

Scientific paper

Analysis of the First Bridge Diagram of Liquid Bromine

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Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

The first bridge diagrams of the classical theory of liquids are discussed for two fluids of Lennard-Jones spheres and for a fluid of a two-centre Lennard-Jones model of liquid bromine. The bridge diagram of liquid bromine is calculated using a biased Monte-Carlo method. We investigate the first bridge diagrams, the bonds of which are either Mayer functions f or total correlation functions h . The Mayer f -bond representation leads to very high values of the first bridge diagram, which can not be used alone in a truncated expansion of the diagrammatic series of the bridge function. We analyse the origin of these high values. In the case of the h -function representation, the bridge function series truncated to the sole first bridge diagram is introduced into the closure of the Ornstein-Zernike equation and leads to some improvement of the pair distribution function upon the HNC result, as compared to the exact simulated values.

Keywords: Bridge function, molecular Ornstein-Zernike equation, liquid bromine

1. Introduction

One of the most important properties in the classical description of isotropic liquids at thermodynamic equilibrium is the molecular pair distribution function g . It describes the structure of the liquid at the two-particle level and is used to calculate various thermodynamic properties such as pressure, internal energy, and dielectric constant.^{1–4} The partial structure factors, which can be measured by neutron diffraction experiments, are closely related to the total pair correlation function $h = g - 1$. The interpretation of neutron diffraction measurements gives insight into the liquid structure and therefore into the underlying intermolecular potential u .^{5–8} Furthermore, g plays an important role in the calculation of non-equilibrium properties like ionic conductivity and diffusion constants. It also affects the relative Brownian dynamics of two molecules. This spatial dynamics induces efficient relaxation of the nuclear spins on the first molecule when

these nuclear spins undergo the fluctuating local magnetic fields due to a paramagnetic moment on the second molecule. These paramagnetic enhancements of the nuclear relaxation rates are responsible of nearly 50% of the improvement of the image contrast due to injected standard paramagnetic gadolinium(III) chelates in magnetic resonance imaging. These enhancements can serve to study the pair distribution functions of solvent and solute molecules for a large variety of representative situations with the help of easily accessible NMR techniques.^{9–12}

It is therefore of fundamental importance to characterize the pair distribution functions in liquids. Their calculation from first principles suffers mainly from three uncertainties: (i) The potential u between the molecules or particles (e.g. micelles) of a liquid is known with limited accuracy only. Usually, the complicated many-particle interactions are approximated by pair potentials. (ii) For a given pair potential, even if the pair distribution function can be computed by Molecular Dynamics or Monte-Carlo

simulation, its convergence can be very slow and the result is always affected by some statistical noise that depends on the performance of the used computer. Nevertheless, computer simulations are considered to be “exact” to within the statistical noise and the resulting pair distribution functions serve as references. (iii) All theoretical methods for determining g from the pair potentials are based on Ornstein-Zernike (OZ) type integral equations and introduce some approximations of the so-called bridge function B appearing in the closures of these equations. It is very difficult to estimate the errors on g stemming from such approximations.

The interest in the bridge functions B of hard body liquids was renewed recently^{13–19} after it had been shown that the multi-dimensional integrals of the first elementary bridge diagrams occurring in the expansion of B can be computed efficiently by Monte-Carlo techniques.²⁰ Moreover, methods have become available to derive the “exact” bridge function from the computed pair distribution function.^{13,16,21} Finally, for the hard-sphere fluids, the simulated pair distribution function could be nearly reproduced thanks to an accurate parametrisation of B .^{22,23} However, our knowledge of the bridge function is essentially limited to hard-body fluids. As far as we know, bridge functions in liquids containing polar molecules and ions have not yet been explored. Bridge function studies for reasonably realistic models of soft atoms are scarce. Here, we further investigate the bridge functions of fluids of atoms of one Lennard-Jones (LJ) centre and molecules of two LJ centres representing bromine Br_2 .

In the integral equation theory of classical fluids, the total correlation function $h(1,2)$, where 1 and 2 stand for the positions and orientations of the first and second molecules, is given by the sum of the so-called direct correlation function $c(1,2)$ and indirect correlation function $\eta(1,2)$ as

$$h(1,2) = c(1,2) + \eta(1,2) \quad (1)$$

Consider a one-component fluid. Let ρ be the number density of the molecules. The functions $c(1,2)$ and $\eta(1,2)$ are obtained simultaneously as the solution of the OZ convolution equation supplemented with a closure equation. The OZ equation reads

$$h(1,2) = c(1,2) + \frac{\rho}{8\pi^2} \int c(1,3)h(3,2)d3 \quad (2)$$

where $\int \dots d3$ represents the integration over the coordinates of position and orientation of molecule 3. The closure equation is

$$c(1,2) = \exp(-\beta u(1,2) + \eta(1,2) + B(1,2)) - 1 - \eta(1,2) \quad (3)$$

The bridge function B can be represented by an infinite series of bridge diagrams involving either Mayer

f -functions with $f = \exp(-\beta u)$, $\beta = 1/(k_B T)$ or total pair correlation functions $h = g - 1$.²⁴ We write $B^{(f)}$ for the representation of B in terms of the Mayer f -functions and $B^{(h)}$ for the representation of B in terms of the total correlation functions h . The diagrams of $B^{(h)}$ and $B^{(f)}$ are integrals over the positions and orientations of k particles, $k \geq 2$. Each diagram carries a multiplicative weight ρ^k . Hence, the bridge function itself can be represented by a power series in ρ^k . In the Mayer f -function representation $B^{(f)}$, the coefficients $b_k^{(f)}$ in the power series are density independent, yielding $B^{(f)} = \lim_{n \rightarrow \infty} B_n^{(f)}$ with $B_n^{(f)} = \sum_{k=2}^n b_k^{(f)} \rho^k$. In the power series of the h -function representation $B^{(h)}$, the coefficients $b_k^{(h)}$ depend on h and hence on the particle density: $B^{(h)} = \lim_{n \rightarrow \infty} B_n^{(h)}$ with $B_n^{(h)} = \sum_{k=2}^n b_k^{(h)} \rho^k$. In the case of $B^{(h)}$ each diagram is an infinite partial sum of diagrams of $B^{(f)}$. Furthermore, each coefficient $b_k^{(h)}$ contains less diagrams than $b_k^{(f)}$ for $n > 2$. Finally, the computation of the h -bond diagrams can be performed over smaller integration hypervolumes than that of the f -bond diagrams, since h is smaller than $f \approx -\beta u$ at large intermolecular distance R_{12} as is often the case. This property is particularly striking in the case of an ionic fluid, for which h is a short-ranged screened function, while the Mayer f -function slowly decays as $1/R_{12}$, preventing the computation of the f -bond diagrams. However, for a fluid of hard spheres of diameter σ at the significant density $\rho \sigma^3 = 0.8$, the progressive incorporation^{15,20} of the terms in $b_2^{(h)}$, $b_3^{(h)}$, and $b_4^{(h)}$ into the approximation of $B^{(h)}$ (see Fig. 8 of Ref. 15) used in the closure is accompanied by a very slow convergence of g towards the “exact” simulated value (see Fig. 9 of Ref. 5). The rather poor estimates of g corresponding to $B_n^{(h)}$ with $n \leq 4$ can be attributed to the fact that the true bridge function B extracted from computer simulations is mostly negative (see Fig. 7 of Ref. 3 and Fig. 6 of Ref. 4). This negative sign also occurs for the first bridge diagram (\boxtimes) of $B^{(f)}$ in the case of hard spheres of diameter σ since this diagram contains 5 Mayer f -bonds such as $f(r) = -1$ for $0 \leq r \leq \sigma$ and $f(r) = 0$ for $r > \sigma$. The first diagram of $B^{(h)}$ has the same topology, but with h -bonds taking quite large positive values which, at $r \approx \sigma$, are the source of positive values of $b_2^{(h)}$, which are absent in the first diagram $b_2^{(f)}$ of $B^{(f)}$ ^{15,20} and lead to incorrect positive values of $B^{(h)} \approx b_2^{(h)} \rho^2$. The terms of $B^{(h)}$ in $b_3^{(h)}$ and $b_4^{(h)}$ are insufficient to cancel the unphysical positive character of $B^{(h)} \approx b_2^{(h)} \rho^2$.

For the more realistic Lennard-Jones potential, it is unknown whether the first term in $B^{(f)}$ is a better approximation of the bridge function B than the first term in $B^{(h)}$. This problem will be discussed hereafter for fluids of LJ atoms and LJ Br_2 .

The article is organized as follows: In section 2, we briefly introduce the numerical algorithm used to compute the bridge diagrams. We discuss the resulting bridge diagrams and their effect on the pair distribution function in section 3 and summarize our results in section 4.

2. Calculation of the First Bridge Diagram

The bridge diagram associated with ρ^2 can be symbolized by ∇ . In the case of $b_2^{(h)}$ all bond functions are total correlation functions h , in the case of $b_2^{(f)}$, all bond functions are Mayer f -functions. The numerical calculation of this diagram can be performed by the application of an expansion of the bondfunction in Legendre polynomials in the case of a system with purely spherical pair potentials. This method was introduced by Barker and Monaghan,²⁵ and Attard and Patey.²⁶ In the more general case of molecules, the angular dependence of the bond function has to be taken into account. In the laboratory frame, denote the position of the mass centre and orientation of a molecule $i = 1, \dots, 4$ by R_i and $\Omega_i := (\alpha_i, \beta_i, \gamma_i)$, where $(\alpha_i, \beta_i, \gamma_i)$ is the set of Euler angles of a molecular frame as defined by Messiah.²⁷ We obtain for $b_2^{(h)}$:

$$b_2^{(h)}(R_{12}, \Omega_1, \Omega_2) = \frac{1}{2(8\pi^2)^2} \times \int_{A \times A} h(R_{13}, \Omega_1, \Omega_3) h(R_{14}, \Omega_1, \Omega_4) h(R_{23}, \Omega_2, \Omega_3) h(R_{24}, \Omega_2, \Omega_4) h(R_{34}, \Omega_3, \Omega_4) dR_3 dR_4 d\Omega_3 d\Omega_4, \quad (4)$$

where $R_{ij} = |R_i - R_j|$ is the intercentre distance and A is the domain $R^3 \times [0, 2\pi[\times [0, \pi[\times [0, 2\pi[$.

In an isotropic liquid, the position and orientation of the molecular frame of molecule 1 in the laboratory frame are arbitrary because of the translation and orientation invariance of the liquid. We choose $R_1 = 0$ and $\mathbf{R}_{12} := R_2 - R_1 = R_2 = R_{12}e_z$ where e_z denotes the unit vector in the direction of the z -axis of the laboratory frame. Hereafter, the angle α_2 of molecule 2 will be simply denoted by α whenever convenient. This means that every function F depending on the distance and the mutual orientation of two molecules can be characterized only by R_{12} , α , β_1 , β_2 , γ_1 , and γ_2 . In the case of linear molecules with a centre of inversion, this is further simplified by the fact, that F is independent of γ_1 and γ_2 . In addition, the following symmetry conditions hold for each F (we write the explicit dependence on R_{12} , α , β_1 , and β_2 only):

$$\begin{aligned} F(R_{12}, \alpha, \beta_1, \beta_2) &= F(R_{12}, 2\pi - \alpha, \beta_1, \beta_2) \\ F(R_{12}, \alpha, \beta_1, \beta_2) &= F(R_{12}, \alpha, \pi - \beta_1, \pi - \beta_2) \\ F(R_{12}, \alpha, \beta_1, \beta_2) &= F(R_{12}, \alpha, \beta_2, \beta_1) \\ F(R_{12}, \alpha, \beta_1, \beta_2) &= F(R_{12}, \alpha + \pi, \beta_1, \pi - \beta_2). \end{aligned} \quad (5)$$

The first two relations follow from the invariance of F through permutation of identical molecules, the last two from the fact that the molecule has a centre of inversion. The numerical calculation of the multiple integral (4) is carried out as described previously.²⁰ We keep the thermalisation periods in the Metropolis algorithm as short as possible by proceeding from one configuration of the mo-

lecules 1 and 2 to another which is “close”: We use the thermalized configurations of the four molecules at larger distances as a starting configuration at shorter distances between 1 and 2. At large distances a change in the orientations of the molecules has a minor effect on the value of the integrand than at shorter ones. Consequently, we use the thermalized configuration at maximum distance as a starting configuration when we change the angles between molecules 1 and 2.

It is necessary to interpolate the values of b_2 obtained on a rather coarse grid of the four variables R_{12} , α , β_1 , and β_2 onto a finer grid. The interpolation will provide a rather smooth bridge function approximation $B \approx b_2\rho^2$ which can be used in a subsequent solution of the molecular Ornstein-Zernike equation. We decided to perform successive one-dimensional interpolations although this method is ambiguous. It is only justified by the fact that we do not find substantial deviations in the results irrespective of the order of successive one dimensional interpolations. We perform first an interpolation with respect to α , then with respect to β_1 , and β_2 , and at the end with respect to R_{12} . For the one dimensional interpolations, we apply the formula of Akima.²⁸

The solution of the Ornstein-Zernike equation is calculated by standard Fourier transform techniques and direct iteration for the systems with spherical molecules and by an expansion in rotational invariants in the case of asymmetric molecules.²⁹

Our Monte-Carlo simulation of the molecular fluid was performed by standard methods applying periodic boundary conditions and the Metropolis sampling scheme.^{30,31} We used 500 molecules in the simulation and generated 11.2×10^6 configurations for the calculation of the mean values.

3. The First Bridge Diagram for Br₂

We first investigate the bridge diagrams of two LJ atoms interacting through LJ potentials P1 and P2 inspired by the LJ potential P3 of the bromine molecule approximated as a dumbbell made of two equal Lennard-Jones centres separated by $L_{\text{Br-Br}} = 2.27 \text{ \AA}$. The parameters for P1–P3 are listed in Table 1.

The diameter σ of the potentials P1 and P2 is defined as the diameter of the hard sphere having the “same” excluding volume as the LJ dumbbell. The excluding vo-

Table 1. Potential parameters

Potential	$\sigma/\text{\AA}$	$\epsilon/(k_B T)$	$L_{\text{Br-Br}}/\text{\AA}$	$\sigma\rho^3$
P1	4.316	1.0788	–	0.94
P2	4.316	3.2364	–	0.94
P3	3.61	1.0788	2.27	0.5528

lume of the dumbbell is simply obtained by rolling one of the spherical atoms of the dumbbell on the surface of a reference dumbbell so as to generate a Connolly surface that is the external surface of the excluding volume. This excluding volume is about 5% larger than the volume of the dumbbell itself. Note that it is a minimal Connolly volume in the sense that the presence of the second LJ atom bound to the rolling dumbbell was not taken into account. The number densities ρ for the systems P1-P3 are all equal. The potential between two bromine molecules is the sum of four site-site LJ potentials. Hence, we have to define a LJ potential for the equivalent atoms which is about four times as strong as the LJ potential between two single sites on two Br₂ molecules. Nevertheless, this is a rough approximation because the site-site distances of two Br₂ molecules generally have different values for an arbitrary configuration of these molecules. Consequently, we decided to investigate various values of the LJ parameter $\beta\epsilon$ of the atomic fluids ranging from the Br site – Br site value $\beta\epsilon_{\text{Br}_2} = 1.0788$ up to $4\beta\epsilon_{\text{Br}_2}$. In this range, we obtained solutions of the Ornstein-Zernike equation with the HNC-closure for $\beta\epsilon$ as large as 3.6. We will show that the values of $B \approx b_2^{(f)}\rho^2$ become very large and can not serve in any bridge function approximation whereas $B \approx b_2^{(h)}\rho^2$ may be a candidate for a bridge function approximation.

In Figure 1, we show the bond functions for the calculation of $b_2^{(f)}$ and $b_2^{(h)}$. In contrast to purely repulsive pair potentials, the Mayer f -function of the Lennard-Jones potential has a positive local maximum at $r = \sigma\sqrt{2}$. In all cases, the “first” maximum (the maximum at smallest distance from the origin) of the corresponding total correlation function h is at lower distances than $r = \sigma\sqrt{2}$. In the case of P1 ($\beta\epsilon = 1.0788$), the maxima of f and h have approximately the same height, but this is not true for P2 ($\beta\epsilon = 3.2364$). In the latter case, the maximum of h reaches a height of about 4.4 whereas the maximum of the Mayer f -function assumes a value of 24.4. We interpret these findings in the following way: The total correlation func-

tion h has its peak at lower distances than the Mayer f -function due to packing effects. The higher the temperature (i.e. the lower the value of $\beta\epsilon$) and thus the higher the energy in the fluid, the closer the particles can approach each other although there is a repulsive component in the Lennard-Jones potential. At low temperatures (high values of $\beta\epsilon$), the average distance between the particles is shifted towards the position of the maximum of the Mayer f -function at which the strongest attraction between the particles occurs. Consequently, the highest peak of h is shifted to larger distances, but it is still below the position of the maximum of the Mayer f -function in our case. Although there is attraction between the particles in this distance regime, the integral over the first peak of the pair distribution function can not exceed the value of the coordination number in a solid crystal or densest sphere packing (12). Thus, the height and width of the first peak in the total correlation function h are limited. Because of these statistical effects limiting the values of the total correlation function h , the values of the first bridge diagram $b_2^{(h)}$ are also limited. This is not true in the case of the Mayer f -function representation $b_2^{(f)}$ because the Mayer f -function only represents the interaction between the particles which may become very large. We demonstrate the effect of the bond function on the values of b_2 in Figure 2 for the systems P1 and P2.

In the case of P2, we also show the bridge function in the parametrization of Duh, Haymet, and Henderson.^{32,33} We did not obtain convergence including this bridge function into the closure relation of the Ornstein-Zernike relation, but we show the approximation obtained from the result of an HNC solution of the Ornstein-Zernike equation.

It is remarkable that the bridge function approximation $B^{(h)} \approx b_2^{(h)}(r)\rho^2$ does not strongly depend on the temperature (or $\beta\epsilon$) and is therefore rather similar for P1 and P2. In contrast to that, $b_2^{(f)}\rho^2$ strongly depends on temperature and assumes values in the order of 0.4×10^5 near σ

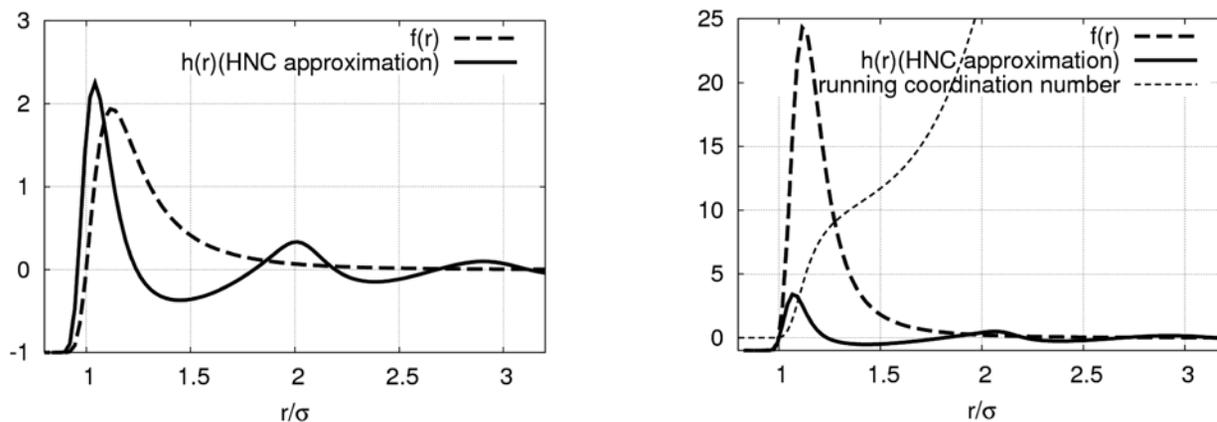


Figure 1. Possible bond functions for the first bridge diagram: Mayer function f and total correlation function h in the HNC-approximation for $\beta\epsilon = 1.0788$ (P1) and $\beta\epsilon = 3.2364$ (P2). We also show the running coordination number calculated from the HNC-approximation of the pair distribution function g .

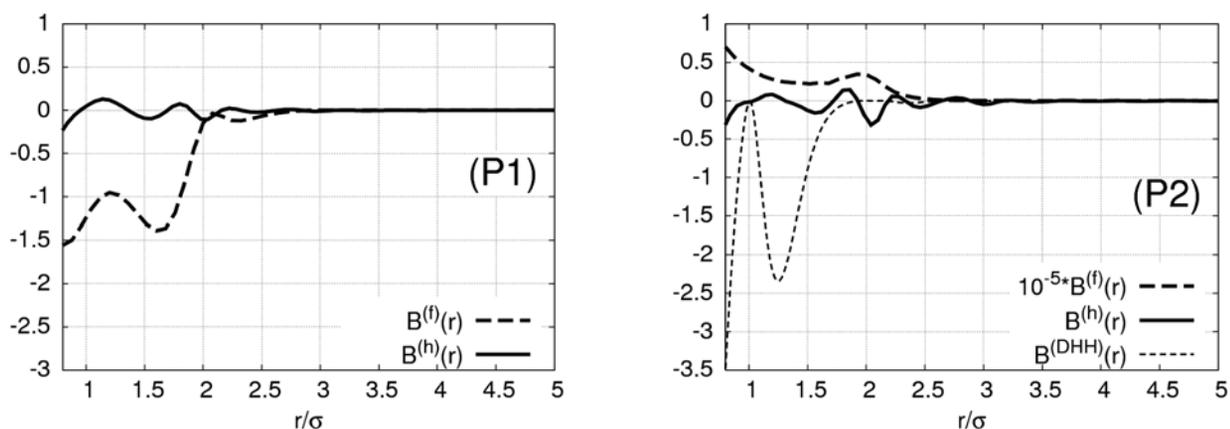


Figure 2. Bridge function approximation $B(r) \approx b_2^{(f)}(r)\rho^2$ and $B(r) \approx b_2^{(h)}(r)\rho^2$ truncated to the first bridge diagram b_2 calculated for the Mayer function f ($b_2^{(f)}$) and for the total correlation function h in the HNC approximation ($b_2^{(h)}$) for the Lennard-Jones parameters $\beta\epsilon = 1.0788$ (P1) and $\beta\epsilon = 3.2364$ (P2). We also show the bridge function approximation $B^{(DHH)}$ by Duh, Haymet, Henderson^{32,33} calculated from the HNC-solution of the Ornstein-Zernike equation for potential P2.

for P2. Only the complete series may give reasonable values at the low temperature of system P2. However, even the convergence is not proven to the knowledge of the authors. A complete discussion of the bridge function of systems P1 and P2 is beyond the scope of this paper, but we

demonstrated that the Mayer f -bond representation is not useful for obtaining bridge function approximations in the case of a system with Lennard-Jones interactions.

The simple two-centre LJ model of bromine (see P3 in Table1) is discussed in the literature.^{6,34} A detailed

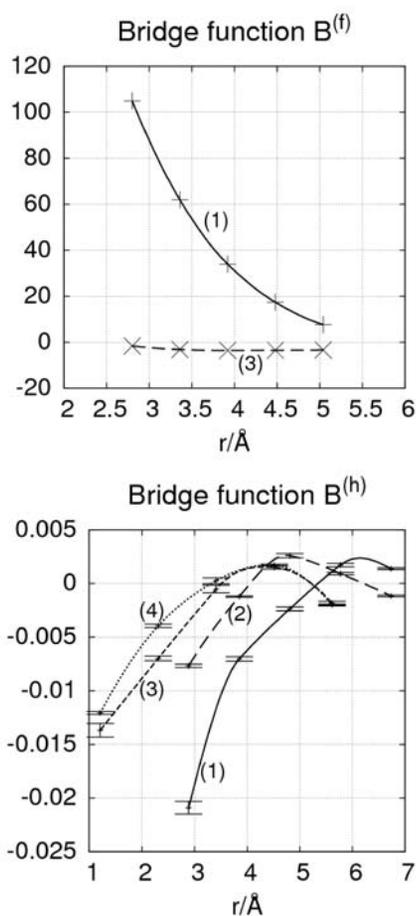
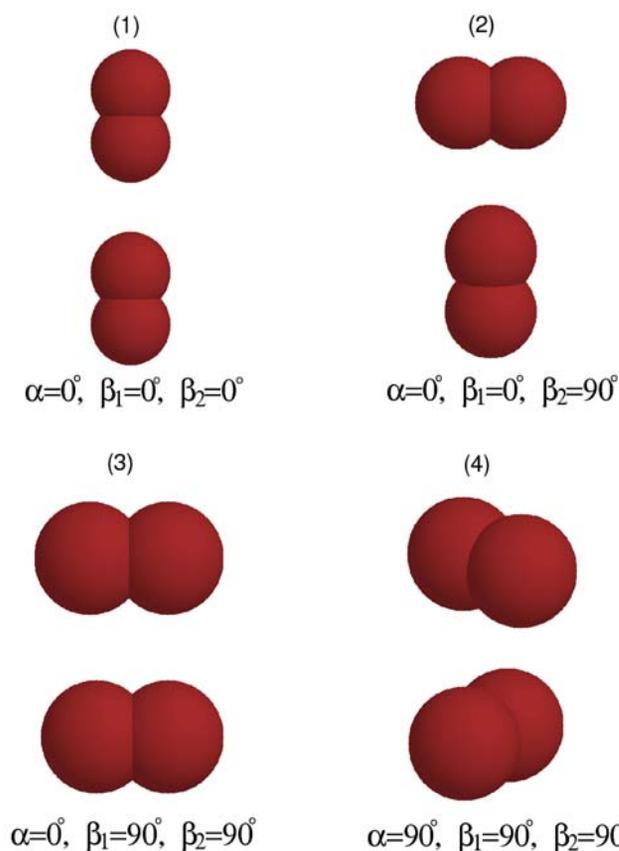


Figure 3. Selected pair configurations of bromine molecules, for which the first bridge diagram was calculated (left): bridge function approximations $B^{(f)} \approx b_2^{(f)}\rho^2$ (top right) and $B^{(h)} \approx b_2^{(h)}\rho^2$ (bottom right). The first bridge diagram $b_2^{(h)}$ was computed with the help of the previously developed biased Monte Carlo method²⁰ with a cut-off radius of 8.3272 Å and 3.28×10^6 Monte-Carlo steps.

analysis of possible model potentials of liquid bromine was published in various articles.^{34–36} For the calculation of $b_2^{(f,h)}(R_{12}, \alpha, \beta_1, \beta_2)$ we rely on the knowledge of the Mayer f -function and the HNC-approximation of $h(R_{12}, \alpha, \beta_1, \beta_2)$ in the rotational invariant expansion, respectively. The most time consuming step is to calculate the f or h -function for each chosen configuration of the molecules via this rotational invariant expansion.

In Figure 3, we present selected configurations of the bromine molecules for which we calculated the first bridge diagram. We also show the bridge function approximation $B^{(f)} \approx b_2^{(f)} \rho^2$, and the approximation $B^{(h)} \approx b_2^{(h)} \rho^2$ for these configurations. Again, the bridge function approximation $B^{(f)}$ has very large values and can not be used as a bridge function approximation in the Ornstein-Zernike equation. In the case of the approximation $B^{(h)} \approx b_2^{(h)} \rho^2$, the bridge function represents an alternately repulsive and attractive potential since $B^{(h)}$ is oscillating around zero. The character of the bridge function is the more repulsive the larger the overlap of the Lennard-Jones sites is. This finding is similar to the spherical Lennard-Jones systems presented in Figure 2. However, the oscillations around zero of our bridge function approximation are in contrast to the non-positivity of the bridge function of spherical systems as it was established in many empirical formulae like the Percus-Yevick approximation,² the Martynov-Sarkisov approximation³⁷ or the more refined form of Duh, Haymet, and Henderson.^{32,33} Whether the higher order terms in the bridge function series change these characteristics of $b_2^{(h)}$ is not yet clear and can only be determined by an inversion of the Ornstein-Zernike equation using computer simulation results. For that purpose, it would be interesting to use the recently developed method^{16,21} to calculate the exact form of the bridge function for angle dependent interactions. A bridge function approximation using the representation $B^{(f)}$ up to the terms in ρ^6 was found to be very successful for the hard sphere poten-

tial,^{13,14} but the present study shows that such a procedure can not be extended to the LJ potentials. Then, the representation $B^{(h)}$ involving the total correlation function h is the only alternative in this case. Should this approximation provide bridge functions with dubious values near $r = \sigma$, another way would be to calculate the bridge function from the Mayer f -functions of a purely repulsive reference potential. This is the essence of the RHNC method, which was successfully applied without optimization of the bridge function of the natural reference hard-sphere system, for instance in the case of the dipolar hard-sphere fluid,³⁸ and with optimization of the bridge functions for this fluid and a water model.^{39,40} RHNC methods are intended for yielding approximate bridge functions on an intuitive basis or optimization criteria. They are beyond the scope of the present analysis of the convergence properties of the bridge diagram series and will not be further discussed here. Besides, it could be tempting to estimate the bridge function $B^{(h)}$ of a given fluid by the n -th order approximation $B_n^{(h_{ref})}$ of the bridge function $B^{(h_{ref})}$ of a reference system in the representation of its total correlation function h_{ref} . However, this would not enable us to discriminate between the possible errors in the bridge function due to the substitution of h by h_{ref} and those due to the truncation of the bridge diagram series, which was the purpose of this work.

In Figure 4, we show the pair distribution functions of the centres of two bromine molecules for the Monte-Carlo simulation ($g_{cc,MC}$),³¹ the HNC approximation ($g_{cc,HNC}$) and the HNC closure including $B^{(h)} \approx b_2^{(h)} \rho^2$ ($g_{cc,HNC+b_2}$). We also depict the differences $\Delta g_{cc,HNC-MC} = g_{cc,HNC} - g_{cc,MC}$ and $\Delta g_{cc,HNC+b_2-MC} = g_{cc,HNC+b_2} - g_{cc,MC}$. We obtain an improvement of the height and position of the first peak of the pair distribution function applying the HNC + b_2 approximation instead of the simple HNC closure, but there is an underestimation of the height of the shoulder around 4 Å in the HNC + b_2 approximation

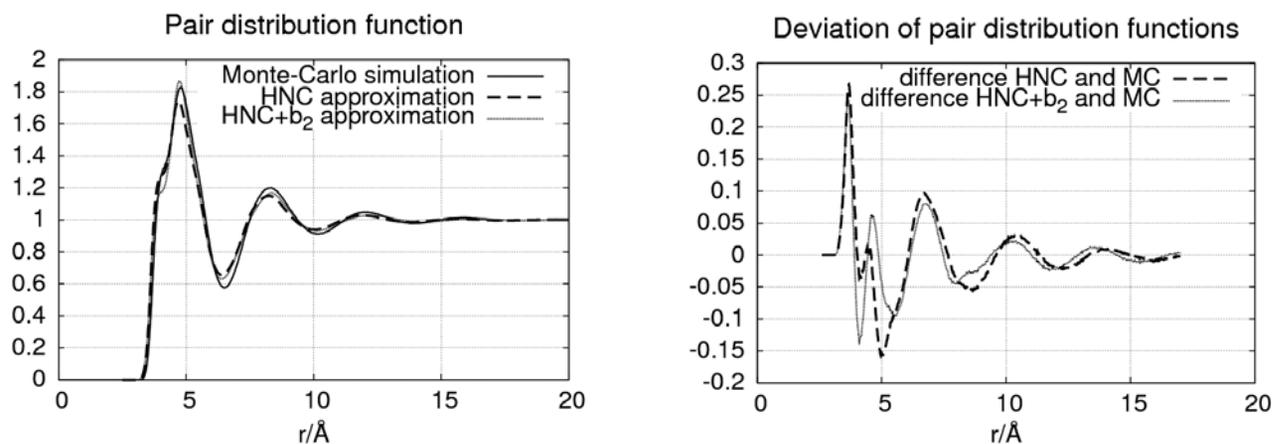


Figure 4. Pair distribution function g_{cc} of the centres (c) of two bromine molecules resulting from the (i) Monte-Carlo (MC) simulation ($g_{cc,MC}$), (ii) HNC approximation ($g_{cc,HNC}$), and HNC closure including $B^{(h)} \approx b_2^{(h)} \rho^2$ ($g_{cc,HNC+b_2}$) (left). Differences $\Delta g_{cc,HNC-MC} = g_{cc,HNC} - g_{cc,MC}$ and $\Delta g_{cc,HNC+b_2-MC} = g_{cc,HNC+b_2} - g_{cc,MC}$ (right).

which is not present in the HNC approximation. We also calculated

$$\Delta_i = 4\pi \int_0^R r^2 \Delta g_i(r) dr, \quad R = 17 \text{ \AA}$$

as a measure of the integral deviation of the various approximations from the Monte-Carlo simulation result. $\Delta_{\text{HNC-MC}} = 338 \text{ \AA}^3$ is 16% larger than $\Delta_{\text{HNC}+b_2\text{-MC}} = 291 \text{ \AA}^3$. We conclude that there is some improvement but higher order terms play a role in the bridge function expansion.

4. Conclusion

In this paper, we analysed the first bridge diagram for two fluids of Lennard-Jones atoms and for a fluid of two-centre Lennard-Jones molecules approximating bromine. We showed that the first bridge diagram of the bridge function series expressed in terms of Mayer f -bonds has a very large amplitude which prevents the convergence of the series towards the much smaller values of the true bridge function because of the statistical uncertainty of the values of the various diagrams of the series. This large amplitude is a direct consequence of the high and broad peak in the Mayer f -function, which occurs either at low temperatures or because of a strong attractive part of the Lennard-Jones potential. It is interesting to note that the total correlation function h is the sum of irreducible diagrams consisting of two white circles, black ρ circles, and f bonds.¹ The function f itself is the lowest order approximation of h . In the case of a significant Lennard-Jones attraction and at normal liquid density, f takes high positive values so that it can not be a reasonable approximation of h as shown, for instance, by the unphysically large values of the coordination number that would be derived from $g = 1 + h \approx 1 + f$. The high positive values of f are cancelled out by the large and/or numerous negative values of the other diagrams to yield a physically relevant total correlation function h . To the opinion of the authors, it is remarkable and quite unexpected that the diagrams of h retained by the Percus-Yevick and HNC approximations also involve diagrams with large positive and negative values that mutually cancel. Such a situation, which results from many high-order spatial correlations among the molecules, is not attainable by a bridge function approximation limited to a small number of f -bond diagrams. In contrast, the h -function representation of the bridge function is a sum of multi-dimensional integrals of products of functions h , for which the large effects of f have been cancelled by the spatial correlations among the molecules. Therefore, $b_2^{(h)}\rho^2$ was shown to be small and the higher order terms $b_k^{(h)}\rho^k$ of the bridge series $B^{(h)}$ are expected to be small too. The term $b_2^{(h)}\rho^2$ is a much more reasonable approximation of B than $b_2^{(f)}\rho^2$.

We calculated the first bridge diagram $b_2^{(h)}$ for a two-centre Lennard-Jones model of liquid bromine. The introduction of $B^{(h)} \approx b_2^{(h)}\rho^2$ into the closure improves the pair distribution function g , even if $b_2^{(h)}$ is calculated from the HNC solution for h and no iteration for the calculation of self-consistent functions h and $b_2^{(h)}$ is performed. However, because $B^{(h)} \approx b_2^{(h)}\rho^2$ takes quite small values, the improvement is modest as shown by the overall reduction of about 16% of the difference between the values of g derived from the integral equation theory and from the simulation. Estimating the number of h -bond diagrams required to get a larger effect is difficult. The present study can be easily extended to fluids of molecules with different interaction potentials, for which the influence of $B^{(h)} \approx b_2^{(h)}\rho^2$ should be estimated.

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Povzetek

Obravnavali smo prvi »bridge« graf po klasični teoriji tekočin za dva primera tekočin predstavljenih z Lennard-Jonesovimi kroglicami, ter model tekočega broma, kjer smo uporabili Lennard-Jones-ov model z dvema centroma. »Bridge« graf za tekoči brom smo izračunali z uporabo adaptirane metode Monte Carlo. Raziskali smo prve »bridge« diagrame, v katerih so vezi lahko Mayerjeve f-funkcije ali celotne korelacijske funkcije h. V primeru Mayerjevih f-funkcij smo dobili izredno visoke vrednosti prvega diagrama, ki same po sebi ne zadoščajo za oceno celotne »bridge« funkcije. V primeru uporabe h-funkcij prvi graf v razvoj predstavlja dobro oceno za celotno »bridge« funkcijo. Parske porazdelitvene funkcije dobljene z Ornstein-Zernike integralno enačbo, kjer približek za »bridge« funkcijo vključimo v HNC približek, se dobro ujemajo z rezultati računalniške simulacije.