

Triplet structure of simple liquids

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A recent comparison of computer simulation data for the triplet structure of hard spheres has revealed that an approach proposed by Attard (the so-called PY3 approximation or “source particle method”) has to be considered at present as the most reliable method available for the determination of the triplet distribution function $g^{(3)}$ of a simple liquid. This holds not only for general three particle arrangements but in particular for those configurations where at least two particles are in direct contact, i.e., where usually the largest discrepancies between different theories are observed. In an effort to study the influence of the interatomic potential on the applicability of the method, we have determined the triplet structure of two classes of simple liquids, namely, soft spheres and liquid metals: we thus varied softness and range of the repulsive potential and the long-ranged attractive potential. In general, agreement with computer experiment is found to be excellent; only for very soft potentials are small discrepancies encountered.

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I. INTRODUCTION

Both improved numerical resources as well as the fact that triplet correlations *do* play an important role in a more reliable description of several physical phenomena (such as, e.g., melting [1]) have lead during recent years to an increased interest in the triplet structure of simple liquids as such. Several methods, proposed during the past 30 years for the determination of the triplet structure [expressed in terms of the triplet distribution function (tDF) $g^{(3)}(r, s, t)$] have been implemented recently; for an overview we refer the reader, e.g., to [2]. In parallel, extensive computer simulations have been performed to test the reliability of the numerical methods [2–5]. From these studies, which have been realized in particular on a large scale for hard spheres [2,4], it was found that the PY3 method proposed by Attard [6] [or named in a similar context “source particle method” (SPM) [7,8], a name to which we will stick in this contribution] represents at present the most reliable method: in comparison with computer experiments excellent agreement was found not only for general configurations but also for particle arrangements where at least two of the three particles are in direct contact. Such configurations, corresponding to the direct contact of the pair case, are — both in the pair and triplet case — known to be very sensitive to the method.

The aim of this contribution is to pass beyond hard spheres and to apply this method to more realistic liquids and to compare the SPM results with computer simulation data, representing thus a more stringent test for the reliability of the numerical method. For this purpose we have chosen soft spheres and liquid metals. With these two types of liquids we have the possibility of varying both the attractive and the repulsive part of the interactions: (i) for soft spheres [$\Phi(r) = \varepsilon (\frac{\sigma}{r})^n$] we can vary the strength (via ε) or equivalently the density [via $\Gamma = \rho\sigma^3(\varepsilon\beta)^{3/n}$, ρ being the number density] and the

softness (via n). We chose three different n values (4, 8, and 12) and for every softness parameter one to three Γ values, approaching as close as possible (from the numerical point of view) towards the freezing point [9]; (ii) with liquid metals, on the other hand, we can study the influence of the characteristic long-ranged Friedel oscillations on the numerical reliability of the method. The two liquid metals, Rb and Ge (just above their respective melting points 373 K and 1250 K), show some characteristic topological disorder: Rb is a typical close-packed liquid metal with approximately 11 nearest neighbors [10], while in Ge — as a reminder of the semiconducting state — an open structure at least for temperatures near the melting point is preferred [11]. This will also be reflected in the triplet structure by the formation of characteristic three particle configurations. These findings were substantiated by calculation of the *pair* structure of both metals along with a close analysis of the number of nearest neighbors [12]. Similar results were also obtained in *ab initio* simulations for liquid Ge [13]. Lennard-Jones systems which also would be appropriate candidates for such a study have already been treated by Fushiki [8]. In this context we would like to point out that a proper determination (i.e., realistic in comparison with experimental data) of the triplet structure of a liquid as Ge would require the inclusion of three-body forces. One of the major drawbacks of the SPM is that its formalism — at least at the present stage — includes two-body forces only. Since our simulations are based on pair forces, too, we find that a comparison on the basis of such forces is legitimate while, on the other hand, we do not claim that such a description is ready for a comparison with experimental structure data.

In this contribution we present results for the triplet structure of the liquids described above; these data were obtained by using the SPM proposed by Attard [6], which we will outline below. These results are complemented by simulation data which serve as a criterion for the reliability of the results. The most crucial parameter which

limits the applicability of the method from the numerical point of view is the range of the potential: for very soft potentials ($n=4$) with Γ values close to the freezing point convergence of the procedure becomes — despite several tricks applied — impossible. As we decrease the strength of the potentials and/or make the potentials more repulsive, no problems at all were encountered. For liquid metals the long-ranged Friedel oscillations do not pose any problems. Summarizing we can say that in all cases where convergence could be achieved we find very satisfactory agreement with results of computer data. Finally, the results for the pair and the triplet structure obey — within numerical accuracy — the required sum rules.

The paper is organized as follows: in the subsequent section we briefly discuss the SPM (leaving, however, a closer discussion to the original paper) and give a few details about our simulations; in Sec. III we discuss the results. The paper is closed with concluding remarks.

II. THE NUMERICAL METHODS

A. The source particle method (SPM)

The SPM is based on an idea of Percus [14] which allows one to relate the distribution functions of a homogeneous N -particle system [characterized by a pair interaction $\Phi(r)$ and a density ρ] with those of an inhomogeneous $(N + 1)$ -particle system by adding a particle

fixed at the origin representing the source of an external field. If the interaction of this particle is identical to $\Phi(r)$, then the *inhomogeneous* one-particle density is related to the pair distribution function (pDF) of the *homogeneous* system via $\rho^{(1)}(\mathbf{r}) = \rho g^{(2)}(0, \mathbf{r}|0)$ and the pDF of the *inhomogeneous* system is given in terms of the tDF of the *homogeneous* system via [14]

$$g^{(2)}(0, \mathbf{r}_1|0)g^{(2)}(0, \mathbf{r}_2|0)g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g^{(3)}(0, \mathbf{r}_1, \mathbf{r}_2|0). \quad (1)$$

The Ornstein-Zernike (OZ) relation for the inhomogeneous system reads

$$\begin{aligned} y^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \int d^3r_3 c^{(2)}(\mathbf{r}_1, \mathbf{r}_3)\rho^{(1)}(\mathbf{r}_3)h^{(2)}(\mathbf{r}_3, \mathbf{r}_2), \end{aligned} \quad (2)$$

where $h^{(2)}$ and $c^{(2)}$ are the total and the direct correlation functions. Equation (2) is solved along with a suitably chosen closure relation. While Attard used in his original paper a Percus-Yevick (PY) closure (generalized to functions in two arguments), we rather stick here to the generalized HMSA closure [i.e., interpolation between HNC and soft mean spherical approximation (SMSA)] [15], as also done by Fushiki [7,8]. This relation was generalized by Kjellander and Sarman [16] to the inhomogeneous case. Our choice is justified by our experience that the HMSA is known to give very reliable results for the pair structure of liquid metals [17]. The closure relation reads

$$g(\mathbf{r}_1, \mathbf{r}_2) = \exp[-\beta\Phi_0(\mathbf{r}_1, \mathbf{r}_2)] \left\{ 1 + \frac{\exp\{f_\alpha(\mathbf{r}_1, \mathbf{r}_2)[h(\mathbf{r}_1, \mathbf{r}_2) - c(\mathbf{r}_1, \mathbf{r}_2) - \beta\Phi_1(\mathbf{r}_1, \mathbf{r}_2)]\} - 1}{f_\alpha(\mathbf{r}_1, \mathbf{r}_2)} \right\}, \quad (3)$$

where $\Phi_0(r)$ and $\Phi_1(r)$ are the attractive and repulsive part of the pair interaction $\Phi(r)$ in the sense of Weeks, Chandler, and Andersen [18]. Equation (3) also includes the Rogers-Young (RY) closure [19] [interpolating between the hypernetted chain approximation (HNC) and PY] for the case $\Phi_1(r) = 0$, as it is found for soft spheres; the SMSA then becomes the PY approximation. The mixing function $f_\alpha(\mathbf{r}_1, \mathbf{r}_2)$ was assumed to depend on the distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ only, with the functional form $f_\alpha(r_{12}) = 1 - \exp[-\alpha|\mathbf{r}_1 - \mathbf{r}_2|]$. α — being a positive parameter — interpolates between the HNC ($\alpha = \infty$) and the SMSA-PY ($\alpha = 0$). In the pair case α is determined to guarantee thermodynamic self-consistency between two equations of state [15,17].

In practice, for an efficient evaluation of the integral in (2) for a spherically symmetric potential $\Phi(r)$, Attard proposed [6] an expansion of the correlation functions in terms of Legendre polynomials, $P_n(\cos \vartheta)$, e.g.,

$$h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = h^{(2)}(r_1, r_2, \vartheta) = \sum_{n=0}^{\infty} \hat{h}_n(r_1, r_2) P_n(\cos \vartheta), \quad (4)$$

ϑ being the angle enclosed by \mathbf{r}_1 and \mathbf{r}_2 . If we now use a well-known relation between the Legendre polynomials, then the OZ equation (2) becomes

$$\begin{aligned} \hat{y}_n(r_1, r_2) &= \frac{4\pi}{2n+1} \int_0^\infty dr_3 r_3^2 \hat{c}_n(r_1, r_3) \\ &\quad \times \rho^{(1)}(r_3) \hat{h}_n(r_3, r_2). \end{aligned} \quad (5)$$

The coefficient functions \hat{c}_n , \hat{h}_n , and \hat{y}_n are calculated from $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, $h^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, and $y^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ according to (4) using a discrete Legendre transform proposed by Attard on 32 ϑ points limiting thus n in (4) to 31. The r grid (Δr , see below) covers 200 (soft spheres) and 150 (liquid metals) points in each dimension.

Numerical errors introduced by truncating the integrals in (5) are minimized following an idea of Fushiki [7,8]: by subtracting the homogeneous OZ relation from the inhomogeneous one and assuming that the homogeneous and inhomogeneous correlation functions are identical for distances larger than a given R , one finally obtains the approximate relation

$$\begin{aligned}
\hat{y}_n(r_1, r_2) &= \hat{y}_n(r_1, r_2|0) \\
&+ \frac{4\pi}{2n+1} \left(\int_0^R dr_3 r_3^2 \hat{c}_n(r_1, r_3) \rho^{(1)}(r_3) \right. \\
&\times \hat{h}_n(r_3, r_2) - \rho \int_0^R dr_3 r_3^2 \hat{c}_n(r_1, r_3|0) \\
&\left. \times \hat{h}_n(r_3, r_2|0) \right). \quad (6)
\end{aligned}$$

The input for the homogeneous distribution functions is taken from computer experiment. The coupled integral equations (3) and (6) are solved iteratively until self-consistency in the following sense is achieved: let

$$\|y^{[j]}\| = \sqrt{\left[\sum \hat{y}_n^{[j]}(r_1, r_2) \right]^2}, \quad (7)$$

where j numbers the iteration cycle and the sum ranges over all n values and the entire (r_1, r_2) grid, then $\|y^{[j]} - y^{[j-1]}\|/\|y^{[j]}\|$ was required to be less than 10^{-5} . Usually a satisfactory convergence in the above sense was obtained after 130 to 200 iterations. For some systems investigated a slight dependence of the convergence speed on the actual value of α was observed.

In solving these equations still an arbitrariness remains in the actual value α appearing in the closure relation (3). One possibility would be to use the exact relation (sum rule)

$$\begin{aligned}
-\frac{\partial}{\partial r_{12}} g^{(2)}(r_{12}) - \frac{\partial}{\partial r_{12}} \left(g^{(2)}(r_{12}) \beta \Phi(r_{12}) \right) \\
= 2\pi\rho \int_{-1}^1 d(\cos \vartheta_{23}) \\
\times \int_0^\infty dr_{13} r_{13}^2 \left[\frac{\partial}{\partial r_{13}} \beta \Phi(r_{13}) \right] \\
\times g^{(3)}(r_{12}, r_{13} \cos \vartheta_{23}) \cos \vartheta_{23} \quad (8)
\end{aligned}$$

$[\beta = 1/(k_B T)]$ for a check of the internal consistency between the pDF and tDF. However, this relation turns out to be not too sensitive to the actual value of α . We have therefore chosen α to be the value which minimizes $\sum_i |g^{\text{MD}}(r_i) - g^{\text{HMSA}}(r_i; \alpha)|$ (sum over grid points). Comparison with computer simulation justifies this choice (see below). For actual calculations or if computer simulation data are not available we propose to fix α by some self-consistency criterion [15,20] since these results have proven to be as accurate as computer simulation data [21].

B. The computer simulation

The computer simulation data were obtained in standard molecular-dynamics (MD) runs: we used 1372 particle ensembles; the sampling of the pDF and tDF has been done every 20 time steps and the simulation has been extended over 4000 time steps. Special care has been taken to avoid the counting of self-correlations in the triplet case (cf., [2,5]). The final results and estimates of the

numerical error were determined by averaging over four independent runs.

III. RESULTS

A. Soft spheres

The parameters of the soft sphere systems investigated in this study are compiled in Table I, along with the values for α , which were determined according to our criterion described above; the interactions are displayed in Fig. 1. The pair potentials are given by

$$\Phi(r) = \varepsilon \left(\frac{\sigma}{r} \right)^n. \quad (9)$$

The system is usually characterized by n and the coupling parameter $\Gamma = \rho\sigma^3(\varepsilon\beta)^{3/n}$. In our study we considered three different n values (4, 8, and 12); Γ actually limits the applicability of the method: we present results for the largest Γ 's for which we could obtain numerical convergence of the SPM. For larger Γ values, i.e., systems closer to the freezing point [9], the numerical algorithm breaks down, despite all of the numerical care taken. The R values [cf., Eq. (6)] and the grid size are compiled in Table II.

For the softest potentials ($n=4$) three different Γ values were considered (cf., Table I). For $\Gamma = 4$ the peak height of the pDF amounts to ~ 2.2 , which shows that the system is rather dense. Figure 2 shows the tDF $g^{(3)}(r, s, \vartheta)$ as a function of ϑ for (r, s) values which correspond to nearest neighbor distances, i.e., for distances where the pDF shows a maximum and where — according to our experience from the hard sphere case — the largest differences between different approaches are encountered. In fact, pure closure relations (HNC and SMSA-PY) differ strongly. If we use a mixed closure relation (in this case the generalized RY closure) we obtain — along with our criterion for the choice of the mixing parameter α — rather good agreement: only a slight phase shift for $\vartheta \sim 100^\circ$ and small differences in the peak height remain. The fact that the simulation data are rather close to the HNC results confirms what we know from the pair case: also there the HNC gives reliable results for soft and/or long-ranged potentials. This tendency is also nicely reflected in the values of the mixing parameters α , compiled in Table I: the soft systems have a rather large value for α (signifying a large HNC component), while

TABLE I. Parameters of the soft sphere systems investigated in this study.

n	Γ	$\alpha\sigma$
4	4	1.68
	2.18	1.76
	1	1.65
8	1.5	0.83
	1	0.86
12	0.862	0.56

the more repulsive systems are characterized by distinctly smaller α 's, i.e., a dominating PY-SMSA contribution. For larger particle distances (r, s) (not displayed here) and less dense systems ($\Gamma = 2.18$ and $\Gamma = 1$; cf., Fig. 2) agreement between the SPM and computer simulation is excellent. Again large differences between the pure closures are observed.

As we increase Γ we encounter numerical problems: convergence of the procedure becomes impossible. Not even a very careful use of the procedure (careful mixing of input and output of subsequent iterations for pair and triplet structure and/or increasing Γ stepwise until the desired values are reached) could overcome these problems. These facts unambiguously point out the limits of the SMP.

For the more repulsive systems ($n = 8$ and $n = 12$) we observe the expected results (Figs. 3 and 4): differences between the curves for the pure closures are now smaller as we increase n ; agreement between the computer simulations and the mixed closure is very satisfactory, even for larger Γ values. This holds in particular

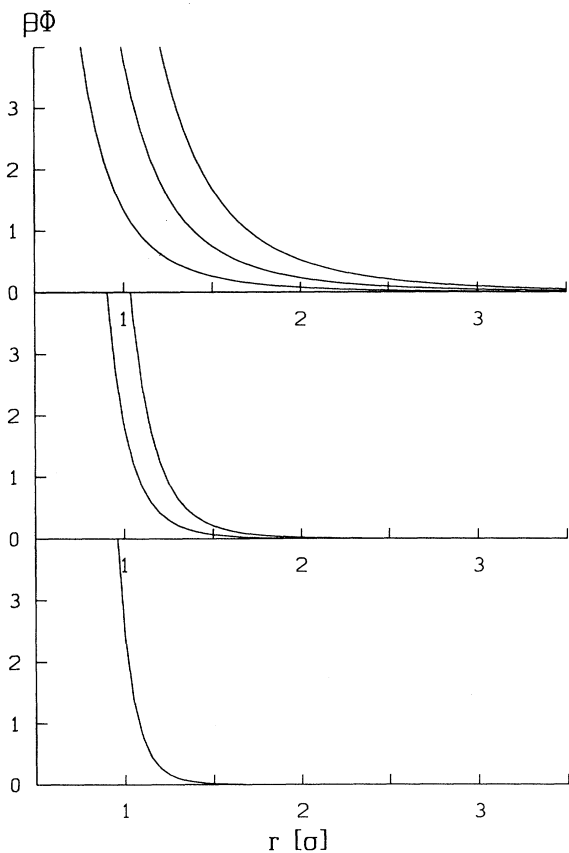


FIG. 1. Reduced dimensionless pair potentials for the soft sphere systems investigated in this study as functions of r/σ ; from top to bottom: $n = 4$ ($\Gamma = 4, 2.18, \text{ and } 1$; from left to right), $n = 8$ ($\Gamma = 1.5 \text{ and } 1$; from left to right) and $n = 12$ ($\Gamma = 0.862$).

for crucial particle configurations (r, s, ϑ) with $r \sim s \sim$ nearest neighbor distance and $\vartheta \sim 60^\circ$. As the configurations expand the differences between the pure and mixed closures vanish and good agreement with computer simulation is observed.

We have also checked the internal consistency of our calculation by using the sum rule (8): in Fig. 5 we present the results for the left-hand side and the right-hand side of Eq. (8) (in arbitrary units). The system chosen is characterized by $n = 8$ and $\Gamma = 1.5$; similar results were found for the other systems. Within numerical accuracy (taking into account the error bars indicated for the simulation data in Figs. 2-4 and 7 and 8) we obtain reason-

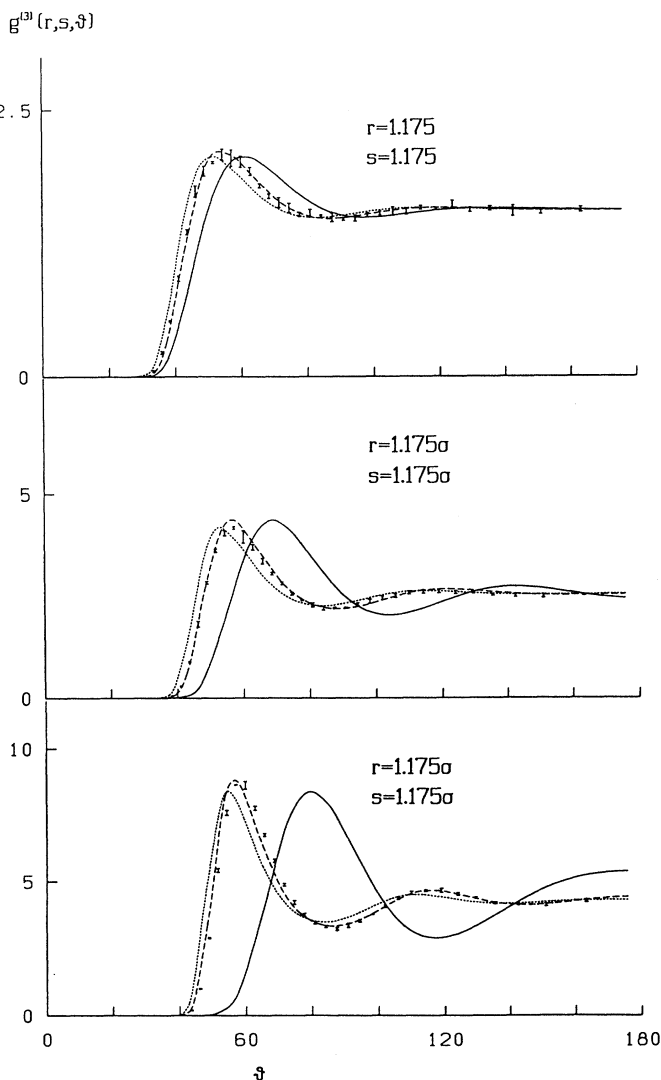


FIG. 2. tDF $g^{(3)}(r, s, \vartheta)$ for three different soft sphere systems ($n = 4$) as functions of ϑ for the (r, s) values as indicated: $\Gamma = 1, 2.18, \text{ and } 4$ (from top to bottom). 1.175σ corresponds to the nearest neighbor distance. Symbols (including error bars): computer simulation results; lines: dotted line ($\alpha = \infty$), full line ($\alpha = 0$), and broken line (α as listed in Table I; cf., text).

TABLE II. Range parameter R [cf., integrals in Eq. (6)], grid spacing Δr for the SPM integrations, and Δt , the time step of the simulations for the systems investigated in this study (in units as indicated). m is the mass of the particles.

System	R	Δr	Δt
Soft spheres	5σ	0.025σ	$0.01\sigma^{-1}\epsilon^{-1/2}m^{-1/2}$
Rb	15 Å	0.1 Å	5 fs
Ge	9.375 Å	0.0625 Å	3 fs

able agreement; discrepancies in the region of the first peak stem from the limited accuracy of the required differentiation of the simulation data for the pDF in that region.

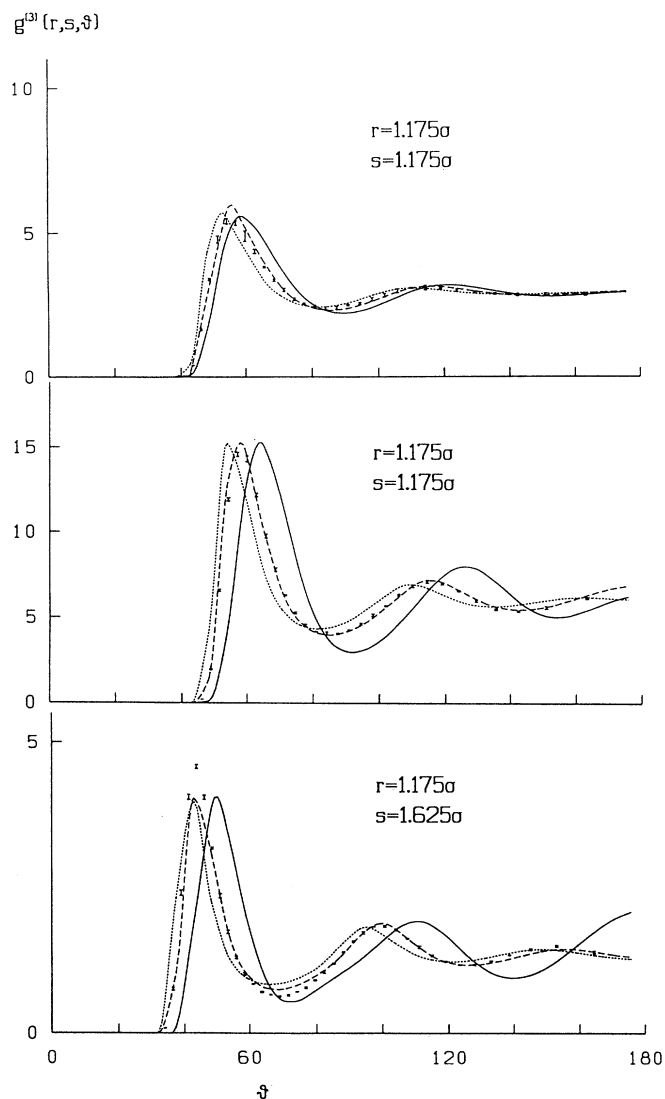


FIG. 3. tDF $g^{(3)}(r, s, \vartheta)$ for three different soft sphere systems ($n = 8$) as functions of ϑ for the (r, s) values as indicated: $\Gamma = 1$ (top) and 1.5 (middle and bottom). 1.175σ corresponds to the nearest neighbor distance, 1.625σ to the first minimum in the pDF. Symbols (including error bars): computer simulation results; lines: dotted line ($\alpha = \infty$), full line ($\alpha = 0$), and broken line (α as listed in Table I; cf., text).

B. Liquid metals

The liquid metals investigated are Rb and Ge just above their respective melting points (373 K for Rb and 1250 K for Ge). The potentials $\Phi(r)$ are based on pseudopotential theory [22], using the Ashcroft empty-core pseudopotential [23] and the expressions of Ichimaru and Utsumi [24] for the local field correction. The core radii are those usually used in literature [22]. The potentials, displayed (along with the pDF obtained in the computer experiment) in Fig. 6, show the characteristic long-ranged Friedel oscillations. Note that $\Phi_{\text{Ge}}(r)$ has a turning point at the distance of the nearest neighbors ($a_{\text{Ge}} \sim$

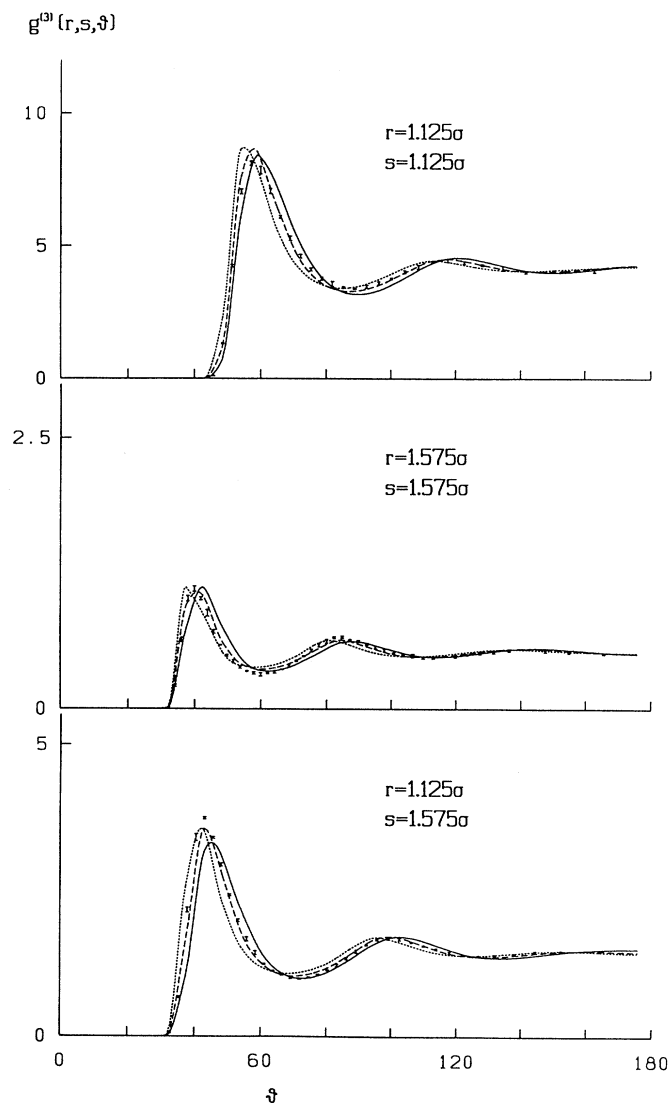


FIG. 4. tDF $g^{(3)}(r, s, \vartheta)$ for three different soft sphere systems ($n = 12$) as functions of ϑ for the (r, s) values as indicated: $\Gamma = 0.862$. 1.175σ corresponds to the first minimum in the pDF, 1.575σ to the second nearest neighbor distance. Symbols (including error bars): computer simulation results; lines: dotted line ($\alpha = \infty$), full line ($\alpha = 0$), and broken line (α as listed in Table I; cf., text).

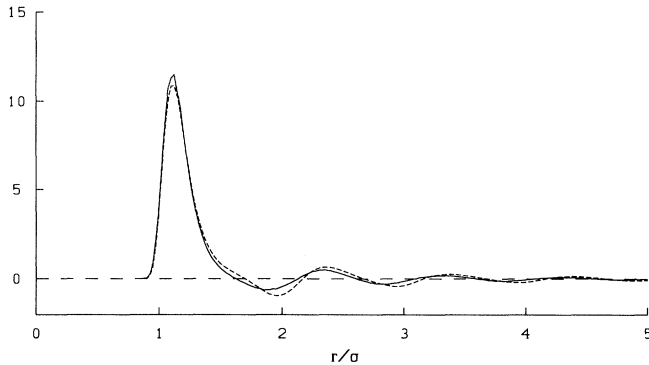


FIG. 5. A check of the internal consistency (via the sum-rules) of our results: left-hand side (full line) and right-hand side (broken line) of Eq. (8) as a function (in arb. units) of r in arbitrary units for a soft sphere system characterized by $n = 8$, $\Gamma = 1.5$, and the optimal α value (cf. Table I).

2.8 \AA) while for $\Phi_{\text{Rb}}(r)$ a pronounced minimum is observed.

Using our proposed criterion for the choice of the mixing parameter we found α to be 0 (i.e., a pure SMSA closure relation) for the case of Rb and $\alpha = 0.5 \text{ \AA}^{-1}$ for Ge. In an effort to give the reader an impression to what extent the closures SMSA and HNC are mixed we have displayed in Figs. 7 and 8 results for the tDF for our choice of α and for the pure closures HNC ($\alpha = \infty$) and SMSA ($\alpha = 0$).

The Rb results for $g^{(3)}(r, s, \vartheta)$ are depicted in Fig. 7 for the following (r, s) pairs as functions of the enclosed angle ϑ : $(4.9, 4.9)$ and $(5.1, 5.1)$, for r and s near the position of the main peak of the pDF; $(8.9, 8.9)$, r and s near the position of the second peak of the pDF; $(4.9, 8.9)$, r being the nearest neighbor distance and s the second nearest neighbor distance. Results are displayed for the mixing parameter $\alpha = \infty$ and 0, the latter being “our” choice for the closure relation (see above). In all four cases we find a very good agreement between the SPM data with computer results and it is obvious that $\alpha=0$ represents a better choice than $\alpha = \infty$. Note the characteristic peak for $\vartheta = 120^\circ$ for those cases where r and s correspond to the nearest neighbor distance: this indicates that the particles tend to arrange in triplet configurations of a close-packed structure.

In Fig. 8 we present the Ge data for the following (r, s) pairs: $(2.8125, 2.8125)$, $(2.5625, 2.5625)$, $(4.1875, 4.1875)$, and $(2.8125, 4.3125)$. The four cases correspond to the particle arrangements discussed above for Rb. Besides the simulation results we have depicted SPM results with three different mixing parameters for the closure relation (2), i.e., 0 (pure SMSA), ∞ (pure HNC), and 0.5 \AA^{-1} , the latter being the mixing parameter of our choice (see above). Again we observe a distinct dependence of the results on the mixing parameter. In all cases displayed (and other configurations investigated) we find that this special choice of α yields the best agreement with com-

puter data. If we consider triangular configurations with $r \sim s \sim a_{\text{Ge}}$ we observe — besides the trivial peak for $\vartheta \sim 60^\circ$ — a side maximum near 109° . This angle corresponds to a tetragonal configuration at the nearest neighbor distance in Ge and may be understood very nicely in terms of the preferred distances in Ge: for this choice of r and s , side t (being opposite to ϑ in this isosceles triangle) is the second nearest neighbor distance in Ge.

We would like to take this opportunity to mention that a realistic description of the pair or triplet structure of liquid Ge would of course require the inclusion of three-body forces. At its present stage the formulation of the SPM only includes pair forces. The main aim of this contribution is *not* a comparison of the triplet structure of the “realistic” Ge but a check of the reliability of the

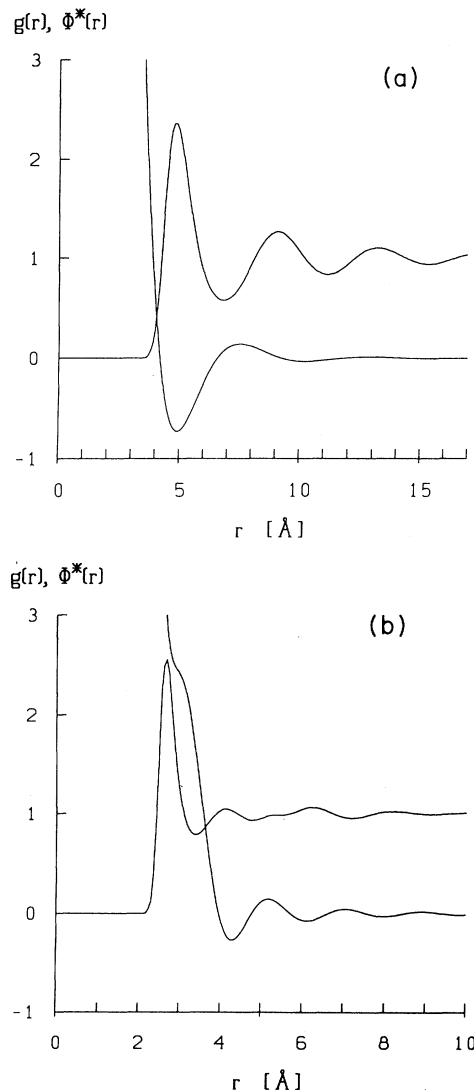


FIG. 6. Reduced dimensionless pair potentials $\Phi^*(r) = \beta\Phi(r)$ and pDFs $g(r)$ as functions of r for Rb (a) and Ge (b) as obtained from the computer experiment. $\beta = 1/k_B T$, with $T = 373 \text{ K}$ for Rb and $T = 1250 \text{ K}$ for Ge.

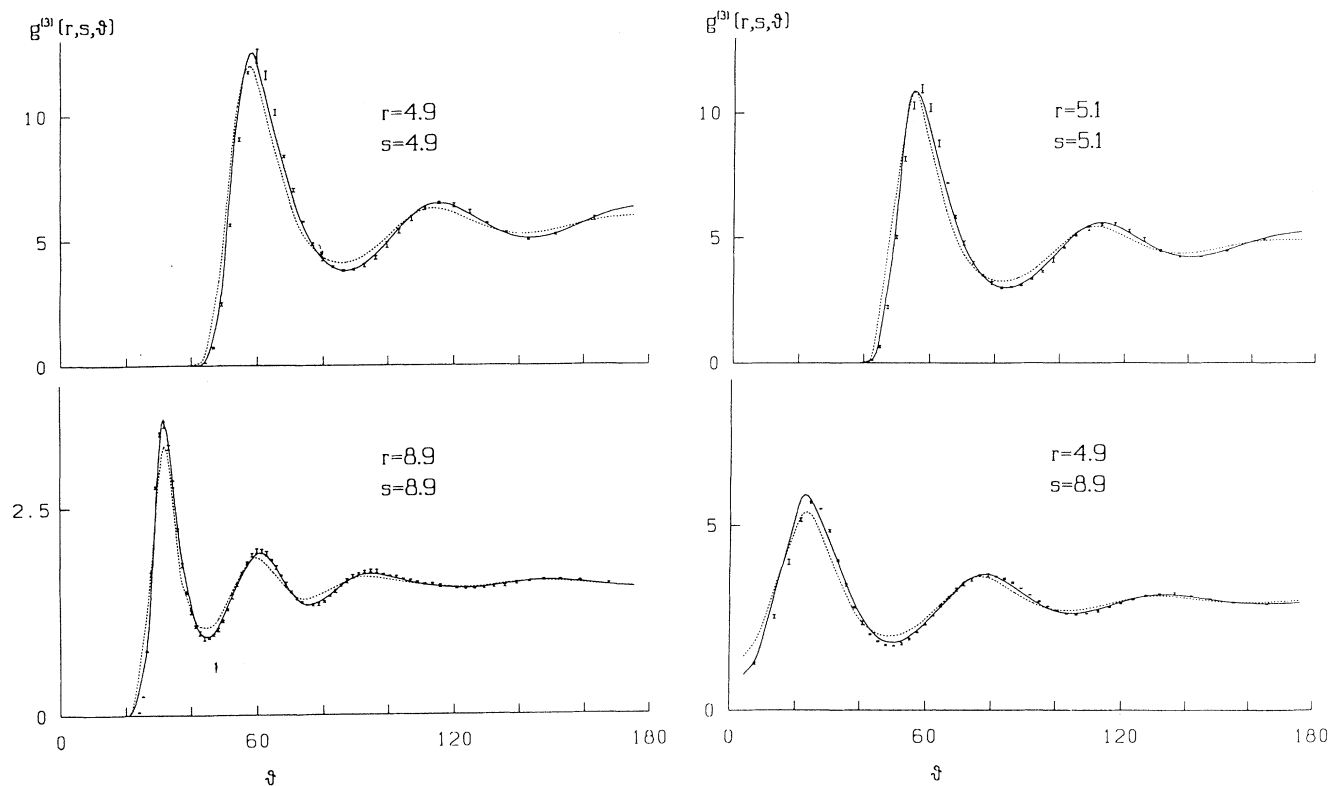


FIG. 7. tDF $g^{(3)}(r, s, \vartheta)$ for liquid Rb at a temperature of 373 K as a function of ϑ for the (r, s) values as indicated (in units of Å). Symbols (including error bars): computer simulation results; lines: broken line ($\alpha = \infty$) and full line ($\alpha = 0$).

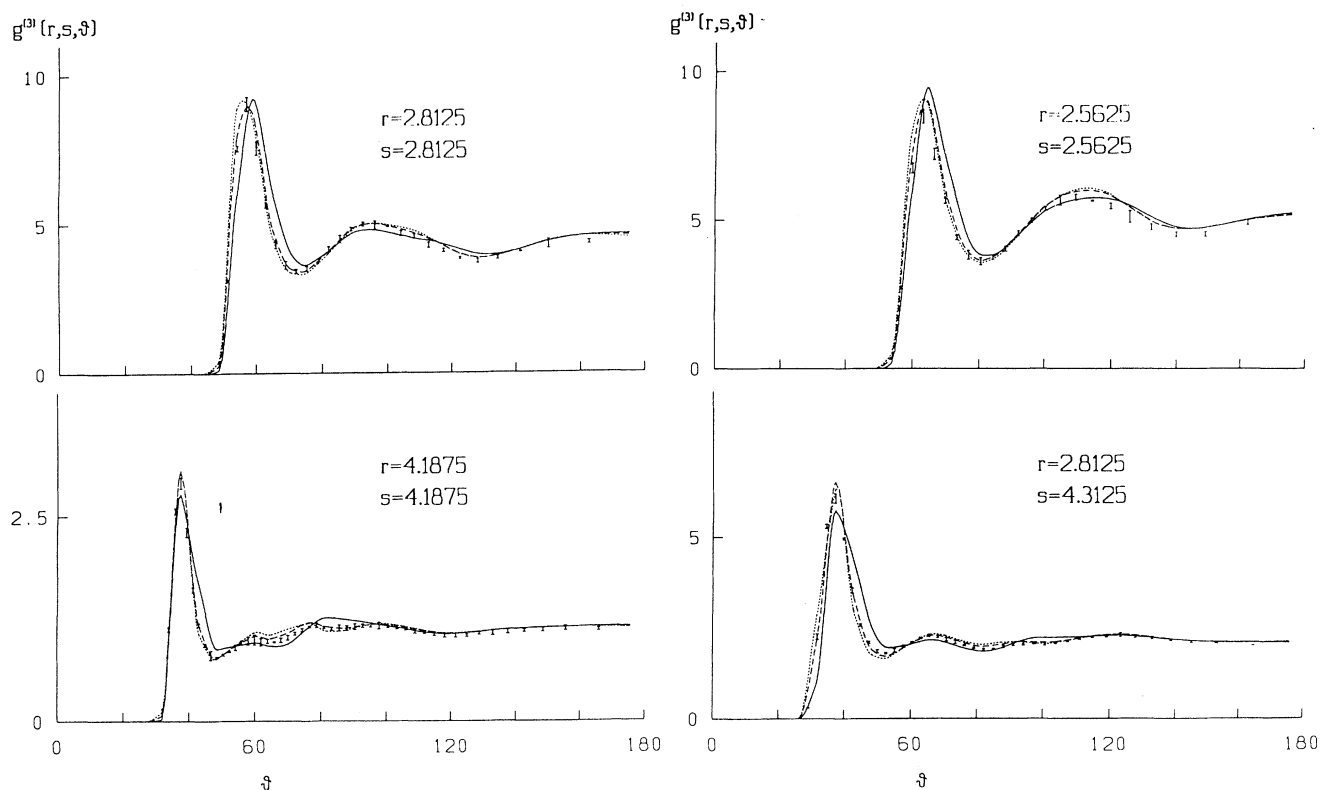


FIG. 8. tDF $g^{(3)}(r, s, \vartheta)$ for liquid Ge at a temperature of 1250 K as a function of ϑ for the (r, s) values as indicated (in units of Å). Symbols (including error bars): computer simulation results; lines: broken line ($\alpha = \infty$), full line ($\alpha = 0$), and dotted line ($\alpha = 0.5 \text{ \AA}^{-1}$).

SPM; furthermore, in the present study the simulations also use pairwise forces, hence a comparison on the basis of two-body forces seems to us to be legitimate.

IV. CONCLUSION

In this contribution we have demonstrated that the SPM for the determination of the triplet structure of a simple liquid is able to yield very reliable results also for a wide range of simple liquids, represented in our study by soft spheres of variable range and strength and by two liquid metals. Results are based on a mixed closure relation (interpolating between “pure” closures) as introduced by Attard. We propose a criterion based on two-body correlation functions for the determination of the mixing parameter in the closure relation and show that this choice is justified by an excellent agreement with computer simulation results. From the soft sphere results we may conclude that in particular the range of the potential represents a limitation of the numerical approach. For rather dense and long-ranged potentials ($n = 4$) no numerical convergence could be obtained. While the pure closure

relations yield strongly different results, we obtain very good agreement for the mixed closure with computer simulation data. As we make the potential more repulsive the discrepancies between the pure closures become less drastic. In general, results for configurations where particles are in close contact are more sensitive to the mixing parameter than for particle arrangements with larger distances; this also holds for the liquid metals. For the two studied cases, the tendencies to a more closed structure (Rb) and a rather open arrangement (Ge) of the particles in the liquid are reflected very nicely in the triplet structure. In all cases investigated the sum rules are preserved within numerical accuracy.

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