LADDER APPROXIMATION FOR THREE AND FOUR-PARTICLE
CORRELATION FUNCTIONS:

Application to thermodynamic perturbation theory

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ABSTRACT

We apply the recently developed ladder approximation (LA) for three- and four-particle correlation functions to the thermodynamic perturbation theory. We calculate the first correction in the perturbative expansion of the pair correlation function, and the second correction in the expansion of the free energy of a fluid of particles interacting via a hard-sphere reference potential plus a perturbing term. Both calculated quantities depend on the three- and four-particle correlation functions of the reference system. The results for the free energy are in good overal agreement with computer-simulation data over a wide range of densities, up to the hard-sphere fluid-solid phase transition. The results for the pair correlation function are in good agreement with computer-simulation data except near contact at high densities.

I. INTRODUCTION

The present paper is one of a series in which a powerful new method of calculating three- and four-particle correlation functions is considered. Our approach is based on the generalized Ornstein- Zernike (OZ) formalism for many-particle correlation functions, developed recently in refs. 1 and 2 (hereafter referred to as I and II). As with the standard OZ equation for the pair correlation function, the generalized OZ equation (GOZE) derived in I is a convenient starting point for approximate evaluation of the three- and four-particle correlation functions in simple fluids. In this paper we apply the simple closure approximation for the GOZE, leading to a ladder approximation[1,2] (LA). The LA corresponds to a resummation of the ladder diagrams in the h-bond Mayer graph expansion of three- and four-particle correlation functions[2,3]; hence its name.

Many-particle correlation functions, in particular three- and four-particle functions, play an essential role in numerous problems of both equilibrium and non-equilibrium statistical physics. Such functions appear in various sorts of thermodynamic perturbation theories,[4,5] in a cluster expansion of the dielectric constant of fluids and suspensions,[6,7] in the theory of depolarized interaction-induced light scattering,[8,9] in the kinetic theory of dense fluids[10−13] and suspensions,[14], in calculating quantum corrections to the equation of state of fluids[15], and in many other applications. While there is a fundamental need for detailed knowledge of three- and four-particle correlation functions, there is still a lack of good evaluation methods. The most frequently used, the Kirkwood superposition approximation (KSA) for the three-particle correlation function and its generalization to the four-particle correlation function, are not reliable. For high densities the superposition approximation often gives poor, results and it is not easy to tell *a priori* for which functionals of three- and four-particle correlation functions it will yield good results.

One of the goals of the present paper, as well as the other papers of this series, is to test the accuracy of the LA by comparing results it yields with computer-simulation data. (In future work we intend also to explore other, more sophisticated approximations based on the GOZE, which facilitate full satisfaction of the core condition for the three-particle correlation functions.[16]) In ref. II the LA was applied to a numerical evaluation of the dipole-dipole-interaction correlation functions for a hard-sphere (HS) fluid. The dipole-dipole-interaction correlation functions are present in expressions for the dielectric constant for nonpolar, polarizable fluids,[17,18] and for the integrated intensity measured in depolarized interaction-induced light scattering experiments[6,7]. The comparison of the LA results with computer-simulation data[19,20] show qualitative agreement for a very wide range of densities, up to the fluid-solid phase transition. On the other hand in this context for high densities the KSA completely fails.

In the present paper we give another example of an application of the LA which is of great importance in liquid-state theory. We present results for thermodynamic perturbation theory.[4,5] We consider a fluid, for which the pair potential can be profitably separated into a short-ranged reference potential and a perturbing term. With such a separation, one can use perturbative techniques to evaluate various properties of the fluid, provided that appropriate properties of the reference system are known. In this paper we are interested in the evaluation of the second-order correction in the expansion of the free energy, and the first correction in the corresponding perturbation expansion of the pair correlation function. To calculate these quantities one needs an appropriate combination of two-, three- and four-particle correlation functions for the reference system which can be expressed in terms of the functional derivative of the Helmholtz free energy with respect to the pair potential. We denote this combination by A. To evaluate the function A we use here the LA. All numerical results we present were obtained for a HS reference potential.

Comparison of the LA results with computer-simulation data allows us to estimate the validity of the LA for various densities and various configurations of particles.

Thermodynamic perturbation theory has previously been considered in many papers. In particular, Smith et al.,[21] Alder et al.,[22] and Henderson et al.[23] have calculated both the second-order term in an expansion of the free energy and the first order term in an expansion of the two-particle correlation functions directly from computer simulations. They considered a square-well fluid with a HS reference potential. Stell and Weis[24] have obtained Monte Carlo (MC) results for the difference between the pair correlation function for a HS and HS with added Lennard-Jones (LJ) tail systems. We use their data to test the LA, along with very new data generated by Weis.[25]

It is interesting to note that the correlation function A of the perturbation theory appears as a natural object of the generalized OZ formalism presented in refs. I and II. In these references the set of functions describing equilibrium correlations between two pairs of particles was considered. A full pair-pair correlation function was defined in a natural way, and it was then separated into the reducible and irreducible parts. The reducible pair-pair correlation function was defined as a sum of the contributions to the full pair-pair correlation function for which the two pairs are correlated through a chain of single intermediate particles. The sum of the remaining contributions, i.e. for which a single intermediate particle cannot be distinguished, forms the irreducible pair-pair correlation function. One can show that the irreducible pair-pair correlation function is equal to the function A appearing in thermodynamic perturbation theory. We will address this point in the present paper.

In the next step the direct and indirect pair-pair correlation functions was introduced. The indirect pair-pair correlation function is a sum of those contributins to the irreducible pair-pair correlation function for which the two pairs are correlated through a sequence of intermediated pairs of particles. This is an extension

of the idea that goes into the usual Ornstein-Zernike equation. The direct pair-pair correlation function is a sum of those terms for which i) an intermediate pair of particles cannot be distinguished, and which ii) cannot be expressed as a simple combination of usual two-particle direct correlation functions. The GOZE derived in I relates the irreducible pair-pair correlation function to the direct pair-pair correlation function and includes also two-particle full and direct correlation functions. The closed integral equation for the irreducible pair-pair correlation function, corresponding to the LA, was obtained by neglecting the direct pair-pair correlation function in the GOZE.

This paper is organized as follows. In Sec. II we introduce the basic formulas of the thermodynamic perturbation theory. In Sec. III the main elements of the generalized OZ formalism are recalled and expressed in the functional differentiation language. Next, the LA for the three- and four-particle correlation functions is formulated. In Sec. IV the numerical results for the perturbative corrections to the pair correlation function and the free energy are presented. We close our paper with some concluding remarks in Sec. V.

II. THERMODYNAMIC PERTURBATION THEORY

We introduce now the basic formulas of the thermodynamic perturbation theory. We express them in a form suitable for the discussion of their relation to the generalized Ornstein-Zernike formalism.[1,2] (For review of various methods of thermodynamic perturbation theory see e.g. refs. 4 and 5).

We consider a uniform equilibrium system of identical classical particles enclosed in a volume V, described by the grand canonical distribution function. The average number of particles is denoted by N, the density by n, the temperature by T, and the standard notation $\beta = 1/k_B T$ is used, where k_B is Boltzmann's constant. The position of ith particle $\mathbf{r}_i$ is denoted by (i).

We assume that the particles i and j interact via a spherically symmetric pair potential $\Phi_2(ij)$ which is divided into a reference part $\Phi_2^r(ij)$ and the perturbation $\epsilon\Phi_2^p(ij)$ so that

$$\Phi_2(ij) = \Phi_2^r(ij) + \epsilon\Phi_2^p(ij). \qquad (2.1)$$

For convenience we have introduced a parameter ϵ which measures the strength of the perturbation. With such a partition of the pair potential, for a given temperature and density, the Helmholtz free energy $F \equiv F[\Phi_2]$ can be expanded around the reference value $F^{(0)} \equiv F[\Phi_2^r]$:

$$F = F^{(0)} + \sum_{k=1}^{\infty} (\beta\epsilon)^k F^{(k)}. \qquad (2.2)$$

The k-th term in expansion (2.2) can be easily expressed in terms of a functional derivative of the reference-system free energy with respect to the pair potential

$$F^{(k)} = \frac{\beta^{-k}}{k!} \int d1 \int d1' \cdots \int dk \int dk' \left(\frac{\delta^k F}{\delta\Phi_2(11')\cdots\delta\Phi_2(kk')} \right)_n \prod_{i=1}^{k} \Phi_2^p(ii'), \qquad (2.3)$$

The functional derivative in eq. (2.3) is defined in a usual way and is evaluated at constant temperature, constant uniform density n, and at $\Phi_2 \equiv \Phi_2^r$.

The expression (2.3) for successive terms in the expansion (2.2) can be simplified by using a well-known relation

$$\frac{1}{2} n_2(ij) = \left(\frac{\delta F}{\delta\Phi_2(ij)} \right)_n, \qquad (2.4)$$

where $n_2(ij) = n^2 g_2(ij)$ is the two-particle reduced distribution function. We assume that the thermodynamic limit is taken in eq. (2.4) after the functional derivative is calculated. Using eq. (2.3), the relation (2.4) specified for a reference system, and the assumption that in bulk the system is uniform one gets in the thermodynamic limit the following expression for the first term in the perturbative expansion of the Helmholtz free energy per particle:

$$f^{(1)} \equiv \frac{F^{(1)}}{N} = \frac{1}{2} n k_B T \int d2\, g_2^{(0)}(12) \Phi_2^p(12), \qquad (2.5)$$

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where the superscript (0) indicates that that the pair distribution function g_2 is evaluated for $\Phi_2 \equiv \Phi_2^c$. The function $f^{(1)}$ depends on the properties of the reference system through the two-particle distribution function only. Since for many systems there are good approximations and a number of computer-simulation data for the two-particle distribution function, calculation of $f^{(1)}$ usually does not cause much difficulty [5,21,22].

To evaluate the second-order term in the expansion of the free energy one needs the first derivative of the two-particle distribution function $n_2(12)$ with respect to the pair potential. We define the function A by the following expression

$$\frac{n^4}{2} A(12 \mid 34) = - \left(\frac{\delta n_2(12)}{\delta \beta \Phi_2(34)} \right)_n. \qquad (2.6)$$

With this notation, in the thermodynamic limit, one obtains from (2.3) and (2.4) the following equation for the second term in perturbative expansion of the Helmholtz free energy per particle:

$$f^{(2)} \equiv \frac{F^{(2)}}{N} = -\frac{1}{8} n^3 k_B T \int d2 \int d3 \int d4 \, A^{(0)}(12 \mid 34) \, \Phi_2^p(12) \Phi_2^p(34), \qquad (2.7)$$

where, similarly as before, the superscript (0) indicates the reference-system value of the function A.

The function $A(12 \mid 34)$ can be expressed in terms of two-, three- and four-particle equilibrium correlation functions of the reference system. Such a relation is discussed in the next section. We will see that the function A can be numerically evaluated in the LA, and the results can be applied to thermodynamic perturbation theory.

The expansion similar to (2.2) can be also introduced for the pair distribution function of the perturbed system:

$$g_2 = g_2^{(0)} + \sum_{k=1}^{\infty} (\beta \epsilon)^k g_2^{(k)}. \qquad (2.8)$$

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In this case already the first-order term $g_2^{(1)}$ depends on the function A:

$$g_2^{(1)}(12) = -\frac{1}{2}n^2 \int d3 \int d4 \, A^{(0)}(12 \mid 34) \Phi_2^p(34). \qquad (2.9)$$

The quantity $g_2^{(1)}$ can be evaluated using the LA and numerical results of the evaluation are presented in this paper.

The problem of calculating the functions $f^{(2)}$ and $g_2^{(1)}$ have been addressed previously in many papers[5,21-24]. The functions have been evaluated for various systems using both computer simulations and the KSA. The comparison of the results shows that the KSA is in substantial error for high densities and that there is need for a better approximation.

III. LADDER APPROXIMATION FOR THE IRREDUCIBLE PAIR-PAIR CORRELATION FUNCTION

In this section we describe an approximate method of evaluating the function A, based on the LA introduced in refs. I and II. To this end first we need to know the relation between the function A, defined by eq. (2.6), and the irreducible pair-pair correlation function discussed in refs. I and II in the framework of the generalized OZ formalism. The problem of this relation has been already considered in ref. 10b) in a different context. It was shown there that the function A and the irreducible pair-pair correlation function are identical. We repeat briefly the arguments appropriate to our present purpose, and we put the generalized OZ formalism in the context of functional differentiation.

Following ref. 10b) we define, in terms of functional derivatives, the set of functions Q_{ij}. For our present purpose it is sufficient to consider $i,j = 1,2$ only. It is convenient at this point to assume that the equilibrium system of particles under

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consideration is subject to an arbitrary external field Φ_1. The local number density at the point (i) is denoted by $n(i)$. With this notation we can conveniently define

$$n^2 Q_{11}(1 \mid 2) = - \left(\frac{\delta n(1)}{\delta \beta \Phi_1(2)} \right)_{\Phi_2}, \qquad (3.1)$$

$$n^3 Q_{21}(12 \mid 3) = - \left(\frac{\delta n_2(12)}{\delta \beta \Phi_1(3)} \right)_{\Phi_2}, \qquad (3.2)$$

$$\frac{n^3}{2} Q_{12}(1 \mid 23) = - \left(\frac{\delta n(1)}{\delta \beta \Phi_2(23)} \right)_{\Phi_1}, \qquad (3.3)$$

and

$$\frac{n^4}{2} Q_{22}(12 \mid 34) = - \left(\frac{\delta n_2(12)}{\delta \beta \Phi_2(34)} \right)_{\Phi_1}. \qquad (3.4)$$

We also introduce the function $Q_{11}^{inv}(1 \mid 2)$ defined by the functional derivative inverse to (3.1):

$$n^{-2} Q_{11}^{inv}(2 \mid 1) = - \left(\frac{\delta \beta \Phi(2)}{\delta n(1)} \right)_{\Phi_2}. \qquad (3.5)$$

(The above definitions, and the definitions of all other quantities introduced in this section are general, valid for any interaction potential. In the application to the thermodynamic perturbation theory the quantities are evaluated for the reference system with $\Phi_1 = 0$.) The functional derivatives of eqs. (3.1) and (3.9) obey the following identity

$$\int d2 \left(\frac{\delta \Phi_1(1)}{\delta n(2)} \right)_{\Phi_2} \left(\frac{\delta n(2)}{\delta \Phi_1(3)} \right)_{\Phi_2} = \delta(1-3). \qquad (3.6)$$

Taking into account known properties of the functional derivatives, it is not difficult to express the functions Q_{ij}, where $ij = 1, 2$, in terms of k-particle equilibrium correlation functions g_k, with $k = 2, 3, 4$. The explicit expressions are as follows:

$$Q_{11}(1 \mid 1') = \frac{1}{n} \delta(1-1') + h_2(1-1'), \qquad (3.7)$$

$$Q_{21}(12 \mid 1') = Q_{12}(1' \mid 12)$$
$$= \frac{1}{n} \left(\delta(1-1') + \delta(2-1') \right) g_2(12) + g_3(123) - g_2(12), \qquad (3.8)$$

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and

$$Q_{22}(12 \mid 1'2') = \frac{1}{n^2} \left[\delta(1-1')\delta(2-2') + \delta(1-2')\delta(2-1') \right] g_2(12)$$

$$+ \frac{1}{n} \left[(\delta(1-1') + \delta(2-1')) g_3(122') + (\delta(1-2') + \delta(2-2')) \bar{g}_3(121') \right]$$

$$+ g_4(121'2') - g_2(12)g_2(1'2') ,$$

$$(3.9)$$

where

$$h_2(12) = g_2(12) - 1. \tag{3.10}$$

Taking into account the expression (3.7) one can easily see that eq. (3.6) is equivalent to the standard OZ equation and that the function Q_{11}^{inv} can be expressed in the form

$$Q_{11}^{inv}(1 \mid 2) = \frac{1}{n}\delta(1-2) - c_2(1-2), \tag{3.11}$$

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

By comparing eqs. (3.7)–(3.9) and (3.11) with eqs. (2.9)–(2.11) and (2.15) of ref. II one immediately arrives at the conclusion that the functions Q, in the present paper defined in terms of functional derivatives, are identical to the functions Q of refs. I and II. In refs. I and II the functions Q_{ij} were defined as the correlation functions between two groups including i and j particles respectively. In particular, the function $A(12 \mid 34)$ describes the correlations between the two pairs of particles (12) and (34); we call this function the pair-pair correlation function.

We are now in position to prove that the function A defined by eq. (2.6) is equal to the irreducible pair-pair correlation function considered in refs. I and II. Let us consider the following functional-derivative identity:

$$\left(\frac{\delta n_2(12)}{\delta \Phi_2(34)} \right)_{\Phi_1} = \int d5 \int d6 \left(\frac{\delta n_2(12)}{\delta \Phi_1(5)} \right)_{\Phi_2} \left(\frac{\delta \Phi_1(5)}{\delta n(6)} \right)_{\Phi_2} \left(\frac{\delta n(6)}{\delta \Phi_2(34)} \right)_{\Phi_1}$$

$$+ \left(\frac{\delta n_2(12)}{\delta \Phi_2(34)} \right)_n . \tag{3.12}$$

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Using notation (2.6) and (3.1)–(3.5) one can rewrite eq. (3.12) in the form

$$Q_{22}(12 \mid 34) = n^2 \int d5 \int d6 \, Q_{21}(12 \mid 5) Q_{11}^{inv}(5 \mid 6) Q_{12}(6 \mid 34)$$
$$+ A(12 \mid 34). \tag{3.13}$$

Eq. (3.13) is identical to eq. (2.13) of ref. II. It describes the decomposition of the pair-pair correlation function Q_{22} into the reducible part (the first term on the rhs of this equation) and the irreducible part (the second term A). It follows immediately that the function A given by eq. (2.6) is identical to the irreducible pair-pair correlation function defined in I and II. (In ref. I the irreducible part was denoted by $^{(\alpha)}Q_{22}^{(\alpha)}$). One can show[1,20] that the reducible pair-pair correlation function, defined in eq. (3.13) corresponds to the situations in which the pairs of particles (12) and (34) are correlated through a chain of a single intermediate particles. The irreducible part $A(12 \mid 34)$ correspond to the case in which no single intermediate particle can be found between (12) and (34).

In ref. I a detailed analysis of the structure of the irreducible pair-pair correlation function A was given. This analysis led to the derivation of the GOZE. The GOZE can be expressed in the following form[2]

$$\frac{n^2}{2} \int d5 \int d6 \, A^{inv}(12 \mid 56) A(56 \mid 34) = I(12 \mid 34), \tag{3.14}$$

where

$$I(12 \mid 34) = \frac{1}{n^2} \left(\delta(1-3)\delta(2-4) + \delta(1-4)\delta(2-3) \right), \tag{3.15}$$

and the inverse integral kernel A^{inv} is decomposed as follows:

$$A^{inv}(12 \mid 34) = \frac{1}{g_2(12)} I(12 \mid 34) - D(12 \mid 34), \tag{3.16}$$

with D given by

$$D(12 \mid 34) = \left(1 + \hat{P}(34)\right) \left[\frac{1}{n} c_2(13)\delta(2-4) \right.$$
$$\left. + \frac{1}{n} \delta(1-3)c_2(24) - c_2(13)c_2(24) \right] \tag{3.17}$$
$$+ C_{22}(12 \mid 34).$$

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The operator $\hat{P}(34)$ in eq. (3.17) permutes the variables (3) and (4). It can be shown that the function $C_{22}(12 \mid 34)$ is the only term on the rhs of eq. (3.17) with a group property, i.e. which vanishes when the distance between any two of the particles (1), (2), (3), and (4) tends to infinity. The Mayer-graph analysis of eqs. (3.14)–(3.17) leads to the conclusion that $C_{22}(12 \mid 34)$ corresponds to the cases in which there are no intermediate pair of particles such that (12) and (34) are correlated only through it. Therefore C_{22} can be naturally interpreted as a direct pair-pair correlation function and eq. (3.14) supplemented with the decomposition (3.16)–(3.17) as a GOZE.

It is interesting to note that the GOZE (3.14) can be cast into a form analogous to (3.10) for the standard OZ equation. Taking into account that the pair potential is symmetric with respect to the permutation of the variables one can rewrite (3.14) as

$$\int d5 \int d6 \left(\frac{\delta \Phi_2(12)}{\delta n_2(56)} \right)_n \left(\frac{\delta n_2(56)}{\delta \Phi_2(34)} \right)_n = \frac{1}{2} \left(\delta(1-3)\delta(2-4) + \delta(1-4)\delta(2-3) \right) \tag{3.18}$$

The underlying structure of a correlation functions is more complicated for the pair-pair GOZE then for the standard OZ equation and the additional decomposition (3.16)–(3.17) of the function A^{inv} is an inherent part of the formalism. Functional-derivative expressions (3.6) and (3.18) form a part of a general scheme. In this scheme the GOZE of an order i can be expressed as a relation analogous to eq. (3.18) but with the functional derivative of the i-particle density n_i with respect to an i-particle potential, with the densities n_j, kept constant for $j = 1, \ldots, i - 1$.[26]

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 the function A, the GOZE has to be supplemented by an appropriate closure approximation for the pair-pair direct correlation function A. The simplest

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possible approximation, corresponding to a resummation of the ladder diagrams in the h-bond expansion of the function A, is obtained by setting

$$C_{22} = 0. \tag{3.19}$$

By inserting expression (3.19) into the GOZE one gets the following closed integral equation for the function A

$$
\begin{aligned}
A(12 \mid 34) - n^2\, g_2(12) \int d5 \int d6 &\left(\frac{1}{n}\delta(1-5)c_2(2-6) \right. \\
&\left. + \frac{1}{n}\delta(2-6)c_2(1-5) - c_2(1-5)c_2(2-6) \right) \times A(56 \mid 34) \\
&= g_2(12)\big(\delta(1-5)\delta(2-6) + \delta(1-6)\delta(2-6)\big).
\end{aligned}
\tag{3.20}
$$

Equation (3.20) allows as to approximately evaluate the function A in terms of the two-particle correlation function.

In ref. II, eq. (3.20) was used to calculate the dipole-dipole interaction correlation functions that appear in the theory of the dielectric constant of nonpolar, polarizable fluids and in the theory of depolarized light scattering. In the present paper we apply this equation in the thermodynamic perturbation theory and calculate the quantities $f^{(2)}$ and $g^{(1)}$ defined by eqs. (2.7) and (2.9).

IV. Numerical results

We are now in position to present our numerical results. We have performed calculations based on the LA for two systems, both with a HS reference potential:

$$\Phi_2^r(ij) = \begin{cases} 0 & \text{for } r_{ij} \le \sigma; \\ \infty & \text{for } r_{ij} > \sigma, \end{cases} \tag{4.1}$$

where σ is a HS diameter and r_{ij} is a distance between particles i and j. The first of the systems considered has a square-well (SW) perturbation correction to a pair potential:

$$\Phi_2^p(ij) = \begin{cases} -1 & \text{for } r_{ij} \le d; \\ 0 & \text{for } r_{ij} > d. \end{cases} \tag{4.2}$$

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In the second case the perturbation potential is a LJ tail:

$$\Phi_2^p(ij) = \begin{cases} -1 & \text{for } r_{ij} \leq 2^{1/6}\sigma; \\ 4\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6\right] & \text{for } r_{ij} > 2^{1/6}\sigma. \end{cases} \qquad (4.3)$$

In both cases the strength of the perturbation is measured by the parameter ϵ in the expression (2.1).

To numerically solve the eq. (3.20) and evaluate the quantities $f^{(2)}$ and $g_2^{(1)}$ given by the respective expressions (2.7) and (2.9), we have used the algorithm which was described in detail in ref. II. As input we have used a Verlet-Weis parametrization of the HS pair correlation function.[27] Without giving details, we only mention that by multiplying eq. (3.5) by the perturbing potential $\phi_2^p(34)$ and integrating with respect to the variables (3) and (4) one arrives directly at an integral equation for the function $g_2^{(1)}$. This greatly simplifies the numerical problem, since in this way one only has to solve an integral equation for a function of one variable. The free-energy correction $f^{(2)}$ can then be evaluated by integrating $g_2^{(1)}$ with a perturbation potential Φ_2^p [cf. eqs. (2.7) and (2.9)]. The integral equation have been solved using fast Fourier transform techniques. It takes only a few minutes of CPU time on a VAX 11/780 to obtain the solution for a given density.

First we describe the results for a SW perturbing potential. We have calculated, using the LA, the second-order correction to the free energy $f^{(2)}$, for a number of SW widths and a wide range of densities. The results are presented in figs. 1–3. In figs. 1 and 2 the dependence of the the LA results for the free energy per particle on the reduced density $n\sigma^3$ for various SW widths are presented. The best fits to the MC data, by Henderson et al.[23], are also given for the comparison. (Henderson et al.[23] and Smith et al.[21] have evaluated the integrals (2.7) and (2.8) for $f^{(2)}$ and $g_2^{(1)}$ directly, using the MC method). One can see that the LA and the MC results are in qualitative agreement for a very wide range of densities. For the SW width

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$d/\sigma = 1.5$ the function $f^{(2)}$ was calculated by Smith et al.[21] using a superposition approximation for the three and four-particle correlation functions:

$$g_3^{(0)} = g_2^{(0)}(12)\, g_2^{(0)}(13)\, g_2^{(0)}(23) \qquad\qquad (4.4)$$

and

$$g_4^{(0)}(1234) = g_2^{(0)}(12)\, g_2^{(0)}(13)\, g_2^{(0)}(14)\, g_2^{(0)}(23)\, g_2^{(0)}(24)\, g_2^{(0)}(34). \qquad (4.5)$$

[eq. (4.5) is a generalization of the the KSA (4.4) to the four-particle correlation function; we refer to both approximations (4.4) and (4.5) as KSA]. We compare in fig. 3 the KSA results for $f^{(2)}$ by Smith et al. with the LA results and the computer-simulation data by Henderson at al.[23] and Alder et al.[22] The KSA results are in great error for high densities, while the LA results qualitatively follow the MC data up to very high densities. This is a similar situation as with the dipole-dipole-interaction correlation functions discussed in II, where analogous behavior of the LA and KSA results with respect to the computer-simulation data was observed.

It is interesting and important to compare the successive terms in the per-turbative expansion (2.2) of the free energy. The reference value $f^{(0)} - f^B$ of the excess free energy per particle, where f^B is the ideal-gas (Boltzmann) value, can be calculated with high accuracy from the approximate analytical expression given by Carnahan and Starling[28] for a hard-sphere fluid. The first perturbative correction $f^{(1)}$ can be easily obtained from eq. (2.5). The values of $\left(f^{(0)} - f^B\right)/k_B T$ and $f^{(i)}/k_B T$, for $i = 1, 2$ et various densities are summarized in the table I. One can see that the first correction is large in absolute magnitude compared to the reference value of the excess free energy. However, for high densities, the expansion converges rapidly, and the the second-order correction constitutes only a few percent of the first correction. Thus the errors in our approximate assessment of $f^{(2)}$, which are quite small over a wide range of densities, give rise to essentialy negligible error in the excess free energy obtained from adding at these densities the contributions from

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$f^{(i)}$ for $i = 0, 1$, and 2. The fast convergence of the perturbative expansion (2.2) for high densities is related to the stringent configurational constraints imposed on the system by the repulsive cores.[4] In fact, it has been shown rigorously in one[29] and in two[30] dimensions that the first-order perturbation thermodynamic theory is exact in the close-packing limit for a short-ranged perturbing potential.

The irreducible pair-pair correlation function A is a sum of terms depending on the correlations between two, three, and four particles. To see this cf. e.g. eqs. (3.7)–(3.11), and (3.13). The respective two-, three-, and four-particle contributions to $A(12 \mid 34)$ are obtained by selecting in eq. (3.13) the terms which include, after integration, two, one, and no Dirac δ functions describing particles common for the pairs (12) and (34). It is important to note, that, individually, the corresponding two-, three- and four-particle contributions to $f^{(2)}$ are big; the smallness of $f^{(2)}$ is due to a substantial cancellation among the individual terms. Indeed, for the square-well fluid the two-particle contribution $f_2^{(2)}$ to the second order term in the expansion of the free energy $f^{(2)}$ is related to the first order term $f^{(1)}$ by

$$f_2^{(2)} = \frac{1}{2} f^{(1)}. \tag{4.6}$$

Taking this into account, one can see from the table I that, for high densities, the total value of $f^{(2)}$ is less than 10% of the two-particle contribution $f_2^{(2)}$. In our calculations the two-particle contribution was determined accurately. Therefore one can conclude that the relative error in the sum of the three- and four-particle contributions obtained from the LA is quite small.

The results for the first perturbative correction to the pair correlation function $g_2^{(1)}$ for the SW widths $d = 1.5\,\sigma$ are represented in figs. 4–7. The MC results by Smith et al.[21b] are also given. The hard-core contact values obtained from the MC simulations by Smith et al. are subject to large uncertainty; we have substituted for them the results obtained from molecular-dynamics data by Michels et al.[31] . Michels et al. have calculated the contact values of the two-particle correlation

function of a square-well fluid for various reduced square-well depths $\epsilon^* \equiv \beta\epsilon$. The contact values of $g_2^{(1)}$ were obtained from Michels' data by extrapolating $\epsilon^* \to 0$. From the results for $g_2^{(1)}$ one gets more detailed information about the accuracy of the approximation than from the results for the free-energy correction. For low and intermediate densities, up to $n = 0.5$ the LA and MC results agree very well for all separations of the particles. For higher densities, however, although the overall agreement is quite good, the LA contact values are in a substantial error. This is a substantial disadvantage of the approximation in applications in which the contact values of correlation functions are very important, for example in a kinetic theory of the HS fluid[10,11]. One should note, however, that, as for $f^{(2)}$, there is strong cancellation among two-, three-, and four-particle contributions to $g_2^{(1)}$. Taking into account that the contact value of the HS pair correlation at the reduced density $n\sigma^3$ is approximately equal to 4, one concludes that the relative error in the sum of the three- and four-particle contributions to the contact value of $g_2^{(1)}$ is on the order of 10%.

In figs. 8 and 9 we compare the first-order perturbation results for the pair-distribution function g_2 of a square-well fluid with the pair distribution function of the hard-sphere reference system $g_2^{(0)}$ at a typical liquid-state density $n\sigma^3 = 0.8$ and the reduced temperature $T^* \equiv k_B T/\epsilon = 1$. The results for the square-well widths $d = 1.375\sigma$ and $d = 1.75\sigma$ are given. One can see that even at this relatively low temperature the perturbative correction is rather small.

Similar calculations have been performed for a HS system with the LJ tail (4.2) as a perturbing potential. The LA results for $g_2^{(1)}$ for the respective densities $n\sigma^3 = 0.6$ and 0.91 are represented in figs. 10 and 11. For the comparison we give also the results of the MC calculations by Stell and Weis[24], augmented by results of Weis[25] of much greater precision required for our present purpose. Weis has evaluated, with great accuracy, the pair distribution function $g_2^{(0)}$ of the reference

HS fluid, and the pair distribution function of the HS+LJ tail fluid for various temperatures. In addition to the LA result we present in figs. 8 and 9 the quantity

$$T^* \left(g_2^{HS+LJ} - g_2^{HS} \right). \tag{4.6}$$

evaluated by Weis at the reduced temperature $T* = 1.6$ for the density $n\sigma^3 = 0.6$ and $T^* = 1.35$ for $n\sigma^3 = 0.91$. The calculations at temperatures higher than presented here shows that the contributions from the terms nonlinear in the perturbing potential are negligible for the considered densities and temperatures, and that the quantity (4.6), essentially, represents the first-order correction to the pair distribution function. The statistical absolute error of the MC results is smaller then 0.01, except for the contact value, which was obtained by extrapolation ($r = 1.01\sigma$ is the smallest distance for which $g_2(r)$ was evaluated directly from the MC simulations). The contact value inaccuracy can be estimated to be less then 0.1. The MC calculations were performed using 1372 particles (which is a number compatible with a fcc crystal structure) and generating between 8 and 11 million configurations. The perturbing LJ potential was cut at $r = 3.2\sigma$, but we found that the influence of this cutoff is negligible for our purpose here.

To illustrate a typical difference between the pair distribution functions of a system of particles with hard-sphere cores and LJ tails and a HS system at high densities we show, in fig. 12, the distribution functions for both systems at reduced temperature $T^* = 0.7$ and density $n\sigma^3 = 0.9$. The pair distribution function for the HS+LJ tail system was evaluated in first order in the perturbing potential, using the LA. The difference between pair correlation functions of the reference and the perturbed systems is very small for the slowly varying perturbing LJ potential. The MC results for the perturbed system would be practically indistinguishable from the theoretical results on the scale of the figure.

Finally, in fig. 13 we represent the LA results for $f^{(2)}$ for the HS+LJ tail system. In this case, due to a long range of the LJ tail, the cancellation between

two-, three-, and four- particle term is particularly strong and the second-order contribution to the free-energy is very small at high densities.

V. Conclusions

In this paper we have presented an application of the LA to the three- and four-particle correlation function in thermodynamic perturbation theory. The LA can be obtained from the GOZE for the pair-pair irreducible correlation function[1,2] by leaving out the direct pair-pair correlation function. This simple closure approximation leads to a closed integral equation from which the three- and four-particle correlation function can be approximately evaluated in terms of the pair correlation function. The LA corresponds to a resummation of the ladder diagrams in the h-bond Mayer graph expansion of the three- and four-particle correlation functions. Evaluating of the correlation functions from the LA is relatively undemanding from the numerical point of view.

We have applied the LA to evaluate the second perturbative correction to the free energy and the first correction to the pair correlation function for two systems, both with a HS reference potential. In the first case we have considered the SW perturbation potential, in the second case the perturbation was the LJ tail. For the second correction to the free energy density $f^{(2)}$ we have obtained good overal agreement with the computer-simulation data for a very wide range of densities, up the HS fluid-solid phase transition. At least for the SW width $d = 1.5\sigma$, for high densities the LA gives much better results than the KSA. For the perturbative correction to the pair correlation function $g_2^{(1)}$ the LA are in very good agreement with computer-simulation data up the the reduced density $n\sigma^3 = 0.5$. For higher densities the LA fails to represent accurately the contact value of the correlation function.

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As we have already discussed in refs. I and II the LA is closely related to the generalized hypernetted-chain approximation (HNC) for a pair-pair correlation function, introduced by Pinski et al.(32) They obtained the generalized HNC approximation by functionally differentiating the two-particle correlation function given in the HNC approximation with respect to the pair potential with the local density held constant. This lead to an integral equation very similar to our eq. (3.20). There are, however, two differences between their and our results. The first difference is that their integral equation includes in its structure the pair correlation function in the HNC approximation. In contrast, our approximation leads to the exact two-particle correlation function. The second and main difference is the interpretation of the function which fulfills the integral equation. Pinski and Campbell assumed that the solution of the integral equation is the full pair-pair correlation function rather then its irreducible part. The reason for the difference stems from an error they made in the functional differentiation. They assumed that the full pair-pair correlation function is given by the functional derivative of the two particle correlation function with respect to the pair potential with *density* held constant, while indeed it is given by eq. (3.4), i.e. by the derivative with *one-particle potential* held constant. We discuss this point in detail in Sec. 3 of the present paper. The error in functional differentiation does not influence most of the numerical results given by Pinski et al. Due to a specific angular dependence of the reducible pair-pair correlation function the difference shows up only in the zero-order Legendre polynomial projection of the function $A(12 \mid 34)$ with respect to the angle between vectors r_{13} and r_{24}. In our present application, however, this difference is essential.

As we have mentioned before, the function A is a combination of the two-, three-, and four- particle terms. For some applications it is important to evaluate those terms individually. This can be done in the LA with the help of the integral eq. (3.20). To evaluate the three-particle term one should select in eq. (3.20) all

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terms which include, after integration, the Dirac δ-function $\delta(1-3)$. (One should take int account in this procedure the Dirac δ-functions included in the function A.) This terms correspond to the cases in which the pairs of particles (12) and (34) have a common particle $(1) \equiv (3)$. After such selection one gets an integral equation for the sum of the two- and three-particle terms. Since the two-particle term is a trivial combination of the two-particle distribution function and Dirac δ-functions such a procedure enables us to evaluate all the contributing terms separately. For details of this procedure see ref. II.

Acknowledgments

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Figure captions

Fig. 1. Plot of $f^{(2)}/k_B T$, with $f^{(2)}$ given by eq. (2.7), as the function of the reduced density $n\sigma^3$ for a for a fluid with a hard-sphere reference potential and a square-well perturbing term ((4.1). Results form the LA, solid lines; the best fit to the MC results, by Henderson et al.,[23] dashed lines. The curves are labeled with the appropriate values of the square-well width d.

Fig. 2. The same as in fig. 1 but with the different values of d.

Fig. 3. Plot of $f^{(2)}/k_B T$, with $f^{(2)}$ given by eq. (2.7), as the function of the reduced density $n\sigma^3$ for a for a fluid with a hard-sphere reference potential and a square-well perturbing term (4.1), for the square-well width $d = 1.5$. Results form the LA, solid line; superposition approximation results (4.4)-(4.5), long-short dashed line; the best fit to the MC results by Henderson, et al.[23] dashed line; MD results by Alder et al.[22] circles.

Fig. 4. The first-order perturbation correction $g_2^{(1)}$ to the pair distribution function, as given by eq. (2.9), for a fluid with a hard-sphere reference potential and a square-well perturbing term ((4.1). Results for the square-well width $d = 1.5\sigma$, at the reduced density $n\sigma^3 = 0.5$. The LA results, solid line; MC results by Smith et al.,[21b] open circles; the interpolated MD result by Michels et al.,[31] for the hard-core contact value, solid line.

Fig. 5. The same as in the Fig. 4, but at the reduced density $n\sigma^3 = 0.7$.

Fig. 6. The same as in the Fig. 4, but at the reduced density $n\sigma^3 = 0.8$.

Fig. 7. The same as in the Fig. 4, but at the reduced density $n\sigma^3 = 0.9$.

fig. 8. The first-order perturbation result for the pair distribution function of the fluid with a hard-sphere reference potential and a square-well perturbing term (4.1). The results for the square-well width $d = 1.375\sigma$ at the reduced temperature $T^* = k_B T/\epsilon = 1$ and the reduced density $n\sigma^3 = 0.8$. The perturbation

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result, $g_2^{HS} + g_2^{(1)}$, dashed line; the pair distribution function of the hard-sphere reference system, g_2^{HS}, solid line.

Fig. 9. The same as in the fig. 8, but with the square-well width $d = 1.75\sigma$.

Fig. 10. The first-order perturbation correction $g_2^{(1)}$ to the pair distribution function, as given by eq. (2.9), for a fluid with a hard-sphere reference potential and a Lennard-Jones perturbing term (4.2), at the reduced density $n\sigma^3 = 0.6$. The LA results, solid line; the MC results of Weis[25], dashed line.

Fig. 11. The same as in the fig. 10 but at the reduced density $n\sigma^3 = 0.91$.

Fig. 12. The first-order perturbation result for the pair distribution function of the fluid with a hard-sphere reference potential and a Lennard-Jones perturbing term (4.2). The results at the reduced temperature $T^* = k_B T/\epsilon = 0.7$ and the reduced density $n\sigma^3 = 0.9$. The perturbation result, $g_2^{HS} + g_2^{(1)}$, dashed line; the pair distribution function of the hard-sphere reference system, g_2^{HS}, solid line.

Fig. 13. Plot of $f^{(2)}/k_B T$, with $f^{(2)}$ given by eq. (2.7), as the function of the reduced density $n\sigma^3$ for a fluid with a hard-sphere reference potential and a Lennard-Jones perturbing term (4.2). Results obtained using the LA.

TABLE 1. The values of the reference excess free energy per particle $f^{(0)} - f^B$, and of the first- and the second-order terms $f^{(1)}$ and $f^{(2)}$ in the perturbative expansion of the free energy per particle of the square-well fluid with a hard-sphere reference potential, at various densities $n\sigma^3$.

$n\sigma^3$	$\frac{f^{(0)} - f^B}{k_B T}$	$\frac{f^{(1)}}{k_B T}$	$\frac{f^{(2)}}{k_B T}$
0.1	0.009	-0.534	-0.248
0.2	0.041	-1.143	-0.343
0.3	0.104	-1.820	-0.359
0.4	0.206	-2.554	-0.352
0.5	0.362	-3.324	-0.346
0.6	0.587	-4.106	-0.338
0.7	0.907	-4.866	-0.322
0.8	1.355	-5.560	-0.300
0.9	1.985	-6.139	-0.281
1.0	2.876	-6.563	-0.276

Fig.

$n\sigma^3$

.9   .7   .5   .3   .1   0

$\dfrac{f(2)}{k_BT}$

-.8   -.7   -.6   -.5   -.4   -.3   -.2   -.1   0

2.0

1.75

1.375

1.125

Fig. 2

$n\sigma^3$

$\dfrac{f(2)}{k_B T}$

1.85

1.625

1.5

1.25

Fig.

$n\sigma^3$

.9   .7   .5   .3   .1   0

$-.50$ $-.45$ $-.40$ $-.35$ $-.30$ $-.25$ $-.20$ $-.15$ $-.10$ $-.05$ 0

$\dfrac{f(2)}{k_B T}$

r/σ

2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0

$n\sigma^3 = 0.5$

$g_2^{(1)}$

-.5 -.4 -.3 -.2 -.1 0 .1 .2 .3 .4 .5 .6

Fig. 5

Fig. 6

$n\sigma^3 = 0.8$

r/σ

1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4

$g_2^{(1)}$

-.8 -.7 -.6 -.5 -.4 -.3 -.2 -.1 0 .1 .2 .3 .4 .5

Fig. 8

r/σ

g_2

$n\sigma^3 = 0.8$

Fig. 9

r/σ

g_2

$n\sigma^3 = 0.8$

$n\sigma^3 = 0.6$

$g_2^{(1)}(r)$

r/σ

Fig. 10

Fig. 1.

$n\sigma^3 = 0.91$

r/σ

$g_2^{(1)}$

Fig. 12 — $n\sigma^3 = 0.9$; axes r/σ and g_2.

Fig 13

$n\sigma^3$

$\dfrac{f(2)}{k_B T}$

0   .1   .2   .3   .4   .5   .6   .7   .8   .9   1.0
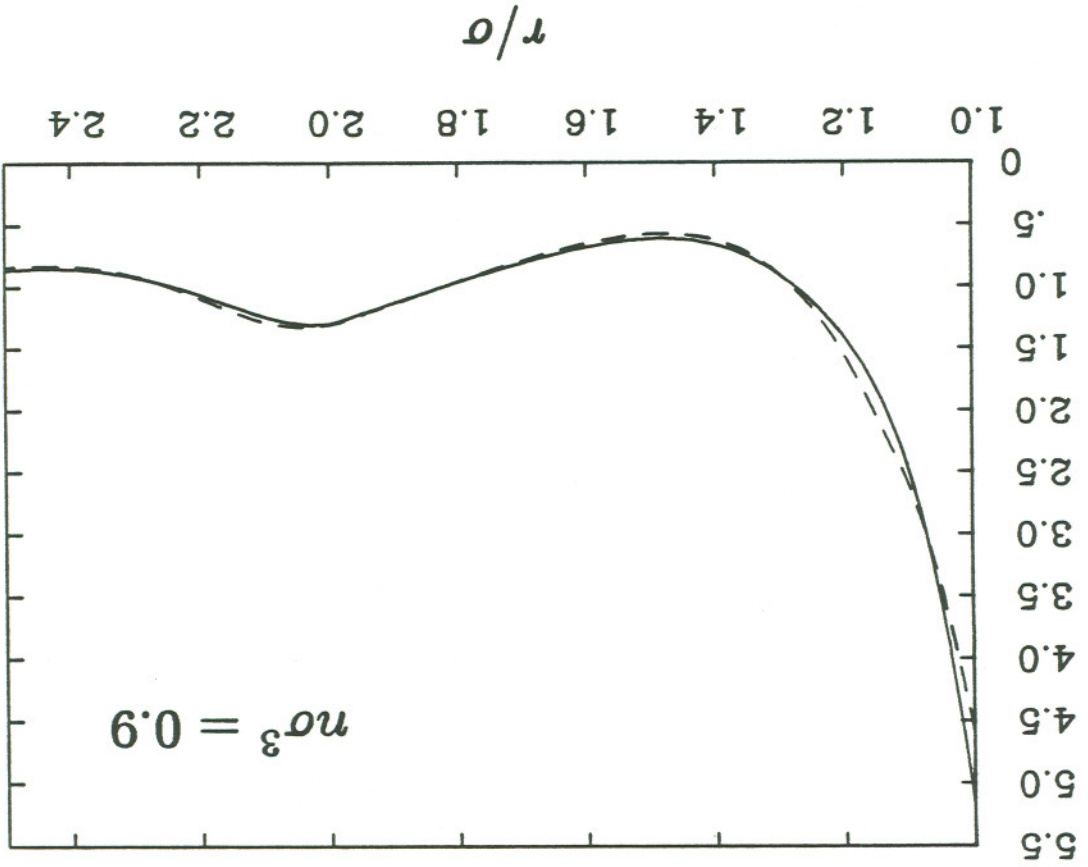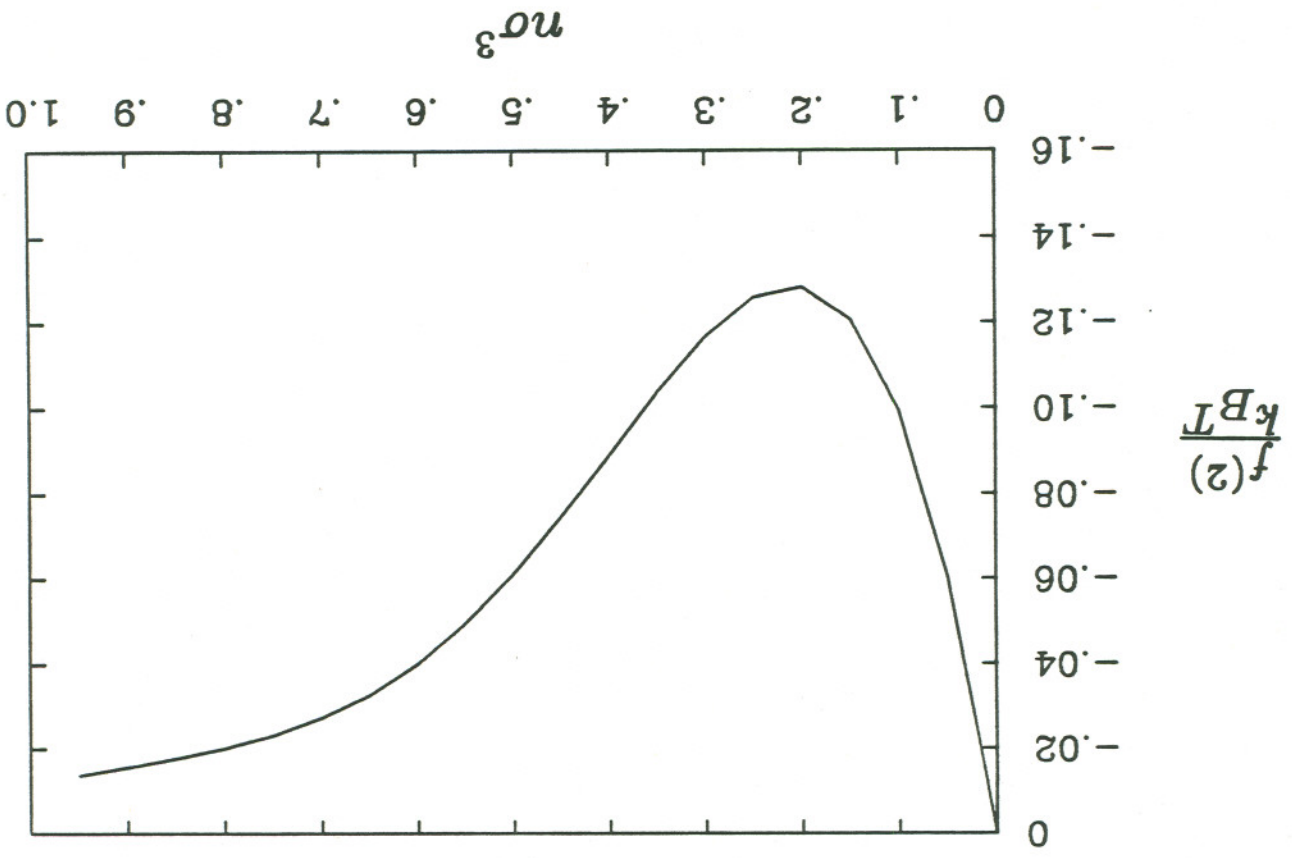
0   -.02   -.04   -.06   -.08   -.10   -.12   -.14   -.16

LADDER APPROXIMATION FOR THREE AND FOUR-PARTICLE

CORRELATION FUNCTIONS:

Application to thermodynamic perturbation theory

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