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EXACT SELF-CONSISTENT INTEGRAL EQUATIONS FOR THE DISTRIBUTION FUNCTIONS OF CLASSICAL FLUIDS

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The source particle method (SPM) due to Percus and Verlet of obtaining the single particle density, and the pair and triplet distribution functions of classical fluids (as well as in the variational theory of Bose liquids) is studied. Generalizations of hypernetted chain (HNC) equations are generated by holding fixed the coordinates of the definite group of source particles. Special attention is paid to the triplet distribution function and to the self-consistent calculation of the bridge function (elementary diagram) contribution in the pair distribution function. A comparison with the other exact integral equation theories including the BBGKY-equations is discussed.

Keywords: Source particle method; Triplet distribution function

1. INTRODUCTION

The most popular methods to calculate thermodynamic properties of a fluid from a given interaction potential $V_2(r)$ are based on approximate integral equations [1, 2] for the pair distribution function $g_2(r)$. The first equation of this kind, the Born–Green–Yvon (BGY) equation [3], was derived already in the 1930's while the accurate numerical solution of this as well as the Percus–Yevick (PY) and the hypernetted chain (HNC) equations introduced in the late 1950's and in the early 1960's became possible during the 1960's, first for the simple fluids [1, 4, 2, 5] and later in the 1970's also for more complex

molecular fluids [6]. A very large number of other approximations have been proposed based more or less closely on one or more of the above theories [7, 8, 2, 1, 4, 6].

It is not obvious which of the three integral equations leads to the best values of the pair distribution function. Generally the PY-equation is now regarded superior for the hard sphere potential [9] while the HNC equation is better for longer range potentials [2, 1] and especially for the Coulomb potential and other ionic interactions [10, 11]. The success of the BGY equation depends crucially on the approximation one has to make for the triplet distribution function in order to get a closed set of equations [1, 4, 5]. Therefore, only very recently it has become possible to compute the pair distribution function *via* the BGY equation with accuracy comparable to the other two equations [12–15].

At supercritical temperatures the agreement with computer simulations is quite good but lowering the temperature makes the approximations worse [1, 8, 5, 2]. On the other hand at subcritical densities the thermodynamic values are not satisfactory and the critical constants differ seriously from the experimental results [16, 17]. Therefore, the differences between the predictions of the simple approximate integral equation theories and the computer simulation remain non-negligible, even for simple liquids.

A long time ago Percus [18] and Verlet [19] introduced a powerful method for deriving systematically a series of approximate integral equations for the distribution functions using the functional Taylor-series expansion method in presence of a single test particle. This approach can be regarded in a sense as a generalization of Kirkwood's coupling parameter method [1]. The source particle method may be generalized also for multiparticle distribution functions by distinguishing a group of particles by holding their coordinates fixed instead of just one test particle [1, 20].

2. PRELIMINARIES

2.1. The Grand Canonical Partition Function

We consider a system of particles interacting through the potential

$$\begin{aligned} \mathbf{V}_N(\vec{r}^N) \equiv \mathbf{V}_N(1, \dots, N) &= \sum_{1 \leq i}^N V_1(i) \\ &+ \sum_{1 \leq i < j}^N V_2(i, j) + \sum_{1 \leq i < j < k}^N V_3(i, j, k) + \dots \end{aligned} \quad (1)$$

in a given volume V and free to exchange both particles and energy with its surroundings. For notational convenience, we use the following shorthand notation for the coordinates adopted from Stell [21] and from Morita and Hiroike [22]. The i, j, k etc., are the coordinates used to describe the micro state of particles. They include in general case specification of both the position vector \vec{r}_i and the orientation vector $\vec{\omega}_i$ of the particle i . In the case of mixtures we use \vec{x}_i to refer to all coordinates except species. The n -particle function $F(1, \dots, n)$ refers therefore in mixtures to an array whose function elements are functions $F_{\alpha_1, \dots, \alpha_n}(\vec{x}_1, \dots, \vec{x}_n)$ for particles of species α_i with a coordinate \vec{r}_i for $i = 1, \dots, n$. The generalized integral symbol, $\int d(i)$ contains now the integration over vectors \vec{r}_i and $\vec{\omega}_i$, and in a mixture also the summation over species α_i

$$\int d(i) \equiv \sum_{\alpha_i} \int d\vec{x}_i = \Omega^{-1} \sum_{\alpha_i} \int d\vec{\omega}_i \int d\vec{r}_i. \quad (2)$$

The grand canonical partition function for a simple classical fluid is then defined by [23, 2, 1]

$$\begin{aligned} \Xi &= \sum_{N=0}^{\infty} \frac{1}{N!} \int \dots \int \prod_{i=1}^N z(i) \exp[-\beta \mathbf{V}_N(1, \dots, N)] d(1) \dots d(N) \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \int \dots \int \exp \left[\sum_{i=1}^N u_1(i) + \sum_{1 \leq i < j}^N u_2(i, j) \right. \\ &\quad \left. + \sum_{1 \leq i < j < k}^N u_3(i, j, k) \right] d(1) \dots d(N) \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \int \dots \int \prod_{i=1}^N z^*(i) \exp \left[\sum_{1 \leq i < j}^N u_2(i, j) \right. \\ &\quad \left. + \sum_{1 \leq i < j < k}^N u_3(i, j, k) \right] d(1) \dots d(N). \end{aligned} \quad (3)$$

We have defined the dimensionless external potential [24]

$$u_1(i) = -\nu \ln(\lambda_{\alpha_i}) + \beta\mu_{\alpha_i} - \beta V_1(i) \quad (4)$$

and the corresponding dimensionless multiparticle potentials

$$u_2(i, j) = -\beta V_2(i, j) \quad (5)$$

$$u_3(i, j, k) = -\beta V_3(i, j, k) \quad (6)$$

while the generalized fugacity is

$$z^*(i) = e^{u_1(i)} = z_{\alpha_i} e^{-\beta V_1(i)}, \quad (7)$$

with the definitions

$$z(i) = z_{\alpha_i} = (\lambda_{\alpha_i})^{-\nu} \exp(\beta\mu_{\alpha_i}); \quad \beta = \frac{1}{k_B T}; \quad \lambda_{\alpha_i} = \left(\frac{2\pi\hbar^2}{m_{\alpha_i} k_B T} \right)^{1/2} \quad (8)$$

and ν is the dimension of the system.

2.2. Distribution Functions

We will summarize below the definitions of the correlation functions [1, 21, 24, 18, 25] needed in this paper for a convenient reference to be used in the following sections.

- The n -particle density (distribution function) [1, 2]

$$\begin{aligned} \rho_n(1, \dots, n) &= \prod_{i=1}^n \rho_1(i) g_n(1, \dots, n) = \langle \hat{\rho}_n^{op}(1, \dots, n) \rangle \\ &= \frac{n!}{\Xi} \frac{\delta \Xi}{\delta u_n(1, \dots, n)} \\ &= \frac{z^*(1) \cdots z^*(n)}{\Xi} \frac{\delta^n \Xi}{\delta z^*(1) \cdots \delta z^*(n)} \end{aligned} \quad (9)$$

- The n -particle Ursell correlation function [18, 21]

$$\begin{aligned} F_n(1, \dots, n) &= \prod_{i=1}^n \rho_1(i) h_n(1, \dots, n) = \langle \hat{\rho}_n^{op}(1, \dots, n) \rangle_C \\ &= z^*(1) \cdots z^*(n) \frac{\delta^n \ln \Xi}{\delta z^*(1) \cdots \delta z^*(n)} \end{aligned} \quad (10)$$

- The n -particle cumulant correlation function [18, 21]

$$\begin{aligned} \hat{F}_n(1, \dots, n) &= \langle \hat{\rho}^{op}(1) \cdots \hat{\rho}^{op}(n) \rangle_C \\ &= \frac{\delta^n \ln \Xi}{\delta u_1(1) \cdots \delta u_1(n)} \end{aligned} \quad (11)$$

- The conditional distribution function [1]

$$\begin{aligned} \rho_{m,n}(1, \dots, m | m+1, \dots, m+n) &= \frac{\rho_{m+n}(1, \dots, m+n)}{\rho_m(1, \dots, m)} \\ &= \prod_{i=m+1}^{m+n} z^*(i) \frac{\delta^{m+n} \Xi}{\delta z^*(1) \cdots \delta z^*(m+n)} \left[\frac{\delta^m \Xi}{\delta z^*(1) \cdots \delta z^*(m)} \right]^{-1} \end{aligned} \quad (12)$$

- The potential of mean force [5]

$$\begin{aligned} \ln \rho_n(1, \dots, n) &= \sum_{j=1}^n \left[\sum_{1 \leq i_1 < \dots < i_j \leq n} W_j(i_1, \dots, i_j) \right] \\ &= \sum_{j=1}^n \left[\sum_{1 \leq i_1 < \dots < i_j \leq n} [u_j(i_1, \dots, i_j) + w_j(i_1, \dots, i_j)] \right] \end{aligned} \quad (13)$$

- The generalized superposition excess function [21]

$$Q_n(1, \dots, n) = \exp[W_n(1, \dots, n)] - 1 \quad (14)$$

$$\begin{aligned} \rho_n(1, \dots, n) &= \prod_{1 \leq i \leq n} \rho_1(i) \prod_{1 \leq i < j \leq n} g_2(i, j) \\ &\quad \times \prod_{m=3}^n \prod_{1 \leq i_1 < \dots < i_m \leq n} [1 + Q_m(i_1, \dots, i_m)] \end{aligned} \quad (15)$$

Here $\hat{\rho}_n^{op}(1, \dots, n)$ is the n -particle density operator defined as

$$\hat{\rho}_n^{op}(1, \dots, n) = \sum_{\substack{1 \leq i_1, \dots, i_n \leq N \\ i_1 \neq \dots \neq i_n}} \langle \delta(\vec{r}_1 - \vec{r}_{i_1}) \cdots \delta(\vec{r}_n - \vec{r}_{i_n}) \rangle \quad (16)$$

and the subscript C indicates the cumulant average [26].

Finally we need the relations between the hatted cumulant correlation functions \hat{F}_n and the Ursell cluster functions F_n

$$\begin{aligned}
 \hat{F}_1(1) &= F_1(1) = \rho_1(1) \\
 \hat{F}_2(1, 2) &= F_2(1, 2) + F_1(1)\delta(1, 2) \\
 \hat{F}_3(1, 2, 3) &= F_3(1, 2, 3) + \sum_3 F_2(1, 2)\delta(1, 3) + F_1(1)\delta(1, 2)\delta(1, 3) \\
 \hat{F}_4(1, 2, 3, 4) &= F_4(1, 2, 3, 4) + \sum_6 F_3(1, 2, 3)\delta(1, 4) \\
 &\quad + \sum_3 F_2(1, 2)\delta(1, 3)\delta(2, 4) + \sum_4 F_2(1, 2)\delta(1, 3)\delta(1, 4) \\
 &\quad + F_1(1)\delta(1, 2)\delta(1, 3)\delta(1, 4). \tag{17}
 \end{aligned}$$

The sums denote the number of topologically similar terms.

2.3. The First Legendre Transformation: Definitions

The first Legendre transformation is defined by [27, 28, 21, 10, 29]

$$\hat{C}[\rho_1, u_2, u_3] = \ln \Xi[u_1, u_2, u_3] - \int \rho_1(1) u_1(1) d(1). \tag{18}$$

In a classical system it is often more convenient to use a functional, which is obtained from \hat{C} by subtracting the ideal gas term

$$\begin{aligned}
 C[\rho_1, u_2, u_3] &= \hat{C}[\rho_1, u_2, u_3] - \int \rho_1(1)[1 - \ln \rho_1(1)]d(1) \\
 &= \ln \Xi[u_1, u_2, u_3] - \int \rho_1(1)[1 - \ln \rho_1(1) + u_1(1)]d(1). \tag{19}
 \end{aligned}$$

The functionals C and \hat{C} are related to the free energy of the system [28, 21]. Recalling the definition of the Helmholtz free energy [23, 30] we note immediately that the functional $-k_B TC$ is proportional to the Helmholtz free energy A_I of the system due to interaction between the particles while the functional $-k_B T\hat{C}$ can be interpreted as the total intrinsic free energy

$$\begin{aligned}
 -k_B TC[\rho_1, u_2, u_3] &= A - A_0 = A_I \\
 -k_B T\hat{C}[\rho_1, u_2, u_3] &= A + \nu k_B T \langle N \rangle \ln \lambda_T + \int V_1(1) \rho_1(1) d(1). \tag{20}
 \end{aligned}$$

The first order functional derivatives of these two free energy functionals, $\hat{C}[\rho_1, u_2, u_3]$ and $C[\rho_1, u_2, u_3]$, with respect to the one-particle density are

$$\hat{c}_1(1) \equiv \frac{\delta \hat{C}}{\delta \rho_1(1)} = -u_1(1) \tag{21}$$

$$c_1(1) \equiv \frac{\delta C}{\delta \rho_1(1)} = -u_1(1) + \ln \rho(1), \tag{22}$$

respectively. The function $c_1(1)$ is in fact equivalent with the function $w_1(1)$, *i.e.*, the potential of the single particle mean force,

$$\rho_1(1) = \exp[u_1(1) + w_1[u_1](1)] = \exp[u_1(1) + c_1[\rho_1](1)], \tag{23}$$

but it is now regarded as a functional of the one-particle density ρ_1 and not a functional of the external potential u_1 or z^* as the single particle thermal potential w_1 is. In homogeneous systems the one particle direct correlation function is the intrinsic chemical potential [28]

$$\frac{\mu}{k_B T} = \ln[\rho \lambda_T^\nu] - c_1(1). \tag{24}$$

2.4. Ornstein – Zernicke Equations

The n -particle direct correlation functions

$$c_n(1, \dots, n) = \frac{\delta^n C}{\delta \rho_1(n) \dots \delta \rho_1(1)} \tag{25}$$

and the corresponding hatted direct correlation functions (equivalent with the one-particle irreducible vertex functions in the field theories [21, 31])

$$\begin{aligned} \hat{c}_n(1, \dots, n) &= \frac{\delta^n \hat{C}}{\delta \rho_1(n) \dots \delta \rho_1(1)} \\ &= c_n(1, \dots, n) + (-1)^n (n-2)! \frac{\delta(1, 2) \dots \delta(1, n)}{[\rho_1(1)]^{n+1}} \end{aligned} \tag{26}$$

are then evaluated by successive functional differentiations from the first order equations

$$\begin{aligned}\rho_1(1) &= \exp[u_1(1) + c_1(1)] \\ u_1(1) &= -\hat{c}_1(1),\end{aligned}\quad (27)$$

respectively.

Since the functional derivative of the density $\rho_1(1)$ with respect to the external potential $u_1(2)$ is the hatted Ursell cumulant function $\hat{F}_2(1, 2)$, the second order derivative is simply the well known Ornstein–Zernicke equation [2, 1]. In terms of the hatted functions it is given by [25, 21]

$$\int \hat{F}_2(1, 1') \hat{c}_2(1', 1) d(1') = -\delta(1, 2). \quad (28)$$

In a more familiar form the Ornstein–Zernicke equation can be written in terms of the total correlation function h_2 and the direct correlation function c_2 as follows

$$h_2(1, 2) = g_2(1, 2) - 1 = c_2(1, 2) + \int \rho_1(1') h_2(1, 1') c_2(1', 2) d(1'). \quad (29)$$

Hence the hatted cumulant function \hat{F}_2 and the direct correlation function $-\hat{c}_2$ are functional inverses of each other. The hatted direct correlation functions correspond in fact the one-particle irreducible vertex function in the field theories while the functional \hat{C} itself corresponds their generating functional, the effective action [31].

The third and higher order equations are evaluated subsequently by straightforward application of functional differentiation into the hatted functions [21, 11, 10]. In the case $n=3$ we get the triplet Ornstein–Zernicke equation [21].

$$\begin{aligned}\hat{F}_3(1, 2, 3) &= \int \int \int \hat{F}_2(1, 1') \hat{F}_2(2, 2') \hat{F}_2(3, 3') \\ &\quad \hat{c}_3(1', 2', 3') d(1') d(2') d(3').\end{aligned}\quad (30)$$

The generalized Ornstein–Zernicke equations for the usual direct correlation functions c_n can be derived readily by using the relations

17 to express hatted Ursell correlation functions in terms of the total correlation functions or applying the chain rule directly to Eq. (29). The three particle equation is then given by

$$\begin{aligned}
 h_3(1, 2, 3) = & h_2(1, 3)h_2(2, 3) + h_2(1, 2)h_2(2, 3) + h_2(1, 2)h_2(1, 3) \\
 & + \int \rho_1(1')h_2(1, 1')h_2(2, 1')h_2(3, 1')d(1') \\
 & + \int \int \int \rho_1(1')\rho_1(2')\rho_3(2')\hat{h}_2(1, 1')\hat{h}_2(2, 2')\hat{h}_2(3, 3') \\
 & \times c_3(1', 2', 3')d(1')d(2')d(3'). \tag{31}
 \end{aligned}$$

The first four Ornstein–Zernicke equations are displayed in diagrammatic forms in Figures 1 and 2.

$$\hat{c}(1) = -u(1)$$

$$\hat{h}(12) = \text{zigzag line}$$

$$\hat{c}(12) = \text{helical line}$$

$$\text{zigzag line} \bullet \text{helical line} = - \text{zigzag line} \text{---} \text{helical line}$$

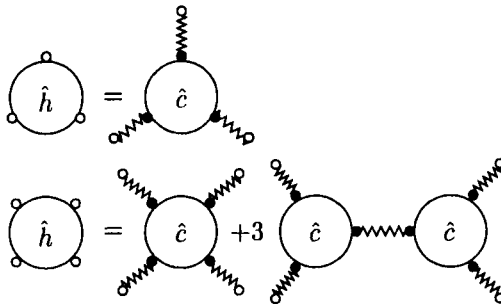


FIGURE 1 Generalized Ornstein–Zernicke equations in terms of the hatted total and direct correlation functions. The bonds drawn with zigzag lines represent cumulant correlation functions \hat{h}_2 and the helical lines are hatted direct correlation functions \hat{c}_2 .

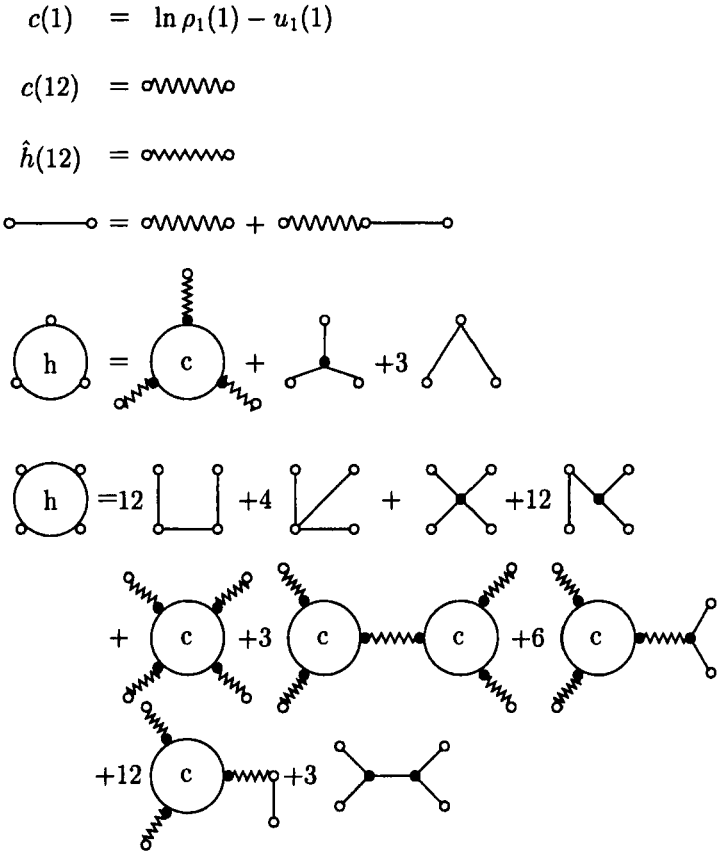


FIGURE 2 Generalized Ornstein–Zernicke equations. Solid bonds represent total pair correlation functions h_2 and zigzag lines are h_2 -functions while the wavy lines are the direct correlation functions.

3. GENERALIZED HNC EQUATIONS

3.1. Percus–Verlet Source Particle Method (SPM)

The basis of the Percus–Verlet method is to introduce an external potential Φ_1 and consider various quantities in the presence of this field. On the other hand one can consider the external field as due to an extra particle added into the system at the coordinate 0. The most common approach is then to study the functional Taylor expansions

of the distribution functions with respect to the one-particle density at a point \vec{r}_i when one adds this extra particle at the origin, $\vec{r}_0 = 0$. The extra test particle is assumed to be fixed while the other n particles move in the external force field caused by the additional $(n+1)$ th particle at the origin. The source particle method may be generalized by distinguishing a group of particles by holding their coordinates fixed instead of just one test particle [1, 20].

Let us consider a system where the total potential energy contains an additional external potential due to the distinguished set of m test particles (labeled with primed coordinates)

$$\begin{aligned} \Phi_m(1', \dots, m' | 1, \dots, N) &= \sum_{i'=1}^m \sum_{j=1}^N V_2(i', j) + \sum_{i'=1}^m \sum_{1 \leq j < k}^N V_3(i', j, k) \\ &+ \sum_{1 \leq i' < j'}^m \sum_{k=1}^N V_3(i', j', k). \end{aligned} \tag{32}$$

The dimensionless total potential of the $N+m$ particles when the m test particles are held fixed is then

$$\begin{aligned} U_N^{(m)}(1', \dots, m', 1, \dots, N) &= -\beta V_N(1, \dots, N) - \beta \Phi_m(1', \dots, m' | 1, \dots, N) \\ &= \sum_{i=1}^N u_1^{(m)}(i) + \sum_{1 \leq i < j}^N u_2^{(m)}(i, j) + \sum_{1 \leq i < j < k}^N u_3^{(m)}(i, j, k). \end{aligned} \tag{33}$$

The single and pair potentials in the presence of the test particles are

$$\begin{aligned} u_1^{(m)}(1) &= u_1(1) + \sum_{i'=1}^m u_2(i', 1) + \sum_{1 \leq i' < j'}^m u_3(i', j', 1) \\ u_2^{(m)}(1, 2) &= u_2(1, 2) + \sum_{i'=1}^m u_3(i', 1, 2) \end{aligned} \tag{34}$$

while in the case of only a single test particle ($r_{1'} = r_0$) we have

$$\begin{aligned} u_1^{(1)}(1) &= u_1(1) + u_2(0, 1) \\ u_2^{(2)}(1, 2) &= u_2(1, 2) + u_3(0, 1, 2). \end{aligned} \tag{35}$$

The partition function in the presence of the external field $\Xi[\Phi]$ is defined by

$$\Xi[\Phi] = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \exp[-\beta\Phi_m(1', \dots, m'|1, \dots, N)] \times \exp[U_N(1, \dots, N)] d(1) \cdots d(N). \quad (36)$$

On the other hand this can be written in terms of a $(N+m)$ -particle potential relabeling the test particles

$$\begin{aligned} \Xi[\Phi] &= \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \frac{\exp[U_{N+m}(1', \dots, m', 1, \dots, N)]}{\exp[U_m(1', \dots, m')]} d(1) \cdots d(N) \\ &= \frac{\Xi}{\exp[U_N(1, \dots, m)]} \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^N}{N!} \int d(m+1) \cdots d(m+N) \\ &\quad \times \exp[U_{N+m}(1, \dots, m, m+1, \dots, m+N)]. \end{aligned} \quad (37)$$

Here Ξ is the partition function in the absence of the external field Φ . Thus we get

$$\Xi[\Phi] = \frac{\rho_m(1, \dots, m)}{\exp[U_m(1, \dots, m)]} \Xi. \quad (38)$$

By similar manipulations we can relate the n -particle distribution functions in the presence of the external field to the conditional $(n+m)$ -particle distribution functions

$$\begin{aligned} \rho_n(1, \dots, n|\Phi) &= \rho_{m,n}(1, \dots, m|m+1, \dots, m+n) \\ &= \frac{\rho_{m+n}(1, \dots, m, m+1, \dots, m+n)}{\rho_m(1, \dots, m)}. \end{aligned} \quad (39)$$

These functions describe the probability of finding the set of n particles within the coordinate set $\{1, \dots, m+n\}$, if it is known that the set of the other m particles has been fixed in positions $\{1, \dots, m\}$ and there is no interactions between the fixed particles.

3.2. Derivation of Generalized HNC Equations Using the Source Particle Method (SPM)

We can make a functional Taylor expansion directly around the value $\Phi_1 = 0$. If this is done we get for example by expanding the Eq. (38) the

well known Kirkwood–Salzburg equation for the activity and similar equations can be derived also for the higher order distribution functions [1]. Kirkwood–Salzburg type equations can be derived also for the one-particle density matrix in inhomogeneous Bose fluids [32].

However, for the short range forces the Kirkwood–Salzburg hierarchy is not practical way to evaluate the distribution functions and in addition integral equations are not in closed form. Instead it is better not to make expansions in Φ_1 but in the one-particle density ρ_1 so as to obtain a faster convergence of the expansion. Since the direct correlation functions c_n and the functions $w_n[\rho_1] = w_n[u_1[\rho_1]]$ (the indirect parts of the potentials of mean force) can be regarded as functionals of ρ_1 it is natural to make expansion for them rather than for the distribution functions as is commonly done in the literature [1].

We consider the external field due to an extra test particle at 0 as a perturbation which is slowly turned on so that finally the extra particle becomes completely indistinguishable from the rest of the n particles

$$\Phi_1(1) \rightarrow V_1^{(1)}(1) = V_1(1) + V_2(0, 1). \tag{40}$$

Hence switching the external field from zero to the value $V_2(0, 1)$, the single particle density changes from $\rho_1(1)$ to the conditional pair distribution function

$$\rho_1(1 | \Phi_1) \rightarrow \rho_{1,1}(0 | 1) = \rho_1(1)g_2(0, 1). \tag{41}$$

Similarly the pair correlation function in the presence of the test particle can be evaluated using the conditional triplet correlation function

$$g_2(1, 2 | \Phi_1) \rightarrow \frac{\rho_{1,2}(0 | 1, 2)}{\rho_{1,1}(0 | 1)\rho_{1,1}(0 | 2)} = g_2(1, 2) + g_2(1, 2)Q_3(0, 1, 2) \tag{42}$$

where Q_3 is the superposition excess function.

3.3. Pair Distribution Function

First we expand the one-particle direct correlation functions c_1 around the unperturbed value $\rho_1(1)$, when $\Phi_1 = 0$. On the other hand

we have the relation for the function c_1

$$c_1(1 | \Phi_1) - c_1(1) = [\ln \rho_1(1 | \Phi_1) - \Phi_1(1) - u_1(1)] - [\ln \rho_1(1) - u_1(1)] \rightarrow \ln g_2(0, 1) - u_2(0, 1) \tag{43}$$

when the external potential is turned on. When we make the functional Taylor-expansion on the left hand side, we get the HNC equation for the radial distribution function

$$\ln g_2(0, 1) - u_2(0, 1) = w_2(0, 1) = N_2(0, 1) + E_2(0, 1) = \int h_2(0, 2) c_2(2, 1) \rho_1(2) d(2) + E_2(0, 1). \tag{44}$$

Here the bridge function E_2 for the elementary diagrams is now given by the following well-known expansion [11, 33]

$$E_2(0, 1) = \frac{1}{2} \int \int h_2(0, 2) h_2(0, 3) c_3(2, 3, 1) \rho_1(2) \rho_1(3) d(2) d(3) + \sum_{n=3}^{\infty} \frac{1}{n!} \int c_{n+1}(1, 2, \dots, n-1) \prod_{i=2}^{n+1} \rho_1(i) h_2(0, i) d(i). \tag{45}$$

Thus first term of the Taylor-expansion (N_2) gives the hypernetted chain (HNC) equation and the rest represents in principle an exact expansion for the elementary diagrams provided that we can calculate the multiparticle direct correlation functions.

3.4. Single Particle Density

The HNC equation for the one-particle density may be obtained similarly as the functional Taylor expansion of the grand partition function [34]. The generating functional of the direct correlation functions in the presence of the test particle is defined as follows

$$C[\Phi_1] = \ln \Xi[\Phi_1] - \int \rho_1(1 | \Phi_1) [u_1(1) + \Phi_1(1) + 1 - \ln \rho_1(1 | \Phi_1)] d(1) \rightarrow \ln[\rho_1(0)\Xi] - u_1(0) - \int \rho_{1,1}(0 | 1) [u_1(1) + u_2(0, 1) + 1 - \ln \rho_{1,1}(0 | 1)] d(1). \tag{46}$$

The evaluation of the Taylor-expansion for $C[\Phi_1] - C$ is then straightforward and we get the result

$$\begin{aligned}
 w_1(0) &= c_1(0) = \ln \rho_1(0) - u_1(0) \\
 &= \int g_2(0, 1) [\ln g_2(0, 1) - u_2(0, 1)] \rho_1(1) d(1) \\
 &\quad + \frac{1}{2} \int \int h_2(0, 1) h_2(0, 2) c_2(1, 2) \rho_1(1) \rho_1(2) d(1) d(2) \\
 &\quad + \sum_{n=3}^{\infty} \frac{1}{n!} \int c_n(1, 2, \dots, n) \prod_{i=1}^n \rho_1(i) h_2(0, i) d(i). \tag{47}
 \end{aligned}$$

Use of the pair HNC equation for the nodal diagrams $N_2(0, 1)$ yields an equation whose leading term is the familiar expression for the chemical potential in HNC approximation [35, 22]

$$\begin{aligned}
 w_1(0) &= c_1(0) = \ln \rho_1(0) - u_1(0) \\
 &= \int [c_2(0, 1) - h_2(0, 1) N_2(0, 1) - g_2(0, 1) E_2(0, 1)] \rho_1(1) d(1) \\
 &\quad + \frac{1}{2} \int \int h_2(0, 1) h_2(0, 2) c_2(1, 2) \rho_1(1) \rho_1(2) d(1) d(2) \\
 &\quad + \sum_{n=3}^{\infty} \frac{1}{n!} \int c_n(1, 2, \dots, n) \prod_{i=1}^n \rho_1(i) h_2(0, i) d(i). \tag{48}
 \end{aligned}$$

This equation (the generalization of the Kirkwood – Buff or Yvon equation) can be written in more compact form using the pair Ornstein – Zernicke equation and the expansion (45) for the bridge function

$$\begin{aligned}
 \ln \rho_1(0) &= u_1(0) + E_1(0) \\
 &\quad + \int \left[c_2(0, 1) - \frac{1}{2} h_2(0, 1) N_2(0, 1) - E_2(0, 1) \right] \rho_1(1) d(1) \tag{49}
 \end{aligned}$$

where the single particle bridge function for the one-particle elementary diagrams is given by the expansion

$$\begin{aligned}
 E_1(0) &= -\frac{1}{3} \int \int \int h_2(0, 1) h_2(0, 2) h_2(0, 3) c_3(1, 2, 3) \\
 &\quad \rho_1(1) \rho_1(2) \rho_1(3) d(1) d(2) d(3) \\
 &\quad - \sum_{n=4}^{\infty} \frac{n-1}{n!} \int \dots \int c_n(1, 2, \dots, n) \prod_{i=1}^n \rho_1(i) h_2(0, i) d(i). \tag{50}
 \end{aligned}$$

3.5. Triplet Distribution Function

For the triplet equation there are several choices for a function to expand:

- the potential of mean force regarded as a functional of the single particle density $w_2(1, 2) = s_2(1, 2) = s_2[\rho_1, u_2](1, 2)$
- the pair direct correlation function $c_2(1, 2)$
- the bridge function E_2 summing the elementary diagrams (it has to be regarded as a functional of the density and the pair potential, $E_2(1, 2) = E_2[\rho_1, u_2](1, 2)$).

We make first an expansion for the function s_2 and get the very same result, which was originally derived by Verlet [19]. A similar equation was discussed already earlier by Percus [18]. The result written in our notation is

$$\begin{aligned} \ln \left[\frac{g_3(0, 1, 2)}{g_2(0, 1) g_2(0, 2) g_2(1, 2)} \right] \\ = \int h_2(0, 3) s_{2,1}(1, 2 | 3) \rho_1(3) d(3) \\ + \frac{1}{2} \int \int h_2(0, 3) h_2(0, 4) s_{2,2}(1, 2 | 3, 4) \rho_1(3) \rho_1(4) d(3) d(4) \\ + \sum_{n=3} \frac{1}{n!} \int \cdots \int s_{2,n}(1, 2 | 3, \dots, n) \prod_{i=1}^n h_2(0, i) \rho_1(i) d(i), \quad (51) \end{aligned}$$

where $s_{2,n}$ are functional derivatives of the pair potential of mean force with respect to the density. The first term of this expansion can be written in terms of the triplet distribution function using the Ornstein–Zernicke equation (44) and the following relation for the functional derivatives of the potential of mean force with respect to the fugacity (labeled as $w_{2,1}$) and with respect to the density (labeled as $s_{2,1}$) [36]

$$w_{2,1}(1, 2 | 3) = \int s_{2,1}(1, 2 | 3') \hat{F}_2(3', 3) d(3'). \quad (52)$$

When we set $s_{2,n} = 0$ for $n \geq 2$ we get the HNC2 equation of Verlet for the triplet distribution function (which we denote as the

HNCII(V) equation)

$$\ln \left[\frac{g_3(0, 1, 2)}{g_2(0, 1) g_2(0, 2) g_2(1, 2)} \right] = \int c_2(0, 3) \rho_1(3) w_{2,1}(1, 2 | 3) d(3). \quad (53)$$

The functional derivative of the potential of mean force $w_{2,1}$ is equivalent with the function α_3 defined by Verlet [19]

$$\begin{aligned} w_{2,1}(1, 2; 3) &= \frac{g_3(1, 2, 3)}{g_2(1, 2)} - g_2(1, 3) - g_2(2, 3) + 1 \\ &= g_2(1, 2) Q_3(1, 2, 3) + h_2(1, 3) h_2(2, 3). \end{aligned} \quad (54)$$

The third case leads to an asymmetric triplet HNC2 equation which is extensively studied by Puoskari and Kallio [37]. Similar equations are discussed also by Attard [38, 39] for classical liquids and by Fertig and Halperin [40] for calculating quasiparticle energies in the fractional quantized Hall effect. Therefore we skip further discussion of this alternative here in order to save space.

In Figures 3 and 4 the first three terms of the iterative solution of Verlet's HNCII equation are shown in the column labeled HNCV while the column labeled HNCW gives the results from the HNC2 equation of Puoskari and Kallio [37]. These results should be compared with the exact expansion for the triplet potential of mean force w_3 also displayed in Figures 3 and 4. In addition the last





No	K	n		Exact	HNCV	HNCW	HNCW
1	0	4		1	1	1	1
2	1	5		3	2	3	3
3	1	5		1	-	1	1

FIGURE 3 The first and second order diagrams in the diagrammatic expansion for the triplet potential of mean force w_3 obtained as the solution of various HNC2 equations: HNCV (Verlet [19]), HNCW (Puoskari and Kallio [37]), HNCW (Wertheim [41]). The solid bonds represent total pair correlation functions h_2 .

No	K	n		Exact	HNCV	HNCP	HNCW
4	2	5		3	1	2	-
5	2	6		1	-	-	-
6	2	6		3	2	3	3
7	2	6		6	-	4	6
8	2	6		6	2	3	-
9	2	6		6	-	3	3
10	2	6		3	-	1	3
11	2	6		3	-	2	3
12	2	6		3	-	1	1
13	2	6		3	1	-	-
14	2	6		3	-	-	3
15	2	6		1	-	-	1

FIGURE 4 The third order diagrams in the diagrammatic expansion for the triplet potential of mean force w_3 obtained as the solution of various HNC2 equations: HNCV (Verlet [19]), HNCP (Puoskari and Kallio [37]), HNCW (Wertheim [41]). The solid bonds represent total pair correlation functions h_2 .

column in these figures gives the results from the HNC2 equation of Wertheim [41]. Unfortunately one can see that already the second order diagrams are not obtained correctly from Verlet's HNCII equation. Furthermore Verlet and Levesque [42] reported that even though numerical results from the corresponding PYII equation are improved for classical Lennard-Jones fluids, they are still bad whenever the original PY or HNC theory is poor. However Attard [38] and Henderson and Sokolowski [43] have reported that the PYII equation provides an accurate method for calculating the bridge functions for the hard sphere system. Nevertheless we feel that Verlet's HNCII equation is not a completely satisfactory extension of the HNC theory and have to look a better way to formulate it [37]. In addition both the HNC2 equation of Verlet as well as that of Puoskari and Kallio are asymmetric with respect to the third coordinate r_0 .

Still another possibility is to expand the pair direct correlation function

$$c_2(1, 2 | \Phi_1) \rightarrow c_2(1, 2) + c_{1,2}(0 | 1, 2) \tag{55}$$

using the functional Taylor-expansion

$$\begin{aligned} c_{1,2}(0 | 1, 2) \equiv & \int h_2(0, 3) \rho_1(3) c_3(1, 23) d(3) \\ & + \frac{1}{2} \int \int h_2(0, 3) h_2(0, 4) \rho_1(3) \rho_1(4) c_4(1, 2, 3, 4) d(3) d(4) \\ & + \sum_{n=5}^{\infty} \frac{1}{n!} \int \cdots \int c_n(1, 2, \dots, n) \prod_{i=2}^n \rho_1(i) h_2(0, i) d(i). \end{aligned} \tag{56}$$

A closure relation between three particle direct correlation function and distribution functions is obtained from the pair Ornstein-Zernicke equation by turning the external potential on. We get then

$$\begin{aligned} h_2(1, 2 | \Phi_1) \rightarrow h_{1,2}(0 | 1, 2) \equiv & \frac{g_3(0, 1, 2)}{g_2(0, 1) g_2(0, 2)} - 1 \\ & = g_2(12) Q_3(0, 1, 2) + h_2(1, 2) \end{aligned} \tag{57}$$

which leads to the triplet HNC equation

$$\begin{aligned} h_{1,2}(0|1,2) &= g_2(12) Q_3(0,1,2) + h_2(1,2) \\ &= c_2(1,2) + c_{1,2}(0|1,2) \\ &\quad + \int [h_2(1,3) + g_2(13) Q_3(0,1,3)] \\ &\quad \times g_2(0,3) [c_2(3,2) + c_{1,2}(0|32)] \rho_1(3) d(3). \end{aligned} \quad (58)$$

Using the pair Ornstein–Zernicke equation this equation can be written in two alternative forms. Eliminating the direct correlation functions c_2 we get the following equation

$$\begin{aligned} g_2(12) Q_3(0,1,2) \\ &= c_{1,2}(0|1,2) + \int [h_2(1,3) + g_2(13) Q_3(0,1,3)] \times g_2(0,3) [c_2(3,2) \\ &\quad + c_{1,2}(0|32)] \rho_1(3) d(3), \end{aligned} \quad (59)$$

which is displayed also diagrammatically in Figure 5. Alternatively using the full triplet distribution function in the form defined by Pinski and Campbell [44]

$$\begin{aligned} T_3(0;1,2) &\equiv g_3(0,1,2) - g_2(0,1) g_2(0,2) \\ &= g_2(0,1) g_2(0,2) g_2(1,2) Q_3(0,1,2) \\ &\quad + g_2(0,1) g_2(0,2) h_2(1,2). \end{aligned} \quad (60)$$

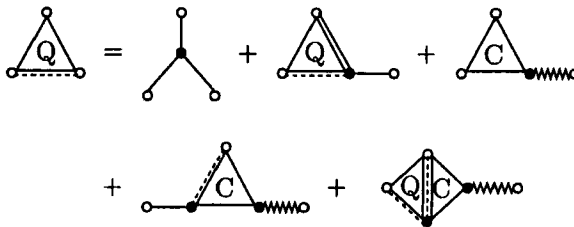


FIGURE 5 The HNC equation for triplet correlation function using the source particle method in the form introduced by Puoskari and Kallio [37]. The solid and dashed bonds represent total pair correlation functions h_2 and radial distribution functions g_2 , respectively, while the zigzag-lines are the hatted correlation functions \hat{h}_2 .

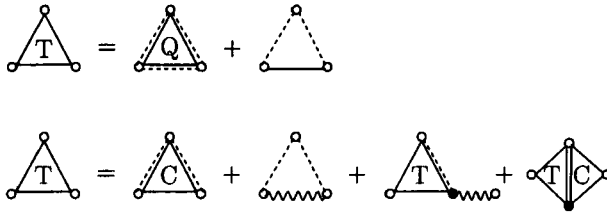


FIGURE 6 The extension of the HNC2 equation of Pinski and Campbell [44] for the triplet correlation function using the source particle method. The solid and dashed bonds represent total pair correlation functions h_2 and radial distribution functions g_2 , respectively, while the wavy line is the direct correlation function c_2 .

we can write the equation in the following form (displayed diagrammatically in Fig. 6)

$$T_3(0, 1, 2) = g_2(0, 1) g_2(0, 2) [c_2(1, 2) + c_{1,2}(0 | 1, 2)] + \int T_3(0, 1, 3) [c_2(3, 2) + c_{1,2}(0 | 3, 2)] \rho_1(3) d(3). \tag{61}$$

Thus we see that the Eq. (58) is an extension of the equation which was derived by Pinski and Campbell [44] using a different method. The triplet HNC equation of Pinski and Campbell is obtained we set $c_{1,2} = 0$. Later also Scherwinski [45] and Pizio [20] have discussed quite similar equations (see also the paper of Puoskari and Kallio [37]).

4. BBGKY EQUATIONS

The Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy is in principle an exact set of equations if the multiparticle correlation functions could be calculated rigorously. With pairwise additive forces the first two BBGKY-equations are [4, 1, 6]

$$\begin{aligned} \nabla_1 \rho_1(1) &= [\nabla_1 u_1(1)] \rho_1(1) + \int [\nabla_1 u_2(1, 2)] \rho_2(1, 2) d(2) \\ \nabla_1 g_2(1, 2) &= [\nabla_1 u_2(1, 2)] g_2(1, 2) \\ &+ \int [\nabla_1 u_2(1, 3)] [g_3(1, 2, 3) - g_2(1, 2) g_2(1, 3)] \rho_1(3) d(3). \end{aligned} \tag{62}$$

The pair equation can be integrated using of the triplet HNC equation of Pinski and Campbell [44]. Differentiating Eq. (61) and substituting the resulting equation to the second BBGKY equation we get

$$\begin{aligned} \nabla_1 \ln g_2(1, 2) &= \nabla_1 u_2(1, 2) \\ &+ \nabla_1 \int [u_2(1, 2) + h_2(1, 2) - \ln g_2(1, 2)] h_2(2, 3) \rho_1(3) d(3) \\ &+ \int \int [\nabla_1 g_2(1, 2)] c_{1,2}(1 | 3, 4) \\ &\quad \hat{F}_2(4, 2) \rho_1(3) \rho_1(4) d(3) d(4). \end{aligned} \tag{63}$$

Using the HNC and Ornstein – Zernicke equations the final result for the solution of the radial distribution function is

$$\begin{aligned} \ln g_2(1, 2) &= u_2(1, 2) + E_2(1, 2) + \int h_2(1, 3) c_2(3, 2) \rho_1(3) d(3) \\ \nabla_1 E_2(1, 2) &= \int [\nabla_1 g_2(1, 3)] c_{1,2}(1 | 2, 3) \rho_1(3) d(3). \end{aligned} \tag{64}$$

Substituting the functional Taylor series expansion for the asymmetric triplet direct correlation function $c_{1,2}$ and integrating over the gradient of the bridge function we end up with exactly same expansion which has been already derived in the previous section by applying the source particle method

$$E_2(1, 2) = \sum_{n=2}^{\infty} \frac{1}{n!} \int c_{n+1}(1, 2, \dots, n+1) \prod_{i=3}^{n+1} \rho_1(i) h_2(1, i) d(i). \tag{65}$$

Substituting the HNC expansion (64) in the first equation and integrating over the particle 1 we get immediately the single particle equation for the chemical potential (48)

$$\begin{aligned} \nabla_1 E_1(1, 2) &= - \int [\nabla_1 E_2(1, 2)] h_2(1, 2) \rho_1(2) d(2) \\ &= - \int \int \nabla_1 [h_2(1, 2) h_2(1, 3)] c_{1,2}(1 | 2, 3) \rho_1(2) d(2) \rho_1(3) d(3) \\ E_1(1) &= - \sum_{n=3}^{\infty} \frac{n-1}{n!} \int \dots \int c_n(2, 3, \dots, n+1) \prod_{i=2}^{n+1} \rho_1(i) h_2(1, i) d(i). \end{aligned} \tag{66}$$

In conclusion we see that both the source particle method and the self-consistent solution of the first two BBGKY-equations lead exactly to the same functional Taylor-expansions for the one and two particle bridge functions (or for the sums of the elementary diagrams) when we use the Taylor-expansion closure (56) for the direct correlation function $c_{1,2}$ together with the triplet HNC2 equation (58) instead of the usual superposition approximation or the Abe expansion for the triplet distribution function.

5. CONCLUSIONS

The Percus–Verlet source particle method is an old approach in deriving various integral equation theories for classical liquids. So the basic ideas of this report are not new.

However the source particle method for the triplet function is extended with several ways. In this paper we have presented a systematic method for choosing the functional to be expanded in the case of one, two and three particle distribution functions and hopefully also made more transparent the connection with the density functional theories.

The well known density expansion of the bridge function is extended also for the one and three particle HNC equations. The one and two particle expansions are also derived by solving the two lowest order BBGKY equations using a new improved and exact expansion for the triplet distribution function.

Finally we note that the asymmetric HNC equation derived using the SPM method turns out to be the basic building block when the two-particle ring diagram expansion of the entropy is generalized for the three particle functions and in the derivation of the triplet HNC2 equations originally developed by Baxter and Wertheim [41, 46].

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