On the triplet structure of binary liquids

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An approach to calculate the triplet structure of a simple liquid, that was proposed some years ago by Barrat, Hansen, and Pastore [Phys. Rev. Lett. **58**, 2075 (1987)] has been tested in the binary case. This approach is based on a factorization ansatz for the triplet direct correlation function $c^{(3)}$; the unknown factor function is determined via the sum rule relating $c^{(3)}$ and the pair direct correlation function which is the only input information of the system that is required in this formalism. We present an efficient and stable numerical algorithm which solves the six (partly coupled) integral equations for the unknown factor functions. Results are given for the case of a binary hard-sphere mixture and complemented by computer simulation data. © *2000 American Institute of Physics.* [S0021-9606(00)52332-0]

I. INTRODUCTION

Concepts to calculate the triplet structure in (simple) liquids date back to the beginning of the 1960s; however, at that time their implementation in computer programs and the actual calculation of the triplet structure were by far out of reach. One of the simplest approximations of the three-particle distribution function $g^{(3)}$ is the Kirkwood superposition approximation (KSA)[1]

$$g^{(3)}(r,s,t)=g(r)g(s)g(t), \tag{1}$$

which is only valid in the low density limit. This has been demonstrated by Egelstaff *et al.*[2] in an attempt to study experimentally the triplet correlation function for liquid argon, relating this function with the isothermal pressure derivative of the structure factor. It has been about fifteen years during which improved computer facilities have made the actual calculation of three-particle correlation functions possible. A large variety of studies have been dedicated to this problem: these investigations have been carried out (mostly) within frameworks based on integral–equation theories and were supplemented by computer simulation results. The increased interest in the triplet structure is, however, not only of purely academic origin: density-functional based approaches that describe freezing phenomena have indeed brought along an improvement of the results if the (approximate) functional that describes the property of the solid is expanded up to third order, i.e., including three-particle correlation functions.[3,4] Among the frameworks proposed during the past two decades to calculate the triplet structure of a liquid, we quote in particular some of those that have been implemented and tested against computer simulation results: they are due to Ashcroft and co-workers,[5,4] Attard,[6] Barrat, Hansen, and Pastore,[7,8] and Leidl and Wagner.[9]

However, up to now—and to the best of our knowledge—only the theory by Rosenfeld[10] has been extended to the study of the hard-sphere mixture fluid, including the calculation of the triplet structure. This method is based on characteristic functions which bear in mind geometrical features of the spheres. In contrast to other theories, the knowledge of the bulk fluid direct correlation function is not a prerequisite, but it can be derived within the framework of the theory together with other properties of the uniform fluid. This approach has been successfully compared with extensive simulation results in Ref. 11. Nonetheless, even if explicit expressions for $c^{(3)}$ for mixtures have been derived within this theory, no results have been presented so far.

This shortage of theories for the calculation of $c^{(3)}$ in the mixture case is somewhat surprising, since differences in size and interaction between the two species are expected to lead to interesting effects in the triplet structure of a binary mixture. As a matter of fact, inclusion of three-body correlation functions should—as in the one-component case—lead to an improved description of the freezing behavior of binary mixtures.[12] Furthermore, it is expected that the triplet structure might give additional information in cases where the pair structure does not appear to have a definite answer[13] as in the case of alloys with marked chemical short range order with the presence of superstructures.[14] In an effort to fill this gap we have generalized one of the above methods due to Barrat, Hansen, and Pastore (BHP)[7,8] to the binary

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case along the lines sketched in Ref. 8. With this purpose we have implemented an efficient and accurate numerical algorithm and have produced data for the triplet structure for a binary hard sphere mixture. The results obtained within this framework are complemented by computer simulation results. In the BHP approach, a symmetric factorization ansatz is made for the triplet direct correlation function in terms of an unknown function $t(r)$. This ansatz is justified by the rotational and translational invariance of the homogeneous liquid and by the lowest order $h^{(2)}$-bond expansion of the triplet correlation function, where $h(r)$ is the total pair correlation function. The only information about the system that is required as input is the density derivative of the pair direct correlation function. The defining relation for the yet unknown factor function $t(r)$ is the sum-rule relating the pair and the triplet direct correlation function: it is an integral equation which can be solved numerically. In terms of functional derivatives this sum-rule reads

$$c^{(n)}(1,...,n)=\frac{\delta c^{(n-1)}(1,...,n-1)}{\delta\rho^{(1)}(n)}=\frac{\delta^n\beta F_{\mathrm{ex}}}{\delta\rho^{(1)}(1)\cdots\delta\rho^{(1)}(n)}. \tag{2}$$

The results presented for $\tilde{c}^{(3)}(\mathbf{k},\mathbf{k}')$ using the BHP theory for long-range potentials (such as Coulombic systems) and soft spheres seem to fit the simulation results. Khein and Ashcroft outlined the unique specification of $t(r)$ according to the sum rule above[4] and made an extension of the BHP theory generating a directly symmetric in k-space $c^{(3)}$ function.[15] The same unambiguity in the determination of $t(r)$ is remarked by Likos *et al.*[3] to use the BHP ansatz of $c^{(3)}$ in the study of the freezing transition in the classical one-component plasma. In this case the results presented favor the ansatz against other theories. Concerning the freezing transition of a hard-sphere system within the framework of the extended modified weighted-density approximation,[16] it is concluded that the factorization ansatz does not predict the stabilization of the expected solid phase.

The extension of the BHP approach to the case of a binary mixture is formally straightforward and has been outlined by Barrat, Hansen, and Pastore.[8] However, the complexity of the expressions and, in particular, their numerical solution increase drastically as the number of components increases. In the binary case the six-factor functions $t_{\alpha\beta}^{\alpha\beta\gamma}(r)$ are determined in six, partly coupled, sets of integral equations. In the original work on the one-component case a single integral equation was solved by minimizing a suitably defined functional with a steepest descent method. Since this method turned out to be unsuitable for our work (in particular with respect to the numerical stability) we present in this study the generalized minimal residual algorithm for nonlinear systems of equations[17] (GMRESNL) introduced some years ago by Fries and Cosnard[18] in the field of liquid state theory. It is a Newton–Raphson-type algorithm and has been applied for the solution of complex integral equations problems dealing with molecular liquids (see for instance Ref. 19).

The rest of this article is organized as follows. In the next section we briefly outline the formalism of the generalized BHP framework and discuss the numerical method we have used to solve the coupled integral-equations. In Sec. III we present results for the model system. The article closes with concluding remarks.

II. THE THEORY

A. The formalism

As an alternative to the KSA factorization of $g^{(3)}$, Jackson and Feenberg[20] proposed a k-space factorization of the triplet structure factor, $S_{\alpha\beta\gamma}^{(3)}(\mathbf{k},\mathbf{k}')$ of the type [$S_{\alpha\beta}^{(2)}(k)$ being the structure factor]

$$S_{\alpha\beta\gamma}^{(3)}(\mathbf{k},\mathbf{k}')=\sum_{\epsilon}\frac{1}{X_e^2}S_{\epsilon\gamma}^{(2)}(|\mathbf{k}+\mathbf{k}'|)S_{\alpha\epsilon}^{(2)}(k)S_{\epsilon\beta}^{(2)}(k'), \tag{3}$$

which via the triplet Ornstein–Zernike (OZ) relation translates into a neglect of the triplet direct correlation function,

$$c^{(3)}(\mathbf{r},\mathbf{r}')=0.$$

This is known as the convolution approximation (CA). A first-order correction for this approximation uses a $h^{(2)}$-bond expansion of $c^{(3)}$ to get

$$c^{(3)}(\mathbf{r},\mathbf{r}')\approx h^{(2)}(r)h^{(2)}(r')h^{(2)}(|\mathbf{r}-\mathbf{r}'|). \tag{4}$$

With this in mind, several years ago, Barrat, Hansen, and Pastore[7,8] proposed the following ansatz for the direct triplet correlation function $c^{(3)}(\mathbf{r},\mathbf{r}')$ of a homogeneous liquid

$$c^{(3)}(\mathbf{r},\mathbf{r}')=t(r)t(r')t(|\mathbf{r}-\mathbf{r}'|), \tag{5}$$

with an unknown function $t(r)$. The expression above reads in k-space

$$\tilde{c}^{(3)}(\mathbf{k},\mathbf{k}')=\frac{1}{2\pi^3}\int\tilde{t}(k'')\tilde{t}(|\mathbf{k}-\mathbf{k}''|)\tilde{t}(|\mathbf{k}'+\mathbf{k}''|)d\mathbf{k}'', \tag{6}$$

where a tilde denotes a Fourier transform.

Now $t(r)$ can be determined via the sum-rule, Eq. (2),

$$\frac{\partial c^{(2)}(r)}{\partial\rho}=\int c^{(3)}(\mathbf{r},\mathbf{r}')d\mathbf{r}'=t(r)\int t(r')t(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'. \tag{7}$$

ρ is the number-density of the system and $c^{(2)}(r)$ is the two-particle direct correlation function, which is the only information about the system that is required as input in this framework. In general, this function is well-known thanks to sophisticated liquid state methods that have been developed during the past years.[21]

The generalization of the formalism to a n-component system is in principle straightforward and has been outlined in Ref. 8. In the binary case, to which the present contribution is dedicated to, the factorization ansatz, Eq. (5) now reads

$$c_{\alpha\beta\gamma}^{(3)}(\mathbf{r},\mathbf{r}')=t_{\alpha\beta}^{\alpha\beta\gamma}(r)t_{\alpha\gamma}^{\alpha\beta\gamma}(r')t_{\beta\gamma}^{\alpha\beta\gamma}(|\mathbf{r}-\mathbf{r}'|). \tag{8}$$

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A closer analysis and taking into account symmetry relations shows that we now have four independent $c^{(3)}$'s, i.e., $c^{(3)}_{\alpha\alpha\alpha}$, $c^{(3)}_{\alpha\alpha\beta}$, $c^{(3)}_{\alpha\beta\beta}$, and $c^{(3)}_{\beta\beta\beta}$ and the six unknown $t^{\alpha\beta\gamma}_{\beta\gamma}$ are related via six equations which explicitly read

$$\frac{\partial c^{(2)}_{\alpha\alpha}(r)}{\partial \rho_\alpha} = t^{\alpha\alpha\alpha}_{\alpha\alpha}(r)\int t^{\alpha\alpha\alpha}_{\alpha\alpha}(r')t^{\alpha\alpha\alpha}_{\alpha\alpha}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = \int c^{(3)}_{\alpha\alpha\alpha}(\mathbf{r},\mathbf{r}')d\mathbf{r}', \tag{9}$$

$$\frac{\partial c^{(2)}_{\alpha\alpha}(r)}{\partial \rho_\beta} = t^{\alpha\alpha\beta}_{\alpha\alpha}(r)\int t^{\alpha\alpha\beta}_{\alpha\beta}(r')t^{\alpha\alpha\beta}_{\alpha\beta}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = \int c^{(3)}_{\alpha\alpha\beta}(\mathbf{r},\mathbf{r}')d\mathbf{r}', \tag{10}$$

$$\frac{\partial c^{(2)}_{\alpha\beta}(r)}{\partial \rho_\alpha} = t^{\alpha\beta\alpha}_{\alpha\beta}(r)\int t^{\alpha\beta\alpha}_{\alpha\alpha}(r')t^{\alpha\beta\alpha}_{\beta\alpha}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = \int c^{(3)}_{\alpha\beta\alpha}(\mathbf{r},\mathbf{r}')d\mathbf{r}', \tag{11}$$

$$\frac{\partial c^{(2)}_{\alpha\beta}(r)}{\partial \rho_\beta} = t^{\alpha\beta\beta}_{\alpha\beta}(r)\int t^{\alpha\beta\beta}_{\alpha\beta}(r')t^{\alpha\beta\beta}_{\beta\beta}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = \int c^{(3)}_{\alpha\beta\beta}(\mathbf{r},\mathbf{r}')d\mathbf{r}', \tag{12}$$

$$\frac{\partial c^{(2)}_{\beta\beta}(r)}{\partial \rho_\alpha} = t^{\beta\beta\alpha}_{\beta\beta}(r)\int t^{\beta\beta\alpha}_{\beta\alpha}(r')t^{\beta\beta\alpha}_{\beta\alpha}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = \int c^{(3)}_{\beta\beta\alpha}(\mathbf{r},\mathbf{r}')d\mathbf{r}', \tag{13}$$

$$\frac{\partial c^{(2)}_{\beta\beta}(r)}{\partial \rho_\beta} = t^{\beta\beta\beta}_{\beta\beta}(r)\int t^{\beta\beta\beta}_{\beta\beta}(r')t^{\beta\beta\beta}_{\beta\beta}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = \int c^{(3)}_{\beta\beta\beta}(\mathbf{r},\mathbf{r}')d\mathbf{r}'. \tag{14}$$

Equations (9) and (14) are decoupled and can be solved independently (as in the one-component case), while the remaining four equations are coupled in pairs.

Once the set of triplet direct correlation functions has been determined, one can use them in the calculation of the three particle distribution functions $g^{(3)}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}')$. This is done by means of the triplet OZ relation [see Eq. (45) in Ref. 8], x_ϵ being the concentration of species ϵ

$$S^{(3)}_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}') = \sum_{\epsilon\sigma\eta}[1/x_\epsilon^2\delta_{\epsilon\sigma}\delta_{\epsilon\eta} + \rho^2\tilde{c}^{(3)}_{\epsilon\sigma\eta}(\mathbf{k},\mathbf{k}')] \times S^{(2)}_{\epsilon\gamma}(|\mathbf{k}+\mathbf{k}'|)S^{(2)}_{\alpha\sigma}(k)S^{(2)}_{\eta\beta}(k'), \tag{15}$$

which also, in terms of total correlation functions, reads[22]

$$\begin{aligned} S^{(3)}_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}') = {} & \delta_{\alpha\beta}\delta_{\alpha\gamma}x_\alpha + \delta_{\alpha\gamma}x_\alpha x_\beta\rho\tilde{h}_{\alpha\beta}(k') \\ & + \delta_{\beta\gamma}x_\alpha x_\gamma\rho\tilde{h}_{\alpha\gamma}(k) \\ & + \delta_{\alpha\beta}x_\beta x_\gamma\rho\tilde{h}_{\beta\gamma}(|\mathbf{k}+\mathbf{k}'|) + x_\alpha x_\beta x_\gamma\rho^2 \\ & \times\int e^{-i\mathbf{k}\mathbf{r}_\alpha}e^{-i\mathbf{k}'\mathbf{r}'_\beta}h^{(3)}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'. \end{aligned} \tag{16}$$

From these two equations one gets the three particle total correlation function $h^{(3)}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}')$ by Fourier inversion of

$$\begin{aligned} \tilde{h}^{(3)}_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}') = {} & \sum_\epsilon[\delta_{\gamma\epsilon}\tilde{h}_{\alpha\epsilon}(\mathbf{k})\tilde{h}_{\beta\epsilon}(\mathbf{k}') + \delta_{\beta\epsilon}\tilde{h}_{\alpha\epsilon}(\mathbf{k})\tilde{h}_{\gamma\epsilon}(-\mathbf{k}-\mathbf{k}') + \delta_{\alpha\epsilon}\tilde{h}_{\beta\epsilon}(\mathbf{k}')\tilde{h}_{\gamma\epsilon}(-\mathbf{k}-\mathbf{k}') \\ & + \rho_\epsilon\tilde{h}_{\alpha\epsilon}(\mathbf{k})\tilde{h}_{\beta\epsilon}(\mathbf{k}')\tilde{h}_{\gamma\epsilon}(-\mathbf{k}-\mathbf{k}')] + \sum_{\epsilon\sigma\eta}\tilde{c}^{(3)}_{\epsilon\sigma\eta}(\mathbf{k},\mathbf{k}')[\delta_{\alpha\sigma}\delta_{\beta\eta}\delta_{\gamma\epsilon} + \delta_{\beta\eta}\delta_{\gamma\epsilon}\rho_\sigma\tilde{h}_{\alpha\sigma}(\mathbf{k}) \\ & + \delta_{\alpha\sigma}\delta_{\gamma\epsilon}\rho_\eta\tilde{h}_{\beta\eta}(\mathbf{k}') + \delta_{\alpha\sigma}\delta_{\beta\eta}\rho_\epsilon\tilde{h}_{\gamma\epsilon}(-\mathbf{k}-\mathbf{k}') + \delta_{\gamma\epsilon}\rho_\sigma\rho_\eta\tilde{h}_{\alpha\sigma}(\mathbf{k})\tilde{h}_{\beta\eta}(\mathbf{k}') + \delta_{\beta\eta}\rho_\sigma\rho_\epsilon\tilde{h}_{\alpha\sigma}(\mathbf{k})\tilde{h}_{\gamma\epsilon}(-\mathbf{k}-\mathbf{k}') \\ & + \delta_{\alpha\sigma}\rho_\eta\rho_\epsilon\tilde{h}_{\beta\eta}(\mathbf{k}')\tilde{h}_{\gamma\epsilon}(-\mathbf{k}-\mathbf{k}') + \rho_\epsilon\rho_\sigma\rho_\eta\tilde{h}_{\alpha\sigma}(\mathbf{k})\tilde{h}_{\beta\eta}(\mathbf{k}')\tilde{h}_{\gamma\epsilon}(-\mathbf{k}-\mathbf{k}')]. \end{aligned} \tag{17}$$

Now the triplet distribution function is simply given by

$$g^{(3)}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}') = h^{(3)}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}') + h_{\alpha\gamma}(r) + h_{\alpha\beta}(r') + h_{\beta\gamma}(|\mathbf{r}+\mathbf{r}'|) + 1. \tag{18}$$

This represents the BHP approximation for mixtures, and the CA is recovered simply by setting $\tilde{c}^{(3)}_{\sigma\epsilon\eta}(\mathbf{k},\mathbf{k}') = 0$ in Eq. (17).

B. The numerical implementation

Due to the fact that Eqs. (10) and (11), and (12) and (13), respectively are coupled, the evaluation of the functions $t^{\alpha\beta\gamma}_{\alpha\beta}(r)$ is now considerably more complex than in the single component case. In their original work, Barrat, Hansen, and Pastore[7,8] used a steepest descent method where a suitably defined functional of $t(r)$ was minimized to yield a solution of Eq. (7); in fact, the gradients of this functional with respect to variations of the function $t(r)$ could be written down explicitly. In principle, one might proceed in the binary case along similar lines but the construction of the gradients is now considerably more cumbersome.

We have therefore decided to use a different numerical approach to solve both the two decoupled equations and the two sets of coupled equations for the t-functions. Our numerical scheme is based on the GMRESNL[17] as formulated by Fries and Cosnard[18] to solve the OZ equation for molecu-

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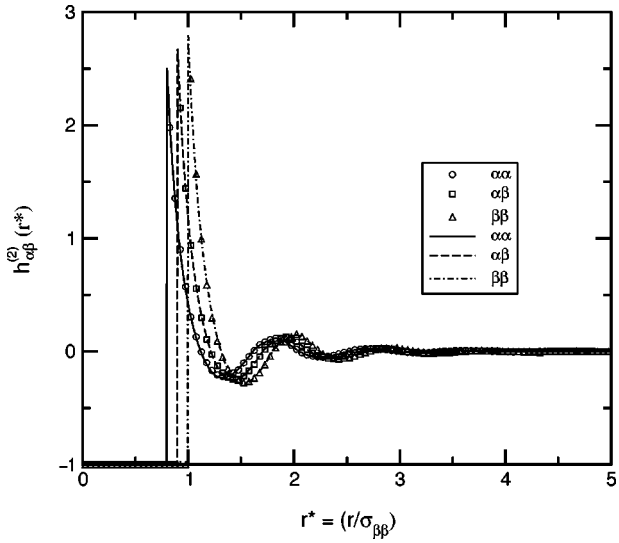

FIG. 1. Pair total distribution functions. Symbols: simulation results, line: OZ with self-consistent VM closure.

lar fluids. This method has two attractive features: (i) it turns out—in particular for the present problem—to be considerably more stable than the steepest-descent method, and (ii) it does not require the determination of the functional derivatives to construct the gradient, which in complex systems like this might represent a formidable task.

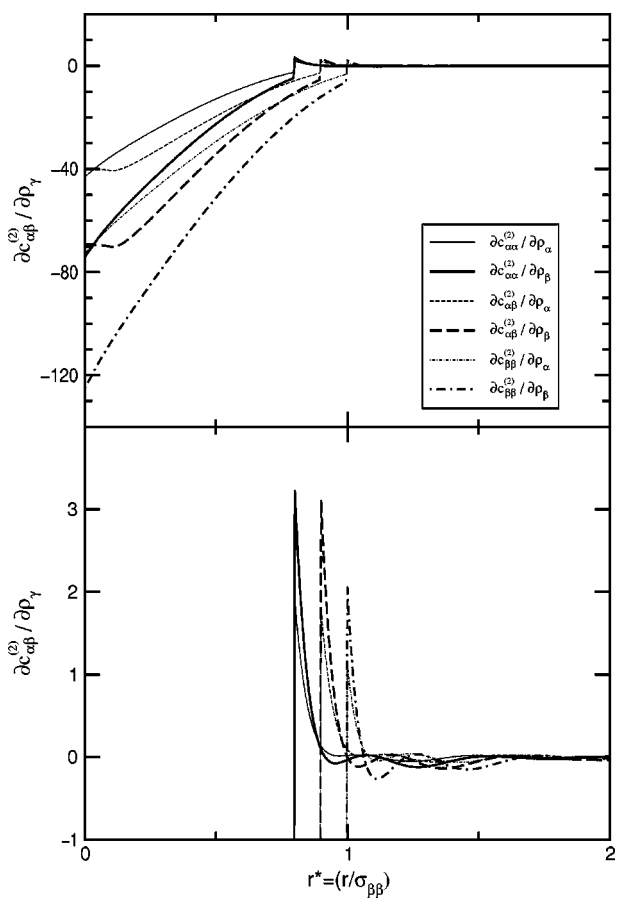

FIG. 2. Density derivatives of the partial pair direct correlation functions at $\eta=0.4$ (upper graph). Zoom of the density derivatives of $c^{(2)}_{\mu\nu}(r)$ (lower graph).

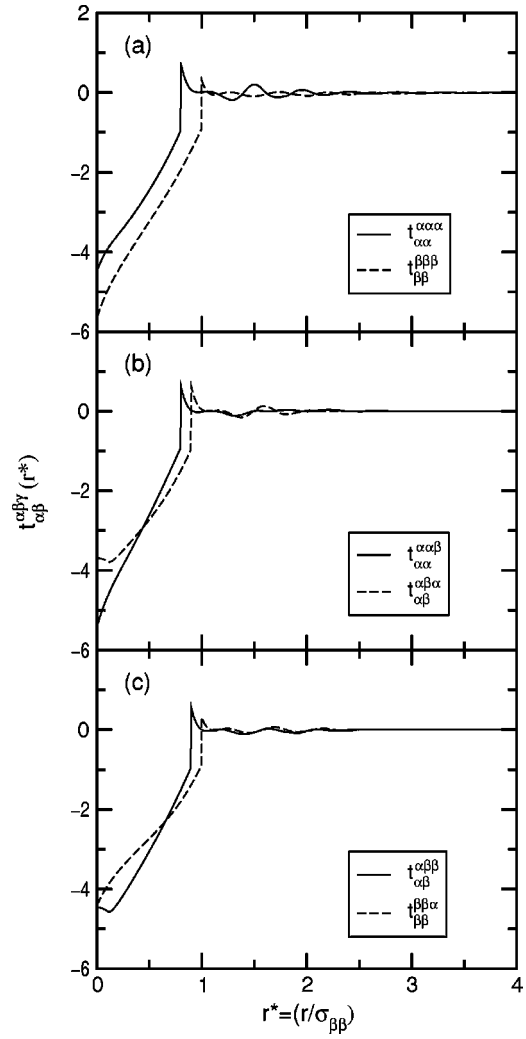

FIG. 3. (a)–(c), $t^{\alpha\beta\gamma}_{\alpha\beta}(r)$'s functions of the BHP factorization ansatz.

We briefly outline the GMRESNL method for the coupled set of Eqs. (10) and (11). Other equations follow similar lines. Introducing a short-hand notation, these equations can be reduced to the following form, omitting the r-arguments

$$C_{\rho_{\alpha\alpha}} - t_{\alpha\alpha}(t_{\alpha\beta} * t_{\alpha\beta}) = 0, \tag{19}$$

$$C_{\rho_{\alpha\beta}} - t_{\alpha\beta}(t_{\alpha\alpha} * t_{\beta\alpha}) = 0, \tag{20}$$

where the given functions $C_{\rho_{\alpha\alpha}}$ and $C_{\rho_{\alpha\beta}}$ represent the density derivatives of the partial direct correlation functions, and the symbol $*$ stands for a convolution. Discretizing the functions on an r-grid and merging the two functions $t_{\mu\nu}$ into a vector $\mathbf{t}$, one searches for the solution of

$$\mathbf{G}[\mathbf{t}] = \mathbf{t} - M[\mathbf{t}] = 0, \tag{21}$$

where $\mathbf{G}[\mathbf{t}]$ is a vector functional of $\mathbf{t}$ and M stands for the convolution operators acting in Eqs. (19)–(20). The

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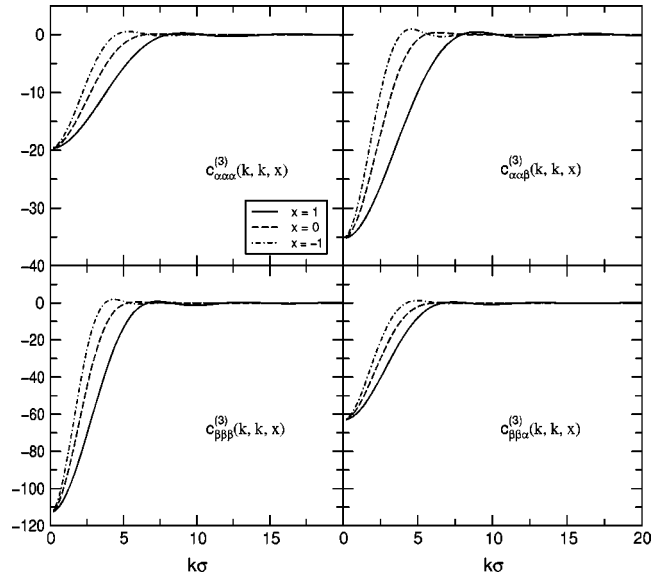

FIG. 4. $c^{(3)}_{\alpha\beta\gamma}(k,k,x)$ vs. $k\sigma$ for the isosceles triangle configuration in a hard-sphere binary mixture at $\eta=0.4$ ($x=\cos\theta$).

directional derivative of $\mathbf{G}$ at some given point $\mathbf{t}$ in the direction $\mathbf{p}$, $\overline{\mathbf{G}}(\mathbf{t};\mathbf{p})$, is given by

$$\overline{\mathbf{G}}(\mathbf{t};\mathbf{p})=\lim_{\epsilon\to 0}\frac{\mathbf{G}[\mathbf{t}+\epsilon\mathbf{p}]-\mathbf{G}[\mathbf{t}]}{\epsilon}=\mathbf{J}_{\mathbf{G}}[\mathbf{t}]\mathbf{p}, \tag{22}$$

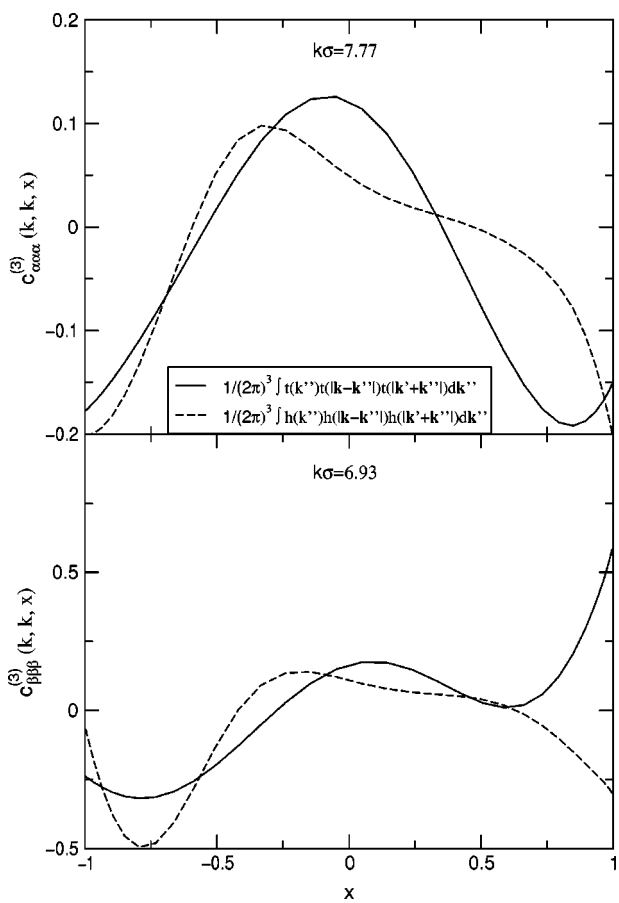

FIG. 5. $c^{(3)}_{\alpha\beta\gamma}(k,k,x)$ vs, x using both Eqs. (5) and (4) for $\eta=0.4$ ($x=\cos\theta$).

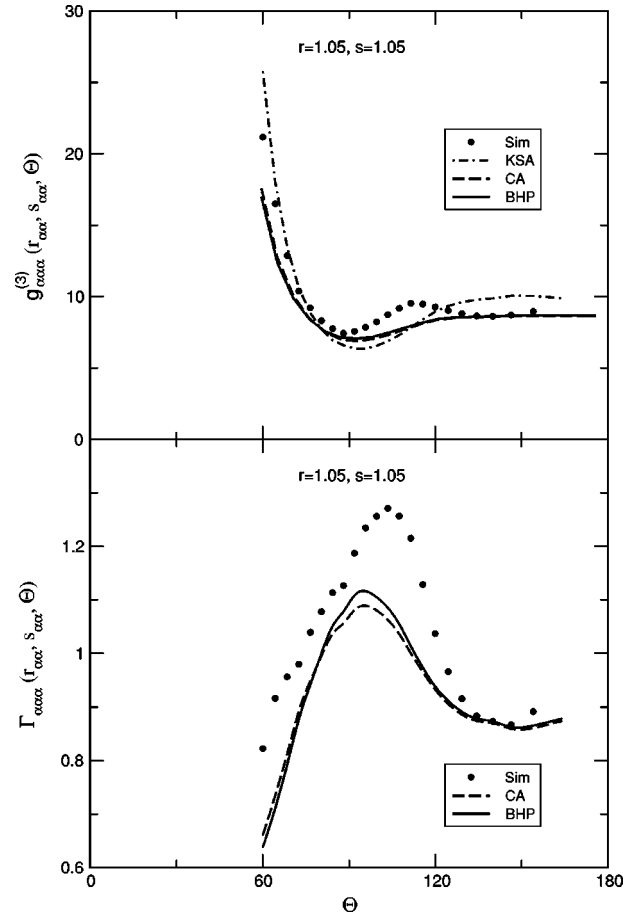

FIG. 6. $g^{(3)}_{\alpha\alpha\alpha}(r_{\alpha\alpha},s_{\alpha\alpha},\theta)$ and $\Gamma_{\alpha\alpha\alpha}(r_{\alpha\alpha},s_{\alpha\alpha},\theta)$ for $\eta=0.4$.

$\mathbf{J}_{\mathbf{G}}$ being the Jacobian matrix of $\mathbf{G}$. We now construct a sequence of $\mathbf{t}_n$, which should tend towards the solution $\mathbf{t}$; they are constructed via

$$\mathbf{t}_{n+1}=\mathbf{t}_n+\delta\mathbf{t}. \tag{23}$$

In principle $\delta\mathbf{t}$ can be calculated from the linearized version of the equation $\mathbf{G}[\mathbf{t}]=0$, i.e., $\mathbf{G}[\mathbf{t}_{n+1}]=\mathbf{G}[\mathbf{t}_n]+\mathbf{J}_{\mathbf{G}}[\mathbf{t}_n]\delta\mathbf{t}=0$, but in practice—in a typical problem we have several thousand grid points—this task (i.e., the inversion of the Jacobian) becomes impossible.

It is therefore more convenient to expand $\delta\mathbf{t}$ in terms of k orthogonal directions $\mathbf{p}_j$, $j=1,\ldots,k$, i.e., $\delta\mathbf{t}=\sum_{j=1}^{k}a_j\mathbf{p}_j$, with

$$\mathbf{p}_0=-\frac{\mathbf{G}[\mathbf{t}_n]}{\|\mathbf{G}[\mathbf{t}_n]\|}. \tag{24}$$

Here $\|\cdot\cdot\|$ denotes the norm of the function, which in the discretized case reduces to the vector modulus. The other $\mathbf{p}_j$'s are determined in a Gram–Schmidt-type orthonormalization procedure. The expansion coefficients a_j are optimized so that $\|\mathbf{G}[\mathbf{t}_n]+\mathbf{J}_{\mathbf{G}}[\mathbf{t}_n]\delta\mathbf{t}\|$ is minimized, i.e.,

$$\|\mathbf{G}[\mathbf{t}_n]+\sum_{j=1}^{k}a_j\mathbf{J}_{\mathbf{G}}(\mathbf{t}_n)\mathbf{p}_j\|=\|\mathbf{G}[\mathbf{t}_n]+\sum_{j=1}^{k}a_j\overline{\mathbf{G}}[\mathbf{t}_n,\mathbf{p}_j]\|. \tag{25}$$

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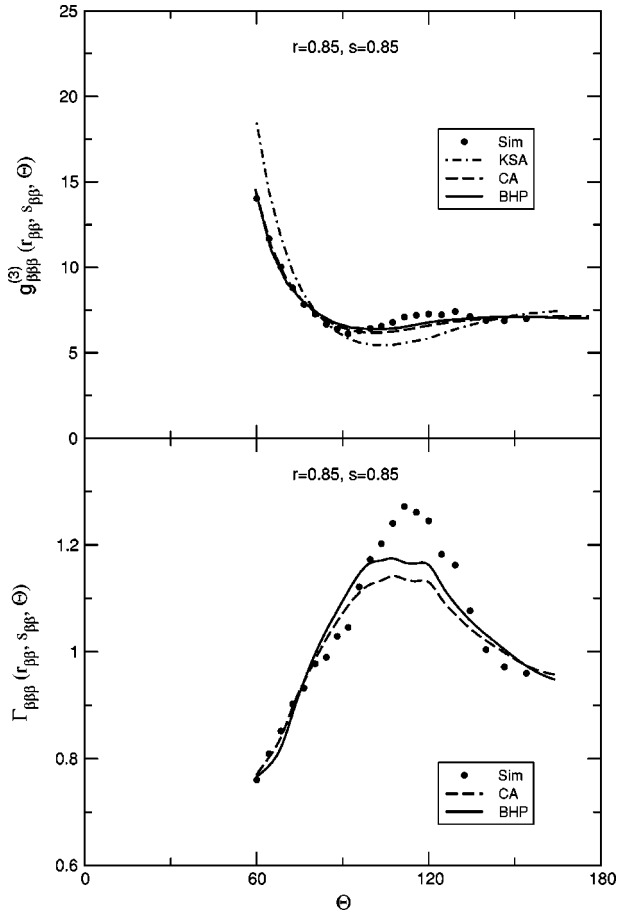

FIG. 7. $g^{(3)}_{\beta\beta\beta}(r_{\beta\beta}, s_{\beta\beta}, \theta)$ and $\Gamma_{\beta\beta\beta}(r_{\beta\beta}, s_{\beta\beta}, \theta)$ for $\eta = 0.4$.

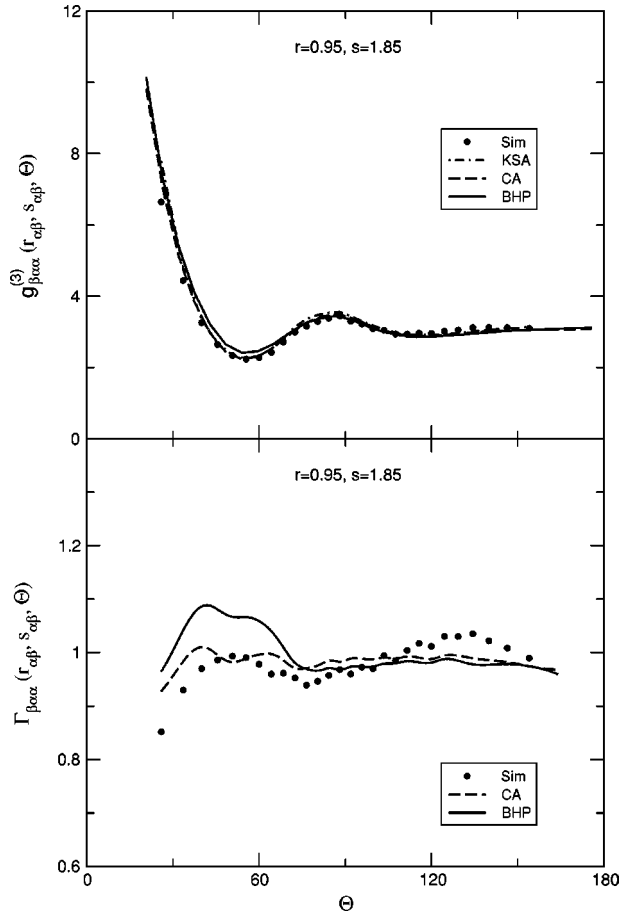

FIG. 8. $g^{(3)}_{\beta\alpha\alpha}(r_{\alpha\beta}, s_{\alpha\beta}, \theta)$ and $\Gamma_{\beta\alpha\alpha}(r_{\alpha\beta}, s_{\alpha\beta}, \theta)$ for $\eta = 0.4$.

The minimization reduces to the solution of a linear set of equations in a_j which can be efficiently dealt with using the QR-decomposition.[23]

The accuracy and stability of the algorithm has been tested initially for simple functions (assuming a simple step function for the t's) and then for our model system. For ϵ we typically set a value of 0.001 and used ten search directions. The functions were discretized on a grid of 2048 points with a mesh size of 0.005σ, where σ is the diameter of the largest sphere in the mixture. Numerical convergence was assumed whenever

$$\frac{\left\| \frac{\partial c^{(2)}}{\partial \rho} - t_n(t_n * t_n) \right\|}{\left\| \frac{\partial c^{(2)}}{\partial \rho} \right\|} < \epsilon, \tag{26}$$

where summation is taken over the grid points of the discretized functions. The value of ϵ was typically of the order of 10^{-10} for the decoupled equations and not larger than 10^{-4} for the coupled case. Depending on the system parameters this was achieved after 10 to 100 iterations.

III. RESULTS

We present results for a binary equimolar mixture of additive hard-spheres with components α and β ($\sigma^*_{\alpha\alpha} = 0.8$, $\sigma^*_{\beta\beta} = 1.0$, being $\sigma^*_i = \sigma_i / \sigma_{\beta\beta}$) and a packing fraction $\eta = (\pi/6)\rho\sigma^3_{\beta\beta} = 0.4$. The simulation results to produce the distribution functions have been obtained from a standard canonical Monte Carlo simulation, and the sampling for the pair and triplet-structure was achieved on a 1100 particle ensemble over 400 configurations.

The pair functions (pair total distribution and direct correlation functions) used to calculate $g^{(3)}_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}')$ in the different approximations were calculated using the OZ equation with a self-consistent closure, implementing virial–isothermal compressibility and chemical potential–virial pressure consistency conditions, derived from Verlet's modified (VM) approximation.[24] The pair distribution functions obtained both from simulation and theory are depicted in Fig. 1, which illustrates the reliability of the theory used on the pair particle level. Alternatively one might resort to a parameterized form of the direct correlation function as typically done in the pure hard-sphere case.[8] This expression although available (see for instance Ref. 25) is not expected to alter significantly the results, given the excellent performance of the self-consistent approximation.

Thus, in the present instance we have calculated $\partial c^{(2)}_{\mu\nu} / \partial \rho_\xi$ using finite differences,

$$\frac{\partial c^{(2)}_{\mu\nu}(r)}{\partial \rho_\xi} = \frac{c^{(2)}_{\mu\nu}(r)(\rho_\xi + \Delta\rho_\xi) - c^{(2)}_{\mu\nu}(r)(\rho_\xi - \Delta\rho_\xi)}{2\Delta\rho_\xi}, \tag{27}$$

with $\Delta\rho_\xi = 0.01$ (see Fig. 2).

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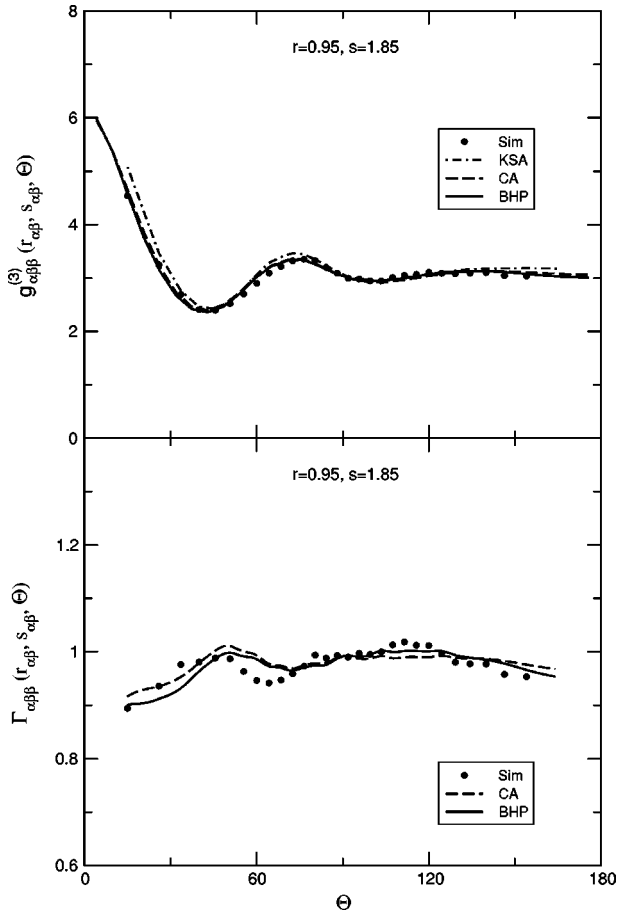

FIG. 9. $g^{(3)}_{\alpha\beta\beta}(r_{\alpha\beta},s_{\alpha\beta},\theta)$ and $\Gamma_{\alpha\beta\beta}(r_{\alpha\beta},s_{\alpha\beta},\theta)$ for $\eta=0.4$.

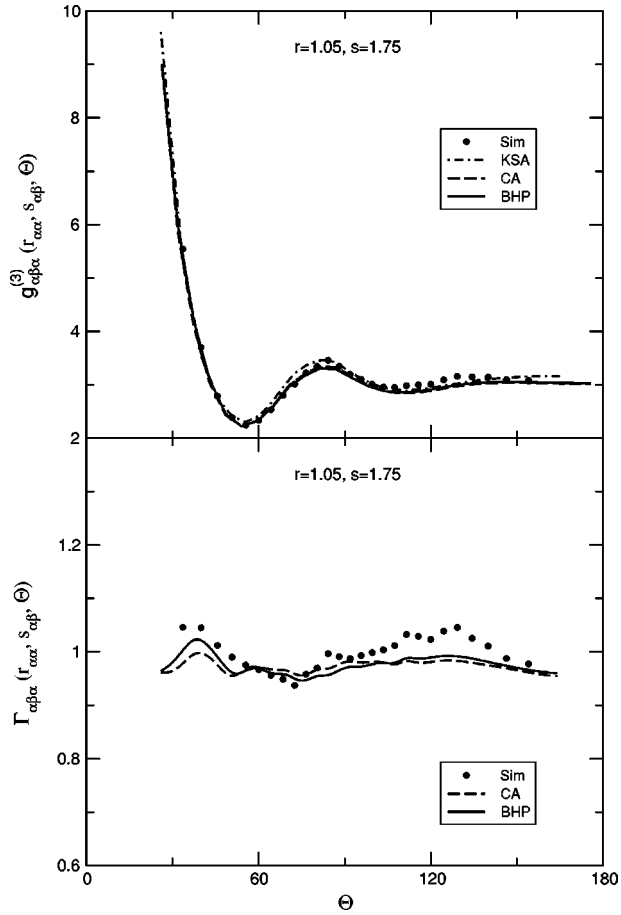

FIG. 10. $g^{(3)}_{\alpha\beta\alpha}(r_{\alpha\alpha},s_{\alpha\beta},\theta)$ and $\Gamma_{\alpha\beta\alpha}(r_{\alpha\alpha},s_{\alpha\beta},\theta)$ for $\eta=0.4$.

Insertion of the corresponding derivatives in Eqs. (9)–(14) leads to the desired t-functions which are plotted in Figs. 3(a)–3(c). As can be seen, the t-functions decay smoothly with r, and exhibit the expected core discontinuity.

In Fig. 4 we present some results of $\tilde{c}^{(3)}_{\alpha\beta\gamma}(k,k',x)$ versus $k\sigma$ for different configurations ($x=\cos\theta=0$, 1, and -1), where θ represents the angle between k and k' in a given isosceles triangle configuration of vectors $\mathbf{k},\mathbf{k}'$, and $\mathbf{k}-\mathbf{k}'$ ($k=k'$). The trends observed are similar to those obtained by Rosenfeld *et al.*[11] for the one-component case.

We include in Fig. 5 results for $\tilde{c}^{(3)}_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}')$ versus $\cos\theta$, where the $\mathbf{k}$ vectors correspond in each case to the first peak in the $\tilde{h}_{\alpha\beta}(k)$ functions. For $\tilde{c}^{(3)}_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}')$ two approximations have been compared: the BHP ansatz, Eq. (5), and the $h^{(2)}$-bond approximation, Eq. (4). If we compare these results with those of Ref. 8 for the one component case, we observe that similar qualitative trends are followed by the two-component mixture. One sees that the $h^{(2)}$-bond approximation agrees qualitatively with the BHP theory, however, much larger discrepancies appear for other k-values not shown here, as was already noticed by Barrat *et al.*[8]

In order to obtain the three-particle distribution functions $g^{(3)}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}')$, it is necessary to calculate the $c^{(3)}$ by means of Eq. (6) and subsequently insert $c^{(3)}$ in Eq. (17) to calculate $h^{(3)}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}')$. The first four terms in Eq. (17) are directly Fourier inverted, and the remaining term is calculated numerically by means of the Hankel–Legendre transform, as already shown in Eq. (A3) of Ref. 26.

When studying the three-particle distribution functions it is common to express its ratio with respect to the KSA,

$$\Gamma(r,s,t)=g^{(3)}(r,s,t)/g^{(2)}(r)g^{(2)}(s)g^{(2)}(t), \tag{28}$$

which somehow represents the deviation from the ideal behavior.

The results of $g^{(3)}_{\alpha\beta\gamma}(r,s,\theta)$ for various theories and simulation together with the corresponding $\Gamma(r,s,\theta)$ ratio are shown for the different configurations in Figs. 6–11. One can see that for the configurations near contact the values of $g^{(3)}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}')$ differ considerably from the KSA estimates. In these cases the Γ-function systematically exhibits a characteristic shape with a marked maximum. As expected, departures from the KSA decrease when the interparticle separation in the triplets is increased, which is clearly illustrated by the r-dependence of the $\Gamma(r,s,\theta)$ function. It is to be noticed that the same features have been observed in the one-component case in a previous work by Bildstein and Kahl.[26] In the present mixture case, for each configuration it can be seen that the CA and BHP results represent a considerable improvement over the KSA. In general, the BHP theory exhibits a better agreement with simulation than the CA in certain regions, for instance in the neighborhood of the

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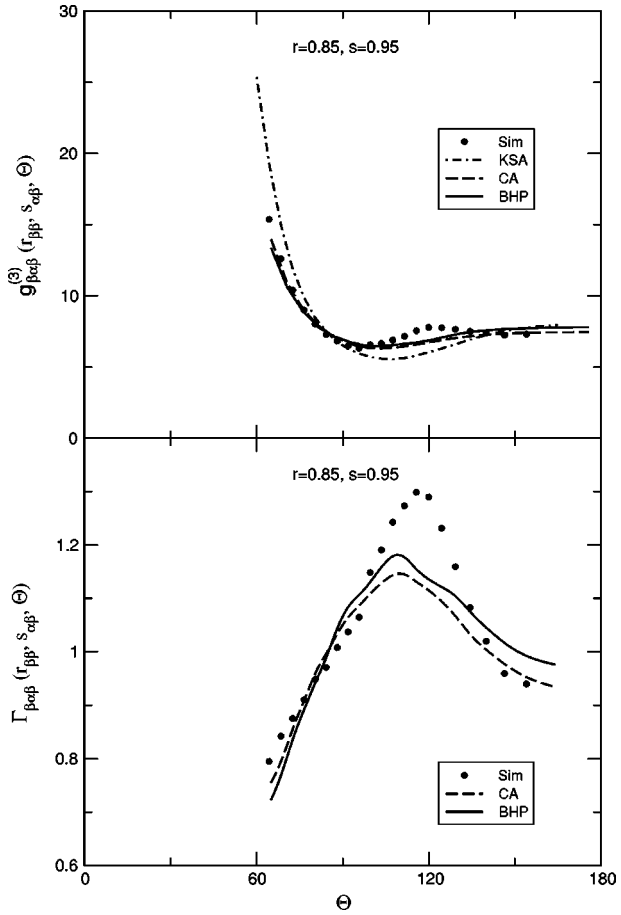

FIG. 11. $g^{(3)}_{\beta\alpha\beta}(r_{\beta\beta}, s_{\alpha\beta}, \theta)$ and $\Gamma_{\beta\alpha\beta}(r_{\beta\beta}, s_{\alpha\beta}, \theta)$ for $\eta = 0.4$.

$\Gamma(r,s,\theta)$ maximum for contact triplets. However, it can also be seen that precisely for these configurations the situation is reversed at low angles.

IV. CONCLUSION

In this article it has been shown that the BHP theory represents an improvement in the description of the triplet structure in fluid mixtures, as found already for pure fluids.[26] The main output of the theory is the direct correlation function, and it remains to be explored whether the results furnished for the hard sphere mixture improve the description of the freezing phenomena in mixtures, by incorporating terms in the density expansion on the three-body level. However, as far as the triplet distribution is concerned, we note here that the improvement over the much simpler CA is relatively small. It will be interesting to see whether the extension to mixtures of other approaches successful in one-component systems like Attard's[6] PY3 or Rosenfeld's theory[10] might also yield a better description of the three-particle distribution function as well as the triplet direct correlation function. Work on these issues is planned.

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