# Inhomogeneous integral equation approach to pair and triple correlations in a glass-forming simple liquid

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A simple model of glass-forming liquid modeled via Dzugutov's pair potential is studied by means of the triplet hypernetted chain approximation as formulated by Attard [P. Attard, J. Chem. Phys. **93**, 7301 (1990)]. This system, which is known to be mostly dominated by microscopic icosahedral ordering, eludes a correct description in terms of classical two-body integral equation theories. However, it is found here that the simple hypernetted chain approximation when applied at the three-particle level can yield a correct semiquantitative description of both the pair and triplet structure of the supercooled state, capturing features which escape more sophisticated closures implemented on the two-particle level.

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## I. INTRODUCTION

Icosahedral ordering (Ih) is known to play an essential role in the glass formation in simple systems [1,2]. However in single-component systems, nucleation of crystallites strongly competes with the glass transition and therefore most metallic glasses presenting long-range icosahedral ordering turn out to be multicomponent systems, whose structure is mostly conditioned by the presence of short-range chemical ordering. Nonetheless, in the early 1990s Dzugutov [3] introduced a model pair potential which considerably facilitated the study of the glass transition by means of molecular-dynamics (MD) simulations stabilizing the short-range icosahedral ordering by precluding competing crystalline configurations. This potential is relatively short ranged and is characterized by the presence of two repulsive ranges and one attractive region. This functional form is not too different from that of some metallic effective potentials (for instance, the aluminum potential proposed by Dagens, Rasolt, and Taylor [4]) and in that sense it is not completely unrealistic. Moreover, it has been suggested that colloidal interactions might be tuned to reproduce the functional form of the Dzugutov potential and thus finally render a colloidal glass. The explicit form of this Ih potential is

$$V(r)=u_1(r)+u_2(r),$$

$$u_1(r)=\begin{cases} A(r^{-m}-B)\exp\left(\dfrac{c}{r-a}\right) & r<a \\ 0 \quad r\geqslant a, \end{cases} \tag{1}$$

$$u_2(r)=\begin{cases} B\exp\left(\dfrac{d}{r-b}\right) & r<b \\ 0 \quad r\geqslant b, \end{cases}$$

where the parameters, in reduced units, are collected in Table I.

Aside from the initial studies in supercooled liquids [3] as precursors of the glass transition, this model has also been used in studies of the freezing transition [5,6], where it was found that the observed solid structure was a monoatomic dodecagonal quasicrystal. Quite recently, Roth and Denton [7] have carried out a detailed simulation and perturbation theory study of the solid phases of the Dzugutov potential.

This remarkably simple potential is perfectly suitable to be studied from the standpoint of liquid state theoretical methods. Preliminary calculations carried out by us indicate that when the system is well within the liquid phase domain (far away from the glass transition), standard integral equations like the reference hypernetted chain equation [8](RHNC), or the self-consistent Zerah-Hansen [9](ZH) approximation can accurately reproduce the pair structure of the fluid, which is by no means surprising. However, when cooling the liquid down below the melting point in such a way the crystallization is precluded, we drive the system into a metastable phase. This undercooled liquid is considered to be precursor of the glass transition and shows, as in glasses, a dominant short-range icosahedral ordering [3] which is exhibited in the splitting of the second coordination shell and in turn translates into the appearance of a marked shoulder in the second maximum of the pair-distribution function. This feature, which is strongly correlated with the glass transition in the Dzugutov liquid, cannot be captured by either the RHNC or the ZH approximations. This is obviously due to the lack of a proper bridge function [10] (or functional, if one is to use Rosenfeld's universality principle of the bridge functional) reflecting the underlying symmetry of the system. Undoubtedly a hard sphere fluid is a poor reference system for an undercooled fluid with Ih ordering.

Moreover, it is clear that the way in which a closure relation like the hypernetted chain approximation (HNC) incorporates the pair potential into the formalism, is not adequate to account for the angular correlations which deviate so much from the full symmetry of fcc-like or bcc-like phases. However, if a similar approximation is introduced at

TABLE I. Parameters of the Dzugutov pair potential.

| *m* | *A* | *c* | *a* | *B* | *d* | *b* |
|---|---|---|---|---|---|---|
| 16 | 5.82 | 1.1 | 1.87 | 1.28 | 0.27 | 1.94 |

 

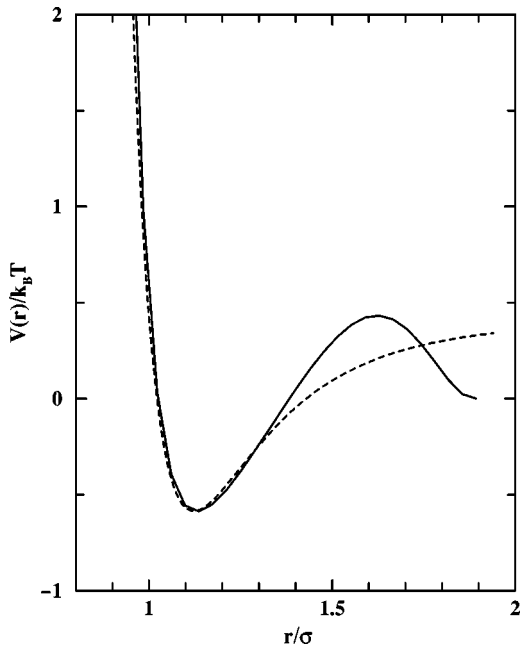


FIG. 1. The two pair potentials used in this work, Ih given by Eq. (1) (solid line) and LJ (dashed line), are plotted together for the sake of comparison. The latter one has been artificially shifted to illustrate the coincidence of both potentials around the minimum and core region.

the three-particle level, even the simple HNC closure will contain direct information regarding the competition between different layers or coordination shells for different triplet configurations. Therefore, we have here explored the inhomogeneous Ornstein-Zernike (OZ) approach proposed by Attard [11,12] to study three-body correlation using Percus source particle method. Within this approach, one can get the density profile, i.e., the new pair-correlation function, using an exact relation like the Triezenberg-Zwanzig-Lovett-Mou-Buff-Wertheim (TZLMBW) equation [13] or the first equation in the Born-Green hierarchy (BG) [14]. Here we have used the former alternative coupled with a HNC closure, which is known as HNC3 (or TZLMBW-HNC3) approach.

We will see that the simple HNC closure, when applied at the three-particle level, is able to capture features in the pair-correlation function (and even in the triplet distribution function) which escape two-particle approximations. For comparison we have also performed calculations for a truncated Lennard-Jones (LJ) fluid ($R_c = 1.94\sigma$, with $\sigma$ being the LJ range parameter) for the state $T^* = k_B T/\epsilon = 0.73$ and $\rho^* = \rho\sigma^3 = 0.85$ for which reference results were available in the literature [15] and which happens to be very close to the corresponding thermodynamic state of interest in the supercooled Ih liquid [3]. This LJ system is obviously well behaved and two-particle approximations yield already excellent results.

In summary, three different cases are presented in this work, namely (a) Truncated LJ potential at $\rho^* = 0.85$ and $T^* = 0.73$ (LJ); (b) Ih pair potential at $\rho^* = 0.88$ and $T^* = 1.60$ (Ih normal liquid); (c) Ih pair potential at $\rho^* = 0.88$ and $T^* = 0.50$ (Ih supercooled liquid).The two potentials are plotted together in Fig. 1.

The rest of the paper is sketched as follows. In Sec. II we summarize the essentials of the inhomogeneous integral equation approach for two and three-body correlations and its numerical implementation is also discussed. Finally, computer simulation details and our most significant results are presented in Sec. III.

## II. INHOMOGENEOUS INTEGRAL EQUATION APPROACH

### A. The formalism

The source particle method of Percus [16] was applied by Attard [11] in order to take advantage of the inhomogeneous integral equation treatments so as to calculate triplet correlation functions. Basically, it reduces to consider a tagged particle as source of an external potential and then use an exact relation between one- and two-particle properties in the presence of external potentials (either the BG equation [14] or one of the TZLMBW equations [13]). Three-particle properties are evaluated by solving the OZ equation supplemented with a given closure. The approximation implicit in the closure corresponds to the three-particle level and it thus turns out to be considerably more accurate when computing two-particle properties. Some examples of the efficiency of this approach using different closure relations for LJ and hard-sphere (HS) fluids can be found in Refs. [15] and [17,18], respectively.

As mentioned before, in this method a given particle in a triplet is considered as the source of an external field, and is therefore responsible for the inhomogeneities in the system that should reflect in the integral equation. One can then calculate density profiles and pair distribution functions conditioned to this particle being taken as a source. Since this source particle is identical to other system particles these quantities are actually two- and three-body properties of the fluid.

The inhomogeneous OZ equation establishes the relationship between the total correlation function $h_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ and the direct correlation function $c_0^{(2)}(\mathbf{r_1},\mathbf{r_2})$ in the presence of the inhomogeneity,

$$h_0^{(2)}(\mathbf{r_1},\mathbf{r_2}) = c_0^{(2)}(\mathbf{r_1},\mathbf{r_2}) + \int d\mathbf{r_4}\rho(\mathbf{r_4})c_0^{(2)}(\mathbf{r_1},\mathbf{r_4})h_0^{(2)}(\mathbf{r_4},\mathbf{r_2}). \quad (2)$$

Although the third particle (source particle) does not explicitly appear in the integral equation, it is implicit in the notation $f_0(\mathbf{r_1},\mathbf{r_2})$ which indicates that particles 1 and 2 are subject to the external potential induced by particle 0. As a consequence, the inhomogeneous pair functions obtained from Eq. (2), $g_0^{(2)}(\mathbf{r_1},\mathbf{r_2})$ represent conditional probabilities which can be used to calculate the three-body distribution function $g^{(3)}$,

$$g^{(3)}(r_0,r_1,r_2) = g^{(2)}(r_1)g^{(2)}(r_2)g_0^{(2)}(\mathbf{r_1},\mathbf{r_2}). \quad (3)$$

while the inhomogeneous density profile will yield the bulk pair-distribution function.

In the present problem the system has axial symmetry because the external potential depends only on the separation from the origin (source). The pair potential $V(r_{12})$ [see Eq. (1)], in the reference frame of the source particle, depends on the distances of the particles from the source and the angle between them. This axial symmetry makes possible to express the integral equation in terms of the polar coordinates

$$s^{(2)}(r_1,r_2,\theta_{12}) = h^{(2)}(r_1,r_2,\theta_{12}) - c^{(2)}(r_1,r_2,\theta_{12}) = \int dr_4 \rho(r_4) c^{(2)}(r_1,r_4,\theta_{14}) h^{(2)}(r_4,r_2,\theta_{42}). \tag{4}$$

As long as three unknown functions are present in Eq. (4), two more equations are needed. One of them is the closure relation connecting the pair potential and the direct correlation function, and the other is the density profile governed by the external field.

Among the possible closures containing translationally invariant functions, and therefore suitable for this problem, the HNC approximation has been used:

$$h^{(2)}(r_1,r_2,\theta_{12}) = \exp[h^{(2)}(r_1,r_2,\theta_{12}) - c^{(2)}(r_1,r_2,\theta_{12}) - \beta V(r_1,r_2,\theta_{12})] - 1, \tag{5}$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature. A hybridized closure, the Zerah-Hansen [9] approach,

$$g^{(2)}(r_1,r_2,\theta_{12}) = \left\{ 1 - \frac{\exp[m(r_{12})(-v_{\mathrm{att}}(r_1,r_2,\theta_{12}) + s^{(2)}(r_1,r_2,\theta_{12}))] - 1}{m(r_{12})} \right\} \exp[-\beta v_{\mathrm{rep}}(r_1,r_2,\theta_{12})] \tag{6}$$

was also used for the LJ case for which it was found to be very accurate. Here $m(r_{12}) = 1 - \exp(-\alpha r_{12})$ and the mixing parameter $\alpha$ is obtained requiring thermodynamic consistency in the approximation at the two-particle level. The interaction potential has been split into repulsive, $v_{\mathrm{rep}}(r)$, and attractive, $v_{\mathrm{att}}(r)$, contributions using the Weeks-Chandler-Andersen decomposition [19]. Following Attard [11], a Legendre transformation is applied to all the angular functions as

$$\hat{f}_n = \frac{2n+1}{2} \int_{-1}^{1} d(\cos\theta) f(\cos\theta) P_n(\cos\theta), \tag{7}$$

$$f(\cos\theta) = \sum_{n=0}^{\infty} \hat{f}_n P_n(\cos\theta), \tag{8}$$

by which the OZ decouples into

$$\hat{h}_n(r_1,r_2) - \hat{c}_n(r_1,r_2) = \frac{4\pi}{2n+1} \int_0^{\infty} dr_4 r_4^2 \hat{c}_n(r_1,r_4) \rho(r_4) \hat{h}_n(r_4,r_2). \tag{9}$$

The density profile has been evaluated via the TZLMBW relation [13]

$$\nabla \rho(\mathbf{r_1}) = -\beta \rho(\mathbf{r_1}) \nabla V(\mathbf{r_1}) - \beta \rho(\mathbf{r_1}) \int d\mathbf{r_2} \rho(\mathbf{r_2}) h(\mathbf{r_1},\mathbf{r_2}) \nabla V(\mathbf{r_2}). \tag{10}$$

After projection of the gradient onto the appropriate direction and integrating over the angular coordinates, the expression above reads

$$\frac{\partial \rho(r_1)}{\partial r_1} = -\beta \rho(r_1) \frac{\partial V(r_1)}{\partial r_1} - 2\pi\beta\rho(r_1) \times \int_{-1}^{1} dx \int_0^{\infty} dr_2 r_2^2 \rho(r_2) h^{(2)}(r_1,r_2,x) x \frac{\partial V(r_2)}{\partial r_2}. \tag{11}$$

Once the Legendre transformation is applied, Eq. (11) reduces to

$$\frac{\partial \rho(r_1)}{\partial r_1} = -\beta \rho(r_1) \frac{\partial V(r_1)}{\partial r_1} - \frac{4\pi\beta\rho(r_1)}{3} \int_0^{\infty} dr_2 r_2^2 \rho(r_2) \hat{h}_1(r_1,r_2) \frac{\partial V(r_2)}{\partial r_2}. \tag{12}$$

### B. Numerical details

The Legendre transforms and the convolution in Eq. (9) constitute the core of the computational costs in this type of calculation. Following Attard we have used a discretized orthogonal version of the Legendre transform, where the nodes of the angular integration are defined by the roots of the Legendre polynomial $P_n(x)$, if the Legendre series include all $P_l(x)$ with $l \leq n$. These transforms have been evaluated using between 60 and 80 roots by means of the quick Legendre transform algorithm suggested in Ref.[11]. The treatment of long ranges follows the ideas proposed by Attard [12] and Fushiki [15], resorting to a replacement of the inhomogeneous distribution functions by their bulk phase counterparts beyond certain cutoff distance, $r_c$ (in this case $r_c = 6\sigma$).

For simple cases, convergence is sufficiently fast using a mixing iterates algorithm, but for the stringent conditions which correspond to a supercooled state, we had to resort to a more effective numerical approach, namely the generalized minimal residual algorithm for nonlinear systems of equations [20]. It basically considers the solution of

$$\mathbf{G}[\mathbf{s}]=\mathbf{s}-\mathbf{M}[\mathbf{s}]=0, \tag{13}$$

where $\mathbf{G}[\mathbf{s}]$ is a vector functional and $\mathbf{M}$ represents the operations involving the OZ equation supplemented by the closure. The elements of $\mathbf{s}$ are the coefficients $s_l(r_1,r_2)$, thus 60 coefficients discretized over 150 grid points will use up 1/2 $60\times150\times150$ words of memory. The previously defined function $\mathbf{s}$, in the $(n+1)^{th}$ iteration is estimated by

$$\mathbf{s}_{n+1}=\mathbf{s}_n+\delta\mathbf{s} \tag{14}$$

and $\delta\mathbf{s}$ is expanded in terms of $k$ orthogonal polynomials which define search directions, $\mathbf{p}_j$, $j=1,\ldots,k$, i.e., $\delta\mathbf{s}=\Sigma_{j=1}^{k}a_j\mathbf{p}_j$, being $\mathbf{p}_0=-\mathbf{r}_0/||\mathbf{r}_0||$ $(\mathbf{r}_0=\mathbf{s}-M[\mathbf{s}])$ and the subsequent $\mathbf{p}_j$ obtained by Gram-Schmidt orthogonalization. The coefficients $a_j$ are optimized so that the norm

$$||\mathbf{G}[\mathbf{s}_n]+\sum_{j=1}^{k}a_j\overline{\mathbf{G}}[\mathbf{s}_n,\mathbf{p}_j]|| \tag{15}$$

is minimized. $\overline{\mathbf{G}}(\mathbf{s};\mathbf{p})$ is the directional derivative of $\mathbf{G}$ at the given point $\mathbf{s}$ in the direction $\mathbf{p}$. For the present problem the optimal balance between storage and efficiency is achieved using five search directions. Note that memory use has to be optimized, since each search direction will occupy the same amount of storage as each set of coefficients $f_l(r_1,r_2)$.

As to the external TZLMBW equation, the Broyles mixing iterative procedure has proven to be efficient enough to guarantee convergence. The particle exchange symmetry in the inhomogeneous pair functions for a given configuration with fixed source particle introduces some simplifications in the calculation, and one of them is the reduction of memory requirements. Thus a typical single precision calculation using 160 grid points for the two radial coordinates of the triplet configuration, 60 angular grid points and five search directions requires about 45 Mb of storage.

## III. RESULTS

In this work, classical MD simulations sampling the canonical ensemble ($NVT$) were performed for comparison purposes, making use of the DL-POLY program [21]. All the systems consisted of 1372 particles embedded in a cubic box with periodic boundary conditions. In particular, the LJ system was simulated at constant reduced density, $\rho^*=0.85$ and $T^*=0.73$. The icosahedral system was simulated at constant reduced density, $\rho^*=0.88$ at both $T^*=1.6$ and $T^*=0.5$, which correspond to a proper liquid and a supercooled state, respectively. The latter was reached by a stepwise equilibrium cooling coupling the system to a heat bath at $T_b^*(t)$. Then we cooled the system linearly in time, $T_b^*(t)=T_s^*-\gamma t$, with $\gamma$ being the cooling rate, and $t$ the simulation time,

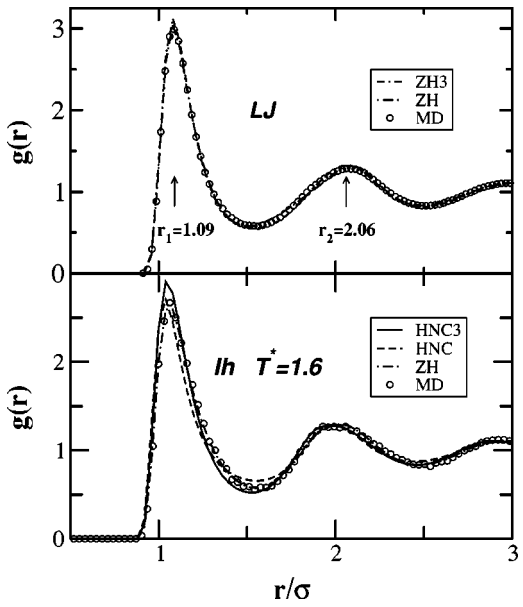


FIG. 2. Pair-distribution functions for LJ system at $T^*=0.73$ (upper frame) and Ih normal liquid case at $T^*=1.6$ (lower frame), obtained both from different theoretical approaches and MD computer simulation.

using a Berendsen thermostat. The system was cooled with $\gamma=4\,10^{10}$ s$^{-1}$ from $T^*=1.6$ down to the supercooled state.

The simulated pair-correlation functions for the LJ system are shown in the upper frame of Fig. 2 together with various theoretical approaches used. One can see that the ZH approach is in extraordinary agreement with the simulation data. If one implements the ZH approximation on the three-particle level to obtain a corresponding ZH3 approach, the results are completely indistinguishable from the simple ZH. Note that the mixing parameter $\alpha$ in the ZH3 is obtained from the two-particle approximation, since the calculation of the isothermal compressibility from the inhomogeneous approach is not accurate enough [12] to implement a thermodynamic consistency loop.

The same can be said for the Ih pair potential in the liquid state $(T^*=1.6)$, whose pair-distribution functions are depicted in the lower graph of Fig. 2. In the latter case one sees that the use of the HNC3 improves upon the pair HNC, as was already established by Attard [12]. Nonetheless the HNC3 is still outperformed by the ZH and RHNC approximations.

Now when the system is cooled down the situation radically changes. First, the ZH equation is unable to reach thermodynamic consistency achieving a minimum discrepancy for $\alpha=0$, i.e., for the soft mean spherical approximation (SMSA). These results together with a RHNC calculation using Lado's free energy optimization criterium for the reference hard-sphere fluid diameter, are presented in Fig. 3. One immediately appreciates that the pair approximations completely miss the clear shoulder appearing on the second coordination sphere, feature which results from the cooling process. Now, on the three-particle level, we observed that implementation of the SMSA yields rather poor results, not included in Fig. 3. This is not surprising given its linear

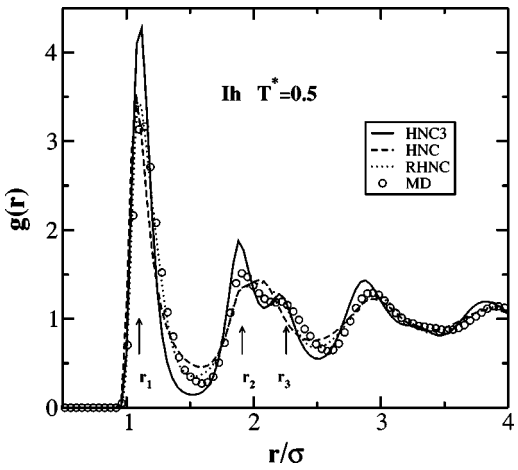


FIG. 3. Pair-distribution functions for Ih supercooled liquid at $T^*=0.5$, obtained both from different theoretical approaches (see text) and MD computer simulations.

nature. On the other hand, the HNC3, although misses somewhat the intensity of the peaks, reproduces the exact position and shape of the shoulder in the second coordination sphere. As mentioned before, this shoulder is a direct consequence of the cooling process and results from the preferential icosahedral ordering of the Dzugutov's supercooled system, which is not present either in the height *T* Ih or LJ liquids. It seems now evident that a correct geometric description of a supercooled structure of a glass-forming system requires approximations at the three-particle level, in particular since the icosahedral ordering strongly deviates from the hard-sphere high density liquid which furnishes the reference system in approximations like the RHNC.

In order to provide some insight into the triplet structure, we have analyzed the behavior of the function $\tau(r,s,t)=\ln[g^{(3)}(r,s,t)/g(r)g(s)g(t)]$. The denominator of the argument is nothing but Kirkwood's superposition approximation (KSA), i.e., the simplest approach for $g^{(3)}(r,s,t)$. Then $\tau(r,s,t)$ is essentially an excess triplet potential of mean force if one considers that the KSA represents the low density (ideal) limit of the three-body correlations. The $\tau(r)=\tau(r,r,r)$, for equilateral triangle configurations, at distances $r$ corresponding to the positions of the first peaks of $g(r)$, are shown in Fig. 4 comparing the LJ liquid with the Ih supercooled case. The departure of $\tau(r)$ from zero measures the correction to the KSA, a positive value means that the triplet is more probable than is predicted by the KSA, and on the contrary, a negative value indicates that such triplets occur less frequently than predicted by the classical ansatz. In the LJ liquid, the HNC3 results are in a good agreement with simulation results particularly at short distances, confirming the remarkable performance of this approximation for this type of system [12,18]. On the other hand, we observed that in the Ih supercooled case the deviations from the KSA are strongly positive at short distances. This and other features of the $\tau(r)$ are qualitatively reproduced by the HNC3. The deviations, which are considerable, can mostly be ascribed to the discrepancies in the amplitude of the $g(r)$, which are magnified in the triple product occurring in the denominator

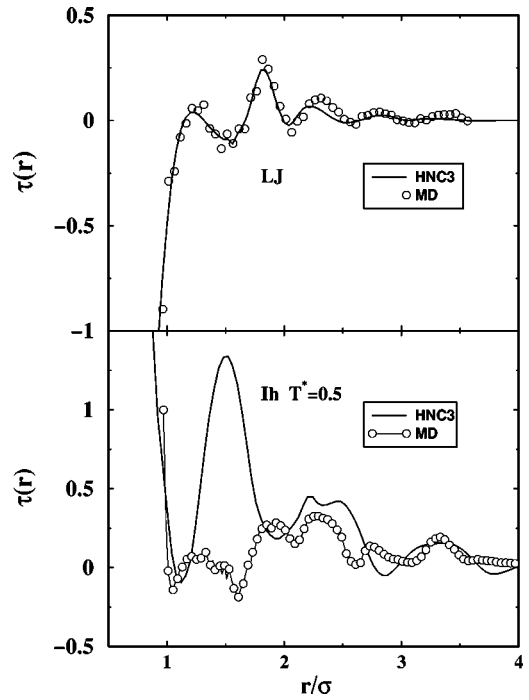


FIG. 4. $\tau(r)$ calculated from the HNC3 approach is compared with MD simulation results, both for the LJ case and the Ih supercooled liquid.

of $\tau(r)$. This is further confirmed below, where triple correlations are directly analyzed and a better agreement is exhibited.

Another alternative to provide a 3D image of the short-range topology of the systems under study is by calculating the triplet correlation function of isosceles triangle configurations, i.e., $g^{(3)}(r,s,\theta)$, with $r=s$, where $\theta$ is the angle between **r** and **s**. These functions have also been computed

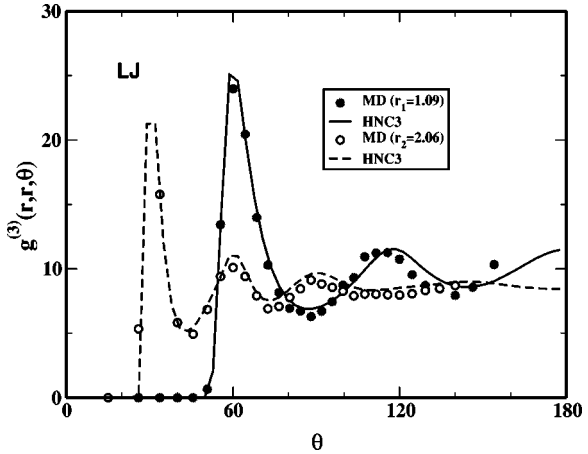


FIG. 5. Theoretical and simulation results of the triplet correlation function of isosceles triangle configurations for the LJ case are plotted vs $\theta$ at the $r$ values corresponding to the first two maxima of $g(r)$ (see Fig. 2). Those values are specified within the legend box. The intensity of $g^{(3)}(r,r,\theta)$ for $r_2=2.06$ has been multiply by 5 to be plotted at the same $y$ axis scale as the one corresponding to the first coordination shell.

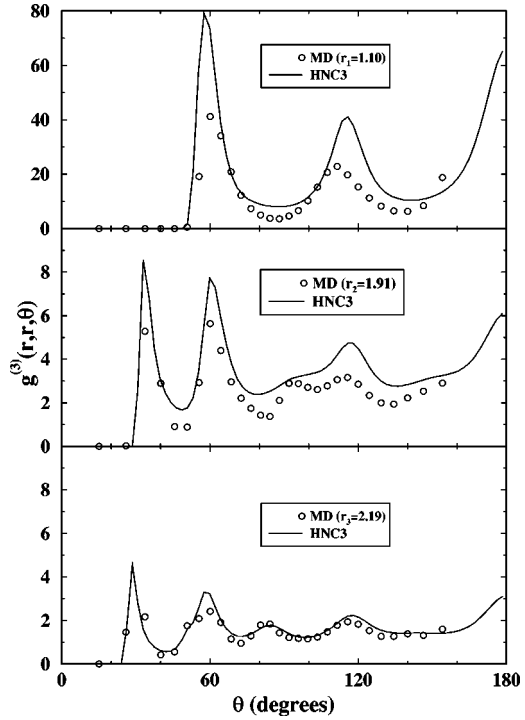


FIG. 6. The same as Fig. 5 for the Ih supercooled case. For the sake of clarity each $r$ value, corresponding to the first two maxima of $g(r)$ plus the position of the shoulder of the second peak (see Fig. 3), are depicted from up to bottom frames (see legend boxes).

and shown in Fig. 5 and 6 for the LJ fluid and Ih supercooled system, respectively. The chosen values of $r$ correspond to the first two maxima of $g(r)$ and the position of the shoulder in the Ih supercooled liquid. Now, the agreement, both for the LJ and Ih cases, is fair. There is a substantial difference in the three-body correlation of the LJ fluid and the Ih supercooled case, in particular the maximum corresponding to the second coordination sphere correlations present around 100° (90° in the LJ fluid) is split in two (110°-120° and 80°-90°) in the latter case. This, in principle, might be ascribed to the larger coordination of the Ih supercooled liquid, and it is correctly reproduced by the HNC3 approximation. It is not obvious whether the five maxima in $g^{(3)}(r,s,\theta)$ for the second-neighbor shell can be correlated with the fivefold-coordination characteristic of icosahedral ordering, but this feature should nonetheless be born in mind for a more detailed geometrical analysis.

In summary, in this work we have analyzed the performance of the inhomogeneous Ornstein-Zernike approach using a HNC closure to determine the pair and triplet structure in a system characterized by an icosahedral short-range ordering that considerably deviates from ''classical'' well behaved liquids like the LJ or HS fluids. This type of system, which proves difficult to tackle in terms of two-particle approximations, is amenable to be described by the HNC3 approach. This indicates that the three-body geometric information implemented in the inhomogeneous closure is essential for a correct description of this class of fluids and presumably glasses. Thus, this approach will be relevant to study other glass-forming systems, in particular highly asymmetric and non additive mixtures. Work on these issues is in progress.

## ACKNOWLEDGMENTS

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[21] DL-POLY is a parallel molecular-dynamics simulation package developed at Daresbury Laboratory by W. Smith and T.R. Forester under the auspices of the former Engineering and Physical Sciences Research Council. The package is property of the Council for the Central Laboratory of the Research Councils.