AN ACCURATE ANALYTICAL REPRESENTATION OF THE BRIDGE FUNCTION OF HARD SPHERES AND A QUESTION OF EXISTENCE OF A GENERAL CLOSURE TO THE ORNSTEIN–ZERNIKE EQUATION

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The bridge function of hard spheres is accurately calculated from computer simulation data on the pair distribution function via the inverted Ornstein–Zernike equation at reduced densities $\rho^* \equiv N\sigma^3/V$ ranging from 0.2 to 1.02, i.e. from low densities through densities in a vicinity of the phase transition to crystal to densities of metastable fluid region. The data are used to propose an analytical representation of the bridge function as a function of the interparticle distance and density. They are further used to construct the so-called Duh–Haymet plot. It is demonstrated that a "general closure" to the Ornstein–Zernike equation in the form $B(r) = f[\gamma(r)]$, where γ is the indirect (or series) correlation function, does not match the data. Nor does an extended closure $B(r) = f[\gamma(r),\rho^*]$ even in the simplest case of the one component hard sphere fluid. A relative success of literature closures to the Ornstein–Zernike equation is discussed.
Keywords: Ornstein–Zernike equation; Closures; Bridge function; Hard spheres.

In molecular theory of fluids the bridge function, B, is defined as an infinite sum of elementary (or bridge) diagrams, E_i,

$$B = \sum_{i=2}^{\infty} E_i \rho^i \tag{1}$$

where E_i is a sum of diagrams with two root points and i field points, without articulation (nodal) points and articulation root pairs[1]. It is related to the pair distribution function, $g(r)$, by

$$g(r) = \exp[-\beta u(r) + \gamma(r) + B(r)] \tag{2}$$

where $\beta = 1/(k_{\mathrm{B}}T)$ is the reciprocal temperature, $u(r)$ is the pair inter-molecular potential, zero or infinity in the case of hard spheres, and $\gamma(r)$ is the indirect or series correlation function. The three functions, g, B, γ, are coupled by the Ornstein–Zernike (OZ) integral equation

$$\gamma(12) = \rho \int [g(13) - 1][g(23) - 1 - \gamma(23)]\, d\mathbf{r}_3 \qquad (3)$$

where $\rho = N/V$ is the number density and (ij) is an abbreviation for $(|\mathbf{r}_i - \mathbf{r}_j|)$ with $|\mathbf{r}_2 - \mathbf{r}_1| = r$. When a relation between $B(r)$ and $\gamma(r)$ is known, the pair distribution function may be calculated by combining Eqs (2) and (3).

There have been proposed a number of relations $B = B(\gamma)$ called closures to the OZ equation. For example, the hypernetted chain (HNC) closure is

$$B(r) = 0, \qquad (4)$$

the Percus–Yevick (PY) closure is

$$B(r) = \ln[\gamma(r) + 1] - \gamma(r), \qquad (5)$$

the Martynov–Sarkisov (MS)[2] closure is

$$B(r) = [1 + 2\gamma(r)]^{1/2} - \gamma(r) - 1, \qquad (6)$$

the Rogers–Young (RY)[3] closure is

$$B(r) = \ln\left\{1 + \frac{\exp[p\gamma(r) - 1]}{p}\right\} - \gamma(r), \quad \text{where } p = 1 - \exp(-0.16r), \qquad (7)$$

and the modified Verlet (VM)[4] closure is

$$B(r) = -\frac{1}{2}\frac{\gamma^2(r)}{1 + a\gamma(r)}, \qquad (8)$$

where $a = 1.1 - \rho^*/3$, $\rho^* = N\sigma^3/V$ is the reduced density, $\sigma \equiv 1$ is the diameter of hard sphere, N and V are number of particles and system volume, respectively. A number of other closures can be found in literature[5], see also ref.[6] for review.

Even though the above and other closures are theoretically or semi-empirically based, they can not give quantitative information on $B = B(r)$ or

$B = B(\gamma)$ due to their approximative nature. Therefore there are only two routes of obtaining accurate values of the bridge function as a function of particle separation and density.

The first route stands in calculation of elementary diagrams, see Eq. (1). The first elementary diagram, E_2, is known analytically[7]. Values of E_3 to E_6 were calculated numerically[8,9]. At low and moderate densities (up to $\rho^* = 0.5$), see Fig. 6 in ref.[9], series (1) truncated after E_6 agrees well with computer simulation results on $B(r)$ of this work. At densities in the vicinity of the phase transition to crystal and in the metastable region it differs as shown in Fig. 1. Attempts to calculate E_7 and higher terms in Eq. (1) would be on the edge or beyond of the present computation technology. There were attempts to accelerate the rate of convergence of the series by replacing f-bonds by h-bonds, where $h = g - 1$ is the total correlation function, but the convergence remained slow[10–13].

The second route of obtaining accurate $B(r,\rho)$ is based on computer simulation of the radial distribution function and its inversion to the bridge function via the OZ equation, Eqs (2) and (3). This route was used by two of the present authors (A.M. and S.L.)[14]. They suggested for the bridge function as a function of interparticle separation distance and density equation
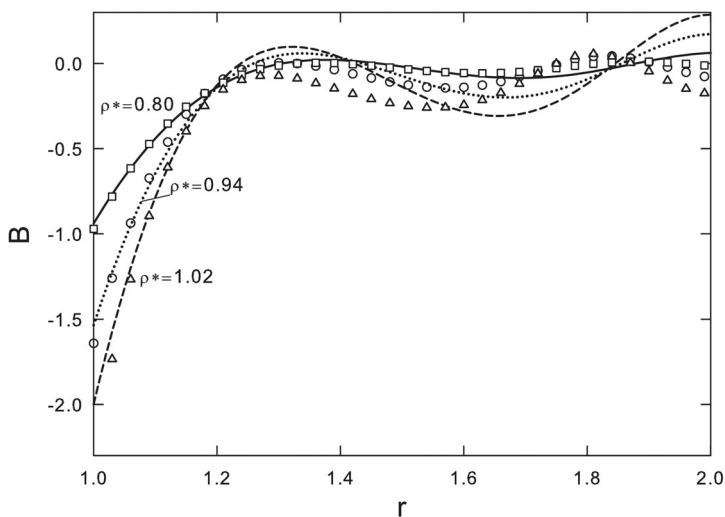

FIG. 1
The bridge function obtained from computer simulations in comparison with the series of elementary diagrams, see Eq. (1), truncated after E_6 at three high densities, $\rho^* = 0.8$, 0.94 and 1.02. Lines are results of the truncated series, points are the inverted simulation results

$$B(r) = -b^2(r) \qquad (9)$$

where

$$b(r) = \begin{cases} (a_1 + a_2 x)(x - a_3)(x - a_4) / a_3 a_4 & \text{for } x \le a_4 \\ A_1 \exp[-a_5(x - a_4)] \sin[A_2(x - a_4)] / r & \text{for } x > a_4 \end{cases} \qquad (10)$$

and $x = r - 1$. In the next text, Eqs (9) and (10) are denoted as the ML formula. Free parameters a_i as functions of density were fitted to computer simulation data on $g(r)$ at low and moderate densities (up to $\rho^* = 0.86$) available (with a reasonable accuracy) in those times.

While the ML formula is reasonably accurate, it has one principal defect: it postulates that $B(r)$ does not change sign, see Eq. (9). One reason for introducing this approximation was an attempt to increase numerical stability of solving a set of highly non-linear equations for unknowns a_i in Eq. (10). Second, the approximation seemed to be reasonable because (i) the known closures to the OZ equation for hard spheres (with the exception of the second order PY theory[15]) predict non-positive values of $B(r)$ and (ii) the first elementary diagram $E_2(r)$ is also non-positive. The postulate of non-positivity of the bridge function was questioned independently by Rast et al.[11] and by Yuste et al.[16]. Their findings and the results of the second order PY theory are inconclusive due to approximations involved. However, they can be further supported by the fact that the higher elementary diagrams, E_3 to E_6, also change sign[8,9]. Thus, a problem of true dependence of the bridge function on a particle separation was reopened.

A few years ago we reexamined the method of determining the bridge function by direct inversion of the computer simulation data on the radial distribution function using the OZ equation[17]. The improved method consists in simulating the radial distribution as accurately as possible, correcting the results on systematic (finite size, grid size, and tail) errors, and finally obtaining values of the bridge function from the corrected $g(r)$ simulation data using the OZ equation. The results of the method were demonstrated for a single density in the vicinity of the phase transition to crystal, $\rho^* = 0.94$ (ref.[17]).

Later, we have calculated $B(r,\rho^*)$ in the whole range of the fluid densities and in the metastable fluid densities up to $\rho^* = 1.02$. These results have been referenced[18], but not explicit formulae have been published. The aim of this paper is to present these data to a broader scientific community and

to express them analytically as functions of interparticle distance and density. The second aim of the paper is to use the fitted $B(r,\rho^*)$ to testing accuracy and reliability of the OZ equation closures.

RESULTS

We have simulated the radial distribution function (RDF) of one-component hard spheres using both Monte Carlo and molecular dynamics methods in the range of the reduced density $\rho^* \in [0.2,1.02]$. The simulation methodology was described earlier[17,19]. The RDF values corrected to systematic computer simulation errors (finite size, grid, tail) and the data on the bridge function obtained from them via the OZ equation are deposited as a supplementary material to this paper.

The data on the bridge function have been fitted as a function of interparticle separation distance and density. Because there is a discontinuity in the second derivative of the bridge function at $r = 2$ (in units of the hard-sphere diameter) and a higher order discontinuity at $r = 3$ (see ref.[9]) we have decided to separate $B = B(r)$ into three parts. There are also discontinuities of higher orders at $r = 1$, $r = \sqrt{3}$ and at distances beyond $r = 3$ but they have not been considered. We have proposed the following form

$$B(r) = \begin{cases} \sum_{i=0}^{13} a_i T_i(r) & \text{for } 1 \le r \le 2 \\ \sum_{i=0}^{9} b_i T_i(r) & \text{for } 2 < r \le 3 \\ \dfrac{1}{r^2}\{\exp(-1.25r)[c_0 \cos(13.75r) + c_1 \sin(13.75r)] + c_2 \exp(-1.5r)\} & \text{for } r > 3 \end{cases} \quad (11)$$

where $T_i(r)$ are Chebyshev polynomials of the first kind; a_i, b_i, c_i have been optimized under the constraints that $B(r)$ and its first derivative are continuous at $r = 2$, and that also the second derivative is continuous at $r = 3$. The values of constants in $a_i = a_i(\rho^*)$, $b_i = b_i(\rho^*)$, $c_i = c_i(\rho^*)$ have been obtained using both the truncated low density expansion, Eq. (1), and the simulation data on $B(r)$. The fitting procedure is described in detail in ref.[20]. The formulae and the values of constants are in the Appendix.

We have tested the fit (11) against the low density expansion data of the elementary diagrams[9] truncated after E_6. At $\rho^* \le 0.2$, the agreement is perfect. The highest deviations between Eq. (*11*) and the truncated series are of the order 10^{-4}. We have also tested the accuracy of the fits of $B = B(r,\rho^*)$ against the computer simulation data of this work. The comparison is shown in Fig. 2 at four selected densities. At the lowest density shown in

the figure, $\rho^* = 0.4$, the differences between the simulated and the fitted values are well bellow the estimated computer simulation errors. At a moderate density, $\rho^* = 0.8$, the deviations are less than 0.002, the highest ones are at $r \approx 2$. At a near vicinity of the phase transition from fluid to crystal,
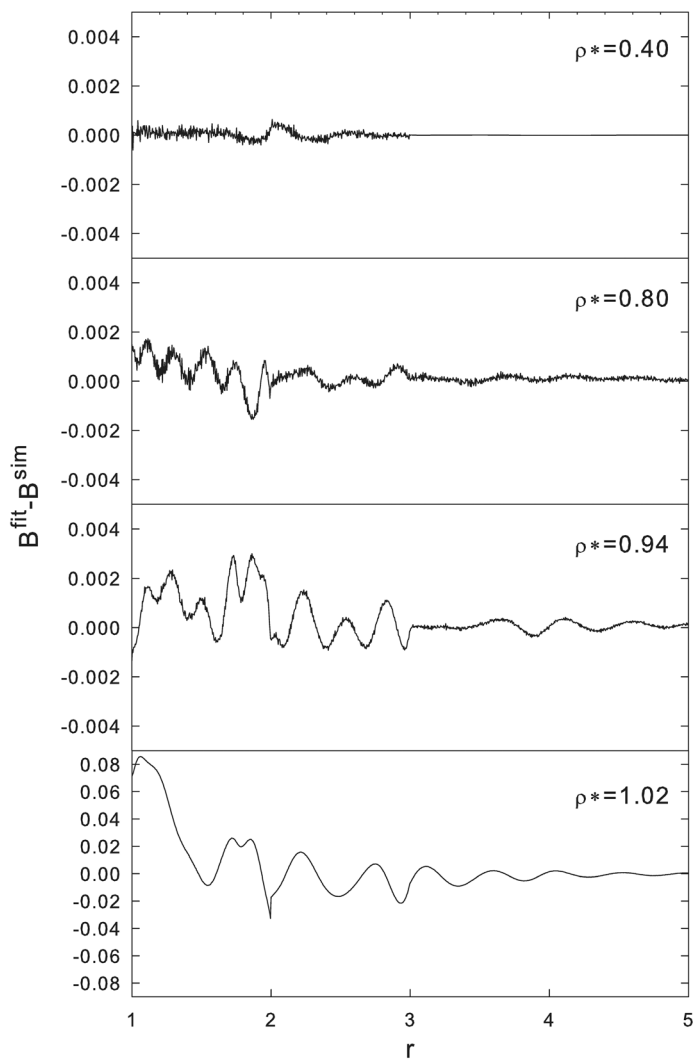

<small>Fig. 2</small>
Deviations between the fitted and simulated values of the bridge function

$\rho^* = 0.94$, deviations between the simulated values and the fitted values are not larger than 0.003, the largest ones are again in the vicinity of $r = 2$. Finally, the figure shows an extrapolation of the fit to the metastable region, $\rho^* = 1.02$. At this density the deviations are by an order higher, but still reasonable. The highest one is in the vicinity of contact (≈ 0.08), the second highest (≈ 0.03) near $r = 2$.

We may conclude that the fit of the bridge function is in a full agreement with the available data: (i) elementary diagrams to E_6, (ii) inverted computer simulation data on $g(r)$ in the region of densities up to the phase transition to crystal. In the metastable region the fit gives semi-quantitative agreement with the simulations.

DISCUSSION

Figure 3 compares the simulated bridge function with the ML equation and the results of several literature closures at a density in the vicinity of the phase transition from fluid to crystal. The classical closures, Percus–Yevick and hypernetted chain, give only qualitative agreement and are not
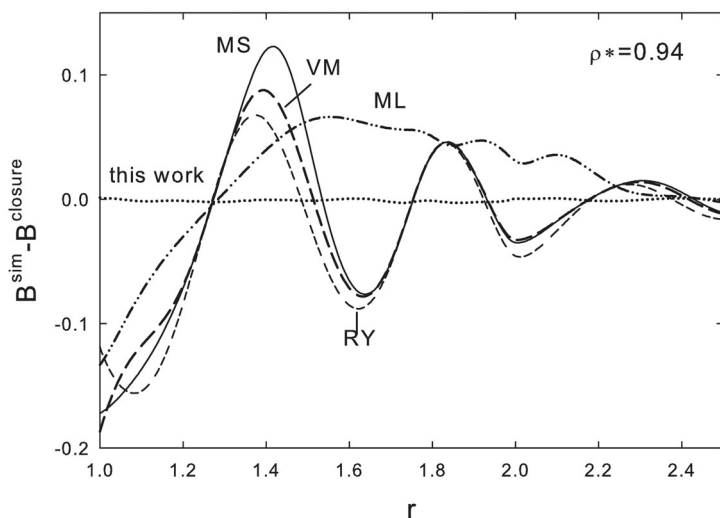
FIG. 3
Comparison of the simulated bridge function B^{sim} with several closures $B^{closure}$ at $\rho^* = 0.94$. Dotted line: this work, Eq. (*11*); solid line: the MS closure; dashed line: the RY closure; long dashes: the VM closure; dash-dot-dot line: the ML formula, Eqs (*9*) and (*10*)

shown in the figure. More sophisticated closures, the Rogers–Young, the Martynov–Sarkisov, and the modified Verlet, agree with the data on the pair distribution function within errors of ≈ 0.1 in magnitude. Within the scale of the figure the fit given by Eq. (*11*) does not differ from the $B(r)$ data. A similar comparison for the pair distribution function, $g(r)$, is in Fig. 4.

The same closures as in Figs 3 and 4 are tested in Fig. 5 but for B as a function of the indirect correlation function γ (so called the Duh–Haymet plot[21]) at a high fluid density. In the interval of $\gamma \in [0.5,3]$ all the considered closures qualitatively agree with the data. From the quantitative point of view, the PY closure is the worst and the VM one is the best. In the interval of $\gamma \in [-0.5,0.5]$, all the literature closures are incorrect in principle as they predict monotonous dependence of $B = f(\gamma)$. In this region, the older ML equation agrees with a much more accurate Eq. (*11*) qualitatively but not quantitatively.

Figures 6 and 7 show B as a function of γ at two high fluid densities and one metastable density. In Fig. 6, the region of γ ranging from 0.5 to 4 is shown. In this region, dependence $B = f(\gamma)$ is monotonous and only weekly depends on density. Figure 7 depicts a region of $\gamma \in [-0.6,0.6]$. The picture is dramatically different. A complicated $\Phi(B,\gamma,\rho^*)$ behavior practically ex-
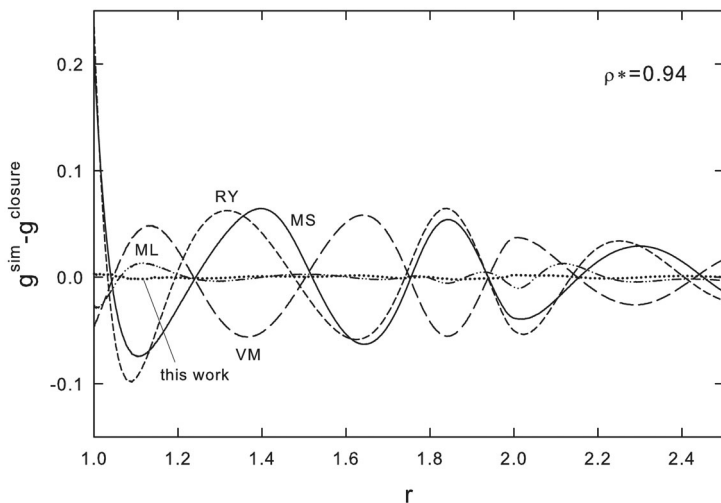

FIG. 4

Comparison of the simulated pair distribution function g^{sim} with results of the theoretical closures and the ML formula $g^{closure}$ at $\rho^* = 0.94$. Notation as in Fig. 3
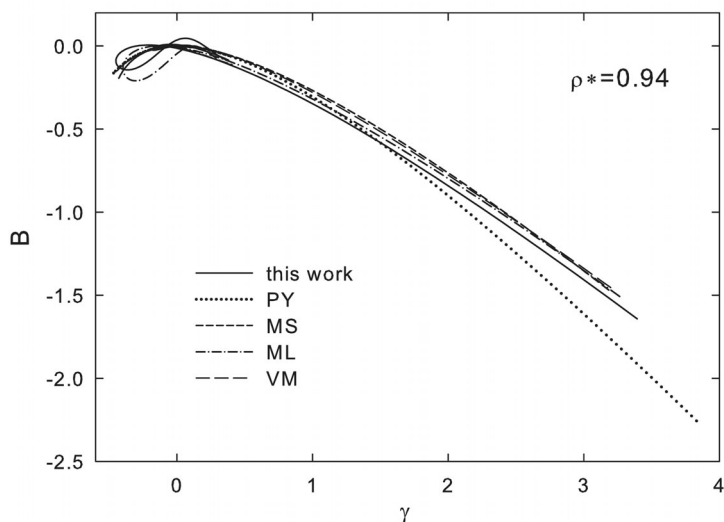
Fɪɢ. 5

Comparison of the bridge function as a function of the indirect correlation function γ with several closures at $\rho^* = 0.94$. Solid line: this work, Eq. (*11*); dashed line: the MS closure; dotted line: the PY closure; long dashes: the VM closure; dash-and-dotted line: the ML formula, Eqs (*9*) and (*10*)
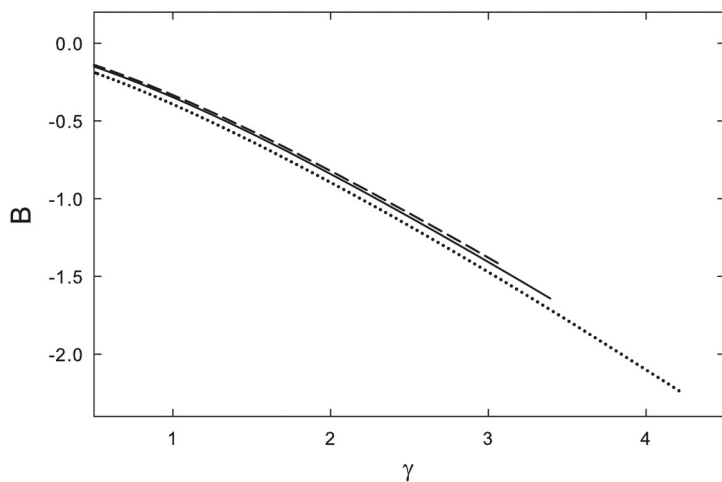

Fɪɢ. 6

The bridge function versus the indirect correlation function at three selected densities, $\rho^* = 0.90$ (dashed line), 0.94 (full line), and 1.02 (dotted line) for γ greater than 0.5

cludes any analytical description. Similar non local behavior was also found for additive and nonadditive hard sphere binary mixtures by Fatoni and Pastore[22].

There is an alternative to the integral equation approach, the fundamental measure theory of Rosenfeld[23], where the bridge function is not a function but a functional of the indirect correlation function. However, results for homogeneous fluids do not reach the accuracy of the integral equation methods up to now.

It may be concluded that the bridge function does not depend on the indirect function at a given density only locally. Then, why the literature closures are (at least partly) successful in describing the fluid structure? The answer is demonstrated in Fig. 6. In the most important region of high (in magnitude) values of B, the bridge function is a simple function of γ almost independent on density. In addition, while calculating the bridge function from the pair distribution function requires an extreme accurate the pair distribution function[17] (the error in g gets multiplied by 1000 at high fluid densities), the opposite is true for determining g from B; an inaccurate B may give an accurate g.
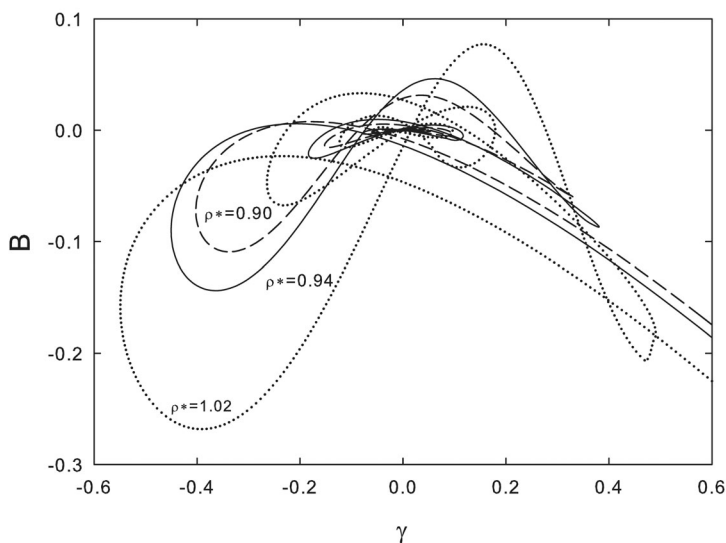

Fig. 7
The bridge function versus the indirect correlation function at three selected densities, $\rho^* = 0.90$ (dashed line), 0.94 (full line), and 1.02 (dotted line) for γ smaller than 0.6

CONCLUSIONS

New highly accurate computer simulation data on the pair distribution function of hard spheres at densities $\rho^* \in [0.2, 1.2]$ have been used to calculate the bridge function via the (inverted) OZ equation. The procedure of the invertion is described in detail in ref.[17]

The results for the bridge function have been fitted to the function of the interparticle separation distance and density. They fitted $B(r,\rho)$ has been used to test directly a few of the most frequently used closures to the OZ equation. It has been shown that none of the considered closures agrees with the present simulation results. More generally, it has been shown that none of the closures based on a local dependence of the bridge function on the indirect correlation function (and density) is able to describe quantitatively the real (i.e. simulated) dependence of the bridge function on a particle separation and density for pure hard spheres and therefore also for more complex fluid systems. A reasonable success of literature closures has been explained.

The fit $B = B(r,\rho^*)$ can be used in the frame of the reference hypernetted chain (RHNC)[24] theory with hard spheres as a reference system. However, the simpler ML equation remains useful for this purpose.

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APPENDIX

Density dependences of constants in Eq. (*11*) have been found by a method of trials and errors (see ref.[20] for details) for densities ρ^* ranging from 0.2 to 0.94. The results are as follows (for simplifying notation ρ is used instead of ρ^*).

Interval $r \in [1,2]$

$$\frac{a_i}{\rho^2} = \sum_{j=0}^{5} \frac{A_{j,i}\rho^j}{\left(1 - \frac{\pi}{6}\rho\right)^{m_i}} \text{, for } i = 0 \text{ to } 4 \text{, and } 7 \tag{12}$$

and

$$\frac{a_i}{\rho^2} = A_{0,i} + A_{1,i}\rho^2 + A_{2,i}\rho^4 + A_{3,i}\rho^6 + A_{4,i}\rho^{12} \text{, for } i = 5, 6, \text{ and } 8 \text{ to } 13. \tag{13}$$

Interval $r \in [2,3]$

$$b_i = B_{0,i}\rho^4 + B_{1,i}\rho^6 + B_{2,i}\rho^8 + B_{3,i}\rho^{12}. \tag{14}$$

Constants of the tail, $r > 3$

$$c_0 = -1.031815\rho^6 + 5.266226\rho^{12} \text{,}$$

$$c_1 = \frac{0.2893272\rho^8 - 0.4913634\rho^{16}}{(0.5235988\rho - 1)^4} \,,$$

$$c_2 = -1.921914\rho^6 - 2.921559\rho^{12} \,. \tag{15}$$

Values of the constants are given in Tables I, II and III. Computer codes on $B = B(r,\rho^\star)$ are available from the first author on request.

TABLE I
Coefficients in Eq. (*12*)

a_i	$A_{0,i}$	$A_{1,i}$	$A_{2,i}$	$A_{3,i}$	$A_{4,i}$	$A_{5,i}$	m_i
a_0	–0.206760	0.369280	0.171548	–0.196882	0.321639	–0.136672	4
a_1	0.321211	–0.364392	0.132817	–0.024998			3
a_2	–0.140573	–0.093559	0.211178	–0.086265			2
a_3	0.027062	0.055775	0.112436	–0.125269			2
a_4	0.001820	–0.002785	0.025128	–0.149103			1
a_5	–3.323 10^{-6}	0.000182	–0.001748	0.003525			3

TABLE II
Coefficients in Eq. (*13*)

a_i	$A_{0,i}$	$A_{1,i}$	$A_{2,i}$	$A_{3,i}$	$A_{4,i}$
a_5	–0.000911	–0.010723	–0.107885	0.150046	
a_6			–0.022374	0.069655	–0.015902
a_8	9.63 10^{-6}	–0.002118	0.011769	–0.003936	
a_9	8.04 10^{-6}	–0.000696	0.005670	–0.009351	
a_{10}	–1.36 10^{-5}	0.000424	–0.000169	0.004596	
a_{11}			0.002958	–0.009630	0.006282
a_{12}			0.000998	–0.000792	0.001137
a_{13}			–0.000974	0.005932	–0.005110

TABLE III
Coefficients in Eq. (*14*)

b_i	$B_{0,i}$	$B_{1,i}$	$B_{2,i}$	$B_{3,i}$
b_0	0.006446	–0.032025		–0.010458
b_1	–0.018374	0.06595		–0.004365
b_2	0.014518	–0.053402	0.054504	
b_3	–0.013088	0.033156	–0.002187	
b_4	0.010724	–0.014752	–0.033415	
b_5	–0.010482	0.002207		0.033602
b_6	–0.008424	0.079268		–0.100056
b_7	–0.002674	0.023253	–0.032579	
b_8	0.002688	–0.011618	0.010049	
b_9	–0.001499	0.004614	–0.002606	