High-order direct correlation functions of uniform fluids and their application to the high-order perturbative density functional theory

Shiqi Zhou* and Eli Ruckenstein†

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York, 14260
(Received 24 August 1999)

Simple analytical expressions for the direct correlation functions of uniform fluids of all orders are derived based on a simple weighted density approximation. The equation thus obtained for the third-order direct correlation function is in satisfactory agreement with simulation data for uniform hard sphere fluids. The obtained expressions are employed to derive two general equations for the perturbative density functional theory of all orders. One of them concerns the direct correlation functions, while the other concerns the direct correlation functions weighted with the present weighting function. The general equations have been used to determine the equilibrium structure about a test molecule immersed in a bulk fluid of the same species. The calculations indicated that both equations with expansions truncated at the fifth order provided for bulk fluids improvements with respect to the second-order perturbative density functional theory (corresponding to the hypernetted-chain closure). The second equation with the bulk density considered as an adjustable parameter, determined by equating the ''virial pressure'' calculated for a bulk fluid to the Carnahan-Starling pressure, provided the best agreement with simulation data. The second equation with an adjusted bulk density was also used to determine the density profile of a hard sphere fluid in a spherical cavity; good agreement with simulation data was obtained.

I. INTRODUCTION

Over the past decade the density functional methods, developed originally for the study of many electron quantum systems [1], has played a key role in providing a comprehensive picture of the complex thermodynamic behavior of fluids in confined geometries, because of its physical clarity and computational simplicity [2–5]. As quite general approaches to the equilibrium distribution in nonuniform fluids, the density functional theories have proven to be some of the most successful, widely applicable approaches to a variety of interfacial phenomena, such as adsorption, wetting, freezing, etc. [6–10]. In the density functional approach, the grand potential of a many particle system is expressed as a unique functional of its local density [11], and acquires its minimum value when calculated for the equilibrium density obtained by solving the corresponding variational problem. In the functional for the grand potential $\Omega[\rho(\mathbf{r})] = F_{id}[\rho(\mathbf{r})] + F_{ex}[\rho(\mathbf{r})] + \int d\mathbf{r}\rho(\mathbf{r})[\varphi_{ext}(\mathbf{r}) - \mu]$, μ is the chemical potential, $\varphi_{ext}(\mathbf{r})$ is the external potential which causes the density distribution $\rho(\mathbf{r})$, the ideal-gas free energy $F_{id}[\rho(\mathbf{r})]$ is given by the exact relation

$$F_{id}[\rho(\mathbf{r})] = \beta^{-1} \int d\mathbf{r}\rho(\mathbf{r})\{\ln[\rho(\mathbf{r})\lambda^3] - 1\},$$

where $\lambda = [h^2/(2\pi m\beta^{-1})]^{1/2}$ is the de Broglie wavelength, and $\beta = 1/kT$ is the reciprocal temperature. However, the exact relation for the excess (over the ideal gas contribution) free energy $F_{ex}[\rho(\mathbf{r})]$ which originates from interparticle interactions is not known. Therefore a major effort in the development of the density functional theory (DFT) has been to approximate the functional in terms of the local density of the system. The basic assumption of all density functional theories is that the thermodynamic potential of a nonuniform system can be obtained from that of the corresponding uniform system. What distinguishes the various theories from one another is the detailed manner in which each formulates the link between the two. The existing DFTs fall mainly into two categories: (1) the weighted (nonperturbative) density functional theories (WDFT) and (2) the perturbative density functional theories (PDFT). In the former, physically motivated *ad hoc* assumptions were made to render the excess free energy of the inhomogeneous system calculable; this was done by constructing an approximation of the local or global excess free energy by mapping the excess free energy per particle or the correlation function of the inhomogeneous system to that of a uniform system with an effective or weighted local density. The WDFT approaches have been mostly employed to predict the structure of a one-component fluid near one or between two walls [12,13], and some of them have been extended to binary mixtures [14–16], electrolyte solutions [17,18], colloidal dispersions [19,20], and also to the study of freezing [21,22] etc. These WDFTs have achieved some success in predicting results in good agreement with computer simulations for hard sphere fluids, but they are computationally demanding. Furthermore, most of the WDFTs [23,24] fail, to a greater or lesser extent, when applied to more realistic potentials such as the inverse-power and Yukawa potentials. In the perturbative density functional theories (PDFT), the excess free energy of the inhomogeneous system is functionally expanded about that of the corresponding uniform system

$$\beta F_{ex}[\rho] = \beta F_{ex}(\rho_b) - \sum_{n=1}^{\infty} \frac{1}{n!} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_n$$

$$\times C_0^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; \rho_b) \nabla \rho(\mathbf{r}_1) \cdots \nabla \rho(\mathbf{r}_n), \quad (1)$$

*Electronic address: chixiayzsq@163.net
†Electronic address: feaeliru@acsu.buffalo.edu

where $\nabla \rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_b$ is the departure of the density from the density ρ_b of a uniform system and $C_0^{(n)}$ are the n order direct correlation functions (DCFs) of the uniform system. In most applications of the theory the expansion has been truncated at the second order due to the lack of information regarding the higher-order direct correlation functions for the uniform system. The second order PDFT has been criticized by Cutrin [25] and Baus and Colot [26], who demonstrated that the perturbative expansion is slowly convergent for hard sphere fluids. In applications to systems characterized by pair potentials such as $\phi(r) \sim r^{-n}$, the second order PDFT has proven even less adequate [27]; in application to the one-component plasma [28], the second order PDFT failed to predict a freezing transition at all. These results pointed to the need for a detailed analysis of the form and behavior of the higher-order direct correlation functions that reside in the omitted terms. In this respect, Barrat, Hansen, and Pastore (BHP) [29] have suggested an approximation for $C_0^{(3)}$ based on the factorization: $C_0^{(3)}(\mathbf{r}, \mathbf{r}'; \rho_b) = t(r) t(r') t(|\mathbf{r} - \mathbf{r}'|)$, with $t(r)$ determined by requiring that $C_0^{(3)}(\mathbf{r}, \mathbf{r}'; \rho_b)$ should satisfy, in the Fourier space, for $n = 3$, the exact relation

$$C_0^{(n)}(\mathbf{k}_1, \ldots, \mathbf{k}_{n-1}, 0; \rho_b) = \frac{\partial}{\partial \rho_b} C_0^{(n-1)}(\mathbf{k}_1, \ldots, \mathbf{k}_{n-1}; \rho_b)$$
$$n \geq 2. \quad (2)$$

Later, Curtin and Ashcroft [30] suggested an approximation for $C_0^{(3)}(\mathbf{r}, \mathbf{r}'; \rho_b)$ based on a weighted-density approximation (WDA) for the excess free energy functional of an inhomogeneous system, while Denton and Ashcroft [31] proposed approximate analytical expressions for $C_0^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n; \rho_b)$ with $n = 3, 4, 5$ based on the WDA for the first-order direct correlation function of an inhomogeneous system [16]. These three approaches have equivalent accuracies and the $C_0^{(3)}(\mathbf{r}, \mathbf{r}'; \rho_b)$ thus calculated were in agreement with simulation data. Among these three approaches, the first required the numerical solution of an integral equation, the second a solution of a differential equation in the Fourier space, while the third became very complicated when extended to higher-order direct correlation functions $C_0^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n; \rho_b)$ with $n > 5$. Recently, Khein and Ashcroft [32] proposed a symmetric algebraic ansatz for $C_0^{(3)}(\mathbf{r}, \mathbf{r}'; \rho_b)$ which provided satisfactory agreement with simulation data. All the above approaches have not been used in the PDFTs approaches mainly because the resulting approximations for high-order direct correlation functions are computationally demanding. Therefore there is a need for simple, analytical expressions for $C_0^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n; \rho_b)$ for all n which can be conveniently employed to develop a PDFT approach beyond the second order. This is the motivation of this paper.

The plan of the present paper is as follows: In Sec. II, approximate analytical expressions for

$$C_0^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n; \rho_b)$$

for all n are derived based on a simple weighted density approximation (SWDA) [33]; the predictions of the expression obtained for the third order direct correlation function of a uniform hard sphere fluid are compared with simulation

data, and the behavior of the higher order direct correlation functions is examined (no simulation data are available in literature for comparison). In Sec. III, the obtained expressions allow to derive two general PDFT equations for all orders, which are employed to determine the equilibrium structure about a test particle immersed in a bulk hard sphere fluid as well as the equilibrium density profile of a hard sphere fluid in a spherical cavity. Finally, Sec. IV summarizes the results.

II. APPROXIMATE ANALYTICAL EXPRESSIONS FOR THE DIRECT CORRELATION FUNCTIONS OF UNIFORM FLUIDS OF ALL ORDERS

In the weighted density approximation [16], $C^{(1)}(\mathbf{r}; [\rho])$, the first order direct correlation function of non-uniform fluids is approximated as

$$C^{(1)}(\mathbf{r}; [\rho]) = C_0^{(1)}(\bar{\rho}(\mathbf{r})), \quad (3)$$

where $C_0^{(1)}(\bar{\rho}(\mathbf{r}))$ is the first order direct correlation function of a uniform fluid for a weighted density $\bar{\rho}(\mathbf{r})$ defined as

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\mathbf{r})). \quad (4)$$

In the simple weighted density approximation [33], $\bar{\rho}(\mathbf{r})$ in the "weighting function" w of Eq. (4) is replaced by ρ_b. While the results obtained in this manner are more approximate than those obtained in Ref. [16], this approximation allows us to derive simple expressions for the DCFs of all orders as the present paper demonstrates. The resulting weighting function w is required to satisfy the usual normalization condition

$$\int dr' w(|\mathbf{r} - \mathbf{r}'|; \rho_b) = 1 \quad (5)$$

and the unique specification of w follows from the relationship:

$$\lim_{\rho(r) \to \rho_b} \left[\frac{\delta}{\delta \rho(\mathbf{r}')} C^{(1)}(\mathbf{r}; [\rho]) \right] = C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b). \quad (6)$$

Equation (6) together with Eqs. (3)–(5) provide the following form for the weighting function:

$$w(|\mathbf{r} - \mathbf{r}'|; \rho_b) = \frac{C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b)}{C_0^{(1)'}(\rho_b)}. \quad (7)$$

Approximate expressions for the DCFs of all orders can be derived on the basis of the equation

$$C_0^{(n)}(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{n-1}; \rho_b) = \lim_{\rho(r) \to \rho_b} \left[\frac{\delta^{n-1} C^{(1)}(\mathbf{r}; [\rho])}{\delta \rho(\mathbf{r}_1) \cdots \delta \rho(\mathbf{r}_{n-1})} \right] \quad (8)$$
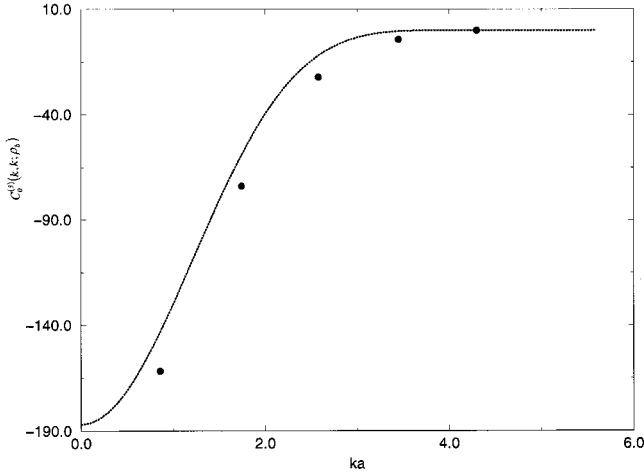
which leads to

FIG. 1. Three-particle direct correlation function (DCF) $C_0^{(3)}$ vs ka for wave vectors of equal magnitude. The curve represents the present approximation for hard sphere; the dots are the MD data of BHP for soft spheres [29].

$$C_0^{(n)}(\mathbf{r},\mathbf{r}_1,\dots,\mathbf{r}_{n-1};\rho_b)$$

$$= w(\mathbf{r},\mathbf{r}_1;\rho_b)\cdots w(\mathbf{r},\mathbf{r}_{n-1};\rho_b)C_0^{(1)^{(n-1)}}(\rho_b)$$

$$= \frac{C_0^{(1)^{(n-1)}}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^{n-1}}C_0^{(2)}(\mathbf{r},\mathbf{r}_1;\rho_b)\cdots C_0^{(2)}(\mathbf{r},\mathbf{r}_{n-1};\rho_b)$$

$$n\geq 2. \quad (9)$$

For $n=3$, Eq. (9) yields

$$C_0^{(3)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2;\rho_b) = w(\mathbf{r},\mathbf{r}_1;\rho_b)w(\mathbf{r},\mathbf{r}_2;\rho_b)C_0^{(1)''}(\rho_b)$$

$$= \frac{C_0^{(1)''}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^2}C_0^{(2)}(\mathbf{r},\mathbf{r}_1;\rho_b)C_0^{(2)}(\mathbf{r},\mathbf{r}_2;\rho_b)$$

$$(10)$$

which in the Fourier space becomes

$$C_0^{(3)}(k,k';\rho_b) = \frac{C_0^{(1)''}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^2}C_0^{(2)}(k;\rho_b)C_0^{(2)}(k';\rho_b).$$

$$(11)$$

All the direct correlation functions should be symmetrical, however, Eqs. (9), (10), and (11) are symmetrical only in the special cases in which the magnitudes of the wave vectors are equal. This deficiency can be corrected [see Eqs. (12) and (23)].

Equation (11) was used to calculate $C_0^{(3)}$ for a hard sphere liquid by employing the Percus-Yevick approximations for $C_0^{(2)}(|\mathbf{r}-\mathbf{r}'|;\rho_b)$ and $C_0^{(1)}(\rho_b)$. The results are plotted in Fig. 1 versus ka, where $a=(3/4\pi\rho_b)^{1/3}$, for the special case $|\mathbf{k}|=|\mathbf{k}'|$; for comparison the MD data [29] for soft spheres are also included. The density $\rho_b\sigma^3=0.871$ at which the hard-sphere $C_0^{(3)}$ was computed, was selected to ensure agreement with the BHP soft sphere approximation [29] at $k=0$. Figure 1 shows that the dependence of $C_0^{(3)}$ on the wave-vector
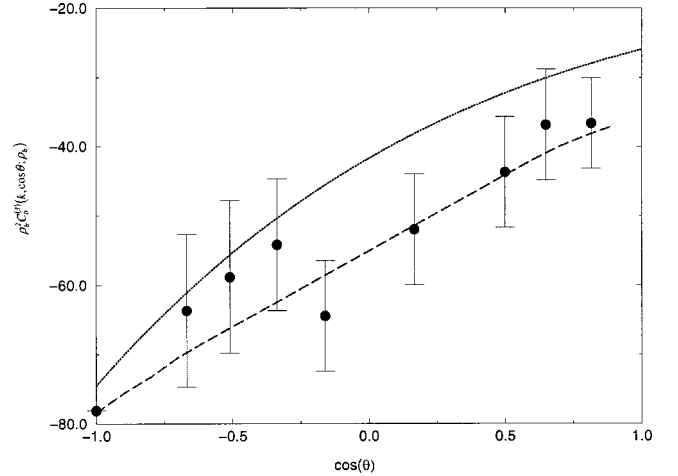

FIG. 2. Three-particle direct correlation function $C_0^{(3)}(k,\cos\theta;\rho_b)$ for $|\mathbf{k}|=|\mathbf{k}'|\equiv k=2.3045$ and a packing fraction $\eta=0.45$; θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. The dotted curve presents the present approximation, the long-dashed curve Eq. (5) in Ref. [32], and the dots are the simulation results with two standard deviation errors bars [34].

magnitude is in satisfactory agreement with the MD data, to within the statistical uncertainty of the MD data.

As suggested previously [31], Eq. (11) can be made symmetrical using the following simple symmetry requirement on Eq. (11):

$$C_0^{(3)}(\mathbf{k},\mathbf{k}';\rho_b) = \frac{1}{3}[C_0^{(3)}(k,k';\rho_b)+C_0^{(3)}(k,|\mathbf{k}+\mathbf{k}'|;\rho_b)$$

$$+C_0^{(3)}(k',|\mathbf{k}+\mathbf{k}'|;\rho_b)]. \quad (12)$$

Equation (11) combined with Eq. (12) has a form similar to Eq. (5) in Ref. [32]. In Figs. 2–4, the $C_0^{(3)}$ given by Eq. (12) is plotted for $|\mathbf{k}|=|\mathbf{k}'|$ and various choices of the wave-vector magnitude, at a packing fraction $\eta=\rho_b\pi\sigma^3/6=0.45$; also included are the Monte Carlo (MC) simulations for a hard-sphere fluid with two standard deviation error bars [34] and the results of Eq. (5) of Ref. [32]. The predictions of Eq. (12) are not in complete agreement with the MC data, but they are almost comparable to those of Eq. (5) in Ref.
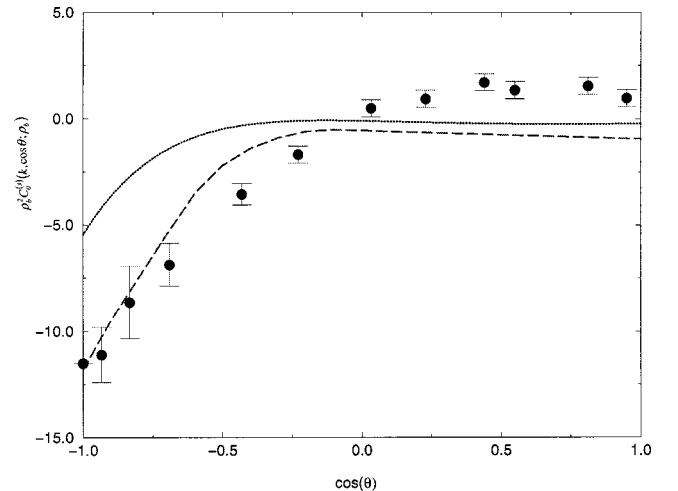

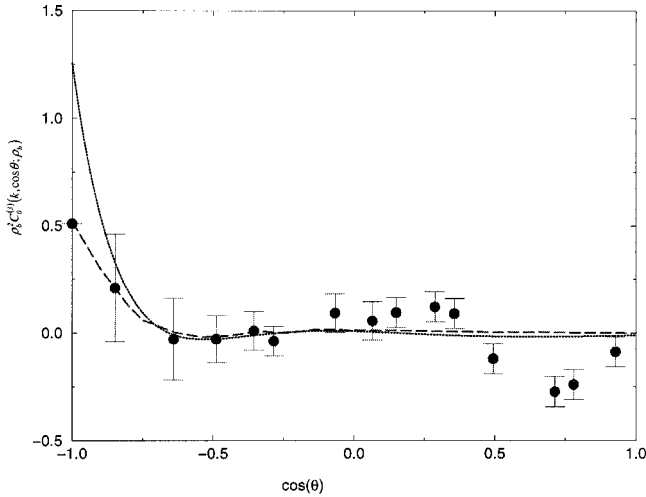FIG. 3. The same as in Fig. 2, but for $k=5.153$.

FIG. 4. The same as in Fig. 2, but for $k=7.0404$.

[32]. From Figs. 2–4 one can observe that as $|\mathbf{k}|=|\mathbf{k}'|=k$ increases, the discrepancy increases; this is expected because the present approximation [Eq. (11) combined with Eq. (12)] satisfies Eq. (2) only for $|\mathbf{k}|=|\mathbf{k}'|=0$:

$$C_0^{(3)}(\mathbf{0},\mathbf{0};\rho_b)=\frac{C_0^{(1)''}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^2}C_0^{(2)}(\mathbf{0};\rho_b)C_0^{(2)}(\mathbf{0};\rho_b)$$

$$=\frac{C_0^{(1)''}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^2}C_0^{(1)'}(\rho_b)C_0^{(1)'}(\rho_b)$$

$$=C_0^{(2)'}(\mathbf{0};\rho_b). \qquad (13)$$

It should be noted that the approximate expressions of Refs. [29,30] satisfied Eq. (2) only for $|\mathbf{k}|=|\mathbf{k}'|=0$ and $\mathbf{k}=-\mathbf{k}'$, while that of Ref. [31] only for $|\mathbf{k}|=|\mathbf{k}'|=0$. It is worth emphasizing that both the present equation and that of Ref. [31] are based on the WDA approximation [16], the former involving the additional approximation due to the substitution of $\bar{\rho}(\mathbf{r})$ in the "weighting function" w by ρ_b. However, that simplification, allowed us to obtain simple

FIG. 6. The same as in Fig. 2, but for large wave vectors.

expressions for the direct correlation functions of any order, while that of Ref. [31], which are given up to the fifth order, are very complex. In some cases, as shown in Figs. 1 and 2, our approximations do not introduce major errors, while in others, shown in Figs. 3 and 4 they produce errors for values of $\cos(\theta)$ near -1. However, as shown later in this paper, the accuracy can be improved both by regarding ρ_b in the derivatives of $C_0^{(1)}(\rho_b)$ as an adjustable parameter and/or by symmetrizing the basic equation (9) as in Eq. (23). While our approximation introduces some inaccuracies, its simplicity allows to extract some information about any order direct correlation function. In Fig. 5, the three, four, and five-particle DCFs are plotted versus ka for a uniform hard-sphere fluid (at a density $\rho_b\sigma^3=0.871$) for small values of k; Fig. 6 presents the results for large values of k. From Fig. 5 one can see that the absolute value of $C_0^{(n)}$ at $k=0$ increases markedly as the order increases; the same behavior is also revealed by Fig. 7 where the normalized functions of $C_0^{(n)}(k;\rho_b)/C_0^{(n)}(0;\rho_b)$ are plotted for $n=2,3,4,5$. From Fig. 6 one can observe that the detailed structure of $C_0^{(n)}(k;\rho_b)$ is increasingly lost with increasing k when the order is raised; this occurs because the direct correlation function of hard sphere fluids is short range.
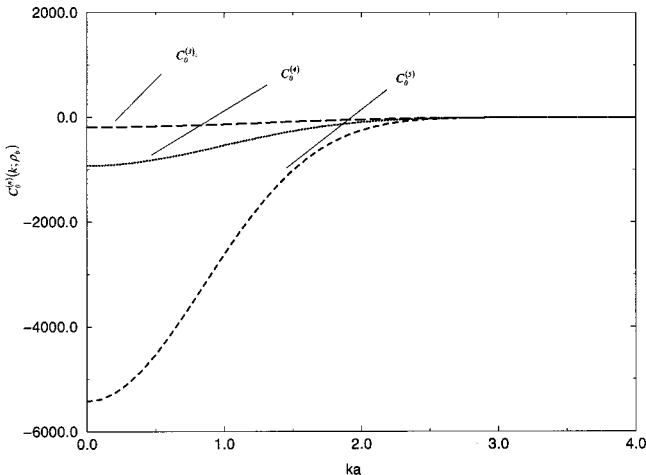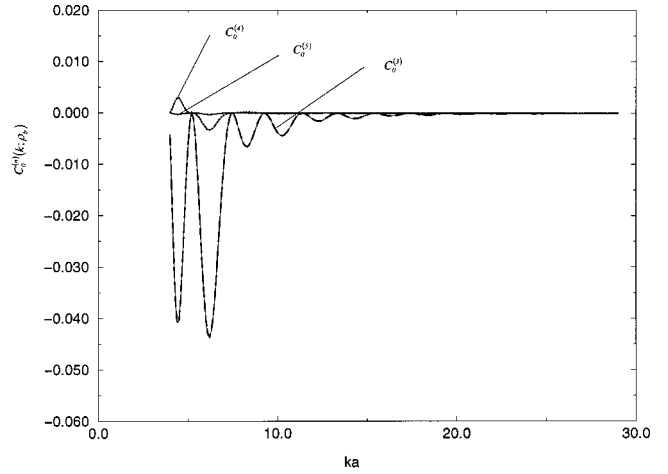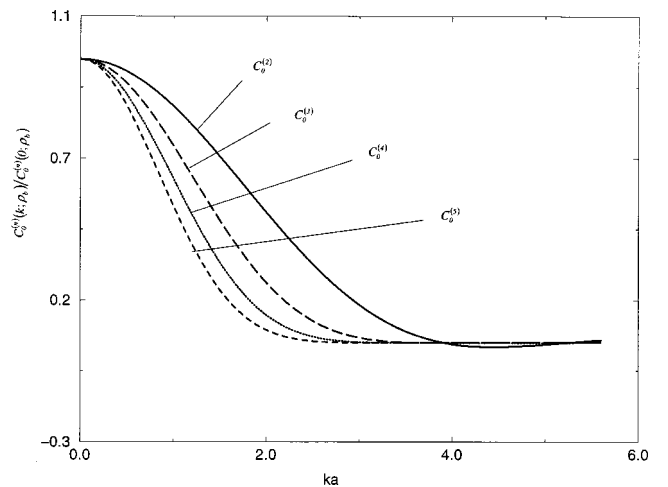

FIG. 5. Approximate four- and five-particle direct correlation functions (DCFs) vs ka for wave vectors of equal magnitude. The three-particle function is also included for comparison.

FIG. 7. Normalized approximate DCFs vs ka for wave vectors of equal magnitude.

III. HIGH-ORDER PERTURBATIVE DENSITY FUNCTIONAL THEORY FOR NONUNIFORM FLUIDS

Let us consider a classical fluid at a fixed temperature $kT = \beta^{-1}$ and chemical potential μ in an external field $\varphi_{\text{ext}}(\mathbf{r})$. In DFT, the density profile of an inhomogeneous fluid is given by the equation

$$\rho(\mathbf{r}) = \rho_b \exp[-\beta \varphi_{\text{ext}}(\mathbf{r}) + C^{(1)}(\mathbf{r};[\rho]) - C_0^{(1)}(\rho_b)]. \quad (14)$$

Expanding the first-order DCF of a nonuniform fluid about an uniform fluid, one can write

$$C^{(1)}(\mathbf{r};[\rho]) = C_0^{(1)}(\rho_b) + \int d\mathbf{r}_1 (\rho(\mathbf{r}_1) - \rho_b) C_0^{(2)}(\mathbf{r},\mathbf{r}_1;\rho_b)$$

$$+ \sum_{n=3}^{\infty} \frac{1}{(n-1)!} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_{n-1}$$

$$\times \prod_{m=1}^{n-1} [\rho(\mathbf{r}_m) - \rho_b] C_0^{(n)}(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{n-1};\rho_b). \quad (15)$$

Substituting expressions (9) for $C_0^{(n)}(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{n-1};\rho_b)$ in Eq. (15), yields

$$C^{(1)}(\mathbf{r};[\rho]) = C_0^{(1)}(\rho_b) + \sum_{n=2}^{\infty} \frac{1}{(n-1)!} \frac{C_0^{(1)^{(n-1)}}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^{n-1}}$$

$$\times \left[\int d\mathbf{r}' C_0^{(2)}(\mathbf{r},\mathbf{r}';\rho_b)(\rho(\mathbf{r}') - \rho_b) \right]^{n-1}, \quad (16)$$

and the density profile equation acquires the form

$$\rho(\mathbf{r}) = \rho_b \exp\left(-\beta \varphi_{\text{ext}}(\mathbf{r}) + \sum_{n=2}^{\infty} \frac{1}{(n-1)!} \frac{C_0^{(1)^{(n-1)}}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^{n-1}} \right.$$

$$\left. \times \left[\int d\mathbf{r}' C_0^{(2)}(\mathbf{r},\mathbf{r}';\rho_b)(\rho(\mathbf{r}') - \rho_b) \right]^{n-1} \right). \quad (17)$$

Let us consider a homogeneous bulk hard sphere fluid and select one of the molecules considered located in the origin as a test molecule; the pair potential $\phi(r)$ between the test molecule and any other molecule is regarded as the external potential $\varphi_{\text{ext}}(\mathbf{r})$

$$\phi(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma. \end{cases} \quad (18)$$

The resulting nonuniform density profile around the test molecule is given by the expression [35]

$$\rho(\mathbf{r}) = \rho_b g(\mathbf{r}), \quad (19)$$

where $g(\mathbf{r})$ is the radial distribution function of the bulk fluid. Thus, for this special type of inhomogeneity, Eq. (17) provides the following equation for $g(\mathbf{r})$:

$$g(\mathbf{r}) = \exp\left(-\beta \phi(\mathbf{r}) + \sum_{n=2}^{\infty} \frac{\rho_b^{n-1}}{(n-1)!} \frac{C_0^{(1)^{(n-1)}}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^{n-1}} \right.$$

$$\left. \times \left[\int d\mathbf{r}' C_0^{(2)}(\mathbf{r},\mathbf{r}';\rho_b)(g(\mathbf{r}') - 1) \right]^{n-1} \right). \quad (20)$$

If the expansion in Eq. (20) is truncated at the second order, one obtains

$$g(\mathbf{r}) = \exp\left[-\beta \phi(\mathbf{r}) + \rho_b \int d\mathbf{r}' C_0^{(2)}(\mathbf{r},\mathbf{r}';\rho_b)(g(\mathbf{r}') - 1) \right]. \quad (21)$$

Combining Eq. (21) with the Ornstein-Zernike (OZ) equation

$$g(\mathbf{r}) - 1 = C_0^{(2)}(\mathbf{r};\rho_b) + \rho_b \int d\mathbf{r}' C_0^{(2)}(\mathbf{r},\mathbf{r}';\rho_b)(g(\mathbf{r}') - 1)$$

leads to

$$g(\mathbf{r}) = \exp[-\beta \phi(\mathbf{r}) + g(\mathbf{r}) - 1 - C_0^{(2)}(\mathbf{r};\rho_b)] \quad (22)$$

which represents the hypernetted-chain (HNC) closure of the OZ equation. Equation (20) with the expansion truncated at different orders was solved in spherical coordinates and the calculations indicated that the predictions of Eq. (20) with the expansion truncated at the third order was in better agreement with simulation data than that truncated at the second order; at the fourth order the accuracy was decreased, while at the fifth order the accuracy was increased. The predictions of the fifth-order PDFT were almost identical to those of the sixth-order PDFT. In Fig. 8, the predictions of Eq. (20) with the expansion truncated at the second and the fifth order are plotted for a bulk density $\rho_b \sigma^3 = 0.6$; the simulation data [36] are also included for comparison. Figure 8 shows that the predictions of Eq. (20) with the expansion truncated at the fifth order are still unsatisfactory at and near the contact point. There are two reasons for the discrepancy: (1) the lack of symmetry with respect to $\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{n-1}$ in the expressions of the high-order direct correlation functions Eq. (9) on which Eq. (20) is based and (2) the approximation made in the calculation of the weighting function w. Consequently, there are two ways to improve Eq. (20): one is to symmetrize expression (9), and another one is to regard ρ_b in the derivatives of $C_0^{(1)}(\rho_b)$ as an adjustable parameter. Consequently, we replace Eq. (9) by Eq. (23) which is the weighted Eq. (9) and is symmetrical with respect to all arguments $\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{n-1}$,

$$C_0^{(n)}(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{n-1};\rho_b)$$

$$= \overline{C_0^{(n)}(\mathbf{r}_0,\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{n-2};\rho_b)}$$

$$= \int C_0^{(n)}(\mathbf{r}_0,\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{n-2};\rho_b) w(\mathbf{r}_0,\mathbf{r}_{n-1};\rho_b) d\mathbf{r}_0$$

$$= \frac{C_0^{(1)^{(n-1)}}(\rho_b)}{[C_0^{(1)'}(\rho_b)]^n} \int C_0^{(2)}(\mathbf{r}_0,\mathbf{r};\rho_b) C_0^{(2)}(\mathbf{r}_0,\mathbf{r}_1;\rho_b) \cdots C_0^{(2)}$$

$$\times (\mathbf{r}_0,\mathbf{r}_{n-2};\rho_b) C_0^{(2)}(\mathbf{r}_0,\mathbf{r}_{n-1};\rho_b) d\mathbf{r}_0,$$
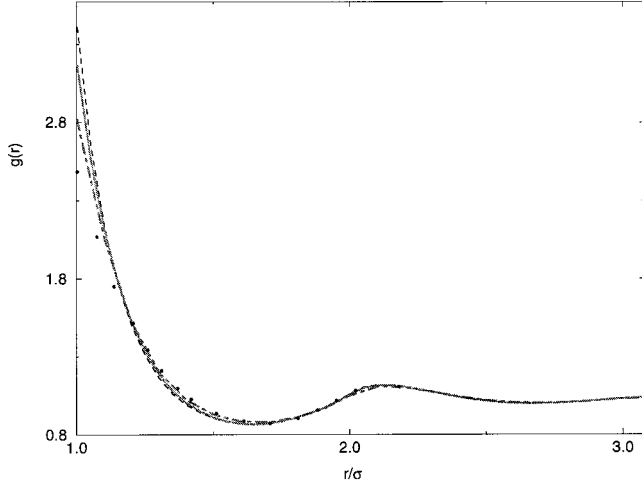
$$n \geq 3. \quad (23)$$

FIG. 8. $g(r)$ for a uniform hard sphere fluid with $\rho_b\sigma^3=0.6$. The dashed curve is given by Eq. (20) with the expansion truncated at the second order, the dotted line is given by Eq. (20) with the expansion truncated at the fifth order, the dot-dashed curve is given by Eq. (26) with the expansion truncated at the fifth order, and the dots represent the simulation data [36].

The substitution of Eq. (23) into Eq. (15) yields

$$
\begin{aligned}
C^{(1)}(\mathbf{r};[\rho]) = &\, C_0^{(1)}(\rho_b) + \int d\mathbf{r}_1(\rho(\mathbf{r}_1)-\rho_b)C_0^{(2)}(\mathbf{r},\mathbf{r}_1;\rho_b) \\
&+ \sum_{n=3}^{\infty} \frac{C_0^{(1)^{(n-1)}}(\rho_b)}{(n-1)![C_0^{(1)'}(\rho_b)]^n} \int C_0^{(2)}(\mathbf{r},\mathbf{r}'';\rho_b) \\
&\times \left[\int C_0^{(2)}(\mathbf{r}',\mathbf{r}'';\rho_b)(\rho(\mathbf{r}')-\rho_b)d\mathbf{r}'\right]^{n-1} d\mathbf{r}''.
\end{aligned}
\tag{24}
$$

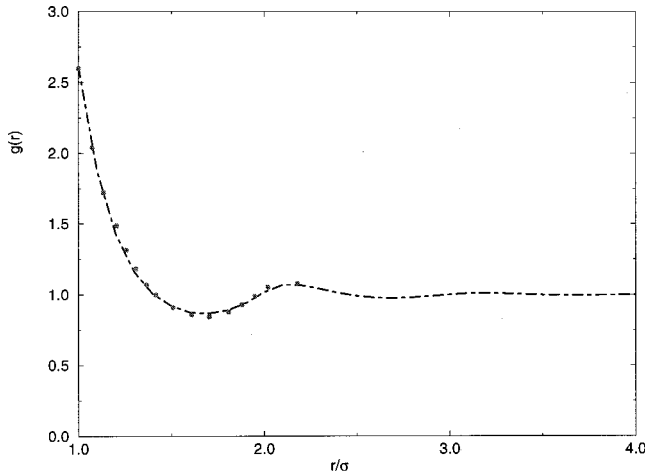Using Eq. (24), one obtains the $\rho(\mathbf{r})$ for a nonuniform fluid

FIG. 9. $g(r)$ for a uniform hard sphere fluid with $\rho_b\sigma^3=0.6$. The curve is given by Eq. (26) with the expansion truncated at the fifth order and ρ_b as an adjusted parameter, and the dots represent the simulation data [36].
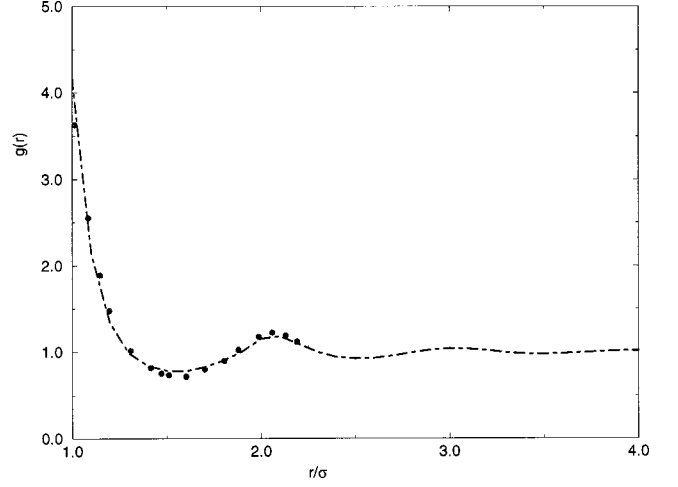

FIG. 10. The same as in Fig. 9, but for $\rho_b\sigma^3=0.8$.

$$
\begin{aligned}
\rho(\mathbf{r}) = &\, \rho_b \exp\Bigg(-\beta\varphi_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}_1(\rho(\mathbf{r}_1)-\rho_b)C_0^{(2)}(\mathbf{r},\mathbf{r}_1;\rho_b) \\
&+ \sum_{n=3}^{\infty} \frac{C_0^{(1)^{(n-1)}}(\rho_b)}{(n-1)![C_0^{(1)'}(\rho_b)]^n} \int C_0^{(2)}(\mathbf{r},\mathbf{r}'';\rho_b) \\
&\times \left[\int C_0^{(2)}(\mathbf{r}',\mathbf{r}'';\rho_b)(\rho(\mathbf{r}')-\rho_b)d\mathbf{r}'\right]^{n-1} d\mathbf{r}''\Bigg),
\end{aligned}
\tag{25}
$$

and the $g(\mathbf{r})$ for a uniform fluid:

$$
\begin{aligned}
g(\mathbf{r}) = &\, \exp\Bigg(-\beta\phi(\mathbf{r}) + \rho_b\int d\mathbf{r}_1(g(\mathbf{r}_1)-1)C_0^{(2)}(\mathbf{r},\mathbf{r}_1;\rho_b) \\
&+ \sum_{n=3}^{\infty} \frac{\rho_b^{n-1}C_0^{(1)^{(n-1)}}(\rho_b)}{(n-1)![C_0^{(1)'}(\rho_b)]^n} \int C_0^{(2)}(\mathbf{r},\mathbf{r}'';\rho_b) \\
&\times \left[\int C_0^{(2)}(\mathbf{r}',\mathbf{r}'';\rho_b)(g(\mathbf{r}')-1)d\mathbf{r}'\right]^{n-1} d\mathbf{r}''\Bigg).
\end{aligned}
\tag{26}
$$

Figure 8 presents the predictions of Eq. (26) for an expansion truncated at the fifth order and shows that they are improved by imposing the symmetry condition on the expressions for the high order direct correlation functions. However, an additional improvement is achieved by regarding ρ_b in the derivatives of $C_0^{(1)}(\rho_b)$ and only in these derivatives as an adjustable parameter, determined by equating the virial pressure predicted by Eq. (26) according to the formula

$$
\frac{\beta p^v}{\rho_b} = 1 - \frac{2\pi\rho_b\beta}{3}\int_0^{\infty} g(r)\frac{d\phi(r)}{dr}r^3 dr
\tag{27}
$$

to the pressure given by the Carnahan-Starling equation [37]

$$
\frac{\beta p^{cs}}{\rho_b} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3},
\tag{28}
$$

where $\eta=\rho_b\pi\sigma^3/6$ is the packing fraction. Figures 9 and 10 present the predictions of Eq. (26) for an expansion truncated at the fifth order and an adjusted parameter ρ_b determined as
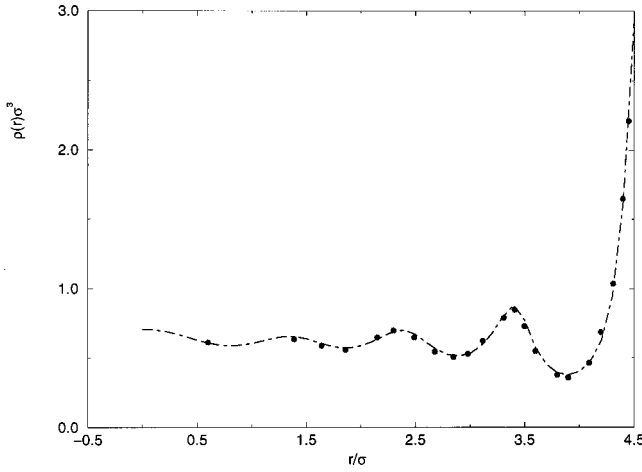
FIG. 11. Density profile of a hard sphere fluid ($\rho_b \sigma^3 = 0.62$) confined in a spherical cavity. The dots represent the simulation data [38], and the curve the predictions of Eq. (29).

FIG. 12. The same as in Fig. 11, but for $\rho_b \sigma^3 = 0.75$.

above, as well as the simulation data [36]. They show that the agreement is much improved.

Equation (25) will be now applied to a hard sphere fluid in a spherical cavity with a hard wall and radius $R + \sigma/2$. In this case, the density profile equation has the form

$$\rho(\mathbf{r}) = \rho_b \exp\left(-\beta\varphi_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}_1 (\rho(\mathbf{r}_1) - \rho_b) C_0^{(2)}(\mathbf{r}, \mathbf{r}_1; \rho_b) \right.$$

$$+ \sum_{n=3}^{\infty} \frac{C_0^{(1)^{(n-1)}}(\rho_b)}{(n-1)! [C_0^{(1)'}(\rho_b)]^n} \int C_0^{(2)}(\mathbf{r}, \mathbf{r}''; \rho_b)$$

$$\times \left. \left[\int C_0^{(2)}(\mathbf{r}', \mathbf{r}''; \rho_b)(\rho(\mathbf{r}') - \rho_b) d\mathbf{r}' \right]^{n-1} d\mathbf{r}'' \right),$$

$$|\mathbf{r}| < R, = 0, \quad |\mathbf{r}| > R, \tag{29}$$

where

$$\varphi_{\text{ext}}(\mathbf{r}) = \infty, \quad |\mathbf{r}| > R$$

$$= 0, \quad |\mathbf{r}| < R \tag{30}$$

and the density ρ_b is a bulk density unaffected by the external field due to the cavity wall [hence at a position far away from the cavity wall ($|\mathbf{r}| \to \infty$)]. Figures 11 and 12 present
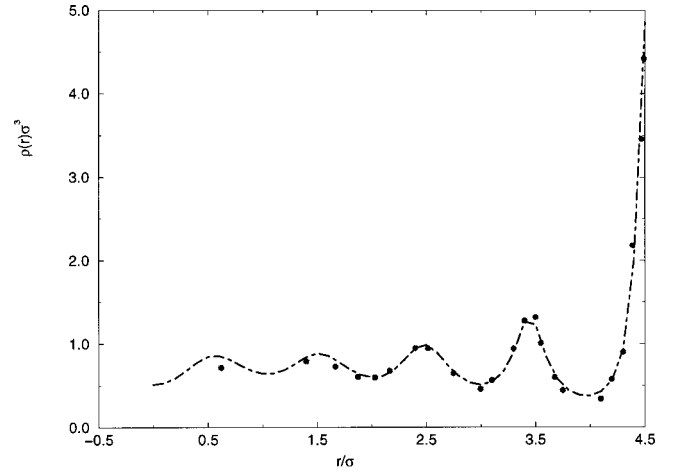
the predictions of Eq. (29) for an expansion truncated at the fifth order and with an adjusted ρ_b in the derivatives of $C_0^{(1)}(\rho_b)$ for two densities and $R = 4.5\sigma$, as well as the computer simulation data [38]. Because $F_{\text{ex}}[\rho(\mathbf{r})]$ is a universal functional for systems involving pairwise additive interactions and independent of the external potential responsible for the inhomogeneity, it is reasonable to consider that the adjusted ρ_b is equal in this case to that obtained above for the radial distribution function in a uniform system; of course, ρ_b at infinity for the former is equal to the bulk ρ_b in the latter [the adjusted ρ_b is used only in the derivatives of $C_0^{(1)}(\rho_b)$]. Figures 11 and 12 show that the predictions of the present theory are in good agreement with simulation data, and at least as good as the results of earlier and more complex theories [39–40].

IV. CONCLUSION

In summary, simple analytical expressions for the direct correlation functions of all orders for uniform fluids are derived, and it is shown that the predictions of the third order direct correlation function are in reasonable agreement with simulation data for hard sphere fluids. Further these expressions are employed to build a perturbative density functional theory of nonuniform fluids beyond the second order whose predictions are in good agreement with simulation data for both a uniform hard sphere fluid and a nonuniform hard sphere fluid in a spherical cavity.

[1] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[2] R. A. Lovett, C. Y. Mou, and F. P. Buff, J. Chem. Phys. **65**, 570 (1976).

[3] M. S. Wertheim, J. Chem. Phys. **65**, 2377 (1976).

[4] N. D. Mermin, Phys. Rev. **137**, A1441 (1965).

[5] J. T. Chayes and L. Chayes, J. Stat. Phys. **36**, 471 (1984).

[6] E. Kerlik and M. L. Rosinberg, Phys. Rev. A **44**, 5025 (1991).

[7] F. van Swol and J. R. Henderson, Phys. Rev. A **40**, 2567 (1989).

[8] F. van Swol and J. R. Henderson, Phys. Rev. A **43**, 2932 (1991).

[9] R. Evans, in *Liquids at Interfaces*, edited by J. Chervolin, J. F. Joanny, and J. Zinn-Justin (Elsevier, Amsterdam, 1989).

[10] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19**, 2775 (1979).

[11] S. K. Ghosh and B. M. Deb, Phys. Rep. **92**, 1 (1982).

[12] T. Zixiang, L. E. Scriven, and H. T. Davis, J. Chem. Phys. **95**, 2659 (1991).

[13] J. G. Powles, G. Rickayzen, and M. L. Williams, Mol. Phys. **64**, 33 (1988).

[14] Z. Tan, U. Marini Bettolo Marconi, F. van Swol, and K. E.

Gubbins, J. Chem. Phys. **90**, 3704 (1989).

[15] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **42**, 7312 (1990).

[16] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **44**, 8242 (1991).

[17] C. N. Patra and S. K. Ghosh, Phys. Rev. E **48**, 1154 (1993).

[18] C. N. Patra and S. K. Ghosh, Phys. Rev. E **47**, 4088 (1993).

[19] N. Choudhury and S. K. Ghosh, J. Chem. Phys. **104**, 9563 (1996).

[20] N. Choudhury and S. K. Ghosh, Phys. Rev. E **53**, 3847 (1996).

[21] A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **74**, 2559 (1981).

[22] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 4701 (1989).

[23] B. B. Laird and D. M. Kroll, Phys. Rev. A **42**, 4810 (1990).

[24] J. L. Barrat, J. P. Hansen, G. Pastore, and E. M. Waisman, J. Chem. Phys. **86**, 6360 (1987).

[25] W. A. Curtin, J. Chem. Phys. **88**, 7050 (1988).

[26] M. Baus and J. L. Colot, Mol. Phys. **55**, 653 (1985).

[27] J. L. Barrat, J. P. Hansen, G. Pastore, and E. M. Waisman, J. Chem. Phys. **86**, 6360 (1987).

[28] M. Rovere and M. P. Tosi, J. Phys. C **18**, 3445 (1985).

[29] J. L. Barrat, J. P. Hansen, and G. Pastore, Phys. Rev. Lett. **58**, 2075 (1987).

[30] W. A. Curtin and N. W. Ashcroft, Phys. Rev. Lett. **59**, 2385 (1987).

[31] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 426 (1989).

[32] A. Khein and N. W. Ashcroft, Phys. Rev. E **59**, 1803 (1999).

[33] S. Zhou, J. Chem. Phys. **110**, 2140 (1999).

[34] Y. Rosenfeld, D. Levesque, and J. J. Weis, J. Chem. Phys. **92**, 6818 (1990).

[35] J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and A. L. Lebowitz (Benjamin, New York, 1964), p. 113.

[36] J. A. Barker and D. Henderson, Mol. Phys. **21**, 187 (1971).

[37] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[38] M. Calleja, A. N. North, J. G. Powles, and G. Rickayzen, Mol. Phys. **73**, 973 (1991).

[39] S. C. Kim, J. K. Suh, and S. H. Suh, Mol. Phys. **79**, 1369 (1993).

[40] S. C. Kim and S. H. Suh, J. Chem. Phys. **104**, 7233 (1996).