

LADDER APPROXIMATION FOR THREE- AND FOUR-PARTICLE CORRELATION FUNCTIONS

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ABSTRACT

An example of an application of a recently developed generalized Ornstein-Zernike formalism to the numerical evaluation of equilibrium three- and four-particle correlation functions is given. Using a simple closure approximation leading to the ladder approximation we have numerically evaluated dipole-dipole-interaction correlation functions for a polarizable nonpolar hard-sphere fluid. These functions depend on the three- and four-particle correlation functions and describe a correction to the Clausius-Mossoti formula for the dielectric constant and an integrated intensity measured in depolarized light scattering experiments. Qualitative agreement with computer simulation data was found for a wide range of densities up to the fluid-solid phase transition. For high densities the ladder approximation yields much better results than the Kirkwood superposition approximation, which becomes useless in this contest at liquid-state densities.

Key words:

many-particle correlation functions, simple fluids, Ornstein-Zernike equation, ladder approximation, Kirkwood superposition approximation, dielectric constant, Clausius-Mossoti formula, depolarized light scattering.

I. INTRODUCTION

The problem of how to efficiently calculate k -particle equilibrium correlation functions, of order $k > 2$, still remains an important challenge, even for simple fluids. Many-particle correlation functions, in particular three- and four-particle, play an essential role in various problems of both equilibrium and non-equilibrium statistical physics. Examples of theories in which expressions for important physical quantities include three- and four-particle correlation functions are the theory of the dielectric constant⁽¹⁻³⁾ and the theory of depolarized interaction-induced light scattering (DILS)^(4,5). Other examples include the thermodynamic perturbation theory^(6,7), the kinetic theory of dense fluids⁽⁸⁻¹³⁾, and the theory of dense suspensions of Brownian particles^(14,15).

While there is a fundamental need for detailed knowledge of the k -particle correlation functions with $k > 2$, there is still a lack of good evaluation methods. The Kirkwood superposition approximation (KSA), the most widely used, is not sufficiently accurate for many applications, particularly at high densities. In the present paper we give an example of an application of an alternative, powerful method, based on an integral-equation approach. Our method is particularly suited for evaluating correlation functions of a general form

$$G_{ab} = \frac{1}{N} \left\langle \sum_{\substack{i,j=1 \\ i \neq j}}^N \delta a(\mathbf{r}_{ij}) \sum_{\substack{k,l \\ k \neq l}}^N \delta b(\mathbf{r}_{kl}) \right\rangle, \quad (1.1)$$

where

$$\delta a(\mathbf{r}_{ij}) = a(\mathbf{r}_{ij}) - \langle a(\mathbf{r}_{ij}) \rangle, \quad (1.2)$$

is the deviation of the function a from its average value; $\langle \dots \rangle$ denotes a canonical ensemble average, \mathbf{r}_{ij} is a relative position of the particles i and j , and N is a total number of particles in the system.

A theoretical framework for the present considerations was given in a recent paper⁽¹⁶⁾, hereafter referred to as I. In this reference a new generalized Ornstein-Zernike (OZ) approach to many-particle correlation functions was introduced. The main object of analysis was a set of functions describing equilibrium correlations between two groups of particles in a fluid. The basic idea was to distinguish a sequence of repetitive terms in the structure of the correlations. Such repetitive terms are short-ranged and play a similar role to the direct correlation function in the standard OZ formalism. The key element in the classification of various terms contributing to the correlation functions was an intermediate set of particles, i.e. a set with the property that the two reference groups are correlated only through it.

The main result of ref. I was a derivation of a generalized Ornstein-Zernike equation (GOZE) for a function describing correlations between two pairs of particles. The analysis was performed in two steps. In the first step, the so called reducible part was subtracted from the pair-pair correlation function. The reducible part was defined as a sum of all contributions for which the two pairs are correlated only through a sequence of single intermediate particles. The important conclusion was that the reducible part of the pair-pair correlation function can be expressed in terms of correlation functions of lower order. The remaining part of the pair-pair correlation function (i.e. that part, for which a single intermediate particle cannot be distinguished) was called irreducible. The structure of this part was considered in the second step of analysis. In this step various contributions were classified in terms of intermediate pairs of particles. The direct pair-pair correlation function was defined as the sum of contributions for which such an intermediate pair cannot be identified. By analyzing repetitive structures of direct correlations the GOZE was derived. The GOZE relates irreducible and direct pair-pair correlation functions and includes full and direct two-particle correlation functions.

As it was pointed out, the GOZE is a convenient starting point for constructing various approximation schemes for calculating three- and four-point correlation

functions. In particular, if one simply drops out the pair-pair direct correlation function one gets a closed, approximate integral equation which relates the pair-pair correlation function to the usual full and direct two-particle correlation functions. One can show that the solution of this approximate integral equation corresponds to the resummation of the "ladder" diagrams in the h -bond expansion⁽¹⁷⁾ of the pair-pair correlation function. In light of this, we call the above-described approximation the ladder approximation (LA).

We should mention at this point that the ladder approximation for the pair-pair correlation function is closely related to the generalized hypernetted-chain (HNC) approximation developed by Pinski and Campbell by an entirely different method⁽¹⁸⁾. Instead of a diagrammatic analysis, their derivation was based on functional derivative techniques. The main difference between the LA and the generalized HNC approximation is a different treatment of the reducible pair-pair correlation function. Pinski and Campbell did not extract this part from the correlation function. Furthermore, the expressions for integral kernels obtained by Pinski and Campbell depend on the two-particle correlation functions given in the HNC approximation rather than on the exact two-particle correlation functions. In LA the exact functions appear.

The main goal of the present paper is to give an example of an application of the formalism developed in ref. I. We present numerical results for two quantities depending on three- and four-particle correlation functions, calculated using the ladder approximation. One quantity is an integrated intensity of DILS spectra^(4,5), and the other is a correction to the Clausius-Mossotti formula for the dielectric constant of a nonpolar, polarizable fluid^(1,2). We have calculated both quantities for a hard-sphere fluid in the dipole-induced-dipole approximation. These quantities serve as a convenient test for the approximation, since there are computer simulation data available for comparison^(19,20). As we will see, our approximation gives results

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in qualitative agreement with computer simulation data for a very wide range of densities, while for high densities the KSA fails completely.

This paper is organized as follows: In section II we summarize the basic elements of the generalized OZ formalism for pair-pair correlation functions. In section III we describe the LA. In section IV we introduce dipole-dipole-interaction correlation functions for which, in section V, numerical results are given. Some details are relegated to appendices.

II. GENERALIZED ORNSTEIN-ZERNIKE EQUATION FOR A PAIR-PAIR CORRELATION FUNCTION

In this section we summarize results of ref. I which are basic for the purpose of approximate evaluation of few-body correlation functions in a simple fluid.

We consider a uniform, equilibrium system of N identical classical particles of mass m , enclosed in volume V . The configuration-space point is denoted by $\mathbf{X} = (1, \dots, N)$, where $(i) = \mathbf{r}_i$ represents the position of the i th particle. We assume that particles i and j interact via a spherically symmetric pair potential $\Phi(r_{ij})$, where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

The essential element of the generalized OZ approach introduced in ref. I was characterization of correlations in terms of functions describing two correlated groups of particles. For our present purpose it is sufficient to consider groups including one or two particles only. However, for the sake of compact notation it is convenient to give a general definition. Following the notation of ref. I we introduce the functions $Q_{ij}([i] | [j'])$ describing equilibrium correlations between two groups of particles with respective coordinates $[i] = (1, \dots, i)$ and $[j'] = (1', \dots, j')$:

$$Q_{ij}([i] | [j']) = n^{-(i+j)} \langle \delta n_i([i]; \mathbf{X}) \delta n_j([j']; \mathbf{X}) \rangle, \quad (2.1)$$

where n is the number density, and $\delta n_i([\mathbf{i}]; \mathbf{X})$ describes the deviation of i -particle microscopic density from its average, i.e.

$$\delta n_i([\mathbf{i}]; \mathbf{X}) = n_i([\mathbf{i}]; \mathbf{X}) - \langle n_i([\mathbf{i}]; \mathbf{X}) \rangle, \quad (2.2)$$

with

$$n_i([\mathbf{i}]; \mathbf{X}) = \sum_{[\mathbf{i}(\mathbf{X})]} \delta([\mathbf{i}] - [\mathbf{i}(\mathbf{X})]). \quad (2.3)$$

In eq. (2.3) the summation runs over all sequences $[\mathbf{i}(\mathbf{X})]$ of i different particle positions included in \mathbf{X} and

$$\delta([\mathbf{i}] - [\mathbf{i}']) = \delta(1 - 1') \cdots \delta(i - i'). \quad (2.4)$$

In particular for $i = 1, 2$ we have

$$n_1(\mathbf{r}; \mathbf{X}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (2.5)$$

and

$$n_2(\mathbf{r}, \mathbf{r}'; \mathbf{X}) = \sum_{i>j=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j). \quad (2.6)$$

In the definition (2.1) the thermodynamic limit is implied. One should notice that, in the thermodynamic limit, the correlation function (1.1) can be easily expressed in terms of the function Q_{22} :

$$G_{ab} = n^3 \int d2 \int d3 \int d4 a(12) Q_{22}(12 | 34) b(34). \quad (2.7)$$

The functions $Q_{ij}([\mathbf{i}] | [\mathbf{j}'])$ are simply related to the usual s -particle normalized average densities $g_s([\mathbf{i}])$, defined by

$$g_s([\mathbf{s}]) = n^{-s} \langle n_s([\mathbf{s}]; \mathbf{X}) \rangle. \quad (2.8)$$

The explicit expressions for $i, j = 1, 2$ are as follows:

$$Q_{11}(1 | 1') = \frac{1}{n} \delta(1 - 1') + h_2(1 - 1'), \quad (2.9)$$

$$\begin{aligned}
Q_{21}(12 | 1') &= Q_{12}(1' | 12) \\
&= \frac{1}{n} (\delta(1 - 1') + \delta(2 - 1')) g_2(12) + g_3(123) - g_2(12),
\end{aligned} \tag{2.10}$$

and

$$\begin{aligned}
Q_{22}(12 | 1'2') &= \frac{1}{n^2} [\delta(1 - 1')\delta(2 - 2') + \delta(1 - 2')\delta(2 - 1')] g_2(12) \\
&+ \frac{1}{n} [(\delta(1 - 1') + \delta(2 - 1')) g_3(122') + (\delta(1 - 2') + \delta(2 - 2')) g_3(121')] \\
&+ g_4(121'2') - g_2(12)g_2(1'2'),
\end{aligned} \tag{2.11}$$

where

$$h_2(12) = g_2(12) - 1. \tag{2.12}$$

We now describe the decomposition of the correlation function Q_{22} into its reducible and irreducible parts. We introduce here simplified notation compared to the general notation of ref. I. The irreducible part $A(12 | 1'2')$ of the pair-pair correlation function is defined by the following formula (in ref. I this part was denoted by $^{(\alpha)}Q_{22}^{(\alpha)}$)

$$\begin{aligned}
Q_{22}(12 | 1'2') &= n^2 \int d1'' \int d1''' Q_{21}(12 | 1'') Q_{11}^{inv}(1'' | 1''') Q_{12}(1''' | 1'2'), \\
&+ A(12 | 1'2')
\end{aligned} \tag{2.13}$$

where the inverse integral kernel Q_{11}^{inv} is defined by integral equation

$$n \int d3 Q_{11}^{inv}(1 | 3) Q_{11}(3 | 2) = \frac{1}{n} \delta(1 - 2). \tag{2.14}$$

Taking into account the explicit expression (2.9) for the function Q_{11} one can easily check that eq. (2.14) is equivalent to the standard OZ equation and the function Q_{11}^{inv} is given by

$$Q_{11}^{inv}(1 | 2) = \frac{1}{n} \delta(1 - 2) - c_2(1 - 2), \tag{2.15}$$

where $c_2(1 - 2)$ is a two-particle direct correlation function.

Mayer-graph analysis supports the following physical interpretation of the decomposition (2.13) of the function $Q_{22}(12 | 1'2')$: The first term corresponds to all situations when the pairs of particles (12) and (1'2') are correlated through a chain of a single intermediate particles, with no other correlations between (12) and (1'2'). Since each correlation function $Q_{21}(12 | 1'')$ and $Q_{12}(2'' | 1'2')$ includes a chain of single intermediate particles, to count such a chain exactly once we have introduced the inverse kernel $Q_{11}^{inv}(1'' | 2'')$ in eq. (2.13). The second term $A(12 | 1'2')$ corresponds to the opposite situation, i.e. when no single intermediate particle can be found between (12) and (1'2'). We call the first and the second terms on the right-hand side (rhs) of eq. (2.13) the reducible and the irreducible pair-pair correlation functions respectively. Decomposition of the form (2.13) has also been considered by various authors in the framework of a linear kinetic theory of dense fluids^(8,9,12,13,15)

The next step of analysis presented in ref. I was a derivation of the GOZE for the function A . The derivation was based on the careful analysis of the structure of the irreducible pair-pair correlations. We will not present detailed arguments; instead we will give explicit form of the equation and limit ourselves to discussing its most important features.

It is convenient at this point to introduce the following shortened notation

$$\tilde{I}(12 | 1'2') = \frac{1}{n^2} (\delta(1 - 1') \delta(2 - 2') + \delta(1 - 2') \delta(2 - 1')), \quad (2.16)$$

Within this notation the GOZE can be represented as the following equation

$$\frac{n^2}{2} \int d1'' \int d2'' A^{inv}(12 | 1''2'') A(1''2'' | 1'2') = \tilde{I}(12 | 1'2'), \quad (2.17)$$

supplemented by the decomposition of the inverse integral kernel A^{inv} :

$$A^{inv}(12 | 1'2') = \frac{1}{g_2(12)} \tilde{I}(12 | 1'2') - D(12 | 1'2'), \quad (2.18)$$

with D given by

$$\begin{aligned}
D(12 | 1'2') &= \left(1 + \hat{P}(1'2')\right) \left[\frac{1}{n} c_2(11') \delta(2 - 2') \right. \\
&\quad \left. + \frac{1}{n} \delta(1 - 1') c_2(22') - c_2(11') c_2(22') \right] \\
&\quad + C_{22}(12 | 1'2').
\end{aligned} \tag{2.19}$$

We call the function C_{22} a pair-pair direct correlation function. The operator $\hat{P}(1'2')$ in eq. (2.19) permutes variables (1') and (2'). The first three terms in expression (2.19) are the combinations of the two-particle direct correlation functions and the Dirac δ -functions. The function $C_{22}(12 | 1'2')$ is the only term on the rhs of eq. (2.19) which has a group property, i.e. which vanishes when the distance between any two of the particles 1, 2, 1', and 2' tends to infinity⁽¹⁾.

Our interpretation of the function C_{22} as the pair-pair direct correlation function is supported by its Mayer-graph representation. According to results of ref. I $C_{22}(12 | 1'2')$ corresponds to the situations where there is no intermediate pair of particles such that the pairs (12) and (1'2') are correlated only through it.

To reveal more clearly the relation of our GOZE to the standard OZ equation we rewrite (2.19) in a different form. To this end let us define the function H by the following decomposition of the function A :

$$A(12 | 1'2') = g_2(12) \tilde{I}(12 | 1'2') + g_2(12) H(12 | 1'2') g_2(1'2'). \tag{2.20}$$

The first term on the rhs of (2.20) corresponds to all of the situations in which the two pairs (12) and (1'2') are identical (cf. eq. (2.11)). The second term correspond to all other situations. By substituting decomposition (2.20) into eq. (2.17) one gets

$$\begin{aligned}
H(12 | 1'2') &= D(12 | 1'2') \\
&\quad + \frac{n^2}{2} \int d1'' \int d2'' D(12 | 1''2'') g_2(1''2'') H(1''2'' | 1'2').
\end{aligned} \tag{2.21}$$

Eq. (2.21) has a form analogous to the standard OZ equation. The underlying structure of the correlations is, however, more complicated than in the standard case and therefore the additional decomposition (2.19) of the function D is required.

The diagrammatic analysis performed in ref. I leads to a physical interpretation of eqs. (2.19) and (2.21). Let us repeat this point: The function $H(12 | 1'2')$, describing the irreducible correlations between two pairs of particles (12) and (1'2'), can be decomposed into direct and indirect correlations. The direct correlations correspond to all the situations, in which there are no intermediate pairs of particles between (12) and (1'2'). The indirect correlations correspond to the opposite situations, i.e. those in which one can find such an intermediate pair of particles (1''2''). An intermediate pair (1''2'') can be always chosen in such a way that there is no other intermediate pair between (12) and (1''2''). As a result the indirect correlation function can be represented as a convolution of the direct correlation functions and the irreducible pair-pair correlation function. The important difference between the standard and the generalized OZ equation is that for the pair-pair problem the choice of an intermediate pair of particles with the above-described properties usually is not unique. This results in a more complicated form of the OZ equation than in the standard case. To understand the role of various terms in the decomposition (2.19) let us consider the following elementary situations.

- i) The particle (1) is correlated with the particles (2), (1') and (2') only through a single intermediate particle denoted by (1'').
- ii) the particle (2) is correlated with the particles (1), (1') and (2') only through a single intermediate particle denoted by (2'');
- iii) both particles (1) and (2) are correlated with remaining particles through a respective single intermediate particles (1'') and (2'');
- vi) there is no single intermediate particle such that the particle (1) or (2) is correlated only through it.

We can always choose the particles (1'') and (2'') in such a way that there is no intermediate particle between (1) and (1'') and non between (2) and (2''). The components of the indirect correlation function which correspond to situation *i*) have an intermediate pair of particles (1''2). On the rhs of eq (2.21) they result from the convolution of the function H with the first term in the square bracket in decomposition the (2.19). Next, the components contributing to *ii*) have an intermediate pair (12'') and they result from the second term in the square bracket. The components corresponding to *iii*) have both the intermediate pairs (1''2) and (12''). Therefore these components result from both the first and the second terms in the square brackets. To cancel the excess components, the third term, with the negative sign, was introduced. Finally, the components corresponding to the situation *iv*) result from the last term C_{22} of the decomposition (2.19).

Before going on to describing our approximation scheme we make the following important remark. The pair-pair correlation function Q_{22} , as well as its reducible, irreducible and direct parts, include components corresponding to the situation in which *i*) the two reference pairs of particles are identical, *ii*) they include one common particle, or *iii*) they do not include any common particles. These components consist of the respective two-, three-, and four-particle correlation functions and the products of the Dirac δ -functions representing the common particles. It is very important that the components of a pair-pair correlation function corresponding to the pairs with different subsets of common particles can be uniquely separated by selecting terms with appropriate combinations of δ -functions. Using this decomposition one can interpret the GOZE as a set of two separate equations for the three- and the four-particle correlation functions. (For the two-particle correlation function we get a trivial result). The three-particle equation can be solved independently from the full four-particle equation and can be used in the approximate evaluation of the three-particle correlation function. In what follows, the parts of the correlation functions Q_{22} and A which correspond to a three-particle problem

We expect the simple closure approximation (3.1) to yield reasonably good results for a pair-pair correlation function for a wide range of densities, at least for fluids with a short-ranged, hard-core interaction potential. The intuitive argument is as follows. The Mayer-graph analysis of the function $C_{22}(12 | 1'2')$, given in ref. I leads to a conclusion that this function is represented by diagrams in which the vertices corresponding to the pairs of particles (12) and (1'2') are multiply connected. Therefore C_{22} is a short-ranged function. On the other hand in the iterative solution of the GOZE equation (2.17), C_{22} is always multiplied by functions which vanish when particle (1) and (2) or (1') and (2') overlap. In this way an overlapping contributions from C_{22} are eliminated. In the final expression for the function A we have only small contributions from the region outside the core. To support our conjecture we will present the LA numerical results for dipole-dipole-interaction correlation functions.

IV. DIPOLE-DIPOLE-INTERACTION CORRELATION FUNCTIONS

We now give two examples of an application of our formalism to numerical evaluation of the correlation functions of forms (A.1) and (1.1). The numerical results presented in this paper were obtained for a hard-sphere fluid, but the same method can be applied for other molecular potentials.

The first calculated quantity R^{zz} describes a correction to the Clausius-Mossoti expression for the dielectric constant of a nonpolar, polarizable fluid. The expansion of the Clausius-Mossoti quantity $(\epsilon - 1)/(\epsilon + 2)$ with respect to the particle polarizability α can be written in the following form

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n\alpha [1 + \Delta + O(\alpha^3)], \quad (4.1)$$

with Δ given by

$$\Delta = (5\alpha^2/2\sigma^6) R^{zz}. \quad (4.2)$$

will be denoted by $Q_{22}^{(s)}$ and $A^{(s)}$. More details related to this problem are given in appendix A.

III. APPROXIMATION SCHEME

As with the standard OZ equation, the GOZE is not a closed integral equation for the irreducible part of the pair-pair correlation function. For the purpose of evaluating of the function $A(12 | 1'2')$, the GOZE has to be supplemented by an appropriate closure approximation for the pair-pair direct correlation function C_{22} . The simplest possible approximation is just to set

$$C_{22} \equiv 0. \quad (3.1)$$

By inserting expression (3.1) into the GOZE (2.17)–(2.19) we get the following closed integral equation for the function A

$$\begin{aligned} A(12 | 1'2') - n^2 g_2(12) \int d1'' \int d2'' \left(\frac{1}{n} \delta(1 - 1'') c_2(2 - 2'') \right. \\ \left. + \frac{1}{n} \delta(2 - 2'') c_2(1 - 1'') - c_2(1 - 1'') c_2(2 - 2'') \right) \\ \times A(1''2'' | 1'2') = g_2(12) \tilde{I}(12 | 1'2'), \end{aligned} \quad (3.2)$$

where we have used a symmetry property of $A(1''2'' | 1'2')$ with respect to a permutation of variables (1'') and (2''). One can show that the solution of eq. (3.2) corresponds to a resummation of the ladder diagrams in the h -bond expansion of the irreducible pair-pair correlation function. Therefore we will call the approximation (3.1) the ladder approximation. (Cf. discussion in Appendix B).

For the three-particle problem one can introduce an approximation similar to (3.1) and derive an equation analogous to (3.2). The details are given in appendix A.

Various authors^(1,2) have derived the following expression for the quantity R^{zz} :

$$R^{zz} = \frac{\sigma^6}{N} \left\langle \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N T_{zz}(ij) \sum_{\substack{m=1 \\ m \neq i}}^N T_{zz}(im) \right\rangle \quad (4.3)$$

where σ denotes the diameter of a sphere, and $T_{zz}(ij)$ is the zz component of the dipole-dipole interaction tensor:

$$T_{zz}(ij) = \frac{2}{r_{ij}^3} P_2(\cos(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{z}})), \quad (4.4)$$

$\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$ and $\hat{\mathbf{z}}$ is the unit vector in the z -axes direction. It is assumed that the average value in (4.4) is calculated for a spherical sample. This is necessary due to the long range behavior of the tensor T_{zz} ; the integrals over the spatial variables in (4.4) are not absolutely convergent. One should note, however, that a careful derivation of the correction to the Clausius-Mossoti formula leads directly to the expression for R^{zz} in which divergent terms are eliminated and therefore an assumption about a shape of the sample is not needed⁽³⁾.

The second quantity S^{zz} for which we present numerical results is related to the integrated intensity I^{DILS} measured in DILS experiments. The relation between I^{DILS} and S^{zz} is given by the following formula

$$I^{DILS} = \frac{3}{4} n(\alpha^4/\sigma^6) S^{zz}, \quad (4.5)$$

and S^{zz} can be expressed by^(4,5)

$$S^{zz} = \lim_{\infty} \frac{\sigma^6}{N} \left\langle \sum_{\substack{i,j=1 \\ i \neq j}}^N T_{zz}(ij) \sum_{\substack{l,m=1 \\ l \neq m}}^N T_{zz}(lm) \right\rangle, \quad (4.6)$$

Again, it is assumed that the average value in (4.6) is calculated for the spherical sample to eliminate divergent terms.

In the framework of the generalized OZ formalism, the quantity R^{zz} corresponds to the three-particle problem described in appendix A, and S^{zz} corresponds

to the full four-particle problem. With the assumption of a spherical shape of a sample, the average value of T_{zz} vanishes. Therefore one can represent the quantities R^{zz} and S^{zz} in the respective forms (A.1) and (1.1):

$$R^{zz} = \sigma^6 C_{T_{zz}T_{zz}}^{(s)} \quad (4.7)$$

and

$$S^{zz} = \sigma^6 C_{T_{zz}T_{zz}}. \quad (4.8)$$

It follows directly from the relations (4.7), (4.8), (2.7) and (A.5) that the quantities R^{zz} and S^{zz} can be expressed in terms of the pair-pair correlation functions $Q_{22}^{(s)}(12 | 1'2')$ and $Q_{22}(12 | 1'2')$. If in addition one uses decompositions (2.13) and (A.6), and the fact that due to angular symmetry the integral containing reducible parts of the correlation functions $Q_{22}^{(s)}$ and Q_{22} vanish, one gets the following important expressions for S^{zz} and R^{zz} in terms of irreducible correlations only:

$$R^{zz} = \sigma^6 n^3 \int d2 \int d1' \int d2' T_{zz}(12) A^{(s)}(12 | 1'2') T_{zz}(1'2'), \quad (4.9)$$

and

$$S^{zz} = \sigma^6 n^3 \int d2 \int d1' \int d2' T_{zz}(12) A(12 | 1'2') T_{zz}(1'2'). \quad (4.10)$$

Because of sufficiently fast decay of the irreducible functions $A^{(s)}(12 | 1'2')$ and $A(12 | 1'2')$ when the distance between any of the particles (1), (2), (1'), and (2') and the remaining particles tends to infinity, all integrals included in eqs. (4.9) and (4.10) are absolutely convergent.

V. NUMERICAL RESULTS

We now describe briefly a procedure of evaluating the correlation functions R^{zz} and S^{zz} and present numerical results obtained using the LA. A detailed account of the algorithm is given in appendices B and C.

In the present paper we consider only evaluation of the integrated quantities of the form (4.9) and (4.10), and therefore we do not need to solve eqs. (3.2) and (A.13) explicitly. Instead it is convenient to evaluate directly an integrated quantity, which for a full four-particle problem is defined by

$$\bar{b}(12) = n^2 \int d1' \int d2' A(12 | 1'2') \bar{\beta}(1'2'), \quad (5.1)$$

where $\bar{\beta}$ has the form

$$\bar{\beta}(12) = \beta(r_{12}) P_2(\cos(\hat{r}_{12} \cdot \hat{z})), \quad (5.2)$$

and β is a function which vanishes sufficiently fast when r_{12} goes to infinity. By multiplying eq. (3.2) by $\bar{\beta}(1'2')$ from the rhs, integrating over $(1'2')$, and taking into account the symmetry of the function \bar{b} with respect to the permutations of the variables we get the following equation

$$\begin{aligned} \bar{b}(12) - 2ng_2(12) \int d2' c_2(2-2') \bar{b}(12') \\ + n^2 g_2(12) \int d1' \int d2' c_2(1-1') c_2(2-2') \bar{b}(1'2') = g_2(12) \bar{\beta}(12). \end{aligned} \quad (5.3)$$

Considerable reduction of numerical effort comes from the fact, that the function A is isotropic, and therefore \bar{b} assumes the form analogous to (5.2)

$$\bar{b}(12) = b(r_{12}) P_2(\cos(\hat{r}_{12} \cdot \hat{z})). \quad (5.4)$$

As result it is sufficient to deal with the function of a single variable only. For

$$\beta = \frac{2}{r^3}, \quad (5.5)$$

the solution of the equation (5.3), can be used for evaluating S^{zz} from the following expression

$$S^{zz} = \frac{4\pi}{5} n \int_0^\infty dr r^2 \beta(r) b(r) \quad (5.6)$$

which one obtains from (4.4), (4.10), (5.1), and (5.4) after performing integration with respect to the angular variables.

Similar set of formulas can be derived also for a three-particle problem. Explicit expressions are given in appendix C.

We have numerically solved eqs. (5.3)-(5.6) and (C.1)-(C.4) and we have evaluated the correlation functions S^{zz} and R^{zz} for hard-sphere fluid for a wide range of densities. As an input we have used the Verlet-Weiss (VW) approximation for a two-particle correlation function. Integral equations (5.3) and (C.4) have been solved by an iterative method using fast Fourier transformation techniques. The details of the algorithm are given in appendices B and C for the four- and three-particle problems respectively. The results of our calculations are presented in figs. 1-2 and tabs. 1-2. Obtaining the value of R^{zz} or S^{zz} for a single density required no more than a few minutes of CPU time of a VAX 11/780.

The LA approximation results for the correlation function R^{zz} versus volume fraction $\phi = \frac{\pi}{6}n\sigma^3$ are plotted in fig. 1. Computer simulation data of Cichocki and Felderhof⁽¹⁹⁾ are given for comparison. We have also plotted results obtained from using the KSA for a triplet correlation function. We find quite good agreement with the simulation data for both LA and KSA up to a volume fraction $\phi = 0.3$. At higher volume fractions LA approximation results are in qualitative agreement with computer simulation data, while in this region the KSA completely fails.

Calculation of the correlation function R^{zz} serves as a quite severe test for an approximation for three-particle equilibrium correlation function. This is due to the cancellation of two- and three-particle terms. The function R^{zz} can be naturally represented in the form

$$R^{zz} = S_2 + S_3, \quad (5.7)$$

where S_2 and S_3 correspond to terms including two- and three-particle correlation function in expression (A.4) for $Q_{22}^{(s)}$. In tab. 1 we give results for R^{zz} , S_2 , and S_3 ,

for the densities at which computer simulation data are available. One can see from this table that for high densities S_2 and S_3 have approximately the same absolute value, but the opposite sign. Due to this cancellation the relative error of S_3 is much smaller than the relative error of R^{zz} . Taking into account that the absolute error of S_2 calculated from VW approximation for the pair-correlation function is less than 0.006 one can see from tab. 1 that the relative error of S_3 does not exceed 3.5%.

The LA results for S^{zz} are given in fig. 2 and tab. 2. The computer simulation data by Alder et al.⁽¹⁸⁾ are also given for comparison. Again, we can see, that LA gives results in qualitative agreement with the computer simulation data for the whole range of densities, up to the fluid-solid phase transition.

As with R^{zz} , the correlation function S^{zz} can be expressed as a sum of two-, three-, and four-particle terms. Namely we have:

$$S^{zz} = 2S_2 + 4S_3 + S_4, \quad (5.8)$$

where S_2 and S_3 are the same quantities as in eq. (5.7), and S_4 corresponds to the term including no δ -functions in A . Results for this quantities are given in tab. 2. Again we observe cancellation among the two-, three-, and four-particle terms.

VI. DISCUSSION

In this paper we have presented an application of a recently developed LA for calculating three- and four-particle equilibrium correlation functions in simple fluids. The LA have been derived in a recent paper⁽¹⁶⁾ in the framework of the generalized OZ formalism. We have obtained this equation from the GOZE by leaving out the direct pair-pair correlation function. In this way we have obtained a closed integral equation relating an irreducible part of the pair-pair correlation function to the full and direct two-particle correlation functions.

We have presented results based on LA for the dipolar density fluctuations R^{zz} and S^{zz} , which quantities depend on the three- and four-particle correlation functions. These calculations were performed for a hard-sphere fluid. We have obtained good agreement of our results with available computer simulations data for a very wide range of densities. For high densities the LA gives much better results than the KSA.

An important advantage of LA is that it does not require extensive computing resources. Indeed, with some effort, quantities like R^{zz} and S^{zz} can be calculated even on a personal computer. This is a big advantage in comparison with the numerically demanding calculations of three-particle correlation function performed by Haymet et al.⁽²¹⁾ (see also refs. 22–26 for other approaches). We should mention, that although our numerical approach was based on solving simplified eqs. (5.3) and (C.4), it is not difficult to develop an algorithm which enables full evaluation of the function $A^{(*)}(12 | 1'2')$ and the function $A(12 | 1'2')$ integrated over the variable $\mathbf{r}_{11'}$. The details of such an algorithm for a closely related approximation was given by Pinski and Campbell⁽¹⁸⁾.

In a series of interesting papers Pinski and Campbell derived approximate integral equations for a pair-pair correlation function, based on the HNC approximation. Their result is closely related to ours. Pinski and Campbell derived their equation using functional-differentiation techniques. To this end they explored the relation of a functional derivative of the two-particle correlation function with respect to the pair potential to a pair-pair correlation function. The generalized HNC approximation for a pair-pair correlation function was obtained by functionally differentiating the two-particle correlation function given in HNC approximation.

Pinski and Campbell derived integral equations which are very similar to eqs. (3.2) and (A.13). However, there are two important differences between their and our results. First of all, for the full four-particle problem they did not subtract the

reducible part from the pair-pair correlation function. This was due to an error in the functional differentiation. The second difference is that their method leads to integral equations with the kernels including two-particle correlation functions calculated in the HNC approximation. In contrast, our closure approximations (3.1) and (4.12) naturally lead to the exact pair-correlation functions in the integral kernels.

Pinski and Campbell have used the generalized HNC approximation to evaluate three- and four-particle equilibrium correlation functions. The above-mentioned error in the derivation of the integral equation does not strongly influence their numerical results. Only the 0th-order Legendre-polynomial projection is influenced, due to an angular symmetry of the reducible part of the correlation function. Taking this into account, their numerical results are consistent with our conclusions on the validity of the approximation.

The LA, while relatively simple, is not free of problems. In particular, the core condition for overlapping particles of different pairs is violated. This observation leads to various new approximations. For the three-particle equation, the simplest approximation beyond the level described in this paper, is to multiply resulting three-particle distribution function g_3 by the function which equals 0 in the core and equals 1 outside. One can also explore the Percus-Yevick idea. To this end one use the exact relation

$$g_3 = 0 \quad \text{in the core} \quad (6.1)$$

and closure approximation

$$C_{22}^{(s)}(12 | 1'2') = 0 \quad \text{for} \quad r_{22'} > 0 \quad (6.2)$$

Such an approach is expected to give better approximations than LA, but is more demanding from the numerical point of view⁽²⁷⁾.

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Appendix A

In this appendix we describe a three-particle version of the GOZE. Such a three-particle equation is particularly useful for evaluating correlation functions of the form

$$G_{ab}^{(s)} = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \delta a(ij) \sum_{\substack{l=1 \\ l \neq i}}^N \delta b(il) \right\rangle, \quad (A.1)$$

i.e. in situations where one particle is common for the two correlated pairs. The correlation functions of this form include only two- and three-particle terms. To develop a GOZE appropriate for our present purpose, it is convenient to introduce the correlation functions $Q_{ij}^{(s)}$ defined as the sum of those parts of the corresponding functions Q_{ij} , which involve a δ -function $\delta(1 - 1')$. For example, from (2.9)–(2.11) one has

$$Q_{11}^{(s)} = \frac{1}{n} \delta(1 - 1'), \quad (A.2)$$

$$Q_{21}^{(s)}(12 | 1') = Q_{12}^{(s)}(1' | 12) = \frac{1}{n} \delta(1 - 1') g_2(12) \quad (A.3)$$

and

$$Q_{22}^{(s)}(12 | 1'2') = \frac{1}{n^2} \delta(1 - 1') \delta(2 - 2') g_2(12) + \frac{1}{n} \delta(1 - 1') g_3(122'). \quad (A.4)$$

One can also define functions $A^{(s)}$, $D^{(s)}$, and $C_{22}^{(s)}$ which are related in an analogous way to the functions A , D , and C_{22} . With the above definitions one can easily

check that in thermodynamic limit the correlation function (A.1) can be expressed in terms of the function $Q_{22}^{(s)}$:

$$G_{ab}^{(s)} = n^3 \int d2 \int d3 \int d4 a(12) Q^{(s)}(12 | 1'2') b(34). \quad (\text{A.5})$$

All integral equations developed in the previous sections can be easily transformed into equations of the functions $Q_{ij}^{(s)}$ and the other related functions. To this end one should simply select all the terms which involve δ -functions corresponding to a distinguished particle common to the two correlated pairs. In this way, after performing integration with respect to the variable ($1'''$) we get from (2.13) the following decomposition of the function $Q_{22}^{(s)}$ into its reducible and irreducible parts:

$$Q_{22}^{(s)}(12 | 1'2') = n \int d1'' Q_{21}^{(s)}(12 | 1'') Q_{12}^{(s)}(1'' | 1'2') + A^{(s)}(12 | 1'2'). \quad (\text{A.6})$$

Taking into account eqs. (A.3) and (A.4) one can derive an explicit expression for the function $A^{(s)}(12 | 1'2')$ in terms of two- and three-particle correlation functions:

$$A^{(s)}(12 | 1'2') = \frac{1}{n^2} \delta(1-1') \delta(2-2') g_2(12) + \frac{1}{n} \delta(1-1') (g_3(122') - g_2(12) g_2(12')). \quad (\text{A.7})$$

The GOZE for a function $A^{(s)}$ can be obtained from eqs. (2.17)–(2.19) in a similar way. Using a shortened notation

$$I(12 | 1'2') = \frac{1}{n^2} \delta(1-1') \delta(2-2') \quad (\text{A.8})$$

one gets the following equation

$$n^2 \int d1'' \int d2'' A_{inv}^{(s)}(12 | 1''2'') A^{(s)}(1''2'' | 1'2') = I(12 | 1'2'), \quad (\text{A.9})$$

supplemented by the decomposition of the inverse integral kernel $A_{inv}^{(s)}$:

$$A_{inv}^{(s)}(12 | 1'2') = \frac{1}{g_2(12)} I(12 | 1' | 2') - D^{(s)}(12 | 1'2'), \quad (\text{A.10})$$

with

$$D^{(s)}(12 | 1'2') = \delta(1 - 1')c_2(22') - C_{22}^{(s)}(12 | 1'2'). \quad (\text{A.11})$$

For the three-particle version (A.9)–(A.11) of the GOZE we propose a closure approximation similar to (3.1):

$$C_{22}^{(s)} \equiv 0 \quad (\text{A.12}).$$

By inserting expression (A.12) into the three-particle GOZE (A.9)–(A.11), and integrating with respect to the variable ($1''$), one gets:

$$\begin{aligned} A^{(s)}(12 | 1'2') - ng_2(12) \int d2'' c_2(2 - 2'') A^{(s)}(1''2'' | 1'2') \\ = g_2(12)I(12 | 1'2'). \end{aligned} \quad (\text{A.13})$$

Eq. (A.13) is an efficient tool for evaluating quantities depending on a three-particle correlation function in simple fluids.

APPENDIX B

In this appendix we describe details of the algorithm which has been used to solve eq. (5.3). Some remaining details for the three-particle problem are given in appendix C.

It is convenient at this point to introduce a compact integral-operator notation. We associate the integral operator \hat{B} with a function $B(12 | 1'2')$. The operator \hat{B} is defined by the following expression

$$(\hat{B} a)(12) = n^2 \int d1' \int d2' B_{22}(12 | 1'2') a(1'2'), \quad (\text{B.1})$$

where $a(1'2')$ is any function for which the integral at the rhs of eq. (B.1) exists. The inverse operator \hat{B}^{-1} is defined by the following equation

$$\hat{B}^{-1}\hat{B} = \hat{I}, \quad (\text{B.2})$$

where the kernel of the identity operator \hat{I} is given by (A.8).

In order to write in a compact form equations related to the ladder approximation we introduce an integral operator \hat{d} defined by the following expression for its integral kernel

$$d(12 | 1'2') = \left(\frac{1}{n} \delta(1-1') + h_2(11') \right) \left(\frac{1}{n} \delta(2-2') + h_2(22') \right). \quad (B.3)$$

Taking into account the standard OZ equation one can easily show that the kernel $d^{-1}(12 | 1'2')$ of the inverse operator \hat{d}^{-1} is given by

$$d^{-1}(12 | 1'2') = \left(\frac{1}{n} \delta(1-1') - c_2(11') \right) \left(\frac{1}{n} \delta(2-2') - c_2(22') \right), \quad (B.4)$$

With the above notation one can rewrite equation (5.3) in the following form:

$$\left[g_2 \hat{d}^{-1} - h_2 \right] \bar{b} = g_2 \bar{\beta}. \quad (B.5)$$

By multiplying both sides of equation (B.5) by \hat{d} , after some simple calculations one gets

$$\bar{b} = -\hat{d} h_2 \left(\hat{d}^{-1} - \hat{I} \right) \bar{b} + \hat{d} g_2 \bar{\beta}. \quad (B.6)$$

An iterative solution of (B.6) with the first term at the rhs treated as a perturbation can be represented in the form

$$\bar{b} = \sum_{i=0}^{\infty} \bar{b}_i, \quad (B.7)$$

where

$$\bar{b}_i = \hat{d} \left[h_2 \left(\hat{d} - \hat{I} \right) \right]^i g_2 \bar{\beta}. \quad (B.8)$$

It is convenient to use eq. (B.6) rather than (B.5) as the basis for perturbative evaluating the function \bar{b} . In such a way one gets the solution in terms of the full two-particle correlation function rather than the direct correlation function. The expansion in terms of the direct correlation function is divergent even for small densities.

The expansion (B.7)-(B.8) justifies the name LA for the closure approximation (3.1).

To get numerical solution for \bar{b} one has to repeatedly evaluate the result of action of the operator \hat{d} on a function of the relative position of the particles (1) and (2). To this end one can use fast Fourier transform techniques. Let

$$\hat{F}_3[a](\mathbf{k}) = \int d\mathbf{r}_{12} e^{i\mathbf{k}\cdot\mathbf{r}_{12}} a(\mathbf{r}_{12}) \quad (B.9)$$

be a three-dimensional Fourier transform of a function $a(\mathbf{r}_{12})$. It is easy to see from (B.1), (B.3) and the properties of the Fourier transform, that

$$\hat{F}_3[\hat{d}a](\mathbf{k}) = S^2(\mathbf{k})\hat{F}_3[a](\mathbf{k}), \quad (B.10)$$

where $S(\mathbf{k})$ is the static structure factor. We have numerically calculated the quantities of the form $\hat{d}a$ which a successive terms of iterative solution by

- i) taking the Fourier transform of the function a ,
- ii) multiplying the result by $S^2(\mathbf{k})$, and
- iii) transforming back to the real space.

To calculate the three-dimensional Fourier transform (B.9) one can use the fact that we consider here functions of the form (5.4). For such functions the three-dimensional Fourier transform can be calculated in terms of one-dimensional transforms. Our algorithm can be applied for a more general angular dependence than (5.4), i.e. for the functions which has the form

$$a_l(\mathbf{r}) = \alpha_l(r)P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{z}}), \quad l = 0, 1, \dots \quad (B.11)$$

It is useful to give here explicit expressions for such a more general case.

The three-dimensional Fourier transform of the function a_l of the form (B.11) can be expressed by the following formula

$$F_3[a_l](\mathbf{q}) = H_l[\alpha_l] P_l(\mathbf{q} \cdot \mathbf{z}), \quad (B.12)$$

where H_l is the l th order Hankel transform:

$$H_l[\alpha_l] = 4\pi (i)^l \int dr r^2 j_l(qr) \alpha_l(r), \quad (B.13)$$

with j_l the spherical Bessel function of the order l . Similarly, the inverse Fourier transform $F_3^{-1}[\tilde{a}]$ of the function

$$\tilde{a}_l(q) = \tilde{\alpha}_l(q) P_l(\hat{\mathbf{q}} \cdot \hat{\mathbf{z}}) \quad (B.14)$$

is given by

$$F_3^{-1}[\tilde{a}_l](\mathbf{r}) = \frac{(-1)^l}{2\pi} H_l[\tilde{\alpha}_l] P_l(\mathbf{r} \cdot \mathbf{z}). \quad (B.15)$$

The Hankel transform H_l can be expressed as the following sequence of integral transforms⁽²⁸⁾

$$H_l[\alpha_l] = 4\pi \int_0^\infty dr \cos(qr) \int_r^\infty dr' r' C_l[\alpha_l](r') \quad \text{for } l \text{ even} \quad (B.16)$$

and

$$H_l[\alpha_l] = 4\pi i \int_0^\infty dr \sin(qr) r \int_r^\infty dr' C_l[\alpha_l](r') \quad \text{for } l \text{ odd} \quad (B.17)$$

with

$$C_l[\alpha_l] = \alpha_l(r) - \int_r^\infty w_l\left(\frac{r}{r'}\right) \frac{\alpha_l(r')}{r'} dr' \quad \text{for } l \text{ even}, \quad (B.18)$$

$$C_l[\alpha_l] = \alpha_l(r) - r \int_r^\infty w_l\left(\frac{r}{r'}\right) \frac{\alpha_l(r')}{(r')^2} dr' \quad \text{for } l \text{ odd}, \quad (B.19)$$

where

$$w_{2s+2}(x) = \frac{2}{s!} \sum_{j=1}^s x^{2j} (-1)^{s-j} \binom{s}{k} \frac{\Gamma(s+j+\frac{5}{2})}{\Gamma(+\frac{3}{2})}, \quad (B.20)$$

$$w_{2s+3}(x) = \frac{2}{s!} \sum_{j=1}^s x^{2j} (-1)^{s-j} \binom{s}{k} \frac{\Gamma(s+j+\frac{7}{2})}{\Gamma(+\frac{5}{2})}, \quad (B.21)$$

and

$$w_0(x) = w_1(x) = 0. \quad (B.22)$$

The integral transforms (B.18)–(B.19) and transforms defined by the second integrals in expressions (B.16)–(B.17) can be calculated by integrating a polynomial interpolation formula for the function α_l . (We have used cubic-spline interpolation for this purpose). The first integrals in (B.16)–(B.17) can be calculated with the help of a fast Fourier transform algorithm. To avoid transforming functions discontinuous at the core we have smoothed-out the integrand functions by adding and subtracting an appropriate function for which the Hankel transform is known.

Similar algorithm can be applied for the three-particle equation (A.13). For details see Appendix C.

For the three-particle problem the iterative solution (C.10) was convergent for all reported densities. For the full four-particle problem straight iteration (B.7)–(B.8) was divergent for a volume fraction of $\phi \geq 0.463$. For those densities and in the region where convergence was slow, we have used Pade approximants for the series. Even for the highest densities we have obtained convergence within at least five decimal places with [8/8] Pade approximant.

Appendix C

In this appendix we describe a method of evaluating the correlation function R^{zz} . This function can be calculated by the similar method as described in appendix B. Appropriate expressions for R^{zz} can be obtained from respective expressions for S^{zz} by retaining only those terms which describe situations when the pairs (12) and (1'2') include a common particle (1) \equiv (1').

The quantity R^{zz} can be evaluated from the following equation

$$R^{zz} = \frac{4\pi}{5} n \int_0^{\infty} dr r^2 \beta(r) b^{(s)}(r), \quad (C.1)$$

where $\beta(r)$ is given by eq. (5.5) and the function $b^{(s)}$ is defined by

$$\bar{b}^{(s)}(12) = b^{(s)}(r_{12})P_2(\hat{r}_{12} \cdot \hat{z}), \quad (C.2)$$

with

$$\bar{b}^{(s)}(12) = n^2 \int d1' \int d2' A^{(s)}(12 | 1'2') \hat{\beta}(1'2'), \quad (C.3)$$

and $\hat{\beta}$ is given by (5.2). Taking into account eq. (A.13) one can show that in LA, $\bar{b}^{(s)}$ is determined by the integral equation of the form

$$\bar{b}^{(s)}(12) - n g_2(12) \int d2' c_2(2-2') \bar{b}^{(s)}(12') = g_2(12) \hat{\beta}(12) \quad (C.4)$$

Using the integral-equation notation of appendix B, eq. (C.4) can be rewritten in the form

$$\left[g_2 \left(\hat{d}^{(s)} \right)^{-1} - h_2 \right] \bar{b}^{(s)} = g_2 \bar{\beta}. \quad (C.5)$$

The operator $\hat{d}^{(s)}$ and the inverse operator $\left(\hat{d}^{(s)} \right)^{-1}$ are given through expressions for their integral kernels $d_{22}^{(s)}(12 | 1'2')$ and $\left(d_{22}^{(s)} \right)^{-1}(12 | 1'2')$

$$d^{(s)}(12 | 1'2') = \frac{1}{n} \delta(1-1') \left(\frac{1}{n} \delta(2-2') + h_2(22') \right) \quad (C.6)$$

and

$$\left(d^{(s)} \right)^{-1}(12 | 1'2') = \frac{1}{n} \delta(1-1') \left(\frac{1}{n} \delta(2-2') - c_2(22') \right). \quad (C.7)$$

Eq. (C.5) can be solved iteratively. To this end it is convenient to transform it into

$$\bar{b}^{(s)} = -\hat{d}^{(s)} h_2 \left[\left(\hat{d}^{(s)} \right)^{-1} - \hat{I} \right] \bar{b}^{(s)} + \hat{d}^{(s)} g_2 \bar{\beta}. \quad (C.8)$$

The iterative solution of the equation (C.8) with the first term at the rhs treated as a perturbation can be represented as

$$\bar{b}^{(s)} = \sum_{i=0}^{\infty} \bar{b}_i^{(s)}, \quad (C.9)$$

where

$$\bar{b}_i^{(s)} = \hat{d}^{(s)} \left[h_2 \left(\hat{d}^{(s)} - \hat{I} \right) \right]^i g_2 \bar{\beta}. \quad (C.10)$$

One can numerically evaluate the perturbative solution (C.10) of the eq. (C.8) using techniques described in appendix B.

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Figure captions

Fig. 1. Plot of the correlation function R^{zz} , defined by eq. (4.3), as a function of the volume fraction ϕ , for a hard-sphere fluid. Results from LA, solid line; results from the KSA, dashed line; Monte Carlo results of Cichocki and Felderhof⁽²⁰⁾, open circles.

Fig. 2. Plot of the correlation function S^{zz} , defined by eq. (4.6), as a function of the volume fraction ϕ , for a hard-sphere fluid. Results from LA, solid line; molecular dynamics data of Alder et al.^(19b): results for 500 particles, solid circles; results for 108 particles, open circles.

Table captions

Table 1. Values of the functions R^{zz} , S_2 , and S_3 , as defined by eqs. (4.3) and (5.7). Values for S_2 from the Verlet-Weiss approximation for the two-particle correlation function; LA, ladder approximation results; KSA, Kirkwood superposition approximation results; MC, Monte Carlo results of Cichocki and Felderhof⁽²⁰⁾.

Table 2. Values of the functions S^{zz} , S_2 , S_3 , and S_4 , as defined by eqs. (4.6) and (5.8). MD, molecular dynamics result of Alder et al.^(19b); other description as for the tab. I.

TABLE 1

ϕ	S_2	S_3 LA	R^{zz} LA	R^{zz} KSA	R^{zz} MC
0.1	0.728	-0.244	0.484	0.488	0.490
0.2	1.650	-0.973	0.677	0.713	0.707
0.3	2.795	-2.146	0.649	0.792	0.723
0.4	4.193	-3.700	0.493	0.996	0.600
0.463	5.216	-4.845	0.371	1.428	0.486
0.5	5.878	-5.580	0.298	1.909	0.415

TABLE 2

ϕ	S_2	S_3 LA	S_4 LA	S^{zz} LA	S^{zz} MD
0.037	0.249	-0.033	0.009	0.375	0.38 ^a
0.074	0.521	-0.134	0.085	0.591	0.62 ^a
0.148	1.146	-0.536	0.568	0.716	0.77
0.247	2.157	-1.471	2.153	0.583	0.68
0.370	3.749	-3.202	5.633	0.323	0.43
0.463	5.216	-4.845	9.121	0.173	0.23
0.463					0.27 ^a
0.494	5.762	-5.452	10.416	0.135	0.22 ^a

^a results for 500 particles; the other simulation results are for 108 particles.

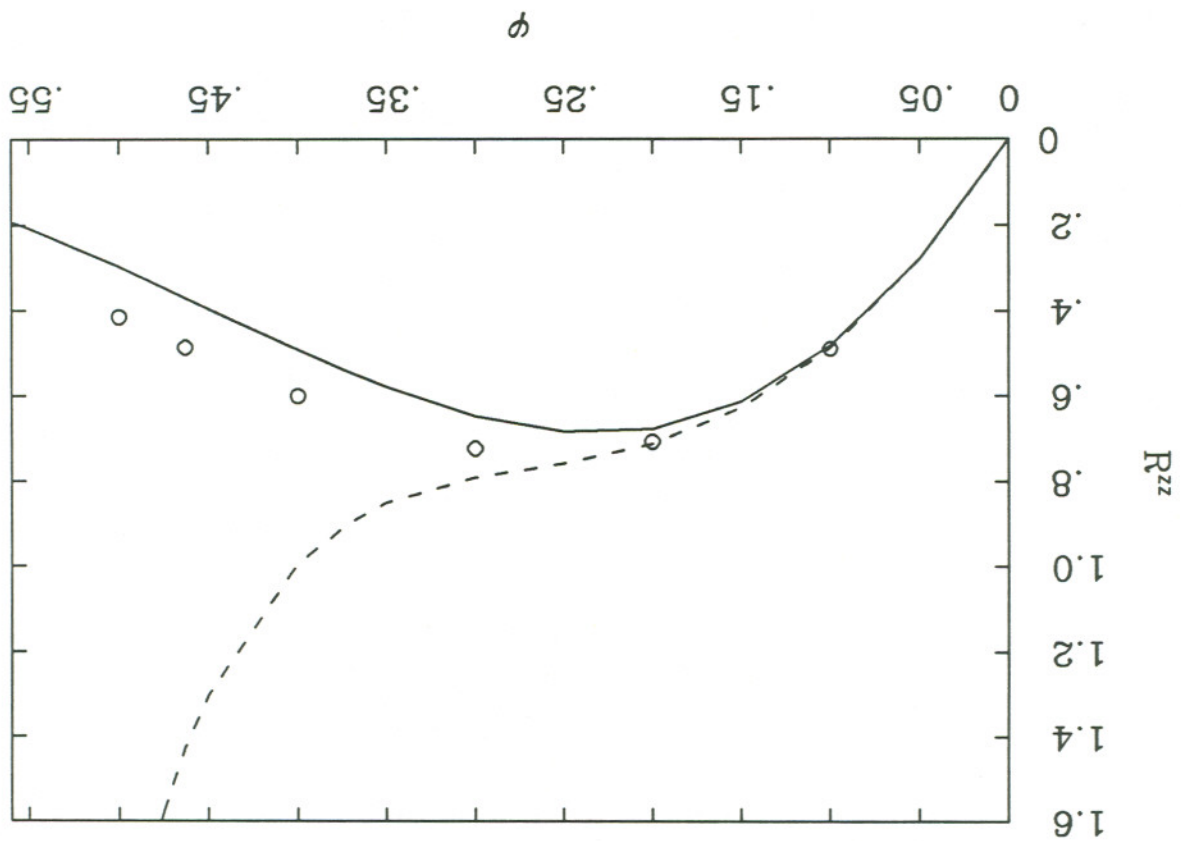


Fig. 2

