

An inhomogeneous integral equation for the triplet structure of binary liquids

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The inhomogeneous integral equation proposed by Attard for the study of triplet correlations [J. Chem. Phys. **91**, 3072 (1989)] has been generalized to multicomponent systems. Defining one of the particles of a triplet as the source of an external field, the three particle distribution functions for the mixture are calculated using the inhomogeneous Ornstein–Zernike equation, an approximate closure relation and the Triezenberg–Zwanzig relation. The proposed theory performs satisfactorily for asymmetric mixtures of Lennard–Jones fluids for which other approximations at the two particle level tend to be rather inaccurate. © 2001 American Institute of Physics.
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I. INTRODUCTION

The crucial role of triplet correlations has already been evidenced in several aspects of simple fluids. For instance, triplet correlations have been used in the characterization of the fluid structure in systems like water, for which the pair distribution functions do not provide enough information.¹ It also plays an important role in the freezing transition of liquids² or in the critical behavior of adsorbed fluids.³ In this context, it would be desirable to devise three body theories for mixtures, since the difference in size of the components of the mixture might result on interesting features in the triplet correlation functions. An attempt to address this problem has been very recently performed by the authors in collaboration with Kahl⁴ by extending the theory of Barrat, Hansen, and Pastore (BHP)² to the multicomponent case. The problem in itself presented formidable technical difficulties and serious convergence problems in certain conditions, in particular for high densities and pronounced size asymmetries. This, and the fact that Bildstein and Kahl⁵ showed that Attard's inhomogeneous integral equation approach⁶ provided better triplet correlations for simple systems, prompted us to formulate the extension to mixtures of the latter theory to multicomponent systems. Attard's original formulation dates back to the late eighties.⁶ Until then, the study of inhomogeneous integral equations^{7,8} had mostly focused in confined fluids, interfaces, wetting transitions or in general surface phenomena. Attard extended the inhomogeneous Ornstein–Zernike (IOZ) integral equation theory to the study of triplet correlation functions exploiting Percus' source particle method.⁹ Considering one of the particles of a given triplet as the source of an external field, one can use the IOZ formalism to provide a fairly complete structural characterization of the fluid in terms of two and three particle correlations.

The external potential stemming from the source particle generates an inhomogeneous density profile which may be related to the pair correlation functions. These two quantities can be linked either by the first member of the Yvon–Born–Green (YBG) hierarchy,¹⁰ or by the Triezenberg–Zwanzig–Wertheim–Lovett–Mou–Buff (TZWLMB)^{11,8} equation. Aside from the density profile, a closure relation is needed to complement the OZ relations. In the present contribution two closures will be used: the hypernetted chain approximation (HNC) and the hybrid HMSA closure (hybrid mean spherical approximation) proposed by Zerah and Hansen¹² which implements a certain degree of thermodynamic consistency. Additionally, in this article we will particularly focus on the performance of the approximation to estimate two body correlations. The fact that the same closure relations when applied at the three particle level yield considerably better results has been well established for hard sphere fluids,^{5,6,13} Lennard–Jones systems,^{14,15} and very recently in glass forming liquids interacting through Dzugutov's potential.¹⁶

It is important to recall that in this kind of approach the choice of the source particle in a triplet conditions the results for the correlation functions, since in principle the positions of the particles are not necessarily equivalent. The effects of this drawback in simple systems have been described elsewhere.¹⁴ Our goal here will be to assess to what extent this feature may affect a system in which different species are present.

We will see that the source particle method can be straightforwardly extended to multicomponent systems. Obviously now there will be several sets of coupled integral equations formed by OZ relations with their corresponding closures plus the TZWLMB equations. Different types of source particles will have to be defined in order to evaluate

the various distribution functions involved, and special attention will have to be paid to the inconsistencies resulting from this choice for a given configuration. The equations thus formulated have been solved in this work for two asymmetric additive Lennard-Jones mixtures, one with size ratio $\sigma_{\alpha\alpha}/\sigma_{\beta\beta}=0.8$ and the other with a more demanding ratio of 0.5. The results of the inhomogeneous HNC and HMSA closure combined with the TZWLMB equation turn out to be in good agreement with the simulation results. Especially in the most asymmetric case, these approaches clearly outperform the more sophisticated self-consistent HMSA approximation at the two particle level.

The rest of the paper is organized as follows. In the next section the theory of Attard is generalized to the multicomponent case and details on the method used to solve the coupled integral equations are introduced. In Sec. III results for pair and triplet distribution functions are presented and discussed.

II. THE THEORY

A. The formalism

1. The inhomogeneous integral equation

The IOZ equation in a mixture of n components (μ, ν, \dots) relates the pair total correlation function $h_{\mu\nu\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ to the pair direct correlation function $c_{\mu\nu\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$,

$$h_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12}) = c_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12}) + \sum_{\lambda=1}^n \int dr_4 \rho_{\lambda\gamma}(r_4) \times c_{\mu\lambda\gamma}^{(2)}(r_1, r_4, \theta_{14}) h_{\lambda\nu\gamma}^{(2)}(r_4, r_2, \theta_{42}). \quad (1)$$

Particles μ and ν are those with corresponding coordinates \mathbf{r}_1 and \mathbf{r}_2 , and the third particle γ , located at the origin of the triplet, represents the source of the inhomogeneity in the system, being $\cos \theta_{ij} = \mathbf{r}_i \mathbf{r}_j / r_i r_j$. This source particle does not appear explicitly in the notation used in other works,^{15,14} but has been included in the present treatment for the sake of clarity since, in contrast with the simple fluid case, in mixtures the identity of the source may change and has therefore to be specified. Hence, in what follows, an underlined subindex will always refer to the source particle.

In a mixture of n components there are $n^2 \times (n+1)/2$ equations like Eq. (1), relating the $n^2 \times (n+1)/2$ independent $f_{\mu\nu\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ inhomogeneous pair functions. The fact that the system is axially symmetric makes it amenable to be Legendre transformed^{6,14} in order to eliminate the angular dependence, and accordingly Eq. (1) reduces to

$$\hat{h}_m^{\mu\nu\gamma}(r_1, r_2) = \hat{c}_m^{\mu\nu\gamma}(r_1, r_2) + \frac{4\pi}{2m+1} \sum_{\lambda=1}^n \int dr_4 r_4^2 \times \rho_{\lambda\gamma}(r_4) \hat{c}_m^{\mu\lambda\gamma}(r_1, r_4) \hat{h}_m^{\lambda\nu\gamma}(r_4, r_2). \quad (2)$$

Here the hatted quantities represent the expansion coefficients of the Legendre transforms of the corresponding inhomogeneous pair functions.

For a mixture of two components α and β one explicitly has six equations like Eq. (1), namely

$$h_{\alpha\alpha\alpha}^{(2)}(r_1, r_2, \theta_{12}) = c_{\alpha\alpha\alpha}^{(2)}(r_1, r_2, \theta_{12}) + \int dr_4 \rho_{\alpha\alpha}(r_4) c_{\alpha\alpha\alpha}^{(2)}(r_1, r_4, \theta_{14}) \times h_{\alpha\alpha\alpha}^{(2)}(r_4, r_2, \theta_{42}) + \int dr_4 \rho_{\beta\alpha}(r_4) \times c_{\alpha\beta\alpha}^{(2)}(r_1, r_4, \theta_{14}) h_{\beta\alpha\alpha}^{(2)}(r_4, r_2, \theta_{42}), \quad (3)$$

$$h_{\beta\beta\alpha}^{(2)}(r_1, r_2, \theta_{12}) = c_{\beta\beta\alpha}^{(2)}(r_1, r_2, \theta_{12}) + \int dr_4 \rho_{\alpha\alpha}(r_4) c_{\beta\alpha\alpha}^{(2)}(r_1, r_4, \theta_{14}) \times h_{\alpha\beta\alpha}^{(2)}(r_4, r_2, \theta_{42}) + \int dr_4 \rho_{\beta\alpha}(r_4) \times c_{\beta\beta\alpha}^{(2)}(r_1, r_4, \theta_{14}) h_{\beta\beta\alpha}^{(2)}(r_4, r_2, \theta_{42}), \quad (4)$$

$$h_{\alpha\beta\alpha}^{(2)}(r_1, r_2, \theta_{12}) = c_{\alpha\beta\alpha}^{(2)}(r_1, r_2, \theta_{12}) + \int dr_4 \rho_{\alpha\alpha}(r_4) c_{\alpha\alpha\alpha}^{(2)}(r_1, r_4, \theta_{14}) \times h_{\alpha\beta\alpha}^{(2)}(r_4, r_2, \theta_{42}) + \int dr_4 \rho_{\beta\alpha}(r_4) \times c_{\alpha\beta\alpha}^{(2)}(r_1, r_4, \theta_{14}) h_{\beta\beta\alpha}^{(2)}(r_4, r_2, \theta_{42}), \quad (5)$$

and a corresponding set of equations with β taken as source particle.

Equation (1) has three sets of unknowns, $h_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12})$, $c_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12})$, and the density profile $\rho_{\lambda\gamma}(r)$. Hence two more equations are needed: an approximate closure relation and an expression linking the density profile with the two particle functions. In the present formulation the density profiles are proportional to the homogeneous pair distribution function according to $\rho_{\mu\gamma}(r) = \rho_{\mu} g_{\mu\gamma}(r)$.

2. The closure relation

The closure relates the interaction potential $v_{\mu\nu}(r_{12})$ to the pair correlation functions, and its exact expression for our inhomogeneous mixture in the source particle approach is

$$g_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12}) = \exp\{-\beta v_{\mu\nu}(r_{12}) + h_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12}) - c_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12}) + B_{\mu\nu\gamma}(r_1, r_2, \theta_{12})\}, \quad (6)$$

where $\beta = 1/K_B T$ is the inverse temperature and $r_{12} = (r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12})^{1/2}$. $B_{\mu\nu\gamma}$ is the bridge function which can be written as a sum over elementary diagrams, but in practice has to be approximated in various ways. Thus, when setting $B=0$ one obtains the hypernetted chain equation

(HNC) which is well suited for long-range potentials. Another possibility is to use a reference system bridge function—e.g., that of a hard-sphere fluid—to construct a reference hypernetted chain equation (RHNC),¹⁷ but for the present problem is yet unclear what the appropriate reference

system should be. A rather efficient alternative is the one proposed by Zerah and Hansen¹² with the HMSA which continuously interpolates between the HNC and the soft core mean spherical approximation (SMSA). For the inhomogeneous mixture case the HMSA reads

$$g_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12}) = \exp\{-\beta v_1^{\mu\nu}(r_{12})\} \left(1 - \frac{\exp\{f(r_{12})[h_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12}) - c_{\mu\nu\gamma}^{(2)}(r_1, r_2, \theta_{12}) - \beta v_2^{\mu\nu}(r_{12})]\} - 1}{f(r_{12})} \right), \quad (7)$$

where $f(r_{12}) = 1 - \exp(-\alpha r_{12})$ is the interpolating function and the potential $v_{\mu\nu}(r_{12})$ is split into a soft core repulsion $v_1^{\mu\nu}$ and an attractive tail $v_2^{\mu\nu}$ following the criterion introduced by Weeks and co-workers.¹⁸ For uniform fluids the parameter α is determined by consistency considerations, requiring that the pressure calculated from the fluctuation theorem and the virial equation be in accordance. In the present instance this is impractical given the difficulty to obtain good estimates for the bulk compressibility from the IOZ.¹⁴ Therefore, following Ref. 8 we have used the same parameter α obtained for the homogeneous fluid subject to the same thermodynamic conditions. Note that when $\alpha \rightarrow 0$ the SMSA is recovered, and $\alpha \rightarrow \infty$ reduces Eq. (7) to the HNC approximation. In a multicomponent system of n species $n \times (n+1)/2$ independent relations like Eq. (7) appear.

In this work we will use both the HNC and HMSA at the two particle level in the closure relation to generate bulk system estimates. The same approximations will be used at the three particle level within the framework of the IOZ equation and will be denoted by HNC3 and HMSA3.

3. The density profile

For inhomogeneous systems the equilibrium density is no longer translationally invariant and an expression of the density profile connecting the density distribution to the pair correlation function is needed. There are several equations that can be used, and following the original ideas of Attard we focus here on the TZWLMB^{8,11} relation

$$\begin{aligned} \nabla \rho(\mathbf{r}_1) = & -\beta \rho(\mathbf{r}_1) \nabla V(\mathbf{r}_1) \\ & -\beta \rho(\mathbf{r}_1) \int d\mathbf{r}_2 \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) \nabla V(\mathbf{r}_2), \end{aligned} \quad (8)$$

where $V(\mathbf{r})$ represents the external potential induced by the source. In our specific problem, being the source one of the particles of the system, $V(\mathbf{r})$ is simply the intermolecular potential and, as mentioned before, the density profile is proportional to the homogeneous pair distribution function. Once the gradient in Eq. (8) has been projected, the remaining integral equation can be solved making use of the boundary condition $\rho(r_\infty) \rightarrow \rho_{\text{bulk}}$. For multicomponent systems the solution of Eq. (8) reads

$$\begin{aligned} \rho_{\mu\gamma}^{(2)}(r_1) = & \rho_\mu \exp\left\{-\beta v_{\mu\gamma}(r_1) - \int_\infty^r \frac{4\pi}{3} \beta \left[\sum_{\lambda=1}^n \int_0^\infty dr_2 r_2^2 \right. \right. \\ & \left. \left. \times \rho_{\lambda\gamma}(r_2) \hat{h}_1^{\mu\lambda\gamma}(r_1, r_2) \frac{dv_{\lambda\gamma}(r_2)}{dr_2} \right] dr_1 \right\}. \end{aligned} \quad (9)$$

In principle n^2 expressions like Eq. (9) can be written in a mixture of n components. The density profile (9) closes the set of Eqs. (1) and (7).

The bulk three particle distribution function can be evaluated through the factorization

$$g_{\mu\nu\gamma}^{(3)}(r_1, r_2, \cos \theta_{12}) = g_{\mu\gamma}(r_1) g_{\nu\gamma}(r_2) g_{\mu\nu\gamma}^{(2)}(r_1, r_2, \cos \theta_{12}), \quad (10)$$

where $g_{\mu\nu\gamma}^{(2)}(r_1, r_2, \cos \theta_{12})$ represents the probability of finding particles μ and ν , respectively at distances r_1 and r_2 from the source γ , θ_{12} is the angle between the vectors \mathbf{r}_1 and \mathbf{r}_2 , and $g_{\mu\nu}(r_i)$ are the homogeneous pair distribution functions.

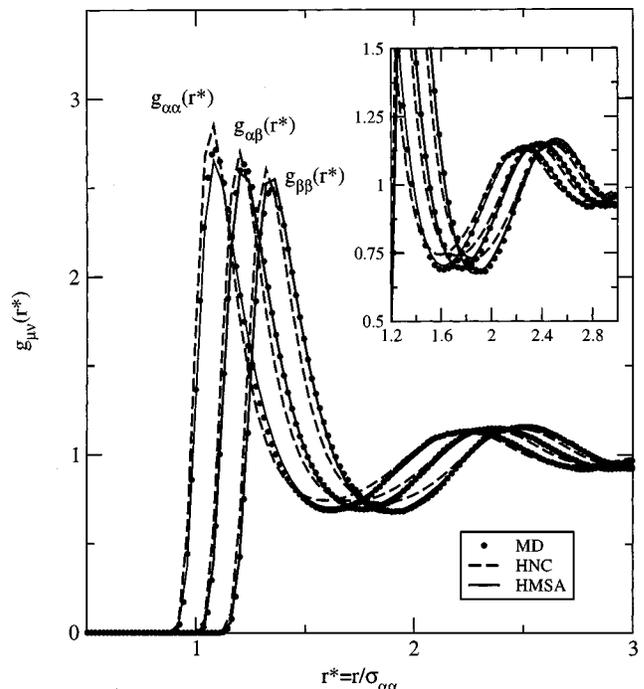


FIG. 1. Pair distribution functions calculated from homogeneous integral equations vs simulation for mixture A. The notation is explained in the legend box.

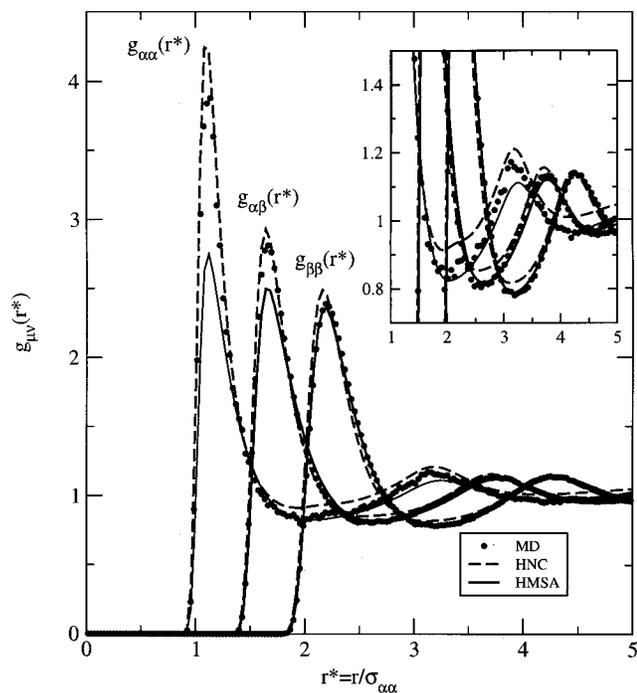


FIG. 2. Same as Fig. 1 for mixture B.

B. The numerical implementation

One has to solve the system of equations (1) and (7) together with the density profile relations (9). It is important to notice that each term in Eq. (1) contains functions with the same source particle, and this decouples equations with source particle α from those with source β . Thus for a binary mixture one could have two sets with Eqs. (3)–(5), and the corresponding set with β as a source, coupled with their respective density profiles. Note that due to the lack of symmetry in source particle exchanges, $\rho_{\alpha\beta}$ and $\rho_{\beta\alpha}$ are not necessarily identical, but as will be shown later, to a good approximation we still can assume $\rho_{\alpha\beta} = \rho_{\beta\alpha}$. This does not preclude the decoupling in two sets of Eqs. (1), provided that the density profile in both of them is calculated with the same degree of accuracy.

The method used to solve each coupled system of equations is the Generalized Minimal RESidual algorithm for nonlinear systems of equations¹⁹ (GMRESNL) previously introduced by Fries and Cosnard²⁰ in the context of liquid state theory. It has also been used in complex problems with molecular liquids,²¹ in the calculation of triplet correlations of hard-sphere mixtures within the BHP approach⁴ and more recently to solve the HNC3 equation in pure simple liquids.¹⁶ We refer the reader to Refs. 19 and 16

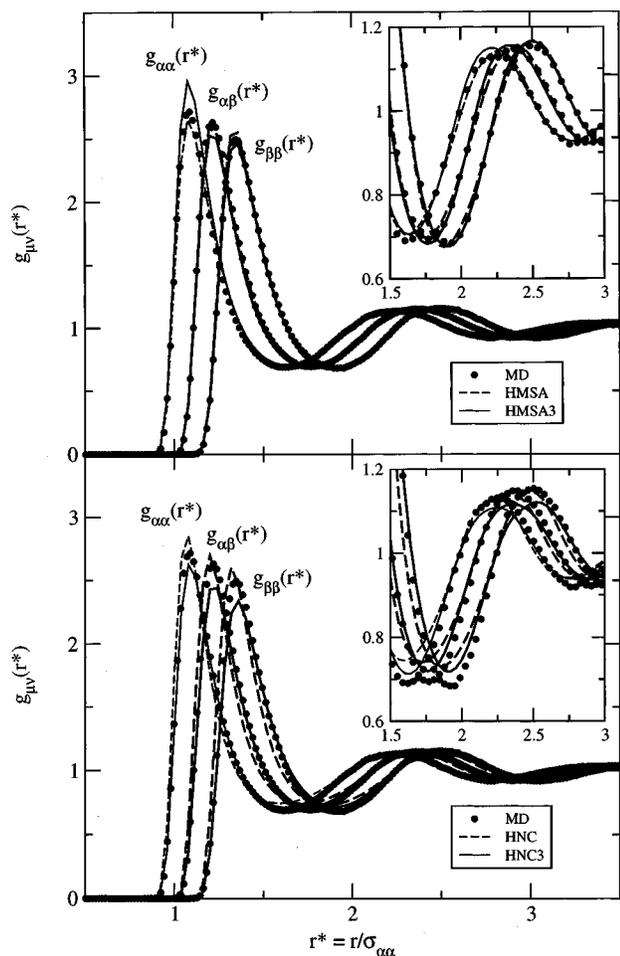


FIG. 3. Pair distribution functions for mixture A evaluated from the inhomogeneous integral equation by means of Eq. (9), compared with MD results. The notation is explained in the legend box.

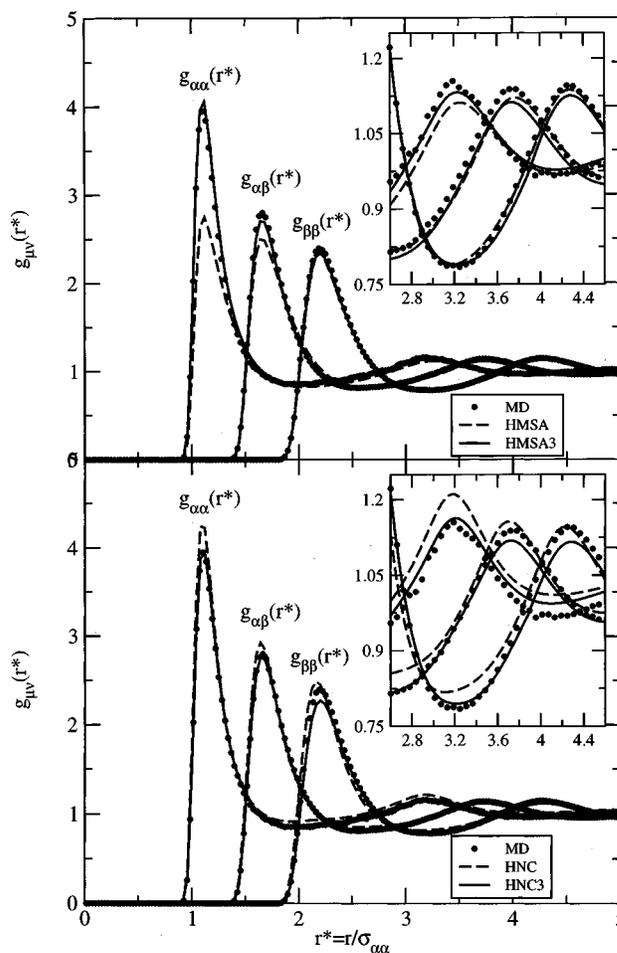


FIG. 4. Same as Fig. 3 for mixture B.

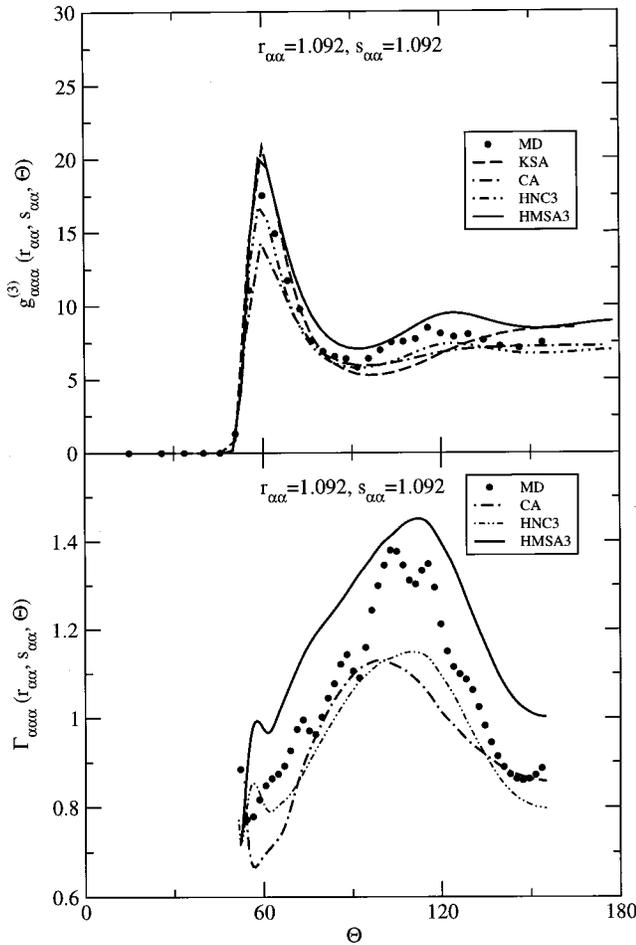


FIG. 5. $g_{\alpha\alpha\alpha}^{(3)}(r_{\alpha\alpha}, s_{\alpha\alpha}, \theta)$ and $\Gamma_{\alpha\alpha\alpha}(r_{\alpha\alpha}, s_{\alpha\alpha}, \theta)$ for mixture A.

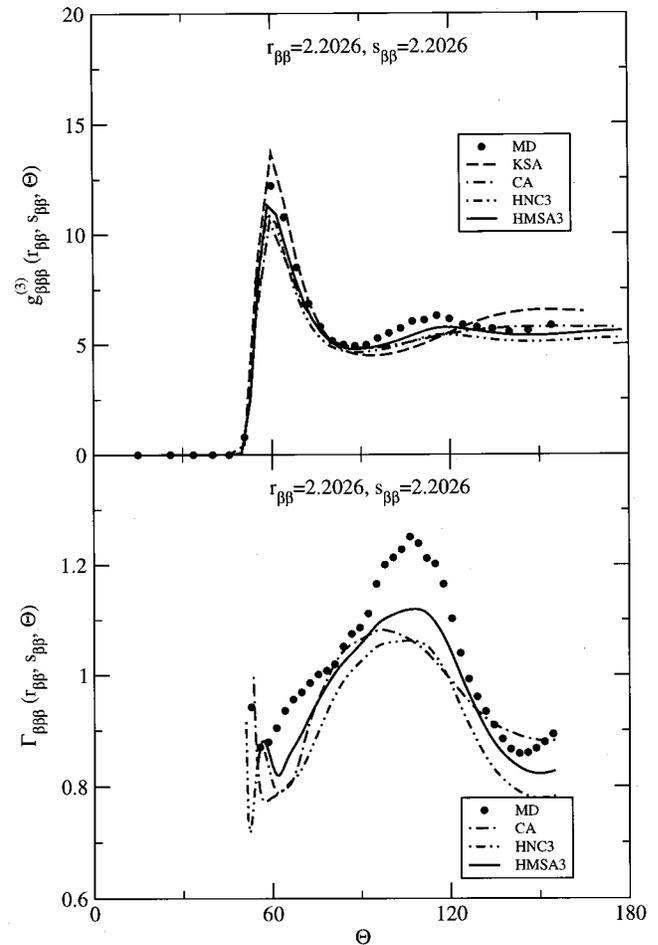


FIG. 6. $g_{\beta\beta\beta}^{(3)}(r_{\beta\beta}, s_{\beta\beta}, \theta)$ and $\Gamma_{\beta\beta\beta}(r_{\beta\beta}, s_{\beta\beta}, \theta)$ for mixture B.

for a detailed exposition of the method. To improve the convergence stability in the calculations, a mixing iterates algorithm²² has been adopted for both the indirect correlation function and the density profile.

In this sort of problem the memory requirements increase rapidly with the number of species and with the number of grid points in the discretized functions, making calculations quite cumbersome. A great simplification can be done bearing in mind that a generic inhomogeneous pair function $f_{\mu\mu\gamma}^{(2)}(r_1, r_2, \theta_{12})$ is symmetric with respect to the variables r_1 and r_2 , regardless of the identity of the source γ . Hence, the dimensions of these matrices are reduced by half.

The homogeneous pair functions calculated in the HNC and HMSA approximations were discretized on a grid of 2048 points and mesh size 0.04σ , σ being the Lennard-Jones range parameter of the smallest particle. A hard-core cutoff of 0.7σ has been used to account for the strong repulsion at small distances. The solutions of the inhomogeneous system of equations (1), (7), and (9) have been obtained using 150 grid points on the radial coordinate, and 60 angular nodes in the discrete Legendre transform. For the GMRESNL algorithm five search directions were used, and the convergence in the correlation functions and the density profile was achieved whenever the condition

$$\sqrt{\frac{\sum_{i=1}^{N_d} (f_i^{n+1} - f_i^n)^2}{N_d - 1}} < \varepsilon \quad (11)$$

was fulfilled for every $f_{\mu\nu\gamma}^{(2)}$ and $\rho_{\mu\gamma}$ function. Here N_d is the number of grid points and n designates a given iteration. For the present problem ε was set to 10^{-3} . The calculations performed under these conditions required about 200 Mbytes of memory for each set of three coupled equations, which can be solved independently.

III. RESULTS

Our theory has been tested for two Lennard-Jones binary mixtures of particles α and β ($\sigma_{\alpha\alpha} < \sigma_{\beta\beta}$). The first case (mixture A) was previously studied by Enciso *et al.*²³ in terms of the RHNC equation and is characterized by $\sigma_{\alpha\alpha}/\sigma_{\beta\beta} = 0.8$, $\rho\sigma_{\alpha\alpha}^3 = 0.5302$, $x_\alpha = 0.5$ and $T^* = 1.0$. In the other test case (mixture B) the difference in size between the particles is increased to $\sigma_{\alpha\alpha}/\sigma_{\beta\beta} = 0.5$, and $\rho\sigma_{\alpha\alpha}^3 = 0.1065$, $x_\alpha = 0.25$ and $T^* = 0.85$. In both cases $\rho = \rho_\alpha + \rho_\beta$, $x_\mu = \rho_\mu/\rho$ and $T^* = K_B T/\epsilon_{\alpha\alpha}$. The interaction parameters in the Lennard-Jones potential are $\epsilon_{\alpha\alpha} = \epsilon_{\alpha\beta} = \epsilon_{\beta\beta}$, the Lorentz rule is employed to define $\sigma_{\alpha\beta}$, and $\sigma_{\alpha\alpha}$ is used as unit of length.

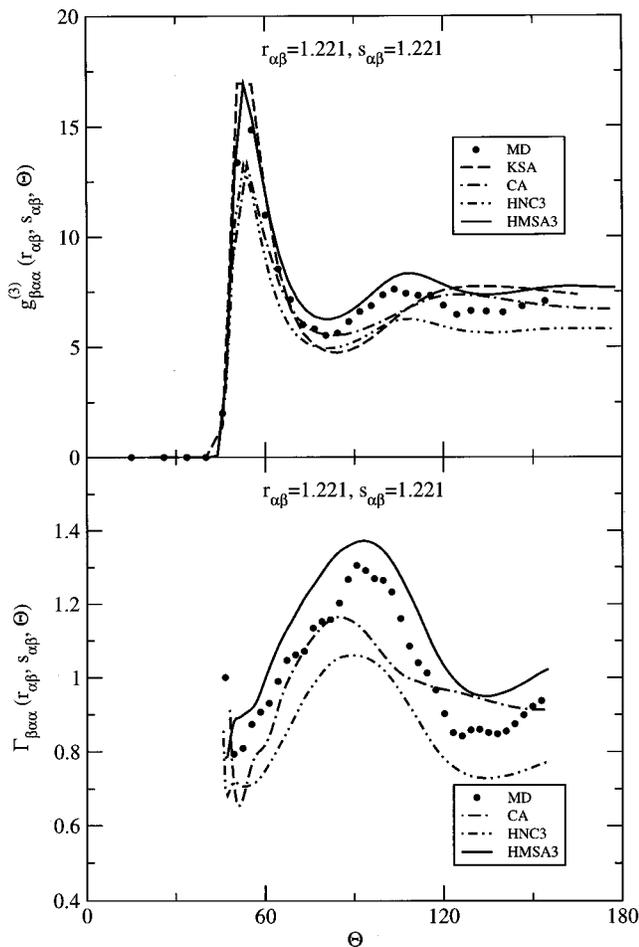


FIG. 7. $g_{\beta\alpha\alpha}^{(3)}(r_{\alpha\beta}, s_{\alpha\beta}, \theta)$ and $\Gamma_{\beta\alpha\alpha}(r_{\alpha\beta}, s_{\alpha\beta}, \theta)$ for mixture A.

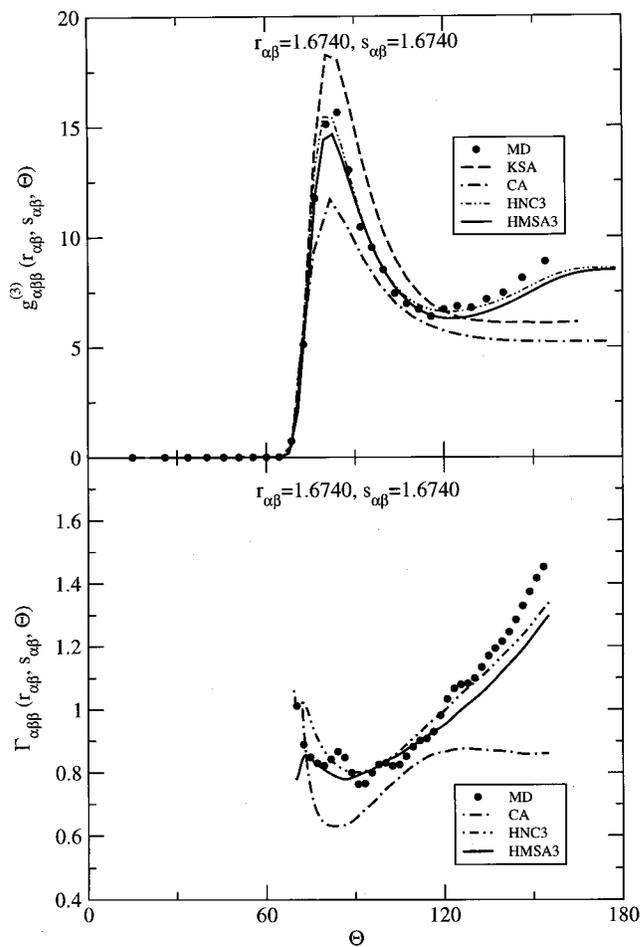


FIG. 8. $g_{\alpha\beta\beta}^{(3)}(r_{\alpha\beta}, s_{\alpha\beta}, \theta)$ and $\Gamma_{\alpha\beta\beta}(r_{\alpha\beta}, s_{\alpha\beta}, \theta)$ for mixture B.

In order to assess the quality of the theory, reference simulation results were generated using canonical ensemble molecular dynamic (MD) simulations.²⁴ Temperature was stabilized using a Berendsen's thermostat with a time constant for temperature coupling of 0.4 ps and the simulation time step was set to 0.001 ps. The equilibration of the system was achieved after 5×10^4 time steps, and around 2.5×10^5 production time steps were employed to calculate ensemble averages on our 864 particle sample.

The IOZ equation requires an initial estimate for the inhomogeneous pair functions and the density profile $\rho_{\mu\gamma}(r)$. As initial guesses, the corresponding homogeneous quantities obtained with HNC and HMSA homogeneous integral equations have been used.

The homogeneous pair distribution functions obtained with both closures are displayed in Figs. 1 and 2 for our two test cases. The improvement of the HMSA over HNC over the whole distance range is notorious for system A in Fig. 1.

When the size asymmetry is increased the quality of the theoretical estimates worsens, and this is particularly evident for the poor HMSA predictions of the $g_{\alpha\alpha}$ and $g_{\alpha\beta}$ first peaks (Fig. 2). This shortcoming of the approximation has already been documented in related asymmetric mixtures.²⁵ Although the HNC results present the characteristic shift in all the peak positions in this case, they are in somewhat better agreement with the simulation.

As mentioned before, when the same closures are applied at the three particle level in the IOZ equation, one should expect an improvement^{14,16} on the pair correlation functions, and indeed this can be seen in Figs. 3 and 4 in which the results of $g_{\mu\nu}$ for HNC3 and HMSA3 are depicted for systems A and B. The ability of the method to improve the two particle closures is more pronounced in the HNC on the medium range, where the shift in the peak positions is corrected, but at short distances the improvement on the HMSA results for the most asymmetric mixture is remarkable. As a whole, we can say that the HMSA3 is slightly better than the HNC3.

Concerning the three particle distribution functions, in Figs. 5–10 we have plotted for systems A and B the six possible $g_{\mu\nu\gamma}^{(3)}$ that appear in a mixture of two components, and compared them with Kirkwood's superposition approximation (KSA)²⁶ and the convolution approximation (CA).²⁷ The lower graphs represent the $\Gamma(r, s, \theta)$ functions

$$\Gamma_{\mu\nu\gamma}(r_1, r_2, \cos \theta_{12}) = \frac{g_{\mu\nu\gamma}^{(3)}(r_1, r_2, \cos \theta_{12})}{g_{\mu\gamma}(r_1)g_{\nu\gamma}(r_2)g_{\mu\nu}(r_{12})} = \frac{g_{\mu\nu\gamma}^{(2)}(r_1, r_2, \cos \theta_{12})}{g_{\mu\nu}(r_{12})}. \quad (12)$$

The chosen configurations represent triplets with interparticle distances corresponding to the first peaks in $g_{\mu\nu}$. In

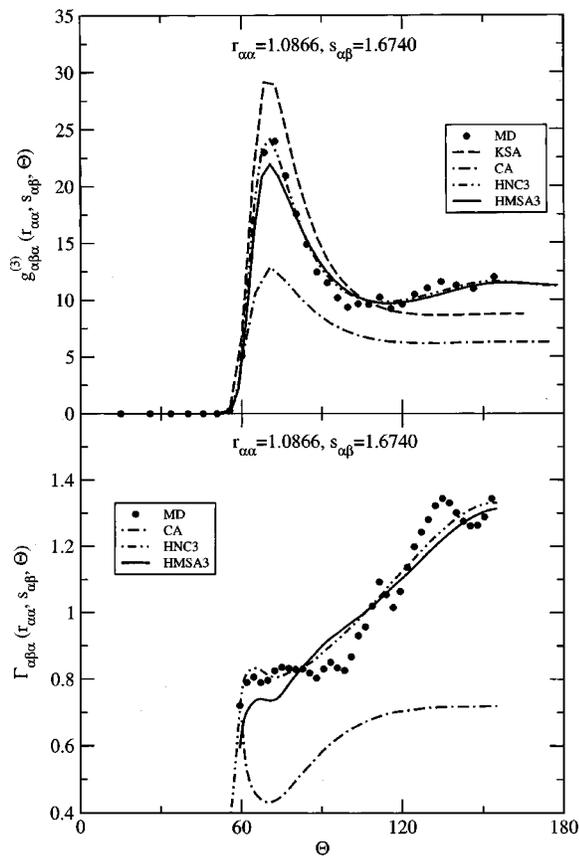


FIG. 9. $g_{\alpha\beta\alpha}^{(3)}(r_{\alpha\alpha}, s_{\alpha\beta}, \theta)$ and $\Gamma_{\alpha\beta\alpha}(r_{\alpha\alpha}, s_{\alpha\beta}, \theta)$ for mixture B.

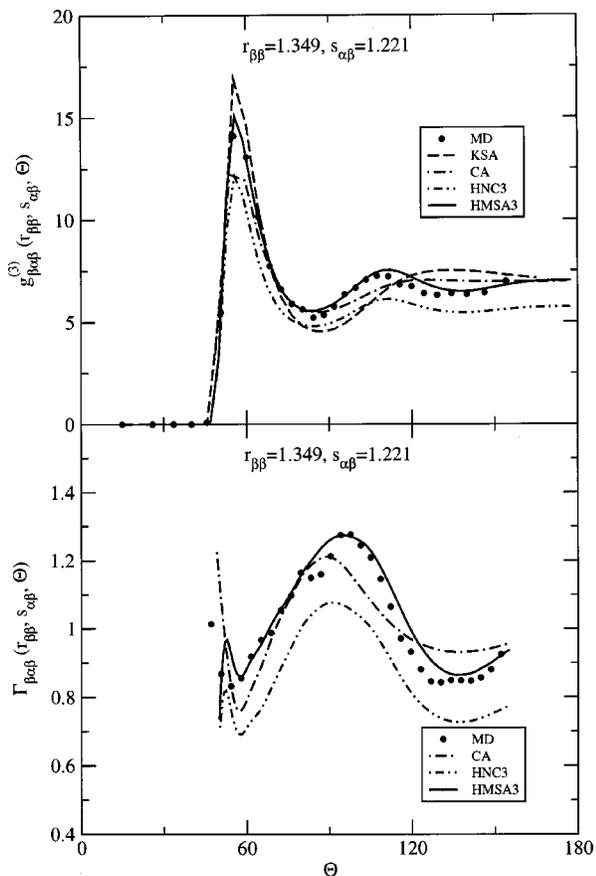


FIG. 10. $g_{\beta\alpha\beta}^{(3)}(r_{\beta\beta}, s_{\alpha\beta}, \theta)$ and $\Gamma_{\beta\alpha\beta}(r_{\beta\beta}, s_{\alpha\beta}, \theta)$ for mixture A.

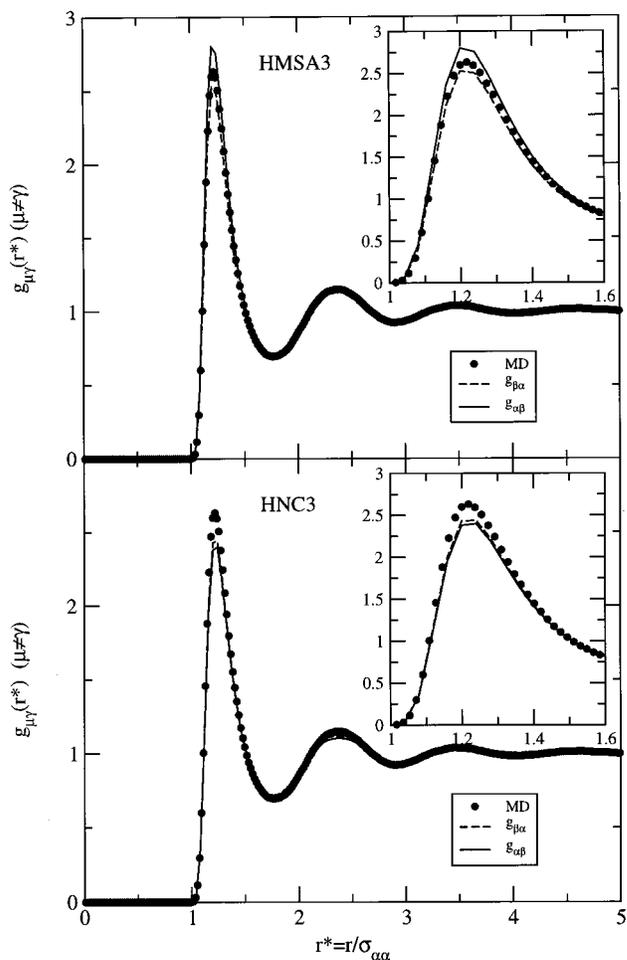


FIG. 11. Dependence of the calculated fluid structure on the choice of the source particle, illustrated on the mixed pair distribution functions $g_{\alpha\beta} \neq g_{\beta\alpha}$, in mixture A.

general one can observe that also here the HMSA3 provides the best approximation to the simulation. Besides, even in those cases when this theory departs more from the MD data, it shows the same trends as the simulation over the whole angular range. Similar observations can be found in the literature for hard-sphere⁵ and Lennard-Jones one component fluids.¹⁴

It has already been mentioned that the interchange of particles in a triplet leads to different approximations for the same function. Despite this, we have decoupled the system of equations and $g_{\alpha\beta}$ and $g_{\beta\alpha}$ have been considered as a unique function. This assumption is obviously an approximation because $g_{\mu\gamma}$ is proportional to the density profile of particles μ around the source γ , and intuitively its estimate should be better the smaller the perturbation induced by the source particle. That is, one should expect to obtain better results when the source particle is small. This is clearly illustrated comparing $g_{\alpha\beta}$ and $g_{\beta\alpha}$ in Figs. 11 and 12 for systems A and B, respectively. First of all it can be seen that the best agreement between $g_{\alpha\beta}$ and $g_{\beta\alpha}$ is obtained when the size asymmetry is minimal. The same argument explains the deviations of $g_{\alpha\beta}$ from simulation both for HNC3 and HMSA3 in systems A and B. Since the β particle is larger in system B, also larger departures are to be expected.

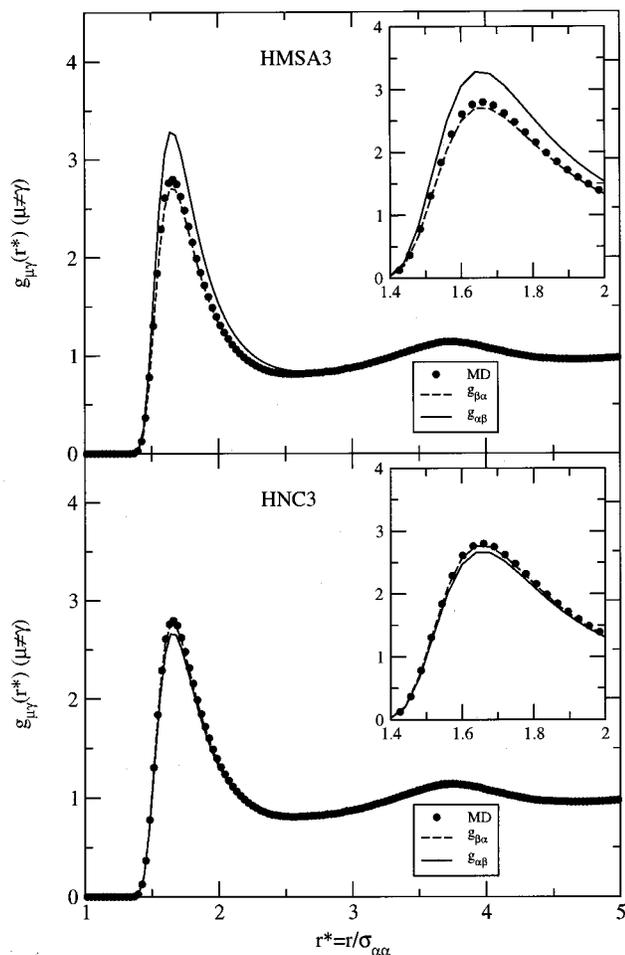


FIG. 12. Same as Fig. 11 for mixture B.

Taking into account that the HMSA closure relation is consistently better than the HNC in simple fluids, it is somewhat surprising to see in Fig. 12 that the disagreement with simulation results is larger for HMSA3 than for HNC3 when β is the source particle. However, we must recall that the mixing parameter in HMSA is determined for the homogeneous integral equation, which does not perform too well as far as the peak heights are concerned, and consequently might be inappropriate for the inhomogeneous case. In this regard, one might use this mismatch between the $g_{\mu\nu}$'s to implement a possible consistency criterion in order to search for a better integral equation approach.

In summary, in this work the validity of the generalization to mixtures of Attard's theory in the study of triplet correlation functions has been investigated and assessed by comparison with reference simulation data. The theory is in good agreement with simulation results, and undoubtedly

performs better than other three body approximations like the KSA and CA.

It has also been confirmed the ability of this approximation to improve the results for pair distribution functions obtained via conventional homogeneous integral equations. Besides, the theory proves to be an efficient tool to characterize mixtures with a high asymmetry, which is one of the greatest challenges for theoretical liquid state methods.

Future research directions should point to a thorough study of more accurate closure relations, incorporating consistency criteria at the three particle level and to a characterization of the dependence of the results on the density profile equation (TZWLMB or YBG) utilized.

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