Hypernetted-chain approximation for three- and four-body correlations in simple fluids

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New approximate integral equations for the three- and four-body correlation functions and structure functions are derived. These approximations are based on the hypernetted-chain resummation. The equation for the three-body correlation function satisfies a self-consistency condition, the Born-Green-Yvon equation, and has the Kirkwood superposition approximation as the leading or nonhomogeneous term. Similarly, the new approximation for the third-order structure function has the convolution approximation as its leading term. In addition to the formalism, numeric solutions are presented for a Lennard-Jones system corresponding to argon at its triple point and at room temperature (with its triple-point density). At this high density, the integral equations give results significantly different from their leading terms.

I. INTRODUCTION

The static properties of a fluid are generally expressed in terms of few-body reduced distribution functions $g_n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)$ or the closely related few-body static correlation functions. The theory of the two-body distribution $g_2(\mathbf{r}_1,\mathbf{r}_2)$ [or radial distribution function $g(r_{12})$] is well developed. In the present work we focus on a theory of the next two higher-order correlation functions, the triplet correlation function and the pair-pair correlation function, both defined below. Aside from providing some additional insights into the structure of fluids, the pair-pair correlation function can be used to calculate the intensity of depolarized light scattered from the fluid[1-4] and in the analysis of the equation of state of a quantum fluid,[3-5] while the triplet correlation function is useful in the theory of the ultraviolet absorption line-shape analysis[6,7] and in the calculation of the kinetic energy of a quantum fluid.[4,8]

The triplet correlation function contains the same information as the three-body distribution function $g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ in an isotropic, homogeneous system. This latter function has been the subject of much attention during the past two decades. Molecular dynamics and Monte Carlo simulations have produced "exact" information about g_3 at special choices of the arguments (e.g., isosceles triangles) in simple fluids such as the Lennard-Jones fluid or hard spheres.[9-13]

Analytic approaches to the theory of the three-body distribution function often begin with the Kirkwood superposition approximation[14] (KSA)

$$g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=g(r_{12})g(r_{23})g(r_{31}) ,$$

although the convolution approximation, given most simply in momentum space as an approximation for the third-order structure function

$$S_3(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)=S(k_{12})S(k_{23})S(k_{31})$$

where $S(k)$ is the liquid structure function, is useful when dealing with long-wavelength properties.[15] While each of these has been found to share some qualitative features of the simulations of the same quantities, the corrections are significant for many purposes.[9-13,16]

A systematic procedure for improving the KSA was given by Abe in the form of an exponentiated linked cluster expansion for the correction factor to the KSA in terms of Mayer cluster integrals.[17] Stell resummed this expansion in terms of diagrams which are functions only of the dressed bond $h=g-1$.[18] Rice, Lekner, and Young demonstrated that the first few Abe corrections produce significant improvement in the evaluation of the higher-order virial coefficients.[19] Lee and Lee examined the effect of the first few terms of the Stell expansion upon the sequential relation, whereby the dimensionless integral over one coordinate in g_3 is given by $(N-2)g$ for an N-particle system.[20]

More recently, Haymet, Rice, and Madden have developed a self-consistent approach to the determination of g and g_3 by making use of truncations of the Stell expansion to provide closure of the Born-Green-Yvon (BGY) equation relating $g(r)$ to g_3:

$$k_B T \nabla_1 g(r_{12}) = -g(r_{12})\nabla_1 V(r_{12})$$
$$-\rho \int d^3 r_3 g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\nabla_1 V(r_{13}) ,$$

where v is the two-body potential.[21] This produces significant improvements over the use of the KSA closure of the BGY equation.

In this paper we take a somewhat different approach to the theory of the triplet correlation function which is a straightforward extension of our earlier theory of the pair-pair correlation function.[1-4] In that work the fact that the pair-pair correlation function is given by the functional derivative of the radial distribution function with respect to the pair potential[4] was used in conjunction with the hypernetted-chain (HNC) resummation of $g(r)$

to produce an exact linear integral equation for the pair-pair correlation function in terms of g. Elementary diagrams in the HNC equation were omitted to simplify the integral equation. This result was employed in a calculation of depolarized light scattering from argon[1] and helium,[2,7] and to produce the equation of state for liquid ^{4}He.[22] In the present work we review this theory and display the results for the pair-pair correlation function as calculated for argon. Perhaps more importantly, we make use of the multicomponent version of the equations to extract a similar linear integral equation for the triplet correlation function for the single component system. Numerical results for various Legendre components of this function are displayed and compared to the KSA. It is also shown that using the HNC *approximation* for this equation as the closure in the BGY equation produces self-consistency with the HNC approximation for $g(r)$.

Section II contains definitions of the functions of immediate interest and an analysis of this general structure and physical applications. In particular, we make use of expansions in Legendre projections to reduce the variables in the system to a manageable number. In Sec. III we review our derivation of the linear integral equation for the pair-pair correlation function, which explicitly has the familiar property that it is a functional only of the radial distribution function in the case when only two-body forces are present.

The results of Sec. III are used in Sec. IV and in Appendix C to produce a related integral equation for the triplet correlation function. It is shown there that the most compact expression of this equation has as its inhomogeneous term the Kirkwood superposition approximation. We also demonstrate the self-consistency of our HNC approximation for the triplet function with the HNC approximation for $g(r)$.

Section V has a similar analysis for the Fourier transforms of the correlation functions, which are most conveniently reexpressed as the structure functions of the system. As in coordinate space, the inhomogeneous term in the linear equation for the third-order structure function is shown to be the simplest approximation for this function, namely, the convolution approximation.

Numerical results for the example of argon are presented in Sec. VI both at its triplet point and at the triple-point density at room temperature. At this high density we find significantly different results from the simpler approximations referred to above. We also show that there are signs of close-packed solidlike correlations appearing in the $l=6$ Legendre component of the triplet correlation function.

In Appendix A we describe Monte Carlo and molecular-dynamics procedures which are relatively straightforward methods for simulating the triplet and pair-pair correlation functions. The molecular-dynamics method has the added advantage that it can be used to simulate the time dependence of the pair-pair correlation function in classical fluids.

II. CORRELATION FUNCTIONS

In this section not only the usual distribution functions are defined, but the new functions—the triplet and pair-

pair correlation functions—are also defined and discussed. For a system of N particles in a volume Ω, the s-body distribution function is defined by

$$n_s(\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_s') = [N!/(N-s)!]$$
$$\times \langle \delta(\mathbf{r}_1 - \mathbf{r}_1') \delta(\mathbf{r}_2 - \mathbf{r}_2') \cdots \delta(\mathbf{r}_s - \mathbf{r}_s') \rangle ,$$
$$(2.1)$$

where the angle brackets denote the usual thermal average. For a uniform system, $n_1(\mathbf{r}) = N/\Omega = \rho$ and $n_2(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(\mathbf{r}_1 - \mathbf{r}_2)$ where g is the radial distribution function. In this definition of g we are implicitly making use of the translational invariance of the fluid, which also requires that the thermodynamic limit be taken, $N \to \infty$, $\Omega \to \infty$, while ρ is held constant. Care must be exercised in taking this limit when the quantities of interest include explicit cancellation of the leading order in N, as is the case, for example, with the pair-pair correlation function defined below. The dimensionless functions g_s are conveniently defined as

$$g_s(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_s) = \rho^{-s} n_s(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_s) . \quad (2.2)$$

A convenient notation exists when the average of an n-body operator is needed. For example, if A_1 and A_2 are one- and two-body operators defined by

$$A_1 = \sum_i a_1(\mathbf{r}_i) \quad (2.3)$$

and

$$A_2 = \sum_{\substack{i,j \\ i<j}} a_2(\mathbf{r}_i - \mathbf{r}_j) , \quad (2.4)$$

then the thermal averages are given by

$$\langle A_1 \rangle = \sum_i \langle a_1(\mathbf{r}_i) \rangle = \rho \int d\mathbf{r}\, a_1(\mathbf{r}) g_1(\mathbf{r}) , \quad (2.5)$$

$$\langle A_2 \rangle = \tfrac{1}{2} \rho^2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 a_2(\mathbf{r}_1 - \mathbf{r}_2) g_2(\mathbf{r}_1, \mathbf{r}_2) . \quad (2.6)$$

For a uniform system the radial distribution function g is then given by

$$g(\mathbf{r}_1' - \mathbf{r}_2') = g_2(\mathbf{r}_1', \mathbf{r}_2')$$
$$= (N\rho)^{-1} \sum_{\substack{i,j \\ i \neq j}} \langle \delta(\mathbf{r}_i - \mathbf{r}_j - \mathbf{r}_1' + \mathbf{r}_2') \rangle . \quad (2.7)$$

The average of A_2 can now be written in terms of g, simply as

$$\langle A_2 \rangle = (N\rho/2) \int d\mathbf{r}\, a_2(\mathbf{r}) g(\mathbf{r}) . \quad (2.8)$$

While these are the most commonly used functions, we now wish to define a new set of functions. These new functions show how the positions of particles are correlated. A useful description of g_2 is the pair distribution function. If the members of the pair are uncorrelated, then g_2 would reduce to a product of g_1's. Thus the pair correlation function $P_{1,1}$ is defined as

$$P_{1,1}(\mathbf{r}, \mathbf{r}') = \rho^{-2} \sum_{i,j} [\langle \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \rangle$$
$$- \langle \delta(\mathbf{r} - \mathbf{r}_i) \rangle \langle \delta(\mathbf{r}' - \mathbf{r}_j) \rangle] , \quad (2.9)$$

or equivalently as

$$P_{1,1}(\mathbf{r},\mathbf{r}')=g_2(\mathbf{r},\mathbf{r}')-g_1(\mathbf{r})g_1(\mathbf{r}')$$
$$+(N\rho)^{-1}\delta(\mathbf{r}-\mathbf{r}')g_1(\mathbf{r}) . \qquad (2.10)$$

If the pair is uncorrelated, only the last term survives, which corresponds to the term where the indices i and j refer to the same particle.

The pair correlation function will also give the explicit correlation between two one-body operators. Recalling the definition of A_1 in Eq. (2.3),

$$\langle A_1B_1\rangle-\langle A_1\rangle\langle B_1\rangle$$

$$=\rho^2\int d\mathbf{r}\int d\mathbf{r}'a_1(\mathbf{r})b_1(\mathbf{r}')P_{1,1}(\mathbf{r},\mathbf{r}') , \qquad (2.11)$$

with B_1 being simply some other one-body operator.

In a similar manner the correlation between two pairs can be defined.[1] The pair-pair correlation function $P_{2,2}$ is defined by

$$P_{2,2}(\mathbf{r},\mathbf{r}')=(N\rho)^{-2}\sum_{\substack{i,j \\ i\neq j}}\sum_{\substack{k,l \\ k\neq l}}[\langle\delta(\mathbf{r}-\mathbf{r}_{ij})\delta(\mathbf{r}'-\mathbf{r}_{kl})\rangle-\langle\delta(\mathbf{r}-\mathbf{r}_{ij})\rangle\langle\delta(\mathbf{r}'-\mathbf{r}_{kl})\rangle] , \qquad (2.12)$$

with $\mathbf{r}_{\alpha\beta}=\mathbf{r}_\alpha-\mathbf{r}_\beta$. If no correlations exist, $P_{2,2}$ becomes a Dirac δ function, coming from the terms when i,j and k,l designate the same pair. Notice that $P_{2,2}$ contains two-, three-, and four-body distribution functions and can be written in terms of g_s's by

$$P_{2,2}(\mathbf{r},\mathbf{r}')=N^{-1}\rho\int d\mathbf{R}[g_4(\mathbf{R},\mathbf{R}+\mathbf{r},\mathbf{r}',0)-g(\mathbf{r})g(\mathbf{r}')]$$

$$+N^{-1}[g_3(\mathbf{r},\mathbf{r}',0)+g_3(-\mathbf{r},\mathbf{r}',0)+g_3(\mathbf{r},-\mathbf{r}',0)+g_3(-\mathbf{r},-\mathbf{r}',0)]+(N\rho)^{-1}[\delta(\mathbf{r}-\mathbf{r}')+\delta(\mathbf{r}+\mathbf{r}')]g(\mathbf{r}) . \qquad (2.13)$$

The correlation between two pair operators A_2 and B_2 is then given by

$$\langle A_2B_2\rangle-\langle A_2\rangle\langle B_2\rangle$$
$$=(N\rho/2)^2\int d\mathbf{r}\int d\mathbf{r}'a_2(\mathbf{r})b_2(\mathbf{r}')P_{2,2}(\mathbf{r},\mathbf{r}') . \qquad (2.14)$$

Since $P_{2,2}$ is not of order unity but in fact is $O(N^{-1})$, the new pair-pair correlation function P_p is conveniently defined as

$$P_p(\mathbf{r},\mathbf{r}')=NP_{2,2}(r,r') . \qquad (2.15)$$

It is also convenient to define a function Q_p which vanishes when the correlations vanish, i.e.,

$$Q_p(\mathbf{r},\mathbf{r}')=P_p(\mathbf{r},\mathbf{r}')-\rho^{-1}[\delta(\mathbf{r}-\mathbf{r}')+\delta(\mathbf{r}+\mathbf{r}')]g(\mathbf{r}) . \qquad (2.16)$$

A contribution to P_p comes from the three-body distribution function due to terms in Eq. (2.12) where the pairs share a particle. Keeping this in mind, the triplet correlation function T is defined by

$$T(\mathbf{r},\mathbf{r}')=(N\rho^2)^{-1}\sum_{i,j,k}{}'[\langle\delta(\mathbf{r}-\mathbf{r}_{ij})\delta(\mathbf{r}'-\mathbf{r}_{kj})\rangle$$

$$-\langle\delta(\mathbf{r}-\mathbf{r}_{ij})\rangle\langle\delta(\mathbf{r}'-\mathbf{r}_{kj})\rangle] , \qquad (2.17)$$

where the prime on the sum means that i, j, and k are never equal. In terms of the g_n's, T is given by

$$T(\mathbf{r},\mathbf{r}')=g_3(\mathbf{r},\mathbf{r}',0)$$

$$-[(N-2)/(N-1)]g_2(\mathbf{r},0)g_2(\mathbf{r}',0) . \qquad (2.18)$$

For a uniform system, T has all the information contained in g_3. The function P_p, however, does *not* possess all the information contained in g_4; note that Eq. (2.13) for P_p contains an integral over g_4. As a further conveni-

ence, the fourth-order correlations Q_4 can be separated out of P_p and are defined as

$$Q_4(\mathbf{r},\mathbf{r}')=(N\rho^2)^{-1}\sum_{i,j,k,l}{}'[\langle\delta(\mathbf{r}-\mathbf{r}_{ij})\delta(\mathbf{r}'-\mathbf{r}_{kl})\rangle$$

$$-\langle\delta(\mathbf{r}-\mathbf{r}_{ij})\rangle\langle\delta(\mathbf{r}'-\mathbf{r}_{kl})\rangle] ,$$

$$(2.19)$$

where the prime on the sum denotes that i, j, k, and l are all different.

The KSA for g_3 is given by

$$g_3^{\text{KSA}}(\mathbf{r},\mathbf{r}',0)\cong g_2(\mathbf{r},0)g_2(\mathbf{r}',0)g_2(\mathbf{r},\mathbf{r}') , \qquad (2.20)$$

which leads to a similar approximation for T [ignoring terms of $O(N^{-1})$] and can be written in terms of g as

$$T^{\text{KSA}}(\mathbf{r},\mathbf{r}')=g(\mathbf{r})g(\mathbf{r}')[g(\mathbf{r}-\mathbf{r}')-1] . \qquad (2.21)$$

This last expression has been written explicitly for two reasons. The first is to see the reason for the unusual subtraction in the definition of T. If r is fixed and r' becomes large, T will vanish. The second reason will become self-evident in Sec. IV where the integral equation for T is discussed. The KSA term will then be seen to be the inhomogeneous term of the HNC integral equation for T.

In a uniform fluid, $Q_p(\mathbf{r},\mathbf{r}')$ and $T(\mathbf{r},\mathbf{r}')$ will depend only on $|\mathbf{r}|$, $|\mathbf{r}'|$, and $\cos\theta=\mathbf{r}\cdot\mathbf{r}'/rr'$. These functions can then be expansed in terms of Legendre polynomials, $\mathscr{P}_l(\cos\theta)$. Any such function can be written as

$$F(\mathbf{r},\mathbf{r}')=(4\pi)^{-1}\sum_l(2l+1)\hat{F}^l(r,r')\mathscr{P}_l(\cos\theta) . \qquad (2.22)$$

For all such expansions, $\hat{F}^l$ depends only on scalar variables. Thus it will be possible to make contour plots of $\hat{F}^l$

for display purposes. These expansion coefficients will be called Legendre projections in the remainder of this paper.

Since $\hat{Q}_p^l(r,r')$ depends upon only two "scalar" variables, relatively simple numerical procedures can be devised to calculate this quantity via Monte Carlo or molecular-dynamics simulations, the latter being easily extended to finite time differences between the coordinates. A brief discussion of this is given in Appendix A.

III. INTEGRAL EQUATION FOR Q_p

In this section we derive a linear integral equation for Q_p by combining the method of functional differentiation with the HNC series resummation method. First, note that the partition function can be used as a generating function for these correlation functions. Defining $u(r) = -v(r)/2k_B T$ for a classical fluid interacting through a pair potential $v(r)$, the partition function at a temperature T has the form

$$Z = \int d^N \mathbf{r} \exp \left[\sum_{\substack{i,j \\ i \neq j}} u(r_{ij}) \right] . \tag{3.1}$$

(This is also the form of the normalization integral for a Jastrow trial function for a boson liquid ground state, e.g., liquid ^{4}He.) A common procedure is to use the partition function as a generating function for the n-body distribution functions defined in Eq. (2.1).[23] The method is to introduce an external one-body potential into Z and then take functional derivatives with respect to this external potential. Moreover, the functional derivatives of the partition function with respect to the pair potential are also related to distribution functions.[4] The first derivative gives $g(r)$,

$$g(\mathbf{r}) = (N\rho)^{-1} \frac{\delta \ln Z}{\delta u(\mathbf{r})} , \tag{3.2}$$

while the second derivative of $\ln Z$ gives the pair-pair correlation function,

$$P_p(\mathbf{r},\mathbf{r}') = (N\rho^2)^{-1} \frac{\delta^2 \ln Z}{\delta u(\mathbf{r}) \delta u(\mathbf{r}')} . \tag{3.3}$$

Combining these two equations, the pair-pair correlation function can be expressed as a functional derivative of g:

$$P_p(\mathbf{r},\mathbf{r}') = \rho^{-1} \frac{\delta g(\mathbf{r})}{\delta u(\mathbf{r}')} . \tag{3.4}$$

The last result permits immediate use of the integral equation for $g(r)$ as a functional of $u(r)$ (i.e., series resummations) to obtain similar approximations for P_p. One such widely used resummation for $g(r)$ is the HNC equation which can be written as

$$\ln g(\mathbf{r}) = u(\mathbf{r}) + u(-\mathbf{r}) + W(\mathbf{r}) + E(\mathbf{r}) , \tag{3.5}$$

where the nodal function

$$W(\mathbf{r}) = g(\mathbf{r}) - 1 - c(\mathbf{r})$$

$$= N^{-1} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} [S(\mathbf{k}) - 1]^2 / S(\mathbf{k}) , \tag{3.6}$$

using the direct correlation function $c(r)$ and the liquid structure function $S(k)$. $E(r)$ is the bridge function con-

sisting of the sum of bridge diagrams. The original HNC approximation, HNC/0, discards the bridge function. For other calculations a nonzero expression for E is used, but in this paper only $E(r) = 0$ will be considered. The functions $S(k)$ and $c(r)$ are defined by

$$S(\mathbf{k}) = 1 + \rho \int d\mathbf{r} \, e^{i\mathbf{k}\cdot\mathbf{r}} [g(\mathbf{r}) - 1] \tag{3.7}$$

and

$$c(\mathbf{r}) = N^{-1} \sum_{k} e^{-i\mathbf{k}\cdot\mathbf{r}} [1 - S^{-1}(\mathbf{k})] . \tag{3.8}$$

Recognizing the relationship between P_p and g, we proceed by simply taking the functional derivative of Eq. (3.5). The resulting integral equation for P_p can be written as

$$\rho P_p(\mathbf{r},\mathbf{r}') / g(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}') + \delta(\mathbf{r} + \mathbf{r}')$$

$$+ \rho^2 \int d\mathbf{R} \, M(\mathbf{r},\mathbf{R}) P_p(\mathbf{R},\mathbf{r}') , \tag{3.9}$$

where the kernal M is given by

$$M(\mathbf{r},\mathbf{R}) = \frac{\delta W(r)}{\delta g(R)} + \frac{\delta E(\mathbf{r})}{\delta g(R)} . \tag{3.10}$$

Notice that when the δ functions are incorporated into P_p in Eq. (3.9) the result is the integral equation for Q_p which explicitly written is

$$Q_p(\mathbf{r},\mathbf{r}') = g(\mathbf{r}) g(\mathbf{r}') [M(\mathbf{r},\mathbf{r}') + M(\mathbf{r}, -\mathbf{r}')]$$

$$+ g(\mathbf{r}) \rho \int d\mathbf{R} \, M(\mathbf{r},\mathbf{R}) Q_p(\mathbf{R},\mathbf{r}') . \tag{3.11}$$

This equation is linear in Q_p. Moreover, Q_p depends explicitly only on g and ρ; the pair potential has disappeared from the equation. In the use of this equation the method of generating g is irrelevant; it need not be an HNC approximation but might be molecular dynamics or some experiment.

In an isotropic fluid the functions Q_p and M depend only on r, r', and $\cos\theta$, and thus can be expanded in Legendre polynomials as in Eq. (2.22). Since Eq. (3.11) is a linear integral equation, the expansion in Legendre polynomials separates this equation into a set of decoupled equations (for even l):

$$\hat{Q}_p^l(r,r') = 2g(r) g(r') \hat{M}^l(r,r')$$

$$+ g(r) \rho \int_0^\infty dR \, R^2 \hat{M}^l(r,R) \hat{Q}_p^l(R,r') . \tag{3.12}$$

The inhomogeneous term in the odd-L equations vanishes. In this case since $g(\mathbf{r}) = g(-\mathbf{r})$, $\hat{Q}_p^l = 0$ is a solution to the odd-l equations which is equivalent to

$$Q_p(\mathbf{r},\mathbf{r}') = Q_p(-\mathbf{r},\mathbf{r}') = Q_p(\mathbf{r}, -\mathbf{r}') = Q_p(-\mathbf{r}, -\mathbf{r}') . \tag{3.13}$$

This follows from the definition of P_p and the assumption that the fluid is isotropic. We have not investigated the existence of nontrivial solutions to the odd-l equations which would be symmetry breaking in nature.

The HNC/0 approximation (also known as the HNC approximation) for $g(r)$ is obtained by setting the bridge function to zero,

$$\text{HNC/0:} \quad E(\mathbf{r}) = 0 . \tag{3.14}$$

To obtain the HNC/0 approximation for Q_p, we use this approximation for E before the functional differentiation in Eq. (3.10). Then M takes the simple form $M(\mathbf{r},\mathbf{r}') \cong M_0(\mathbf{r}-\mathbf{r}')$ which is given by

$$M_0(\mathbf{x}) = 2c(\mathbf{x}) - \rho \int d\mathbf{y}\, c(\mathbf{y})c(\mathbf{y}-\mathbf{x}) \ . \tag{3.15}$$

In momentum space one obtains the simpler expression

$$M_0(k) = 1 - S^{-2}(k) \ . \tag{3.16}$$

The results of this integral equation using the HNC/0 approximation were implicitly used in the "paired phonon" analysis of ^{4}He (Ref. 22) and explicitly in the calculation of depolarized light scattering from ^{4}He (Ref. 2) and from room-temperature argon.[1,5] In Sec. VI there is further discussion of the resulting functions from these equations. The method of solving the integral equation is given in Appendix B.

IV. TRIPLET AND QUARTIC CORRELATION FUNCTIONS

The integral equation of Sec. III made possible calculations of the pair-pair correlation function which include both the triplet, T, and quartic, Q_4, correlation functions. In this section an integral equation for T is discussed. (The details of the derivation are in Appendix C.) In particular, consider a two-component system, N_a and N_α, in a volume Ω. These particles interact via pair potentials v_{aa}, $v_{a\alpha}$, and $v_{\alpha\alpha}$. An integral equation for T appears in the limit when the v's become equal. The result of Appendix C shows how, within the HNC/0 approximation, an integral equation for T is derived, and it is simply written as

$$T(\mathbf{r},\mathbf{r}') = g(\mathbf{r})g(\mathbf{r}')c(\mathbf{r}-\mathbf{r}')$$
$$+ g(\mathbf{r})\rho \int d\mathbf{R}\, c(\mathbf{r}-\mathbf{R})T(\mathbf{R},\mathbf{r}') \ . \tag{4.1}$$

Thus, using only the results of the HNC/0 equations for a two-component system and functional derivatives, a simple, linear integral equation for T can be found. As the rest of this section shows, it has several interesting features.

The first fact is that this equation can be made even more revealing by a transformation. Consider the function $P_{1,1}$ defined in Eq. (2.10) which can be rewritten for an isotropic system as

$$P_{1,1}(\mathbf{r},\mathbf{r}') = N^2[g(\mathbf{r}-\mathbf{r}') - 1 + \delta(\mathbf{r}-\mathbf{r}')/\rho] \ . \tag{4.2}$$

Defining $F(\mathbf{r},\mathbf{r}') = N^{-2}P_{1,1}(\mathbf{r},\mathbf{r}')$ the inverse of F is defined by

$$\rho \int d\mathbf{R}\, F(\mathbf{r},\mathbf{R})F^{-1}(\mathbf{R},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')/\rho \tag{4.3}$$

and is given by

$$F^{-1}(\mathbf{R},\mathbf{r}') = -c(\mathbf{r}-\mathbf{r}') + \delta(\mathbf{r}-\mathbf{r}')/\rho \ . \tag{4.4}$$

The integral equation for T [Eq. (4.1)] can then be made to be

$$\frac{\rho[g(r)-1]T(\mathbf{r},\mathbf{r}')}{g(r)g(r')} + \delta(\mathbf{r}-\mathbf{r}')$$
$$= F^{-1}(\mathbf{r},\mathbf{r}') + \rho \int d\mathbf{R}\, F^{-1}(\mathbf{r},\mathbf{R})T(\mathbf{R},\mathbf{r}') \ . \tag{4.5}$$

Multiplying by $F(\mathbf{s},\mathbf{r})$ and integrating over r, the new equation becomes

$$\frac{\rho \int d\mathbf{r}[g(r)-1]F(\mathbf{s},\mathbf{r})T(\mathbf{r},\mathbf{r}')}{g(r)g(r')} + F(\mathbf{s},\mathbf{r})$$
$$= \frac{\delta(\mathbf{s}-\mathbf{r})}{\rho} + \frac{T(\mathbf{s},\mathbf{r}')}{g(r')} \ , \tag{4.6}$$

which leads to the remarkable result

$$\frac{T(\mathbf{s},\mathbf{r}')}{g(s)g(r')} = g(\mathbf{s}-\mathbf{r}') - 1$$
$$+ \rho \int d\mathbf{r}[g(\mathbf{s}-\mathbf{r})-1][g(\mathbf{r})-1]$$
$$\times \frac{T(\mathbf{r},\mathbf{r}')}{g(r)g(r')} \ . \tag{4.7}$$

Notice that the inhomogeneous term is the KSA for T. [See Sec. II, Eq. (2.21).] Notice also that T is given explicitly by knowledge of g and ρ and independent of the potential. This approximation is also linear; each Legendre projection can be obtained independently.

Another property of this approximation for T is its self-consistency. The BGY hierarchy connects g_2 and g_3 through an exact integral equation. Our approximation, when used for g_3 in the BGY equation, leads to the HNC/0 equation for g_2. To see this we write the second equation in the BGY hierarchy in terms of T:

$$\nabla g(\mathbf{r}) = -g(\mathbf{r})\nabla v(\mathbf{r})/k_B T$$
$$+ \rho \int d\mathbf{r}'\nabla[v(\mathbf{r}')/k_B T]T(\mathbf{r},\mathbf{r}') \ . \tag{4.8}$$

Note that only the three-body part of T contributes to the integral. Using the expressions in Eq. (4.1) and making use of Eq. (4.7) the result is

$$\nabla g(\mathbf{r}) = g(\mathbf{r})\nabla[g(\mathbf{r}) - 1 - c(\mathbf{r}) - v(\mathbf{r})/k_B T] \ , \tag{4.9}$$

which is the gradient of the HNC/0 approximation. This further justifies the identification of Eq. (4.7) [or its equivalent, Eq. (4.1)] as the HNC/0 approximation for the three-body distribution function.

This self-consistency has further significance in the Jastrow theory of boson quantum fluids since it is this self-consistent approximation for $T(\mathbf{r},\mathbf{r}')$ and $g(r)$ which establishes the formal identity of the Jackson-Feenberg[8] and Clark-Westhaus[8] expressions for the kinetic energy. This exact identity is violated when the usual procedure of calculating the Clark-Westhaus kinetic energy is used, i.e., when the KSA is employed together with the HNC/0 approximations for $g(r)$.[23]

V. MOMENTUM SPACE FORMULATION

The Fourier transforms of the correlation functions are useful in describing the elementary excitations of a fluid. These functions are more directly determined by experiment since experimental conditions usually include conservation of momentum. The liquid structure function is measured in x-ray and neutron scattering experiments, is related to the pair distribution, and can be written in terms of the density fluctuation operator ρ_q which is defined as

$$\rho_q = \sum_j e^{-i\mathbf{q}\cdot\mathbf{r}_j} \ . \tag{5.1}$$

The liquid structure function $S(q)$ is then expressed as

$$S(\mathbf{q}) = N^{-1}\langle \rho_q \rho_{-q} \rangle \ . \tag{5.2}$$

The higher-order structure functions can now be calculated using the momentum space integral equations equivalent to those presented in Sec. IV. First, the fourth-order function will be considered. The derivation is similar to the above work; only the equations will be included for completeness.

In a uniform fluid a product of four ρ_q's which depends only on two momenta and whose expectation value does not vanish is $\langle \rho_k \rho_{-k} \rho_l \rho_{-l} \rangle$. This is simply the Fourier transform of the pair-pair correlation function. It can be broken into a connected piece $S_4(\mathbf{k},l)$ and disconnected pieces. The convention is to define S_4 to be of $O(1)$, and therefore it is defined

$$NS_4(\mathbf{k},l) = \langle \rho_k \rho_{-k} \rho_l \rho_{-l} \rangle - N^{-1}\langle \rho_k \rho_{-k} \rangle \langle \rho_l \rho_{-l} \rangle$$
$$- (\delta_{k,l} + \delta_{k,-l})\langle \rho_k \rho_{-k} \rangle^2 \ . \tag{5.3}$$

The HNC/0 approximation for S_4 is given by a linear integral equation.[2] The equation expresses S_4 completely in terms of S and ρ and is

$$\frac{S_4(\mathbf{k},l)}{S(\mathbf{k})^2} = S(k+l) - 1 + S(k-l) - 1$$
$$+ (2\pi)^{-3}\rho^{-1}$$
$$\times \int d\mathbf{h}[S(k-h) - 1][S(h)^2 - 1]\frac{S_4(\mathbf{h},l)}{S(\mathbf{h})^2} \ . \tag{5.4}$$

This linear equation can be broken up into decoupled equations for each Legendre projection as has been discussed previously.

The derivation of the equation for the third-order structure function evolves from the equation for T, Eq. (4.1). To facilitate the algebra, a third-order modified Ursell function is defined as

$$F_3(\mathbf{x},\mathbf{y}) = \delta(\mathbf{x}-\mathbf{y})g(\mathbf{x})/\rho + T(\mathbf{x},\mathbf{y}) \tag{5.5}$$

and is equivalent to eliminating the prime on the sum in the definition of T [see Eq. (2.1)]. The equation for F_3 can be seen to be simply

$$F_3(\mathbf{x},\mathbf{y}) = \delta(\mathbf{x}-\mathbf{y})g(x)/\rho$$
$$+ g(\mathbf{x})\rho \int d\mathbf{R}\, c(\mathbf{x}-\mathbf{R})F_3(\mathbf{R},\mathbf{y}) \ . \tag{5.6}$$

The significance of F_3 is that its Fourier transfer is easily related to S_3 by

$$S_3(\mathbf{k},l) = \rho^2 \int d\mathbf{x} \int d\mathbf{y}\, e^{i\mathbf{k}\cdot\mathbf{x}}e^{il\cdot\mathbf{y}}F_3(\mathbf{x},\mathbf{y}) - \delta_{\mathbf{k},l}S(k) \ , \tag{5.7}$$

where the definition of S_3 can be viewed as the connected piece of the product of three ρ_q's and is explicitly given by

$$NS_3(\mathbf{k},l) = \langle \rho_k \rho_{-l} \rho_{l-k} \rangle - N^{-1}\langle \rho_k \rho_{-k} \rangle \langle \rho_l \rho_{-l} \rangle$$
$$- \delta_{k,l}\langle \rho_k \rho_{-k} \rangle \ . \tag{5.8}$$

The integral equation for S_3 is linear and expresses S_3 in terms of only $S(k)$ and ρ. The HNC/0 approximation for S_3 can be found by taking the Fourier transform of Eq. (5.6) and is

$$\frac{S_3(\mathbf{k},l)}{S(\mathbf{k})S(l)} = S(\mathbf{k}-l) - 1$$
$$+ N^{-1}\sum_q [S(\mathbf{k}-\mathbf{q}) - 1][S(\mathbf{q}) - 1]\frac{S_3(\mathbf{q},l)}{S(\mathbf{q})S(l)} \ . \tag{5.9}$$

Notice that the inhomogeneous term is the convolution approximation for S_3.

VI. NUMERICAL RESULTS

As examples of the possible numerical calculations that can be achieved from this formalism, we have looked at a system which only has a two-body, Lennard-Jones potential. The potential parameters were taken to be $\sigma = 3.41$ Å and $\epsilon = 122$ K, corresponding to argon. The reduced density was $\rho^* = \rho\sigma^3 = 0.80$; two different temperatures were examined—$T_1^* = k_B T_1/\epsilon = 0.73$ (the triplet point) and $T_2^* = 2.44$ (room temperature). The 6-12 Lennard-Jones potential can be written as

$$U(r) = -v(r)/k_B T = -4[(r^*)^{-12} - (r^*)^{-6}]/T^*$$

with $r^* = r/\sigma$. The new equations for the higher correlations depend only on $g(r)$ and $S(q)$ and therefore these could have been obtained from experiment or computer simulation. The approximation for the three-body correlation function may be more accurate if the input function $g(r)$ were exact. In this paper we have chosen the HNC/0 approximation because we could do the calculations quickly. This is in keeping with the spirit of this section to show examples of these functions and the information they contain. Comparison with previous calculations is difficult because to our knowledge no one has previously displayed results in terms of Legendre projections. Typically the triplet correlation function has been calculated for particles whose positions determine equilateral or isosceles triangles. The regeneration of these functions from our results would take a prohibitively large number of terms in their Legendre expansions. In the future we hope that these projections will be calculated exactly and have presented an appendix showing how this can be accomplished (Appendix A).

In Fig. 1 we display the input functions $g(r)$ and $S(q)$ used in our calculation, which are solutions to the HNC/0 approximation [Eqs. (3.5) and (3.14)]. At the higher temperature, $g(r)$ shows that more of the core region is accessible to a neighboring particle, i.e., the nearest-neighbor (nn) peak, including the sharp rise, is shifted to smaller distances. At the lower temperature, the nn peak is 50% larger. Similar differences exist in $S(q)$. At the lower temperature, the first peak in $S(q)$ is 30% larger and shifter to a slightly smaller momentum when compared to the higher-temperature result.

In the next two figures (Figs. 2 and 3), Legendre projections $l=0$ and 6 of the triplet correlation function are
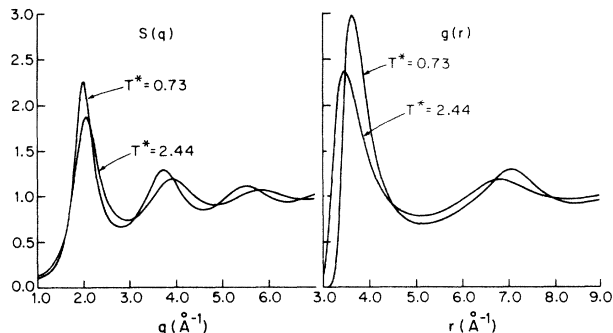
FIG. 1. Liquid structure function $[S(q)]$ and radial distribution function $[g(r)]$ at the triple-point density $\rho^*=0.80$ at two temperatures: triplet point ($T^*=0.73$) and room temperature ($T^*=2.44$).

given. It should be recalled the Legendre projections of $T(r,s)$ are defined by

$$\hat{T}^{l}(r,s)=2\pi \int_{-1}^{1} d(\cos\theta)[g_3(r,s,|r-s|)$$

$$-g(r)g(s)]\mathscr{P}_{l}(\cos\theta)$$

and that since these projections only depend on the scalar variables $r=|r|$ and $s=|s|$ they can be presented as contour plots. Furthermore, this function, as well as all the projections, are symmetric in r and s, i.e., $\hat{T}^{l}(r,s)=\hat{T}^{l}(s,r)$; therefore, only one-half of the contour plots are shown. The contour plots in this paper use the following convention: The upper half contains results at the higher temperature, and below the diagonal the lower-temperature regions are plotted.

Consider the $l=0$ projection of T which is displayed is Fig. 2. The major feature is the large negative peak when r and s correspond to the nearest neighbor, R_{nn}, peak in
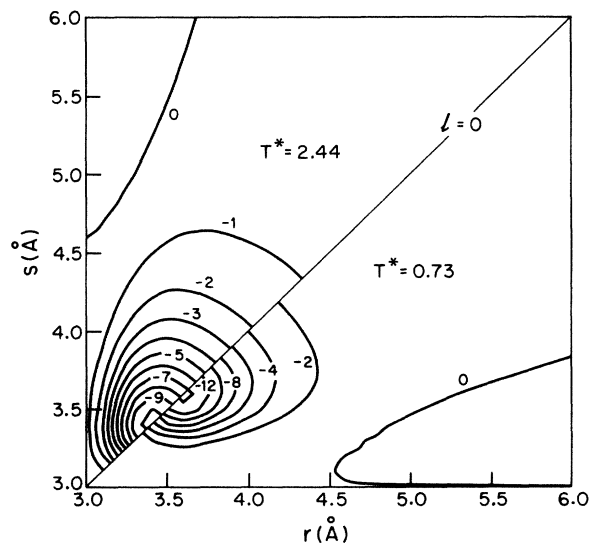

FIG. 2. Contours of the HNC approximation for the $l=0$ Legendre triplet correlation function, $T^{(0)}(r,s)$, at the temperatures and densities of Fig. 1.
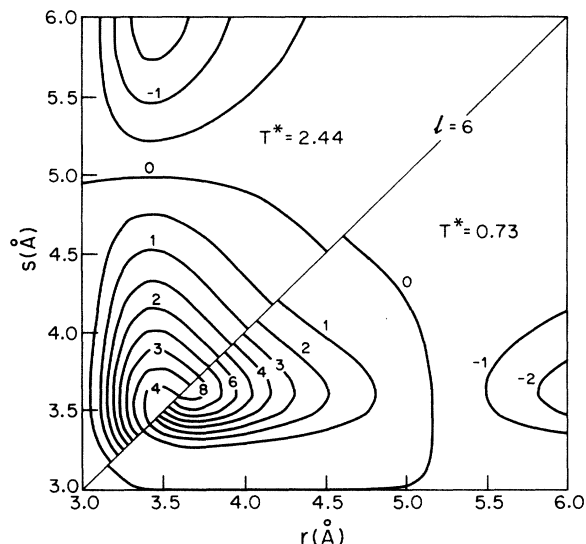

FIG. 3. Contours of the HNC approximation for the $l=6$ Legendre triplet correlation function, $\hat{T}^{(6)}(r,s)$, at the temperatures and densities of Fig. 1.

$g(r)$. This is an excluded volume effect. There exists a hole in $g_3(r,r,r\sqrt{2(1-\cos\theta)})-g(r)g(r)$, near $\theta=0$, due to the core, which gives a large negative contribution to the $l=0$ projection. This hole is also described by the KSA, because for small θ, $g_3(r,r,r\sqrt{2(1-\cos\theta)})$ $\approx G(r)^2 g(r\theta)$. The difference between the HNC approximation for T and the KSA for $l=0$ is given in Fig. 4. At the large negative peak, the percent difference at low temperature is 32% and at high temperature is 29%.

The other interesting feature in the $l=0$ projection of T is the enhancement over the KSA at $r=R_{nn}$, $s=R_{MIN}$ where R_{MIN} is the position of the first valley of $g(r)$ beyond the nearest-neighbor peak R_{nn}. In Fig. 3 these positive peaks are in the vicinity of $r=3.4-3.6$ Å and $s=3.0-5.5$ Å. At both temperatures, this corresponds to a ratio of $s/r\approx 1.5$ (which is larger than $\sqrt{2}$). However, this enhancement does not show up as a peak in $\hat{T}^{l=0}$ (see Fig. 2). In the $l=8$ projection (not shown), for both the KSA and the HNC approximation for T, a positive peak exists when $r\approx 3.7$ Å (3.6 Å) and $s\approx 5.3$ Å (4.9 Å) for low (high) temperature. At low temperature this ratio $s/r\approx 1.43$, while at high temperature the peak is much less defined and this ratio is 1.36. The $l=8$ projection emphasizes integer multiples of 45°. For a simple cubic crystal structure of the same density, the nearest-neighbor distance would be 3.6 Å and the second-nearest-neighbor distance would be 5.1 Å. The angle between the ray drawn from an atom to its nearest neighbor and the ray to its second nearest neighbor is 45°. The structure in the $l=8$ projection at the lower temperature is sensitive to the tendency to form the simple cubic structure.

The $l=6$ projection (Fig. 3) shows the tendency for the atoms to be close packed, i.e., triangular coordination. In particular, the major feature in these projections is a large positive peak, when $r=s=R_{nn}$. This is also true for the KSA, but the peak for the HNC approximation for T is enhanced by 9% at high temperature and by 13% at low
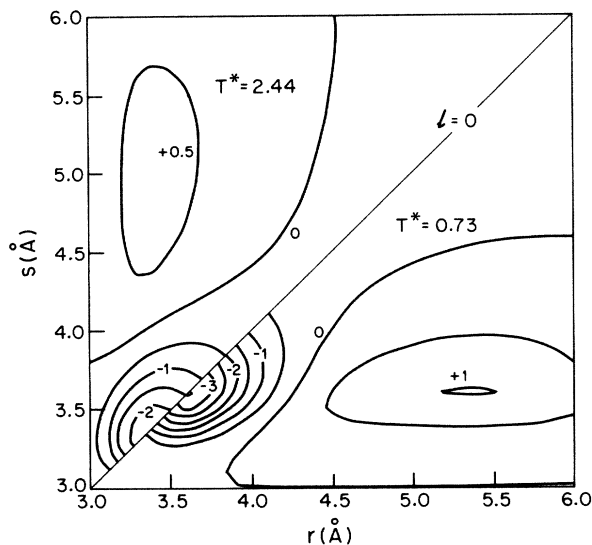
FIG. 4. Contours of the difference between the HNC approximation and the KSA for the $l=0$ Legendre component of the triplet correlation function, as in Figs. 2 and 3.

FIG. 5. Contours of the HNC approximation for the $l=0$ fourth-order correlation function, $\hat{Q}_4^{(0)}(r,s)$, as in Fig. 2.

temperatures. This triangular coordination is not found in a simple cubic structure but is in a face-centered-cubic (fcc) crystal. However, the peak in the $l=6$ projection occurs at $r=s=R_{nn}$, a distance which is too small for an fcc, since for an fcc crystal with the same density the first neighbor would be at 4.0 Å. However, a density change to $\rho^*=1.17$ would give the correct spacing to the $l=6$ peak with the $\sqrt{2}$ ratio of the second-neighbor distance and nn distance being preserved. These correlations therefore are suggestive of a closed-packed structure such as an fcc or hcp crystal at a density larger than that of the fluid. These correlations can be considered as a response function exhibiting the tendency to solidify in a particular crystal structure. The overly large density change may come from the breakdown of the HNC/0 equation, which is known to move the nn peak in $g(r)$ to smaller distances than exact calculations. We have performed the calculations for $l \leq 12$ projections of T using Eq. (4.7). Space limitations prohibit more plots, and the physical interpretations of the other projections are not clear.

We now consider the fourth-order correlation function $Q_4(r,s)$. This function describes the correlation between two distinct pairs, one pair separated by $\mathbf{r}$, the other pair separated by $\mathbf{s}$, but only after integrating over the center-of-mass coordinates of each pair. This function can also be expanded in Legendre projections. In Fig. 5 the $l=0$ projection is plotted. The major feature is a large positive peak where the triplet correlation function had a negative peak at $r \approx s \approx R_{nn}$. At low temperature this peak is 1.3 times larger than at the higher temperature. The other even projections of Q_4 are very similar; the peak at $r=s=R_{nn}$ is the dominant structure. The odd projections of Q_4 vanish in an isotropic fluid, unless the symmetry is broken.

The momentum space equations can also be solved. The next two graphs (see Figs. 6 and 7) show projections
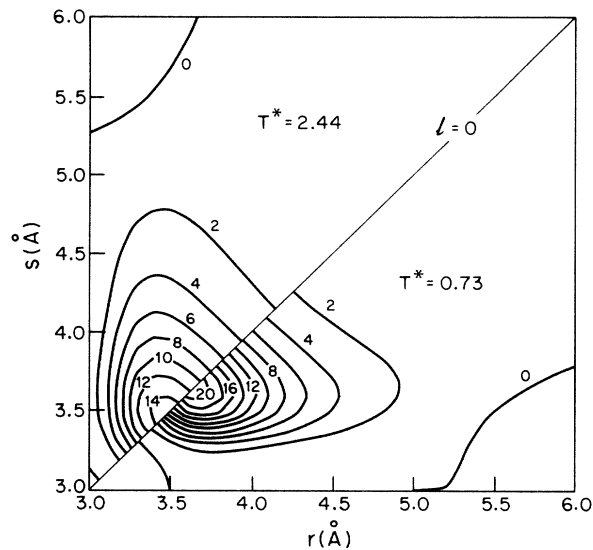
of S_3. The structure function $S_3(\mathbf{k},l)$ is related both to the Fourier transform of T and to $\langle \rho_k \rho_{-l} \rho_{l-k} \rangle$ (see Sec. V). The $l=0$ projection (not shown) has one major feature: a large negative peak at $k \approx l \approx 2$ Å^{-1} for either temperature. As can be seen in Fig. 1, the first peak in $S(q)$ is at nearly the same value of q for either temperature. This fact is reflected in the position of the peaks in S_3 (and S_4). The peak for the $l=0$ projection of S_3 (not shown) at the low temperature is -5.2 (-4.0 at the high temperature). The $l=6$ projections of S_3 are shown in Fig. 6. The positive peak is again located at $k \approx l \approx 2$ Å^{-1}. For both temperatures there is a substantial differ-
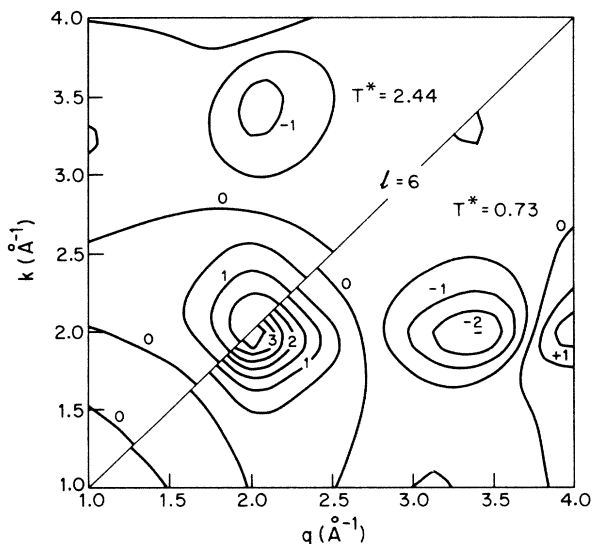

FIG. 6. Contours of the HNC approximation for the $l=6$ Legendre component of $S_3(\mathbf{k},l)$ at the triplet-point density $\rho^*=0.80$ at two temperatures: triplet point ($T^*=0.73$) and room temperature ($T^*=2.44$).
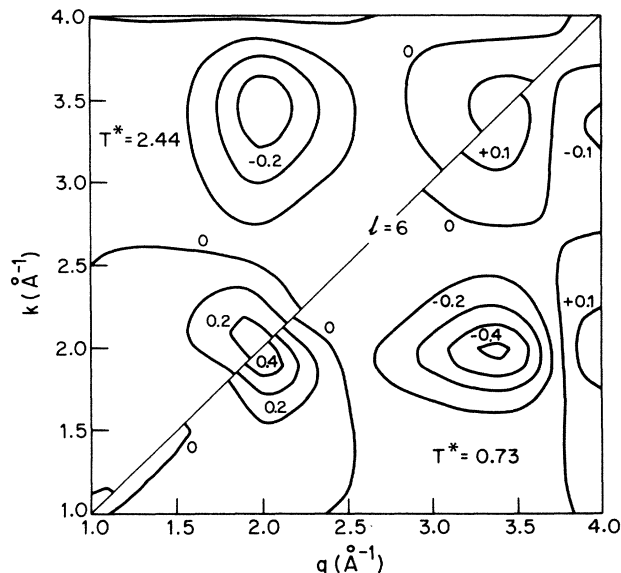
FIG. 7. Contours of the difference between the HNC and convolution approximations for $S_3(\mathbf{k},l)$, as in Fig. 6.

ence between S_3 and the convolution approximation. This is demonstrated in Fig. 7, where the difference for the $l=6$ projection is plotted. The positive peak is shifted and the other structure is missing in the convolution approximation.

In this section we have shown a few examples of the richness of this formalism. We have looked at various projections of the triplet function and their analogs in momentum space. The $l=6$ projection showed particularly interesting features indicating significant preference for close-packed structures.

VII. CONCLUSION

In this paper we have derived an HNC/0 equation for the three-body correlation function and for a particular four-body correlation function. The new approximation for the triplet function is consistent with the BGY equation. In particular, by using this approximation for the three-body correlation function and the BGY equation, we recover the HNC/0 equation for $g(r)$.

We have solved these new equations for the Lennard-Jones system at two temperatures. Major differences exist between this new approximation and the superposition approximation. We have looked at some examples of the information contained in the angular projections of the triplet correlation functions. The accuracy of these approximations is unknown, although the evidence suggests that the overall structure is well described. In the future, we hope that comparisons with molecular-dynamics results will answer this question. The formalism in this paper represents a new step in the theory of fluids, whereby certain three- and four-body correlations can be easily included in many theories at a level of approximation beyond the KSA.

APPENDIX A

In this appendix the Monte Carlo method of evaluating the functions Q_p and P_p is explained. This approach has the advantage of being exact within the statistical errors. The usual Monte Carlo procedure is a biased random walk.[25] The biasing is done by the Boltzmann factor, $\exp(-V/k_BT)$, of the particular configuration where

$$V = \sum_{\substack{i,j \\ i<j}} v(r_{ij}) \tag{A1}$$

is the total potential energy. Then the partition function for N particles in a volume Ω is

$$Z = \int \left[\prod_i d\mathbf{r}_i \right] \exp(-V/k_BT) . \tag{A2}$$

The expectation value of F_s, an s-body operator (depending only on position), is

$$\langle F_s \rangle = Z^{-1} \int \left[\prod_i d\mathbf{r}_i \right] \exp(-V/k_BT)$$
$$\times F_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s) . \tag{A3}$$

The Monte Carlo method samples sets of particle positions; one such set is called a configuration. For a calculation using N_c configurations, the expectation of F_s is simply given by

$$\langle F_s \rangle = N_c^{-1} \sum_c F_s(\mathbf{r}_1^c,\mathbf{r}_2^c,\ldots,\mathbf{r}_s^c) , \tag{A4}$$

where r_i^c is the position of the ith particle in the configuration c.

The pair distribution function g is related to an expectation value of a Dirac δ function. Using the Monte Carlo method, g can only be obtained on a finite grid; using equal increments of r^2 will save computer time. For one configuration, a function which counts the number of pairs separated by a distance x is $G_c(x^2)$ which is

$$G_c(x^2) = \sum_{\substack{i,j \\ i<j}} \int_{x^2-\Delta^2/2}^{x^2+\Delta^2/2} d(y^2)\delta(y^2-r_{ij}^2) , \tag{A5}$$

where Δ^2 is the increment of the r^2 grid. The pair distribution function g is then calculated by summing over configurations, i.e., by

$$N^2\Delta^2\pi x g(x)/\Omega = N_c^{-1} \sum_c G_c(x^2) . \tag{A6}$$

The Legendre projections of the pair-pair correlation function can be calculated in a similar manner. First, a function $\hat{G}_c^l$ must be calculated. For a given configuration, G_c is found by adding one to the appropriate bin

corresponding to the interparticle distance. $\hat{G}_c^l(x^2)$ is calculated by adding $Y_{lm}(\theta_{ij},\phi_{ij})$ to a bin designated again only by the interparticle distance. $\hat{G}_c^l(x^2)$ is then given by

$$\hat{G}_c^l(x^2) = \sum_{\substack{i,j \\ i<j}} Y_{lm}(\theta_{ij},\phi_{ij}) \int_{x^2-\Delta^2/2}^{x^2+\Delta^2/2} d(y^2)\delta(y^2-r_{ij}^2) \ . \tag{A7}$$

For an isotropic fluid, the choice of m is arbitrary. Note that $G_c(x^2)=\sqrt{4\pi}\hat{G}_c^{l=0}(x^2)$.

The lth Legendre component of the pair-pair correlation function is then given by

$$N^4\Delta^4 xz\hat{P}_{2,2}^l(x,z)/\Omega^2$$

$$= N_c^{-1} \sum_c \hat{G}_c^l(x^2)\hat{G}_c^l(z^2)$$

$$- N_c^{-2} \left[\sum_c \hat{G}_c^l(x^2) \right] \left[\sum_c \hat{G}_c^l(z^2) \right] \ . \tag{A8}$$

The last term will be zero for $l\neq0$ in a uniform fluid. A δ function contributes the only leading-order term to $P_{2,2}$. The function Q_p does not have this term and is given by

$$\hat{Q}_p^l(x,z) = N\hat{P}_{2,2}^l(x,z) - \delta_{x,z}(4\pi N_c)^{-1} \sum_c G_c(x^2) \ . \tag{A9}$$

This exact method can be used for testing the accuracy of our approximations if a sufficient number of configurations are used. Since Q_p is a fluctuation requiring the cancellation of the leading order in N, it requires many more configurations then, e.g., $g(r)$. The advantage of the HNC approximation introduced in this paper is its relative ease of calculation and its need for a relatively small amount of computer time.

APPENDIX B

The correlation functions Q_p, T, S_3, and S_4 described in this paper can be approximated by linear integral equations of the form

$$F(\mathbf{x},\mathbf{y}) = D(|\mathbf{x}-\mathbf{y}|) + \int d\mathbf{h}\,K(|\mathbf{x}-\mathbf{h}|)F(\mathbf{h},\mathbf{y}) \ . \tag{B1}$$

Expanding F, D, and K in spherical harmonics, which is given for F by

$$F(\mathbf{x},\mathbf{y}) = \sum_{l,m,l',m'} \hat{F}_{l'm'}^{lm}(x,y)Y_{lm}(\theta_x,\phi_x)Y_{l'm'}(\theta_y,\phi_y) \ , \tag{B2}$$

it is clear that since D and K depend on x,y and $\cos\theta=\mathbf{x}\cdot\mathbf{y}/xy$ only, both $l=l'$ and $m=m'$ contribute. Furthermore, $\hat{F}_{lm}^{lm}=\hat{F}_{lM}^{lM}$ and will be designated simply by $\hat{F}^l$. The integral equation splits into separate equations for each l, and they can be written as

$$\hat{F}^l(x,y) = \hat{D}^l(x,y) + \int_0^\infty dh\,h^2\hat{K}^l(x,h)\hat{F}^l(h,y) \ . \tag{B3}$$

The integral can then be approximated by a sum (using Simpson's rule or a similar method). This then is a matrix equation (on a regular grid),

$$\hat{F}_{ij}^l = \hat{D}_{ij}^l + \Delta^3 \sum_p p^2 a_p \hat{K}_{ip}^l\hat{F}_{pj}^l \ , \tag{B4}$$

where $a_p=1$ for the trapezoid rule (with $\frac{1}{2}$ at the end points) and $a_p=\frac{4}{2}$, $\frac{2}{3}$, or $\frac{1}{3}$ for Simpson's rule. We define

$$\kappa_{ij}^l = \Delta^3 j^2 a_j \hat{K}_{ij}^l \ . \tag{B5}$$

Then the equation can be written as

$$[\underline{1}-\underline{\kappa}]\hat{\underline{F}}^l = \hat{\underline{D}}^l \ . \tag{B6}$$

Standard methods exist for solving linear equations. In this calculation the matrices were dimensioned to be 150×150, and partial Gaussian pivoting was sufficient in getting our results using Simpson's rule with $\Delta=0.1$ Å.

The calculation of $\hat{D}^l(x,y)$ was done by recognizing

$$\hat{D}^l(x,y) = 2\pi \int_{-1}^1 dw\,D[(x^2+y^2+2xyw)^{1/2}]\mathscr{P}_l(w) \ . \tag{B7}$$

Defining $z=|\mathbf{x}-\mathbf{y}|$, the expression for $\hat{D}^l$ can be written as

$$\hat{D}^l(x,y) = 2\pi/xy \int_{|x-y|}^{x+y} z\,dz\,D(z)$$

$$\times \mathscr{P}_l(z^2-x^2-y^2/2xy) \ . \tag{B8}$$

This can be further simplified by defining the moments of D as

$$I_m(r) = 2\pi \int_0^r dh\,h^{m+1}D(h) \ . \tag{B9}$$

Then the expression for $\hat{D}_l$ becomes

$$\hat{D}^l(x,y) = \sum_n A_n^l(x,y)[I_{2n}(x+y)-I_{2n}(|x-y|)]/xy \ , \tag{B10}$$

where the $A_n^l(x,y)$ are rational functions coming from the Legendre polynomial expanded as

$$\mathscr{P}_l(z^2-x^2-y^2/2xy) = \sum_{n=0}^l A_n^l(x,y)z^{2n} \ . \tag{B11}$$

The matrix $\hat{D}_l$ can be constructed from a tabulation of the functions $I_n(Z)$. The functions A_n^l for $l=0$, 1, and 2 are given in Table I.

APPENDIX C

In this appendix the hypernetted-chain equation for the triplet correlation function is derived. The starting point is the partition function of a two-component system. Functional derivatives of the partition function give the

TABLE I. The function $A_n^l(x,y)$ for the first three Legendre polynomials. For $n>l$, these functions vanish. We define $\gamma=x^2+y^2$ and $\xi=2xy$.

$A_0^0(x,y)=1$
$A_0^1(x,y)=-2\gamma\xi^{-1}$
$A_1^1(x,y)=\xi^{-1}$
$A_0^2(x,y)=\frac{3}{2}\gamma^2\xi^{-2}-\frac{1}{2}$
$A_1^2(x,y)=-3\gamma\xi^{-2}$
$A_2^2=\frac{3}{2}\xi^{-2}$

various pair distribution functions. The second functional derivatives define the various pair-pair distributions. The HNC/0 approximation for a binary system is then used as a basis for the integral equation for the pair-pair correlation functions.[26] In the limit of vanishing distinction between component particles, the difference of two correlation functions is the triplet function. The integral equations can themselves be subtracted giving the integral equation for the triplet function [Eq. (4.1)].

The details are now presented. The binary system will consist of N_a particles of type 1 and N_α particles of type 2 in a volume Ω. Lower-case italic letters a, b, c, and d will always refer to particles of type 1; Greek letters α, β, γ, and δ will refer to type 2. Italic letters i, j, k, and l will be used to designate type, i.e., one or two. The partition function can be written as

$$Z = \int \left[\prod_a d\mathbf{r}_a \right] \left[\prod_\alpha d\mathbf{r}_\alpha \right] \exp U , \tag{C1}$$

where the potential energy is given by

$$U = \sum_{\substack{a,b \\ a \neq b}} u_{11}(r_{ab}) + \sum_{a,\alpha} u_{12}(r_{a\alpha})$$

$$+ \sum_{\alpha,a} u_{21}(r_{\alpha a}) + \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}} u_{22}(r_{\alpha\beta}) , \tag{C2}$$

where $u = -v/2k_B T$ as before and there is a formal distinction between u_{12} and u_{21}. Then the pair distribution functions are

$$g_{ij}(\mathbf{r}) = \Omega N_i^{-1} N_j^{-1} \frac{\delta \ln Z}{\delta u_{ij}(\mathbf{r})} , \tag{C3}$$

and the partial structure functions are

$$S_{ij}(\mathbf{q}) = \delta_{ij} + N_i^{1/2} N_j^{1/2} \Omega^{-1} \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}} [g_{ij}(\mathbf{r}) - 1] . \tag{C4}$$

The HNC/0 equations are written as[26]

$$\ln g_{11}(\mathbf{r}) = u_{11}(\mathbf{r}) + u_{11}(-\mathbf{r})$$
$$+ N_1^{-1} \sum_q e^{-i\mathbf{q}\cdot\mathbf{r}} [S_{11}(\mathbf{q}) - 2 + S_{22}(\mathbf{q})/D(\mathbf{q})] ,$$
$$\tag{C5}$$

$$\ln g_{12}(\mathbf{r}) = u_{12}(\mathbf{r}) + u_{21}(-\mathbf{r})$$
$$+ N_1^{-1/2} N_2^{-1/2}$$
$$\times \sum_q e^{-i\mathbf{q}\cdot\mathbf{r}} [S_{12}(q) - S_{21}(\mathbf{q})/D(\mathbf{q})] ,$$

where $D(\mathbf{q})$ is the usual determinant,

$$D(\mathbf{q}) = S_{11}(\mathbf{q}) S_{22}(\mathbf{q}) - S_{12}(\mathbf{q}) S_{21}(\mathbf{q}) . \tag{C6}$$

The functional derivative of g_{11} with respect to u_{11} gives $P_{11,11}$ and is a combination of two-, three-, and four-particle distributions. However, $\delta g_{11}(\mathbf{r})/\delta u_{22}(\mathbf{r}')$ does not contain any two- or three-particle contributions. A suitable difference becomes the usual triplet function in the limit in which the particles become indistinguishable.

We define the function Q_{ijkl} as

$$Q_{ijkl}(\mathbf{r},\mathbf{r}') = (N_i N_j N_k N_l)^{-3/4} \Omega^2 \frac{\delta^2 \ln Z}{\delta u_{ij}(\mathbf{r}) \delta u_{kl}(\mathbf{r}')}$$
$$- \delta_{ik}\delta_{jl} N_i^{-1/2} N_j^{-1/2} \Omega g_{ij}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$$
$$- \delta_{il}\delta_{jk} N_i^{-1/2} N_j^{-1/2} \Omega g_{ij}(\mathbf{r})\delta(\mathbf{r}+\mathbf{r}') . \tag{C7}$$

Then the integral equations for the Q_{1111} can be written as

$$g_{11}^{-1}(\mathbf{r}) Q_{1111}(\mathbf{r},\mathbf{r}') = g_{11}(\mathbf{r}')[M_1(\mathbf{r}+\mathbf{r}') + M_1(\mathbf{r}-\mathbf{r}')]$$
$$+ N_1 \Omega^{-1} \int d\mathbf{h}\, M_1(\mathbf{r}-\mathbf{h}) Q_{1111}(\mathbf{h},\mathbf{r}') + N_1 \Omega^{-1} \int d\mathbf{h}\, M_2(\mathbf{r}-\mathbf{h}) Q_{1211}(\mathbf{h},\mathbf{r}')$$
$$+ N_1 \Omega^{-1} \int d\mathbf{h}\, M_3(\mathbf{r}-\mathbf{h}) Q_{2111}(\mathbf{h},\mathbf{r}') + N_1 \Omega^{-1} \int d\mathbf{h}\, M_4(\mathbf{r}-\mathbf{h}) Q_{2211}(\mathbf{h},\mathbf{r}') , \tag{C8}$$

where the functions M are defined as

$$M_1(\mathbf{x}) = N_1^{-1} \sum_q e^{-i\mathbf{q}\cdot\mathbf{x}} \{1 - [S_{22}(\mathbf{q})/D(\mathbf{q})]^2\} , \tag{C9a}$$

$$M_2(\mathbf{x}) = N_1^{-5/4} N_2^{1/4} \sum_q e^{-i\mathbf{q}\cdot\mathbf{x}} S_{21}(\mathbf{q}) S_{22}(\mathbf{q})/D(\mathbf{q})^2 , \tag{C9b}$$

$$M_3(\mathbf{x}) = N_1^{-5/4} N_2^{1/4} \sum_q e^{-i\mathbf{q}\cdot\mathbf{x}} S_{12}(q) S_{22}(\mathbf{q})/D(\mathbf{q})^2 , \tag{C9c}$$

$$M_4(\mathbf{x}) = N_1^{-3/2} N_2^{1/2} \sum_q e^{-i\mathbf{q}\cdot\mathbf{x}} S_{12}(q) S_{21}(\mathbf{q})/D(q)^2 . \tag{C9d}$$

Now we allow the distinction to vanish. Defining $N = N_1 + N_2$ and $f_i = N_i/N$, $f_1 + f_2 = 1$ and f_i is the frac-

tion of particles of type i. In that case, the following is true:

$$S_{11}(\mathbf{q}) = f_1 S(q) + f_2 , \tag{C10a}$$

$$S_{12}(\mathbf{q}) = S_{21}(-\mathbf{q}) + f_1^{1/2} f_2^{1/2}[S(q) - 1] , \tag{C10b}$$

$$D(\mathbf{q}) = S(q) , \tag{C10c}$$

where $S(q)$ is the usual liquid structure function of the total system. Then the M's can be written as

$$M_1(x) = 2f_2 c(x) + f_1 M(x) , \tag{C11a}$$

$$M_2(x) = M_3(x)$$
$$= f_1^{-3/4} f_2^{3/4}(f_2 - f_1)c(x) + f_1^{1/4} f_2^{3/4} M(x) , \tag{C11b}$$

$$M_4(x) = -f_1^{-1/2} f_2^{1/2} M_1(x) , \tag{C11c}$$

where M and c have been defined before. The Q's can be decomposed into components that look like the pair-pair and the triplet functions. Schematically, this becomes

$$Q_{1111} \rightarrow f_1 Q_p + 4 f_2 T , \qquad (C12a)$$

$$Q_{1211} \rightarrow f_1^{-1/4} f_2^{1/4} [f_1 Q_p - 2(f_1 - f_2)T] , \qquad (C12b)$$

$$Q_{2211} \rightarrow f_1^{-1/2} f_2^{1/2} (f_1 Q_p - 4 f_1 T) . \qquad (C12c)$$

By use of the equation for Q_p, Eq. (C7) becomes the HNC equation for the triplet function which was written as Eq. (4.1). This equation is, of course, independent of the choice of f_1 and f_2. The most convenient choice if $f_1 = f_2 = \frac{1}{2}$, which makes M_2 and M_3 proportional to M and Q_{1211} proportional to Q_p. Subtracting the equations for Q_{1111} and Q_{1211} leads to Eq. (4.1).

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