappa')$ for any diagonalizable matrix $\kappa$. In I, we discussed generalized chains as well as generalized rings. The generalized chain between mole-
THE FOURIER INTEGRAL REPRESENTATION OF PHIV (r), EQUATION (3.4), CAN BE USED IN WHICH CASE CIV (1, 2), FOR EXAMPLE, IS

\[ C^{(1, 2)} = (\rho/\Omega)^{-1} (2\pi)^{-1} \int d^3 d^3 (2n+2) \]

\[ \times \sum_{\mathbf{k}, \mathbf{k}_1} \sum_{\mathbf{r}, \mathbf{r}_1} F_d(1, 3) \phi_{\mathbf{v}}(\mathbf{r}_1, \mathbf{r}, \mathbf{k}_1, \mathbf{k}) F_d(4, 5) F_d(6, 2) \]

\[ \times \exp[i \mathbf{k}_1 \cdot (\mathbf{r}_1 - \mathbf{r}) + i \mathbf{k}_2 \cdot (\mathbf{r}_2 - \mathbf{r}_1)]. \]

The integrations over the configurations of molecules 4 and 5 are done with the aid of Eq. (3.5) to give

\[ C^{(2)} = (\rho/\Omega)^{-1} (2\pi)^{-1} \int d^3 d^3 (2n+2) \]

\[ \times \sum_{\mathbf{k}, \mathbf{k}_1} \sum_{\mathbf{r}, \mathbf{r}_1} \phi_{\mathbf{v}}(\mathbf{r}_1, \mathbf{k}_1) \Gamma(\mathbf{r}, \mathbf{k}_1) \]

\[ \times F_d(1, 3) F_d(6, 2) \exp[i \mathbf{k}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)]. \]

The remaining integrations are done simply if \( F_d(1, 3) \) and \( F_d(6, 2) \) are represented by Fourier integrals; that is,

\[ F_d(1, 3) = (2\pi)^{-1} \int d^3 \mathbf{k} \left[ (\rho/\Omega) \delta(\mathbf{R}_1 - \mathbf{R}_3) + (\rho/\Omega) h(\mathbf{k}) \right] \]

\[ \times \exp[i \mathbf{k} \cdot (\mathbf{R}_1 - \mathbf{R}_3)]. \]

With this formula, one finds

\[ C^{(1, 2)} = (2\pi)^{-1} \int d^3 \mathbf{k} \sum_{\mathbf{r}} \left[ \frac{\partial}{\partial \mathbf{r}} \right] \Gamma(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \left[ \frac{\partial}{\partial \mathbf{r}} \right] \frac{\partial}{\partial \mathbf{r}} \exp(-i \mathbf{k} \cdot \mathbf{r}) \]

\[ \times \left[ 1 + \rho \alpha(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \right] \exp(-i \mathbf{k} \cdot \mathbf{r}). \]

The generalized chain with \( n \) perturbation bonds is analyzed in the same way. The result is

\[ C^{(1, 2)} = (2\pi)^{-1} \int d^3 \mathbf{k} \sum_{\mathbf{r}} \left[ \frac{\partial}{\partial \mathbf{r}} \right] \Gamma(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \left[ \frac{\partial}{\partial \mathbf{r}} \right] \frac{\partial}{\partial \mathbf{r}} \exp(-i \mathbf{k} \cdot \mathbf{r}) \]

\[ \times \left[ 1 + \rho \alpha(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \right] \exp(-i \mathbf{k} \cdot \mathbf{r}). \]

Thus, the sum over all generalized chains \( (n \geq 1) \) gives

\[ C(1, 2) = \sum_{n=1}^{\infty} C^{(n)}(1, 2) \]

\[ = \sum_{n=1}^{\infty} (2\pi)^{-1} \int d^3 \mathbf{k} \left[ \frac{\partial}{\partial \mathbf{r}} \right] \Gamma(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \left[ \frac{\partial}{\partial \mathbf{r}} \right] \frac{\partial}{\partial \mathbf{r}} \exp(-i \mathbf{k} \cdot \mathbf{r}) \]

\[ \times \left[ 1 + \rho \alpha(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \right] \exp(-i \mathbf{k} \cdot \mathbf{r}). \]

By making use of our convention that site 1 is at the center of the sphere (I.e., \( \mathbf{r}_1 = \mathbf{R}_i \)), Eq. (3.12) can be expressed in the convenient form

\[ C(1, 2) = \sum_{n=1}^{\infty} C_{n\rho}(\mathbf{r}_1, \mathbf{r}_2) \]

\[ \times \exp[i \mathbf{k}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)]. \]

Here, \( A(\mathbf{k}) \) is the matrix

\[ A(\mathbf{k}) = 1 + \rho \mathbf{H}(\mathbf{k}) \mathbf{a}(\mathbf{k}), \]

where \( \mathbf{H}(\mathbf{k}) \) is the matrix with elements

\[ H_{av}(\mathbf{k}) = \delta_{av} \delta_{av} \delta(\mathbf{R}_1 + \mathbf{R}_2 - \mathbf{r}). \]

In addition to the sum of generalized chains, given in Eqs. (3.12)–(3.12''), which is dependent upon the orientations and separation of the two molecules, another function is also of interest. This function is obtained by holding one site on 1 and another site on 2 fixed and averaging \( C(1, 2) \) over all orientations of the two molecules. The precise definition is

\[ \bar{C}_{av}(\mathbf{r}) = \Omega^{-2} \int d^3 d^3 (2n+2) \]

\[ \times \delta(\mathbf{R}_1 + \mathbf{R}_2 - \mathbf{r}). \]

This function depends only on the separation between the two sites, and it should be noted that it is distinctly different from \( C_{av}(\mathbf{r}) \) introduced in (3.12'). By employing Eq. (3.12) and performing the integrations in Eq. (3.13), one finds

\[ \bar{C}_{av}(\mathbf{r}) = \rho^{-2} (2\pi)^{-1} \int d^3 \mathbf{k} \exp(-i \mathbf{k} \cdot \mathbf{r}) \]

\[ \times \left[ (\Gamma(\mathbf{k}) \hat{\Phi}(\mathbf{k}) [1 - \Gamma(\mathbf{k}) \hat{\Phi}(\mathbf{k})]^{-1} \Gamma(\mathbf{k}) \right] \hat{\Phi}(\mathbf{k}). \]

The same result can also be obtained by taking a functional derivative of the sum of generalized rings. In particular, by employing Eq. (3.9) one finds

\[ \bar{C}_{av}(\mathbf{r}) = (2/\rho)^2 [\partial \phi_{av}(\mathbf{r})/\partial \phi_{av}(\mathbf{r})] \]

\[ \times (\text{Tr} \Gamma(\mathbf{k}) \hat{\Phi}(\mathbf{k}) + \ln \det[1 - \Gamma(\mathbf{k}) \hat{\Phi}(\mathbf{k})]) \]

\[ \times (\Gamma(k) \hat{\Phi}(k) [1 - \Gamma(k) \hat{\Phi}(k)]^{-1} \Gamma(k) \hat{\Phi}(k)) \]

\[ \times [1 - \Gamma(\mathbf{k}) \hat{\Phi}(\mathbf{k})]^{-1} \Gamma(\mathbf{k}) \hat{\Phi}(\mathbf{k})]. \]

To derive the last equality in Eq. (3.15), it is useful to note that \( \hat{\Phi}(\mathbf{k}) \) and \( \Gamma(\mathbf{k}) \) are symmetric matrices.

B. Equations for the Free Energy and Distribution Functions

The principal approximations discussed in Paper I are the ORPA and the ORPA+B2 approximations for the free energy and the ORPA and the exponential approximations for the two-particle distribution function. These approximations represent truncations of formally exact infinite cluster expansions and are opti-
mized in the sense that they are to be evaluated using a perturbation which inside the core is chosen so as to satisfy an optimization condition. This condition makes the infinite cluster series converge more quickly than they would without optimization, and it also eliminates unphysical divergences associated with ring and chain sums. For the embedded site model these approximations are

$$\varrho_{\text{ORPA}} = \varrho_{\text{HTA}} + \varrho_{\text{RING}},$$  \hspace{1cm} (3.16)

$$\varrho_{\text{ORPA}+B_2} = \varrho_{\text{ORPA}} + B_2,$$  \hspace{1cm} (3.17)

$$g_{\text{ORPA}}(R_{12}, \Omega_1, \Omega_2) = g_d(R_{12}) + \mathcal{C}(1, 2),$$  \hspace{1cm} (3.18)

$$g_{\text{exp}}(R_{12}, \Omega_1, \Omega_2) = g_d(R_{12}) \exp[\mathcal{C}(1, 2)],$$  \hspace{1cm} (3.19)

where

$$\varrho_{\text{HTA}} = \varrho_d + \frac{1}{2} \frac{(\rho/\Omega)^2}{(\partial^2 \varrho/\partial \Omega^2)} \sum_{\alpha \gamma} V_{\alpha \gamma}^*(d(1) d(2)) \times \mathcal{C}(R_{12}) \phi_{\gamma \alpha}(|r_{\alpha \gamma} - r_{\gamma \alpha}|),$$

$$= \varrho_d + \frac{1}{2} \rho^2 \sum_{\alpha \gamma} \left[ \phi_{\gamma \alpha}(0) + (2\pi)^{-3} \times \int d \Omega \phi_{\gamma \alpha}(k) \phi_{\gamma \alpha}(k) z_{\alpha \gamma}(k) z_{\gamma \alpha}(k) \right],$$  \hspace{1cm} (3.20)

$$B_2 = \frac{1}{2} \frac{(\rho^2/\Omega)^2}{(\partial^2 \varrho/\partial \Omega^2)} \int dR_{12} d\Omega_1 d\Omega_2 g_d(R_{12}) \times \left[ \mathcal{C}(1, 2) + (1, 2) - \frac{1}{2} (\partial^2 \varrho/\partial \Omega^2) \right]$$

$$+ \frac{1}{2} \frac{(\rho^2/\Omega)^2}{(\partial^2 \varrho/\partial \Omega^2)} \int dR_{12} d\Omega_1 d\Omega_2 h_d(R_{12}) \times \left[ \mathcal{C}(1, 2) + (1, 2) - \frac{1}{2} (\partial^2 \varrho/\partial \Omega^2) \right],$$  \hspace{1cm} (3.21)

and the remaining functions, \( \varrho_{\text{RING}} \) and \( \mathcal{C}(1, 2) \), are given in Eqs. (3.9) and (3.12), respectively. By averaging over \( g_{\text{ORPA}} \) [see Eq. (2.6)], or equivalently by taking a functional derivative [Eq. (2.7)], one also has

$$g_{\text{ORPA}}(r) = \int g_d(|r - l_{\alpha \gamma} - l_{\gamma \alpha}|) d\Omega_1 d\Omega_2 / \Omega^2 + \bar{c}_{\alpha \gamma}(r),$$  \hspace{1cm} (3.22)

where \( \bar{c}_{\alpha \gamma}(r) \) is given in Eq. (3.14).

The simplicity of these equations is remarkable. They represent generalizations, to the case of highly anisotropic molecules, of formulas which can be very accurate when applied to atomic liquids. Nevertheless, the numerical procedures required by these equations are just inversion of \( m \times m \) matrices and one dimensional Fourier transform integrations except for \( B_2 \), while the calculation for \( B_2 \) is comparable in difficulty to the calculation of a molecular second virial coefficient. Thus they offer a very practical approach to the statistical mechanical study of dense molecular liquids, and there is good reason to expect that they, like their atomic counterparts, will be quite accurate if the perturbation potential for physically impossible separations is chosen properly, that is, if the appropriate optimization conditions for ESM molecules can be found.

C. Optimal Choice of the Perturbation Potentials

The quantities \( \varrho_{\text{RING}} \) and \( \mathcal{C}(1, 2) \) are functionals of the perturbation potentials \( u_{\alpha \gamma}(r) \). They depend on \( u_{\alpha \gamma}(r) \)

for \( r < d - l_{\alpha \gamma} - l_{\gamma \alpha} \) even though the total potential energy of the system makes site-site separations smaller than \( d - l_{\alpha \gamma} - l_{\gamma \alpha} \) physically impossible. Because these site-site separations are impossible, one is free to choose \( u_{\alpha \gamma}(r) \) for \( r < d - l_{\alpha \gamma} - l_{\gamma \alpha} \) to be any finite function.

The corrections to the approximations given in Eqs. (3.17) and (3.19) can be expressed in terms of an infinite diagrammatic series involving \( \mathcal{C}(1, 2) \) and reference system (hard sphere fluid) correlation functions. These corrections are analyzed in Paper I. It is shown that if, by varying the perturbations inside the cores, the chain sum can be made zero for \( R_2 < d \), the convergence of the infinite series is enhanced and the analogs of Eqs. (3.17) and (3.19) may be very accurate. Unfortunately this condition cannot be enforced on \( \mathcal{C}(1, 2) \) in the embedded site model. However, it is possible to insure that the site-site averages of \( \mathcal{C}(1, 2) \), namely the \( \bar{c}_{\alpha \gamma}(r) \) functions, are zero for \( r < d - l_{\alpha \gamma} - l_{\gamma \alpha} \). We believe that such a choice for \( u_{\alpha \gamma}(r) \) should be sufficient to allow Eqs. (3.17) and (3.19) to be accurate. Thus, when using the approximations given above, they should be supplemented with the optimization condition

$$\bar{c}_{\alpha \gamma}(r) = -2 k_B T / \rho^2 \left[ \delta \varrho_{\text{RING}} / \delta u_{\alpha \gamma}(r) \right] = 0,$$

$$r < d - l_{\alpha \gamma} - l_{\gamma \alpha}. \hspace{1cm} (3.23)$$

This represents \( m(m+1)/2 \) coupled variational equations that must be solved simultaneously. This optimization condition is analogous to the simple fluid optimization condition given in I for several reasons. First, the two variational formulations, (3.23) above and (4.3) of I are very similar. Secondly, (3.23) demands that the ORPA result for \( \bar{c}_{\alpha \gamma}(r) \) satisfy the excluded volume restrictions imposed by the hard sphere forces, which is similar to the meaning of optimization of the RPA for simple liquids. Thirdly, in the limit that all the sites are moved to the center of the molecule, (3.23) becomes equivalent to the simple fluid optimization condition.

Equations (3.16)–(3.22), (3.9), and (3.12), together with the optimization condition (3.23), are our major results for the embedded site model. They represent computationally convenient approximations for the thermodynamic and structural properties of this class of molecular fluids. Experience with the simple fluid analogs of these results leads us to expect that these approximations will be very accurate.

IV. THEORY FOR INTERACTION SITE MODEL

To treat the interaction site model, two essentially separate problems must be solved. First, one must determine the properties of the reference system in which the pair interactions are

$$u_{\text{ref}}(1, 2) = \sum_{\alpha \gamma = 1}^m u_{\text{ref}}(\{ r_{\alpha \gamma} - r_{\gamma \alpha} \}). \hspace{1cm} (4.1)$$
The second problem is to describe the effects of the perturbations. This second problem can be solved straightforwardly by employing the techniques described in Paper I and Sec. III of this paper. The description of the reference system seems to be harder to solve. Our theory for treating it is an integral equation for the site-site distribution function that is analogous to the Percus–Yevick equation\textsuperscript{80} for hard spheres. The theory has the convenient feature that it reduces the description of the reference system to a variational problem that is simple to solve numerically even when the molecular geometry is complicated.

A. Theory for Reference System

For a molecular system one defines the direct correlation function $c(1,2)$ by the general Ornstein–Zernike (OZ) equation. In particular,

$$h(1,2) = c(1,2) + \langle p/\Omega \rangle d(3)c(1,3)h(3,2), \quad (4.2)$$

where $h(1,2) = g(R_{12}, \Omega_1, \Omega_2) - 1$. The reference fluid for the interaction site model is composed reference interaction site model (RISM) molecules; that is, the pair interaction is infinite when one or more spheres on molecule 1 overlap with one or more spheres on molecule 2, and it is zero otherwise. The Percus–Yevick\textsuperscript{80} closure relation for such a fluid of hard molecules is

$$c_{\text{P}}(1,2) = 0, \quad \text{no overlap},$$

$$h_{\text{P}}(1,2) = -1, \quad \text{overlap}.$$  

The second of these equations is exact. But the first is an approximation. Even so, the Percus–Yevick theory for hard sphere fluids is fairly accurate. We suspect it would also be an accurate theory for describing the reference system in the interaction site model. Unfortunately, the solution of Eq. (4.2) with the Percus–Yevick closure would in general be extremely difficult.

The iterative solution of the OZ equation expresses $h(1,2)$ as the sum of $c$-bond chains. In general, the angular dependence of $c(1,2)$ is so complicated that the sum of $c$-bond chains cannot be handled with analytic techniques. The methods developed in Sec. III do show that chain sums of two-molecule functions can be treated analytically if the functions are sums of site-site functions. This fact motivates us to write the RISM direct correlation function in two parts:

$$c_{\text{R}}(1,2) = c_0(1,2) + \Delta c(1,2), \quad (4.3)$$

where

$$c_0(1,2) = \sum_{\alpha, \gamma} c_{\alpha \gamma}(\mid r_{1\alpha} - r_{2\gamma} \mid), \quad (4.4)$$

with

$$c_{\alpha \gamma}(r) = 0, \quad r > d_{\alpha \gamma}. \quad (4.5)$$

The condition that $c_{\alpha \gamma}(r)$ is zero for $r > d_{\alpha \gamma}$ is suggested by the Percus–Yevick approximation. If $c_{\alpha \gamma}(r)$ were nonzero for distances larger than $d_{\alpha \gamma}$, then $c(1,2)$ would be nonzero when the RISM molecules did not overlap unless there were a fortuitous cancellation by $\Delta c(1,2)$.

If $\Delta c(1,2) = 0$, the techniques of Sec. III could be used to solve the OZ equation for $h_{\text{R}}(1,2)$ in terms of the $c_{\alpha \gamma}$ functions. But it is clear, from the cluster expansion for $c(1,2)$, that $\Delta c(1,2)$ is not zero. Our hope, however, is that there is a “best” choice for the $c_{\alpha \gamma}(r)$ functions for which the approximation $c_{\text{R}}(1,2) \approx c_0(1,2)$ is useful.

Let $h_0(1,2)$ denote the solution to Eq. (4.2) when $\Delta c(1,2) = 0$; that is,

$$h_0(1,2) = c_0(1,2) + \langle p/\Omega \rangle d(3)c_0(13)h_0(32). \quad (4.6)$$

Then,

$$h_{\text{R}}(1,2) = h_0(1,2) + 0(\Delta c), \quad (4.7)$$

where the second term on the right would vanish if $\Delta c$ were identically zero. Since $c_0(1,2)$ is a sum of site-site functions, $h_0(1,2)$ is also a sum of site-site functions (see Sec. III). As a result, the neglect of $\Delta c$ terms in Eq. (4.7) would be a poor approximation since it would be impossible to insure the physical requirement that $h_{\text{R}}(1,2) = -1$ when molecules 1 and 2 overlap. This leads one to investigate the RISM site-site correlation functions defined by

$$h_{\text{R}}^{\alpha \gamma}(r) = \Omega^{-\frac{1}{2}}d(1)d(2)\delta(R_3 + R_4 - r) \times \delta(R_3 + k \cdot r - k)h_{\text{R}}(1,2). \quad (4.8)$$

With Eq. (4.8) and the methods developed in Sec. III, we obtain [see Eq. (3.14)]

$$h_{\text{R}}^{\alpha \gamma}(r) = (2\pi)^{-\frac{1}{2}}d(1)d(2)\Omega^{-\frac{1}{2}}\times \exp(-ik \cdot r)e_{\alpha \gamma}(r), \quad (4.9)$$

where the $\omega(k)$ matrix is defined in Eq. (3.6), and $\hat{c}(k)$ is the matrix with elements

$$e_{\alpha \gamma}(k) = \int dr \exp(-ik \cdot r)c_{\alpha \gamma}(r). \quad (4.10)$$

It is now possible to neglect the $\Delta c$ terms without producing unphysical features. Thus, we write

$$h_{\text{R}}^{\alpha \gamma}(r)_{\text{RISM}} = (2\pi)^{-\frac{1}{2}}d(1)d(2)\Omega^{-\frac{1}{2}}\times \{\omega(k)\hat{c}(k)\omega(k)\}_{\alpha \gamma} \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (4.11)$$

where the subscripts RISM are used to note the approximation that $\Delta c$ has been neglected. The apparent “best” choice for the $e_{\alpha \gamma}(r)$ functions is the one which makes

$$h_{\text{R}}^{\alpha \gamma}(r) = -1, \quad r \leq d_{\alpha \gamma}. \quad (4.12)$$

Equations (4.5), (4.11), and (4.12) form a closed set of equations for RISM site-site correlation functions.
We call them the RISM equations. They reduce to the Percus-Yevick equation\(^{10}\) for hard spheres when the RISM molecules are composed of concentric hard spheres.

The solution of the RISM equations can be performed with a variational method. In particular, the functional

\[
I_{\text{RISM}} = \rho^2 \sum_{\alpha, \gamma} \hat{c}_{\alpha \gamma}(0) - (2\pi)^{-3} \int \! d \mathbf{k} \left[ \text{Tr} \phi(\mathbf{k}) \hat{c}(\mathbf{k}) + \ln \text{det} [1 - \rho \omega(\mathbf{k}) \hat{c}(\mathbf{k})] \right] \tag{4.13}
\]

satisfies the functional derivative relation

\[
\rho^{-2} \frac{\partial I_{\text{RISM}}}{\partial \hat{c}_{\alpha \gamma}(r)} = \left[ \frac{g_{\text{ref}}^{\alpha \gamma}(r)}{I_{\text{RISM}}} - 1 \right] \tag{4.14}
\]

Thus, Eq. (4.12) can be expressed as

\[
\frac{\partial I_{\text{RISM}}}{\partial \hat{c}_{\alpha \gamma}(r)} = 0, \quad r \leq d_{\alpha \gamma}. \tag{4.15}
\]

Equations (4.11) and (4.12) are the principal results of this part of Sec. IV. They represent a set of approximate equations for the site-site correlation functions of a class of anisotropic molecules which interact via repulsive hard core forces. Equations (4.13) and (4.15) provide a variational method for solving these equations. These results are generalizations of the hard sphere Percus-Yevick theory.

**B. Theory for Perturbations**

The knowledge of \(g_{\text{ref}}^{\alpha \gamma}(r)\) allows one to calculate the thermodynamic properties of the reference hard molecule fluid. The effects of the perturbations, \(u_{\alpha \gamma}(r) = \omega_{\alpha \gamma}(r) - u_{\text{HTA}}(r)\), can be calculated from a perturbation theory. The simplest of these is the high temperature approximation (HTA)

\[
\omega_{\text{HTA}} = \omega_{\text{ref}} + \left( \frac{\rho^2}{2 k T} \right) \int \! d \mathbf{R} \int \! d \mathbf{R}' \int \! d \mathbf{\Omega} \int \! d \mathbf{\Omega}' g_{\text{HTA}}(\mathbf{R}, \mathbf{R}', \mathbf{\Omega}, \mathbf{\Omega}')
\]

\[
= \omega_{\text{ref}} + \left( \frac{\rho^2}{2} \right) \sum_{\alpha, \gamma} \int \! g_{\text{ref}}^{\alpha \gamma}(r) \phi_{\alpha \gamma}(r) \, d r. \tag{4.16}
\]

Corrections to this approximation must account for the effects of the perturbations on the structure. It is a straightforward matter to obtain the ring diagram sum for describing corrections to the HTA. The general ring diagram contributing to the ORPA is given by Eq. (3.2) with \(F_{\text{d}}(1, 2)\) replaced by

\[
F_{\text{ref}}(1, 2) = (\rho/\Omega) \delta(\mathbf{R}_1 - \mathbf{R}_2) \delta(\mathbf{\Omega}_1 - \mathbf{\Omega}_2) + (\rho/\Omega)^3 h_{\text{ref}}(1, 2).
\]

The integrations are performed using the same methods exhibited in Sec. III. The result is

\[
\omega_{\text{RING}} = \sum_{n=2}^{\infty} \delta(n) = -\left[ 2(2\pi)^{-3} \right] \int \! d \mathbf{k} \left[ \text{Tr} \Lambda(\mathbf{k}) \hat{\phi}(\mathbf{k}) \right]
\]

\[
+ \ln \text{det} [1 - \Lambda(\mathbf{k}) \hat{\phi}(\mathbf{k})], \tag{4.17}
\]

where \(\Lambda(k)\) is the matrix with elements

\[
\Lambda_{\alpha \gamma}(k) = \rho \omega_{\alpha \gamma}(k) + \rho \hat{h}_{\text{ref}}^{\alpha \gamma}(k). \tag{4.18}
\]

When the reference system is a hard sphere fluid, \(\Lambda_{\alpha \gamma}(k)\) reduces to the \(G_{\alpha \gamma}(k)\) function introduced in Sec. III.

The ORPA for the free energy is

\[
\omega_{\text{ORPA}} = \omega_{\text{HTA}} + \omega_{\text{RING}}. \tag{4.19}
\]

To obtain correlation functions in this approximation, one takes the functional derivative of \(\omega_{\text{ORPA}}\). The result is

\[
g_{\text{ORPA}}^{\alpha \gamma}(r) = g_{\text{ref}}^{\alpha \gamma}(r) + \rho^2 (2\pi)^{-3} \int \! d \mathbf{k} \exp(-i \mathbf{k} \cdot \mathbf{r})
\]

\[
\times [\Lambda(\mathbf{k}) \hat{\phi}(\mathbf{k}) [1 - \Lambda(\mathbf{k}) \hat{\phi}(\mathbf{k})]^{-1} \Lambda(\mathbf{k})]_{\alpha \gamma}. \tag{4.20}
\]

When evaluating Eqs. (4.19) and (4.20), the optimized perturbation should be used. Optimization is done by ensuring that the second term on the right-hand side of Eq. (4.20) is zero for \(r < d_{\alpha \gamma}\). Thus, the optimized perturbation is the solution to the following variational problem:

\[
\frac{\partial \omega_{\text{RING}}}{\partial u_{\alpha \gamma}(r)} = 0, \quad r < d_{\alpha \gamma}. \tag{4.21}
\]

Equations (4.16) and (4.19)–(4.21) represent ways of calculating the thermodynamic properties and site-site correlation functions for ISM molecules when these quantities for the reference fluid of hard molecules are known. Information about the reference fluid can be obtained from solving the RISM equations of Part A above, but in the future it may also be available from Monte Carlo and molecular dynamics studies.

In the special case that the RISM equations are used to give \(g_{\text{ref}}^{\alpha \gamma}(r)\), Eqs. (4.20) and (4.21) can be shown to be equivalent to the following integral equation for \(g^{\alpha \gamma}(r)\) in the interaction site model:

\[
g^{\alpha \gamma}(r) = 1 - \bar{h}^{\alpha \gamma}(r)
\]

\[
= (2\pi)^{-3} \int \! d \mathbf{k} \exp(i \mathbf{k} \cdot \mathbf{r}) \left[ \omega(\mathbf{k}) \hat{c}(\mathbf{k}) \right]
\]

\[
\times [1 - \rho \omega(\mathbf{k}) \hat{c}(\mathbf{k})]^{-1} \omega(\mathbf{k}) \hat{c}(\mathbf{k}), \tag{4.22}
\]

where \(\hat{c}(\mathbf{k})\) is the matrix with elements \(c_{\alpha \gamma}(k)\) which are the Fourier transforms of \(c_{\alpha \gamma}(r)\). The latter are defined by

\[
c_{\alpha \gamma}(r) = -u_{\alpha \gamma}(r)/k_b T, \quad \text{for} \quad r \geq d_{\alpha \gamma}, \tag{4.23}
\]

and are determined for \(r < d_{\alpha \gamma}\) by the condition

\[
h_{\alpha \gamma}(r) = 1, \quad r < d_{\alpha \gamma}. \tag{4.24}
\]

The solution of Eqs. (4.22)–(4.24), which we call the interaction model (ISM) equations, can be performed by the same type of variational procedure discussed for the RISM equations. When all the interaction sites on a molecule lie at the same point, the ISM equations reduce to the mean spherical model (MSM) equation.\(^{11}\)
C. Alternative Derivation of the ISM Equations

It is shown in Paper I that the OZ equation for spherical molecules can be stated in terms of a functional derivative equation. In particular, \( \delta \sigma / \delta c_0(r) = \rho^2 g(r) / 2 \), where \( c_0(r) \) is the direct correlation function and \( \sigma \) is defined in terms of the sum of the ring diagrams involving \( c_b \) bonds. The analogous procedure for the ISM is to define \( c_{\sigma \gamma}(r) \) in terms of \( g^\sigma_\gamma(r) \) by the equation

\[
[\delta \Sigma_{\text{ISM}} / \delta c_{\sigma \gamma}(r)] = \rho^2 g^\sigma_\gamma(r) / 2,
\]

where \( \Sigma_{\text{ISM}} \) is expressed in terms of the ring diagrams involving \( c(1, 2) = \sum_{\sigma \gamma} c_{\sigma \gamma}(r_\sigma - r_\gamma) \) bonds. That is,

\[
\Sigma_{\text{ISM}} = \left\{ \text{The diagram in which two black } \rho \text{ circles are connected by one } c \text{ bond plus the sum of all diagrams which are rings containing black } \rho \text{ circles and } c \text{ bonds} \right\}.
\]

Here, one should recall Eq. (2.8) in order to convert the diagrams defined in I to diagrams appropriate to molecular fluids. The explicit form for \( \Sigma_{\text{ISM}} \) is determined with the techniques developed in Sec. III. One finds that

\[
\Sigma_{\text{ISM}} = \frac{\rho^2}{4} \sum_{\sigma \gamma} c_{\sigma \gamma}(0) - (2\pi)^{-1} \int d\theta \rho \omega(\theta) \tilde{c}(\theta)
\]

\[
+ \ln \det[1 - \rho \omega(\theta) \tilde{c}(\theta)] \right].
\]

Since (4.25) and (4.26) serve only as equations relating \( g_{\sigma \gamma}(r) \) and \( c_{\sigma \gamma}(r) \) (together, they are a kind of OZ equation), a closure of the equations is needed in order to have a theory for the ISM. This closure is created with an analogy to the MSM equation (see Sec. IV of I). In particular, we write

\[
g^\sigma_\gamma(r) = 0, \quad r < d_{\sigma \gamma}, \quad \text{(4.27a)}
\]

and

\[
c_{\sigma \gamma}(r) = \phi_{\sigma \gamma}(r), \quad r > d_{\sigma \gamma}. \quad \text{(4.27b)}
\]

Equation (4.27a) is exact, and (4.27b) is the approximation. Combined with Eqs. (4.25) and (4.26), they are the ISM equations discussed in the previous part of this section.

V. CONCLUDING REMARKS

There are few practical techniques for employing equilibrium statistical mechanics for the study of realistic models of dense molecular fluids. Most of the available methods are either limited in applicability to very special situations (such as those of low density, weak interactions, or only slightly nonspherical forces) or else they require formidable amounts of computer time for their use. The methods presented here are not subject to these limitations.

The models studied herein simulate the short range repulsions in liquids with hard core interactions. Further they do not consider the possibility of many body forces, such as those arising from nonadditive polarizability effects. However, both of these restrictions can be eliminated. The "softening" of the hard core repulsions can be done with techniques already presented. Polarizability effects can be included by allowing the sites to vibrate in the molecule. Ring and chain sums can still be performed simply despite this added feature of the model.

Thus, the methods we have presented give rise to theories which are applicable to a large variety of molecular fluids. Since they are molecular analogs of techniques which are very accurate for simple liquids, there is good reason to expect them to be quite accurate and useful tools for the study of the liquid state.

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7 See, for example, J. R. Sweet and W. A. Steele, J. Chem. Phys. 47, 3029 (1967).
8 Generalizations to several components can be derived with the same techniques used herein.
9 A restriction of additive diameters, i.e., that \( d_{\sigma \gamma} = (d_{\sigma} + d_{\gamma}) / 2 \), need not hold.
11 J. L. Lebowitz and J. K. Percus, Phys. Rev. 144, 251 (1966); see also Sec. IV of Ref. 1.