

A Variational Approach to Distribution Function Theory

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Received January 17, 1990; final May 9, 1990

We present a novel formalism for the generation of integral equations for the distribution functions of fluids. It is based on a cumulant expansion for the free energy. Truncation of the expansion at the K th term and minimization of the resulting approximation leads to equations for the distribution functions up to K th order.

The formalism is not limited to systems with two-body interactions and does not require the addition of closure relations to yield a complete set of equations. In fact, it automatically generates superposition approximations, such as the Kirkwood three-body superposition approximation or the Fisher-Kopeliovich four-body one.

The conceptual approach is adapted from the cluster variation method of lattice theory.

KEY WORDS: Liquid theory; distribution function theory; integral equations.

1. INTRODUCTION

The goal of the statistical mechanical theory of liquids is: given the interactions between the molecules, predict the structure, thermodynamic properties, and range of stability of the liquid phase.⁽¹⁾ The difficulty here does not lie in the principle involved, since all one has to do is to evaluate the appropriate partition functions and ensemble averages, but a practical one: in all but the most simple of cases, theory requires one to perform a feat that surpasses all conceivable levels of computational effort. Thus, liquid theory is approximation theory, and a wealth of techniques has been

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employed to generate approximate theories for at least the first few of the k -body distribution functions $g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)$, from which structure and thermodynamic properties may be inferred: diagrammatic techniques, functional differentiation, perturbation methods, and density functional methods, to name a few well-known approaches.^(2,3)

The same problem of approximation is, of course, central to the theory of phase behavior of the solid state. The localization of the atoms allows for a space discretization (lattice models), which considerably simplifies the mathematics of the statistical aspects of microscopic theories; consequently, for lattice models the field of analytic approximations (as opposed to numerical simulation) has reached a mature stage, where almost all approximate theories can be understood and derived within the framework of a single formalism, namely the generalized cluster variation method.⁽⁴⁻⁶⁾ In this formalism a Möbius transformation⁽⁷⁾ is used to generate a cumulant expansion⁽⁸⁾ for the free energy, and approximations result from minimization of truncated versions of this expansion.

Here we present an adaptation of that same formalism to the liquid-state theory. It is conceptually very simple and straightforward, it is not limited to systems with only two-body interactions, it is free from auxiliary assumptions such as the closure relations employed in the Yvon-Born-Green theory, and it is free from the fairly arbitrary choices that must be made in applying functional differentiation methods or density functional theory. The only freedom is in choosing the number of terms to be kept in the cumulant expansion of the free energy. This also means that the way to improve upon any given approximation is clear: include the next term, involving the next-higher-order distribution function. The formalism applies to homogeneous and inhomogeneous fluids alike.

While the conceptual advantages of our approach are thus manifold, and it parallels a method proven to be highly successful in solid-state theory, we want to make clear from the outset that at present we make no claims as to its practical usefulness. The algebraic complexity is such that it is unlikely that more than four or maybe five terms in the cumulant expansion can be kept, and so far only preliminary numerical calculations have been done (using a pairwise Lennard-Jones potential). However, it is our belief that even as a purely theoretical exercise the approach presented here is of value, in that it may help gain a better insight into the structure of other approximate theories. One interesting result in this direction is the following: keeping K terms in the cumulant expansion results in a set of equations for the first K distribution functions; the equation for $g^{(K)}$ has the form of a superposition approximation. In this fashion, we can *derive* both the Kirkwood superposition approximation⁽⁹⁾ for $g^{(3)}$ and the Fisher-Kopeliovich relation⁽¹⁰⁾ for g .⁽⁴⁾

In the next section we shall introduce the cumulant expansion for the free energy. This is done in the formalism of the canonical ensemble. The minimization of the truncated free energy expansion is discussed in Section 3. The resulting equations for the distribution functions depend explicitly on the number of particles N and the volume V , and it is necessary to derive their asymptotic form, valid in the thermodynamic limit $N, V \rightarrow \infty$, with $\rho = N/V$ fixed. Sections 4 and 5 present details of the asymptotic analysis for the cases in which three and four terms in the expansion are kept. We limit our presentation to the case of a homogeneous fluid, to avoid excessively tedious algebra. Section 6 contains concluding remarks.

The equations of the triplet approximation of Section 4 and the quartet approximation of Section 5 have also been obtained by Kikuchi and Van Baal in an earlier attempt to adapt the cluster variation method to the theory of liquids.⁽¹¹⁾ They started from a lattice-based formulation and then considered the limit of the lattice constant going to zero. The approach presented here is more direct and stays within the continuum space formulation.

2. A CUMULANT EXPANSION FOR THE FREE ENERGY

We use the canonical formalism and thus consider N identical particles of mass m in a volume V . The particles are numbered 1 to N and they interact with k -body potentials $\Phi^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)$, $k = 1, \dots, N$. If the particles 1 to N are at positions \mathbf{r}_1 to \mathbf{r}_N in the volume V , then the potential energy of the system is

$$E^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{k=1}^N \sum_{\substack{\text{k-tuples} \\ \{i_1, \dots, i_k\} \subseteq \{1, \dots, N\}}} \Phi^{(k)}(\mathbf{r}_{i_1}, \dots, \mathbf{r}_{i_k}) \quad (1)$$

We assume that each potential function $\Phi^{(k)}$ is invariant under permutation of its arguments. The one-body potential $\Phi^{(1)}$ describes an external force field.

We now consider the joint probability of finding particle i in a volume element $d\mathbf{r}_i$ at \mathbf{r}_i , $i = 1, \dots, N$ and we denote the associated probability density by $P^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N)$. For the situation of thermodynamic equilibrium this density is

$$P_{\text{eq}}^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) = Z_N^{-1} \exp[-\beta E^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N)] \quad (2)$$

where Z_N is the configurational integral

$$Z_N(V, T) = \int_{V^N} d^N \mathbf{r} \exp[-\beta E^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N)] \quad (3)$$

and $\beta = (k_B T)^{-1}$.

For any such probability density $P^{(N)}$, not just for the equilibrium one, we may define the n -particle density functions $\rho_N^{(n)}$ by

$$\rho_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{N!}{(N-n)!} \int d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N P^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (4)$$

(Integration over a particle coordinate is implicitly assumed to be over the volume V .)

The n -particle distribution function $g_N^{(n)}$ is traditionally defined as

$$g_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{\rho_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)}{\prod_{i=1}^n \rho_N^{(1)}(\mathbf{r}_i)} \quad (5)$$

but for this work we found it more convenient to work with slightly modified functions,

$$G_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \rho^{-n} \rho_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \quad (6)$$

where ρ denotes the average particle density, $\rho = N/V$. For a homogeneous system, for which the local density $\rho_N^{(1)}(\mathbf{r})$ equals the average density ρ , the G -functions are identical to the distribution functions.

The $G_N^{(n)}$ satisfy the following reduction relations:

$$\rho \int d\mathbf{r}_{n+1} G_N^{(n+1)}(\mathbf{r}_1, \dots, \mathbf{r}_{n+1}) = (N-n) G_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \quad (7)$$

and they are normalized according to

$$\rho^n \int d\mathbf{r}_1 \cdots d\mathbf{r}_n G_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{N!}{(N-n)!} \quad (8)$$

The excess internal energy U_N of the system in a state described by a probability density $P^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is

$$U_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N P^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) \cdot E^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (9)$$

We introduce a configurational entropy S_N^{conf} by the definition

$$S_N^{\text{conf}} = - \int d\mathbf{r}_1 \cdots d\mathbf{r}_N P^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) \log P^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (10)$$

The difference $\beta U_N - S_N^{\text{conf}}$ takes its minimum value if and only if the probability density $P^{(N)}$ equals the equilibrium density $P_{\text{eq}}^{(N)}$ [Eq. (2)].

Consequently, this equilibrium density may be characterized by the variational principle

$$\min_{P^{(N)}} \{ \beta U_N - S_N^{\text{conf}} \} \quad (11)$$

rather than explicitly by Eq. (2). We shall use this variational characterization, which of course is just the statement that in thermodynamic equilibrium the free energy of the system takes its minimum value, to set up a hierarchy of approximations.

Since all the potential functions $\Phi^{(k)}$ are, by assumption, invariant under permutation of their arguments, $P_{\text{eq}}^{(N)}$ has the same invariance, and we may restrict the variation in Eq. (11) to such invariant probability densities. Consequently, we shall consider only probability densities $P^{(N)}$ that are invariant under permutations of the arguments. The functions $G_N^{(n)}$ then inherit the same invariance property.

The energy U_N may then be written as

$$U_N = \sum_{k=1}^N \frac{\rho^k}{k!} \int d\mathbf{r}_1 \cdots d\mathbf{r}_k G_N^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \Phi^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \quad (12)$$

This representation derives its usefulness from the fact that the contribution of the k -body potential $\Phi^{(k)}$ is expected to decrease rapidly with increasing k . Actually, many systems are adequately modeled with two-body potentials only. The idea behind the transformation to be defined below is to isolate k -body contributions to the configurational entropy in a similar manner, so that they also decrease rapidly with increasing k . Thus, to express S_N^{conf} in a way analogous to the energy representation of Eq. (12), we define transforms $\gamma_N^{(n)}$ of the functions $G_N^{(n)}$ as follows:

$$\log \gamma_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \sum_{k=1}^n (-1)^{n-k} \sum_{\{i_1, \dots, i_k\} \subset \{1, \dots, n\}} \log G_N^{(k)}(\mathbf{r}_{i_1}, \dots, \mathbf{r}_{i_k}) \quad (13)$$

The second summation is over all the subsets of k elements of the set of indices $\{1, \dots, n\}$. The definition makes sense since the $G_N^{(k)}$ have the invariance property mentioned above. The $\gamma_N^{(k)}$ share this property. The inverse of Eq. (13) is

$$\log G_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \sum_{k=1}^n \sum_{\{i_1, \dots, i_k\} \subset \{1, \dots, n\}} \log \gamma_N^{(k)}(\mathbf{r}_{i_1}, \dots, \mathbf{r}_{i_k}) \quad (14)$$

Comparing this equation with Eq. (1), one sees that the relationship between $\log G$ and $\log \gamma$ is the same as the relationship between the energy E and the potential Φ . It is a version of a cumulant expansion that is meant to separate contributions from all the subgroups of particles within the total system of N particles.

With the help of the γ -functions, the configurational entropy S_N^{conf} may be expressed as a sum, analogous to the sum representation of U_N in Eq. (12). The transformation leads to the following representation for the difference:

$$\beta U_N - S_N^{\text{conf}} = -\log N! + N \log \rho + \sum_{k=1}^N \frac{\rho^k}{k!} \int d\mathbf{r}_1 \cdots d\mathbf{r}_k G_N^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \times [\beta \Phi^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) + \log \gamma_N^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)] \quad (15)$$

Approximations are generated by truncating the summation in this expression at $k=K$. The resulting approximation for $\beta U_N - S_N^{\text{conf}}$ will be denoted by $F_N^{(K)}$. Equations for $G_N^{(k)}$, $k=1, \dots, K$, will follow from minimizing $F_N^{(K)}$, in accordance with the variational characterization of thermodynamic equilibrium expressed in Eq. (11). In the final step the asymptotic form of the equation for N , $V \rightarrow \infty$ with $\rho = N/V$ fixed will be derived.

3. MINIMIZATION OF THE TRUNCATED CUMULANT EXPANSION

We proceed to find the functions $G_N^{(k)}$, $k=1, \dots, K$, that minimize the truncated expansion for $\beta U_N - S_N^{\text{conf}}$:

$$F_N^{(K)} = -\log N! + N \log \rho + \sum_{k=1}^K \frac{\rho^k}{k!} \int d\mathbf{r}_1 \cdots d\mathbf{r}_k G_N^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \times [\beta \Phi^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) + \log \gamma_N^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)] \quad (16)$$

Note that $F_N^{(K)}$ is a functional of $G_N^{(K)}$ only, since this function determines all the lower-order functions $G_N^{(k)}$, for $k=1, \dots, K-1$, through the reduction relations (7), and the collection $G_N^{(k)}$, $k=1, \dots, K$, determines all the $\gamma_N^{(k)}$, $k=1, \dots, K$, through Eq. (13). At its minimum value the functional $F_N^{(K)}$ is stationary with respect to variations $\delta G_N^{(K)}(\mathbf{r}_1, \dots, \mathbf{r}_K)$ that are invariant under argument permutations and that satisfy the condition

$$\int d\mathbf{r}_1 \cdots d\mathbf{r}_K \delta G_N^{(K)}(\mathbf{r}_1, \dots, \mathbf{r}_K) = 0 \quad (17)$$

[Equation (17) is a consequence of the normalization condition (8).] A straightforward calculation translates this stationarity requirement into the following equation, which may be regarded as the basic equation of this approach:

$$\sum_{k=1}^K \frac{(K-k)!}{(N-k)!} \sum_{\{i_1, \dots, i_k\} \subset \{1, \dots, K\}} \{ \beta \Phi^{(k)}(\mathbf{r}_{i_1}, \dots, \mathbf{r}_{i_k}) + \log \gamma_N^{(k)}(\mathbf{r}_{i_1}, \dots, \mathbf{r}_{i_k}) \} = \text{const} \quad (18)$$

In combination with $K-1$ reduction relations linking $G_N^{(1)}$ to $G_N^{(2)}$ to ... to $G_N^{(K)}$, this equation determines the distribution functions that approximately describe thermodynamic equilibrium. The constant is determined by the normalization condition (8) applied to any one of the G 's.

In the next sections we shall consider two specific approximations and derive asymptotic forms of the equations valid in the thermodynamic limit $N = \rho V \rightarrow \infty$.

4. THE TRIPLET APPROXIMATION FOR A HOMOGENEOUS FLUID

In this section we consider the triplet approximation, which results from taking $K=3$ in the foregoing. That is, all contributions to the internal energy and the configurational entropy that involve distribution functions of order 4 or more are neglected.

For notational convenience we introduce another set of functions $\psi_N^{(k)}$ by

$$\psi_N^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) = \gamma_N^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \exp[\beta \Phi_N^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)] \quad (19)$$

We also introduce a shorthand notation for the functions g , G , γ , ψ , and Φ by dropping the subscript N that refers to the size of the system and indicating the argument list and the order of the function by a list of subscripts and their total number. Thus, γ_{34} stands for $\gamma_N^{(2)}(\mathbf{r}_3, \mathbf{r}_4)$, Φ_{123} stands for $\Phi^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, etc.

With this notation and $K=3$, Eq. (18) yields

$$\frac{2}{(N-1)(N-2)} \log(\psi_1 \psi_2 \psi_3) + \frac{1}{N-2} \log(\psi_{12} \psi_{23} \psi_{31}) + \log \psi_{123} = \text{const} \quad (20a)$$

We may take the constant on the right-hand side of this equation to be zero if we agree to change the potentials Φ by additive constants afterward so as to satisfy the normalization conditions. With this convenient choice, Eq. (20) can be rearranged to read

$$G_{123} = \frac{G_{12} G_{23} G_{31}}{G_1 G_2 G_3} e^{-\beta \Phi_{123}} (\psi_{12} \psi_{23} \psi_{31})^{-1/(N-2)} (\psi_1 \psi_2 \psi_3)^{-2/(N-1)(N-2)} \quad (20b)$$

Since the reduction relations that couple the various G 's are not readily applied after the thermodynamic limit $N, V \rightarrow \infty$ has been taken, we combine them with Eq. (20b) at this stage of the proceedings.

Integrating Eq. (20b) over \mathbf{r}_3 and using Eq. (7) with $n=2$, we can divide both sides of the equation by G_{12} and rearrange the result to obtain the following equation:

$$\begin{aligned} & (\psi_{12})^{1/(N-2)} (\psi_1 \psi_2)^{2/(N-1)(N-2)} \\ &= \frac{\rho}{N-2} \int d\mathbf{r}_3 (\gamma_3 \gamma_{13} \gamma_{23} e^{-\beta\Phi_{123}}) (\psi_{23} \psi_{31})^{-1/(N-2)} (\psi_3)^{-2/(N-1)(N-2)} \end{aligned}$$

With the abbreviation

$$\begin{aligned} J_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &\equiv J_{12} \\ &\equiv \left\{ \frac{\rho}{N-2} \int d\mathbf{r}_3 (\gamma_3 \gamma_{13} \gamma_{23} e^{-\beta\Phi_{123}}) (\psi_{23} \psi_{31})^{-1/(N-2)} \right. \\ &\quad \left. \times (\psi_3)^{-2/(N-1)(N-2)} \right\}^{N-2} \end{aligned} \quad (21)$$

this reads

$$\psi_{12} = J_{12} (\psi_1 \psi_2)^{-2/(N-1)} \quad (22)$$

Next, we isolate G_{12} by rearranging Eq. (22):

$$G_{12} = G_1 G_2 e^{-\beta\Phi_{12}} J_{12} (\psi_1 \psi_2)^{-2/(N-1)}$$

Integrating over \mathbf{r}_2 , dividing by G_1 , rearranging, and introducing $J_N^{(1)}$ by

$$J_N^{(1)}(\mathbf{r}_1) \equiv J_1 \equiv \left\{ \frac{\rho}{N-1} \int d\mathbf{r}_2 (\gamma_2 J_{12} e^{-\beta\Phi_{12}}) (\psi_2)^{-2/(N-1)} \right\}^{N-1} \quad (23)$$

leads to

$$\psi_1 = (J_1)^{1/2} \quad (24)$$

We now collect Eqs. (20), (22), and (24) into the set

$$\log \psi_{123} = -\frac{1}{N-2} \log(\psi_{12} \psi_{23} \psi_{31}) - \frac{2}{(N-1)(N-2)} \log(\psi_1 \psi_2 \psi_3) \quad (25a)$$

$$\log \psi_{12} = \log J_{12} - \frac{2}{N-1} \log(\psi_1 \psi_2) \quad (25b)$$

$$\log \psi_1 = \frac{1}{2} \log J_1 \quad (25c)$$

We have used the reduction relations that define G_1 and G_{12} in terms of G_{123} [cf. Eq. (7)] to derive Eqs. (25b) and (25c) from Eq. (25a) [which is Eq. (20a) with the constant chosen to be zero, i.e., absorbed into the interactions]. Hence the above set of three equations is equivalent to the set consisting of Eq. (20a) plus the two reduction relations. It is a convenient starting point for the consideration of the thermodynamic limit, to which topic we turn next.

We shall only consider the case of a homogeneous fluid here. The local density $\rho^{(1)}(\mathbf{r})$ then equals the average density ρ everywhere and $\gamma_N^{(1)}(\mathbf{r}) = G_N^{(1)}(\mathbf{r}) = g_N^{(1)}(\mathbf{r}) = 1$. This explicit information replaces Eq. (25c). (Obviously, the potentials must allow for a homogeneous equilibrium state.) The asymptotic ($N \rightarrow \infty$) form of Eq. (25a) is clearly

$$\log \psi_{123} = 0 + O(1/N) \tag{26}$$

To find the asymptotic form of Eq. (25b), we must consider the asymptotic form of $\log J_{12}$. The reduction relation (7) with $n = 2$ can be rearranged to read

$$\rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} \gamma_{123} = N - 2 \tag{27}$$

Equation (25a) implies that to leading order, $\gamma_{123} = \exp(-\beta\Phi_{123})$. These observations imply that the integral in the definition of J_{12} , Eq. (21), is roughly $(N - 2)/\rho$. This leads us to write

$$\begin{aligned} \log J_{12} &= (N - 2) \log \left\{ \frac{\rho}{N - 2} \int d\mathbf{r}_3 (\gamma_3 \gamma_{13} \gamma_{23} e^{-\beta\Phi_{123}}) \right. \\ &\quad \left. \times (\psi_{23} \psi_{31})^{-1/(N-2)} (\psi_3)^{-2/(N-1)(N-2)} \right\} \\ &= (N - 2) \log \left\{ 1 + \frac{\rho}{N - 2} \int d\mathbf{r}_3 \gamma_3 (\gamma_{13} \gamma_{23} e^{-\beta\Phi_{123}} - \gamma_{13} - \gamma_{23} + 1) \right. \\ &\quad \left. + \frac{\rho}{N - 2} \int d\mathbf{r}_3 (\gamma_3 \gamma_{13} \gamma_{23} e^{-\beta\Phi_{123}}) \right. \\ &\quad \left. \times (\psi_{23} \psi_{31})^{-1/(N-2)} (\psi_3)^{-2/(N-1)(N-2)} - 1 \right\} \end{aligned}$$

where we have used that

$$\rho \int d\mathbf{r}_2 \gamma_2 \gamma_{12} = N - 1 \tag{28}$$

which follows from Eq. (7) with $n = 1$.

We now expand the above expression in powers of N^{-1} , boldly assuming that our manipulations can be justified in a mathematically rigorous fashion. We shall freely interchange summations and integrations; moreover, we make the following assumptions as regards the order of the integrals that we shall encounter (recall that all coordinate integrations are over the volume $V = N/\rho$):

1. Integration of any product of factors γ and/or factors $\exp(-\beta\Phi)$ over a coordinate \mathbf{r}_i yields a result of $O(N)$.
2. Integration of any integrand that contains a factor $\log \psi_{1\dots k}$ over one or more (up to $k-1$) coordinates \mathbf{r}_i out of $\mathbf{r}_1, \dots, \mathbf{r}_k$ yields a result of $O(1)$; integration over all k coordinates yields a result of $O(N)$.

The first assumption is based on the expectation that such an integrand will approach unity if any coordinate becomes very large, and the second assumption derives from the expectation that the quantity $\beta U_N - S_N$ should be proportional to N for large N and that the same holds for each of the separate contributions in the expansion of Eq. (15).

With the abbreviation

$$E_{12} = \rho \int d\mathbf{r}_3 \gamma_3 (\gamma_{13} \gamma_{23} e^{-\beta\Phi_{123}} - \gamma_{13} - \gamma_{23} + 1) \quad (29)$$

a straightforward calculation yields

$$\begin{aligned} \log J_{12} = E_{12} - \frac{1}{2} \frac{(E_{12})^2}{N-2} \\ - \frac{\rho}{N-2} \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} e^{-\beta\Phi_{123}} \log(\psi_{23} \psi_{31}) + O\left(\frac{1}{N}\right) \end{aligned} \quad (30)$$

Since the integral in Eq. (30) is $O(1)$ according to our second assumption, we obtain the asymptotic form of Eq. (25b) as

$$\log \psi_{12} = E_{12} + O\left(\frac{1}{N}\right) \quad (31)$$

Collecting our results from Eqs. (26) and (31), assuming sufficiently smooth behavior so that the $O(1/N)$ terms can be neglected, using homogeneity to substitute unity for $\gamma^{(1)}(\mathbf{r}_i)$, and reexpressing the equations in terms of the standard pair and triplet distribution functions $g^{(2)}$ and $g^{(3)}$, we find

$$g_{123} = g_{12} g_{23} g_{31} \exp(-\beta\Phi_{123}) \quad (32a)$$

$$g_{12} = \exp \left[-\beta\Phi_{12} + \rho \int d\mathbf{r}_3 (g_{13} g_{23} e^{-\beta\Phi_{123}} - g_{13} - g_{23} + 1) \right] \quad (32b)$$

Recall that we adopted the convention that the potentials $\Phi^{(2)}$ and $\Phi^{(3)}$ incorporate the freedom of an additive constant each, to allow for proper scaling of $g^{(2)}$ and $g^{(3)}$. Proper scaling is best effected by using the fact that the distribution functions should approach unity whenever the separation between any two of their arguments approaches infinity. It follows from Eq. (32) that this can be ensured by adjusting the potentials so as to approach zero for infinite separations, which is the usual choice anyway.

Equation (32a) is an explicit equation for the triplet distribution function, which in the absence of a triplet interaction, i.e., $\Phi^{(3)} \equiv 0$, is seen to be just the Kirkwood superposition approximation. It is an automatic result of our formalism rather than an additional assumption. Equation (32b) is an integral equation for $g^{(2)}$, which, in the absence of a triplet interaction and with the (standard) notations $g_{12} \exp(\beta\Phi_{12}) = y_{12}$ and $g_{12} - 1 = h_{12}$, can be written as

$$y_{12} = \exp\left(\rho \int d\mathbf{r}_3 h_{13} h_{32}\right) \quad (33)$$

This same equation results if the hypernetted chain (HNC) assumption⁽¹²⁾ is combined with a linearized version of the Ornstein–Zernike (OZ) relation,⁽¹³⁾ as follows. The OZ relation, which defines the direct pair correlation function $c^{(2)}$, is

$$h_{12} - c_{12} = \rho \int d\mathbf{r}_3 h_{13} c_{32} \quad (34)$$

A version linearized in ρ is

$$h_{12} - c_{12} = \rho \int d\mathbf{r}_3 h_{13} h_{32} \quad (35)$$

Upon combination with the HNC approximation

$$y_{12} = \exp(h_{12} - c_{12}) \quad (36)$$

this produces Eq. (33). In this sense our triplet approximation for $g^{(2)}$ is a linearization of the HNC approximation, just as the Percus–Yevick (PY) approximation⁽¹⁴⁾ $y_{12} = 1 + h_{12} - c_{12}$ can be considered as such.

It is also possible to obtain the PY equation from Eq. (33) by linearizing the right-hand side as follows:

$$\begin{aligned}
 y_{12} &= 1 + \rho \int d\mathbf{r}_3 h_{13} h_{32} + O(\rho^2) \\
 &= 1 + \rho \int d\mathbf{r}_3 h_{13} g_{32} \left(1 - \frac{1}{g_{32}}\right) + O(\rho^2) \\
 &= 1 + \rho \int d\mathbf{r}_3 h_{13} g_{32} [1 - \exp(\beta\phi_{32})] + O(\rho^2)
 \end{aligned}$$

Dropping the $O(\rho^2)$ term now results in the PY equation.

Two comments may be in order. First, to truncate the general equation (15) and to minimize the expression in Eq. (16) is exactly the basic procedure of the cluster variation method for lattice models. Second, the fact that Kirkwood's superposition approximation (32a) is *derived* from this truncation procedure can be interpreted as this truncation (the very basis of the cluster variation method) being equivalent to the closure procedure which uses the superposition approximation.

5. THE QUARTET APPROXIMATION FOR A HOMOGENEOUS FLUID

In this section we present the next higher approximation out of the hierarchy, namely the quartet approximation, which results if we take $K=4$ in Eq. (18). Again we incorporate the constant on the right-hand side of that equation in the potentials. The quartet version of Eq. (18) then leads to

$$\begin{aligned}
 \log \psi_{1234} &= -\frac{1}{N-3} \log(\psi_{123} \psi_{124} \psi_{134} \psi_{234}) \\
 &\quad -\frac{2}{(N-2)(N-3)} \log(\psi_{12} \psi_{13} \psi_{14} \psi_{23} \psi_{24} \psi_{34}) \\
 &\quad -\frac{6}{(N-1)(N-2)(N-3)} \log(\psi_1 \psi_2 \psi_3 \psi_4) \quad (37)
 \end{aligned}$$

In exactly the same fashion as in the treatment of the triplet equation, we use the reduction relations to derive the following equations:

$$\begin{aligned}
 \log \psi_{123} &= \log J_{123} - \frac{2}{N-2} \log(\psi_{12} \psi_{13} \psi_{23}) \\
 &\quad -\frac{6}{(N-1)(N-2)} \log(\psi_1 \psi_2 \psi_3) \quad (38)
 \end{aligned}$$

with

$$\begin{aligned}
 J_{123} = & \left[\frac{\rho}{N-3} \int d\mathbf{r}_4 (\gamma_{124} \gamma_{134} \gamma_{234} \gamma_{14} \gamma_{24} \gamma_{34} \gamma_4 e^{-\beta\Phi_{1234}}) \right. \\
 & \times (\psi_{124} \psi_{134} \psi_{234})^{-1/(N-3)} (\psi_{14} \psi_{24} \psi_{34})^{-2/(N-2)(N-3)} \\
 & \left. \times (\psi_4)^{-6/(N-1)(N-2)(N-3)} \right]^{N-3} \quad (39)
 \end{aligned}$$

and

$$\log \psi_{12} = \frac{1}{2} \log J_{12} - \frac{3}{N-1} \log(\psi_1 \psi_2) \quad (40)$$

with

$$\begin{aligned}
 J_{12} = & \left[\frac{\rho}{N-2} \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} J_{123} e^{-\beta\Phi_{123}} (\psi_{13} \psi_{23})^{-2/(N-2)} \right. \\
 & \left. \times (\psi_3)^{-6/(N-1)(N-2)} \right]^{N-2} \quad (41)
 \end{aligned}$$

Note that J_{12} for the quartet approximation is not identical to the J_{12} we defined earlier for the triplet case.

We can also write a similar equation for $\log \psi_1$, but since we shall again restrict our attention to homogeneous fluids, we shall not need such an equation, but will use the explicit knowledge $\gamma^{(1)}(\mathbf{r}) = 1$ to complete the set of equations.

The final step is to find the asymptotic form of Eqs. (37), (38), and (41), valid for large N and V , with $\rho = N/V$ fixed. The asymptotic form of Eq. (37) is clearly

$$\log \psi_{1234} = 0 + O\left(\frac{1}{N}\right) \quad (42)$$

In finding the large- N behavior of $\log J_{123}$ we employ the reduction relations [Eq. (7)] with $n = 0, 1, 2$ and 3 in the form

$$\rho \int d\mathbf{r}_4 \gamma_4 = N$$

$$\rho \int d\mathbf{r}_4 \gamma_4 \gamma_{14} = N - 1$$

$$\rho \int d\mathbf{r}_4 \gamma_4 \gamma_{14} \gamma_{24} \gamma_{124} = N - 2$$

$$\rho \int d\mathbf{r}_4 \gamma_4 \gamma_{14} \gamma_{24} \gamma_{34} \gamma_{124} \gamma_{134} \gamma_{234} \gamma_{1234} = N - 3$$

to write

$$\begin{aligned} \log J_{123} = (N-3) \log \left\{ 1 + \frac{\rho}{N-3} \int d\mathbf{r}_4 (\gamma_4 \gamma_{14} \gamma_{24} \gamma_{34} \gamma_{124} \gamma_{134} \gamma_{234} e^{-\beta\Phi_{1234}} \right. \\ - \gamma_4 \gamma_{14} \gamma_{24} \gamma_{124} - \gamma_4 \gamma_{14} \gamma_{34} \gamma_{134} - \gamma_4 \gamma_{24} \gamma_{34} \gamma_{234} \\ + \gamma_4 \gamma_{14} + \gamma_4 \gamma_{24} + \gamma_4 \gamma_{34} - \gamma_4) \\ + \frac{\rho}{N-3} \int d\mathbf{r}_4 (\gamma_4 \gamma_{14} \gamma_{24} \gamma_{34} \gamma_{124} \gamma_{134} \gamma_{234} e^{-\beta\Phi_{1234}}) \\ \times [(\psi_{124} \psi_{134} \psi_{234})^{-1/(N-3)} (\psi_{14} \psi_{24} \psi_{34})^{-2/(N-2)(N-3)} \\ \left. \times (\psi_4)^{-6/(N-1)(N-2)(N-3)} - 1 \right] \Big\} \end{aligned}$$

We introduce the abbreviations

$$\begin{aligned} E_{123} = \rho \int d\mathbf{r}_4 (\gamma_4 \gamma_{14} \gamma_{24} \gamma_{34} \gamma_{124} \gamma_{134} \gamma_{234} e^{-\beta\Phi_{1234}} \\ - \gamma_4 \gamma_{14} \gamma_{24} \gamma_{124} - \gamma_4 \gamma_{14} \gamma_{34} \gamma_{134} - \gamma_4 \gamma_{24} \gamma_{34} \gamma_{234} \\ + \gamma_4 \gamma_{14} + \gamma_4 \gamma_{24} + \gamma_4 \gamma_{34} - \gamma_4) \end{aligned} \quad (43)$$

and

$$F_{123} = \rho \int d\mathbf{r}_4 [\gamma_4 \gamma_{14} \gamma_{24} \gamma_{34} \gamma_{124} \gamma_{134} \gamma_{234} e^{-\beta\Phi_{1234}} \log(\psi_{124} \psi_{134} \psi_{234})] \quad (44)$$

Then, employing the rules of operation as assumed in the previous section, we can write

$$\log J_{123} = E_{123} - \frac{(E_{123})^2}{2(N-3)} - \frac{F_{123}}{N-3} + O\left(\frac{1}{N^2}\right) \quad (45)$$

so that we find the asymptotic form of Eq. (38) to be

$$\log \psi_{123} = E_{123} + O\left(\frac{1}{N}\right) \quad (46)$$

The $O(N^{-1})$ contributions to J_{123} will play a role in the asymptotic behavior of J_{12} , which we shall consider next. In the by now familiar way we derive

$$\log J_{12} = \rho \int d\mathbf{r}_3 \gamma_3 (\gamma_{13} \gamma_{23} J_{123} e^{-\beta\Phi_{123}} - \gamma_{13} - \gamma_{23} + 1) + O\left(\frac{1}{N}\right)$$

into which result we substitute the expansion for J_{123} that follows from Eq. (45) to find

$$\begin{aligned} \log J_{12} &= \rho \int d\mathbf{r}_3 \gamma_3 (\gamma_{13} \gamma_{23} e^{E_{123} - \beta \Phi_{123}} - \gamma_{13} - \gamma_{23} + 1) \\ &\quad - \frac{\rho^2}{N-3} \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} e^{E_{123} - \beta \Phi_{123}} \\ &\quad \times \int d\mathbf{r}_4 \gamma_4 \gamma_{14} \gamma_{24} \gamma_{34} \gamma_{124} \gamma_{134} \gamma_{234} e^{-\beta \Phi_{123}} \log \psi_{124} + O\left(\frac{1}{N}\right) \end{aligned}$$

The second term results from part of F_{123} and is kept since the integral is $O(N)$: interchanging the order of integration and using [cf. Eqs. (42) and (46)]

$$\begin{aligned} e^{-\beta \Phi_{1234}} &= \gamma_{1234} + O\left(\frac{1}{N}\right) \\ e^{E_{123} - \beta \Phi_{123}} &= \gamma_{123} + O\left(\frac{1}{N}\right) \end{aligned}$$

we see that this second term is

$$\begin{aligned} & - \frac{\rho^2}{N-3} \int d\mathbf{r}_4 \gamma_4 \gamma_{14} \gamma_{24} \gamma_{124} \log \psi_{124} \\ & \quad \times \int d\mathbf{r}_3 \left[\gamma_3 \gamma_{13} \gamma_{23} \gamma_{43} \gamma_{123} \gamma_{143} \gamma_{243} \gamma_{1243} + O\left(\frac{1}{N}\right) \right] \\ & = - \frac{\rho^2}{N-3} \int d\mathbf{r}_4 \gamma_4 \gamma_{14} \gamma_{24} \gamma_{124} \log \psi_{124} \cdot \left[\frac{N-3}{\rho} + O(1) \right] \\ & = - \rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} \gamma_{123} \log \psi_{123} + O\left(\frac{1}{N}\right) \end{aligned}$$

and thus

$$\begin{aligned} \log J_{12} &= \rho \int d\mathbf{r}_3 \gamma_3 (\gamma_{13} \gamma_{23} e^{E_{123} - \beta \Phi_{123}} - \gamma_{13} - \gamma_{23} + 1) \\ &\quad - \rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} \gamma_{123} \log \psi_{123} + O\left(\frac{1}{N}\right) \end{aligned} \tag{47}$$

Since Eq. (46) only determines γ_{123} to leading order and $O(1/N)$ contributions may not be neglected if γ_{123} occurs in an integrand, we must

replace the factor $\gamma_{123} \log \psi_{123}$ by an expression in terms of E_{123} . From Eqs. (38) and (45)

$$\log \psi_{123} = E_{123} - \frac{(E_{123})^2}{2(N-3)} - \frac{F_{123}}{N-3} - \frac{2}{N-2} \log(\psi_{12} \psi_{13} \psi_{23}) + O\left(\frac{1}{N^2}\right)$$

from which one may deduce that

$$\begin{aligned} & \rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} \gamma_{123} \log \psi_{123} \\ &= \rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} E_{123} e^{E_{123} - \beta\Phi_{123}} - \rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} \gamma_{123} \log \psi_{123} \\ & \quad - 2 \log \psi_{12} + O\left(\frac{1}{N}\right) \end{aligned}$$

which yields the following relation:

$$\begin{aligned} & \rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} \gamma_{123} \log \psi_{123} \\ &= -\log \psi_{12} + \frac{1}{2} \rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} E_{123} e^{E_{123} - \beta\Phi_{123}} + O\left(\frac{1}{N}\right) \quad (48) \end{aligned}$$

Combining Eqs. (40), (47), and (48), we find for the asymptotic form of Eq. (40)

$$\begin{aligned} \log \psi_{12} &= \rho \int d\mathbf{r}_3 \gamma_3 (\gamma_{13} \gamma_{23} e^{E_{123} - \beta\Phi_{123}} - \gamma_{13} - \gamma_{23} + 1) \\ & \quad - \frac{1}{2} \rho \int d\mathbf{r}_3 \gamma_3 \gamma_{13} \gamma_{23} E_{123} e^{E_{123} - \beta\Phi_{123}} + O\left(\frac{1}{N}\right) \quad (49) \end{aligned}$$

Collecting our results, dropping the $O(1/N)$ terms, and expressing the equations in terms of the standard quartet, triplet, and pair distribution functions, we obtain, after some rearrangement, the following set of equations for the homogeneous fluid:

$$g_{1234} = \frac{g_{123} g_{124} g_{134} g_{234}}{g_{12} g_{13} g_{14} g_{23} g_{24} g_{34}} \exp(-\beta\Phi_{1234}) \quad (50a)$$

$$\begin{aligned} g_{123} &= g_{12} g_{23} g_{31} \exp \left[-\beta\Phi_{123} + \rho \int d\mathbf{r}_4 \left(\frac{g_{1234}}{g_{123}} - \frac{g_{124}}{g_{12}} - \frac{g_{134}}{g_{13}} \right. \right. \\ & \quad \left. \left. - \frac{g_{234}}{g_{23}} + g_{14} + g_{24} + g_{34} - 1 \right) \right] \quad (50b) \end{aligned}$$

$$g_{12} = \exp \left[-\beta\Phi_{12} + \rho \int d\mathbf{r}_3 \left(\frac{g_{123}}{g_{12}} - g_{13} - g_{23} + 1 \right) - \frac{1}{2} \rho \int d\mathbf{r}_3 \frac{g_{123}}{g_{12}} \left(\beta\Phi_{123} + \log \frac{g_{123}}{g_{12} g_{23} g_{31}} \right) \right] \quad (50c)$$

Equation (50a) has the form of a superposition approximation. For $\Phi_{1234} = 0$ it is just the relation proposed by Fisher and Kopeliovich. Here it is generated by the formalism itself.

The additive constants that have been absorbed into the potentials must again be adjusted so that the potentials approach zero at infinity.

6. CONCLUDING REMARKS

We have presented a new formalism for the generation of integral equations to approximate distribution functions of fluids. It is an adaptation of the conceptual approach underlying the cluster-variation method (CVM) of lattice theories. It is straightforward and generally applicable; it can handle many-body interactions and inhomogeneous fluids.

This work represents the very beginning of a new application of the ideas behind the CVM. There are many important questions that we cannot answer at this stage; in particular, we do not want to make any claims as to the accuracy of the approximations. Nevertheless, we want to lend credence to our approach by showing one result of a first application (which will be presented in full detail in a forthcoming publication). It

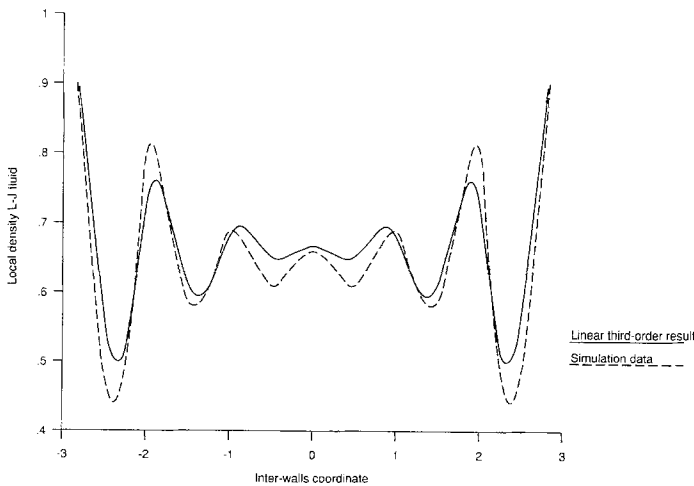


Fig. 1. Density profile of Lennard-Jones fluid between attracting walls. (—) Linearized triplet approximation, (---) Monte Carlo simulation. The temperature is given by $kT/\epsilon = 2$, with ϵ the Lennard-Jones energy parameter.

concerns an inhomogeneous system; although we have not presented the equations for the inhomogeneous case explicitly, they can be derived in a straightforward manner in our formalism, as stated earlier. The example that we show in Fig. 1 concerns a fluid that is confined between two parallel walls. The fluid-wall potential is attractive and exponentially decaying; the fluid molecules interact with a truncated Lennard-Jones potential. The walls are six molecular diameters apart. We used the triplet approximation of our approach. In the inhomogeneous case this results in two coupled integral equations that must be solved. We simplified these equations by linearizing one of the two with respect to the overall density ρ ; the resulting approximation is referred to as the linearized triplet approximation for the density profile.

In Fig. 1 its result is compared with the Monte Carlo simulation result for the same system. Note that this agreement is obtained without any input other than the wall and fluid potentials; state-of-the-art density functional approaches generally need structural information from the homogeneous fluid to achieve comparable results. A detailed presentation of the inhomogeneous equations and the numerical results will be given elsewhere in the near future.⁽¹⁵⁾

NOTE ADDED IN PROOF

The validity of the assumption that $O(1/N)$ corrections may be neglected in the final equations may be questioned. A more detailed asymptotic analysis, to be presented in the near future, clarifies this point.

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