

Percus-Yevick bridge functions in a thermodynamic self-consistent theory of hard sphere mixtures

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Two component hard sphere mixtures are studied by means of a modified hypernetted-chain (MHNC) approach in which Percus-Yevick (PY) bridge functions are employed. The thermodynamic self-consistency of the theory is obtained by using as adjustable parameters the hard sphere diameters entering the expressions of the bridge functions. Thermodynamically consistent calculations are also performed in the Rogers-Young (RY) approximation in terms of two consistency parameters. A wide range of diameter ratios and of relative concentrations of the particle species is explored, with particular attention to strongly asymmetric mixtures in the highly diluted regime of the bigger-sized component. Comparison with Monte Carlo results, and with well known parametrizations of computer simulation data, shows that the MHNC predictions for thermodynamic and structural quantities are generally very accurate and slightly superior to the RY ones. It also turns out that the PY bridge functions, which yield the thermodynamic consistency, reproduce fairly well those of the actual mixture as obtained from the parametrizations of simulation results. Such an agreement remains valid up to diameter ratios as great as 3, and down to 2% concentration of the bigger-sized component. [S1063-651X(97)00212-2]

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I. INTRODUCTION

Several authors [1–6] have recently addressed the problem of determining both the bridge functions and other functions relevant in the structural description of two-component fluids. Hard sphere mixtures have been, in particular, the object of an intense theoretical investigation and this has yielded a number of works based on liquid state integral equation theories [7,8–12], the density functional formalism [13–15], and other approaches [16–18].

Most of these studies do actually concern hard sphere mixtures characterized by a strong size asymmetry of the two particle species, and by a high dilution of the bigger-sized component. Such mixtures are in fact believed to model with sufficient accuracy real systems (such as, e.g., certain colloidal suspensions) for which neither experiments [19] nor computer simulations [20] have as yet clearly established whether (under appropriate temperature conditions) a liquid-liquid or a liquid-solid phase separation takes place. On the other hand, theoretical studies based on integral equation approaches predict that a phase segregation process does actually occur [8], although the nature of the coexisting phases is still a matter of debate [8,11,12].

Under such conditions it becomes particularly necessary to perform extensive tests of the most accurate theories available, in view of further determinations of the phase behavior of such fluids. To this aim, we consider here the modified hypernetted chain (MHNC) approach of Rosenfeld and Ashcroft [21], and devote this paper to an investigation of the performances of this theory in the description of hard sphere mixtures.

As is well known, in the MHNC a crucial role is played

by the knowledge of the hard sphere bridge function. In the one component hard sphere fluid case the latter was determined [21] by making use of “zero separation theorems” and of an accurate representation for the cavity distribution function $y(r)$ [22], together with extensively tested parametrizations of computer simulation data for thermodynamic and structural quantities [23–26].

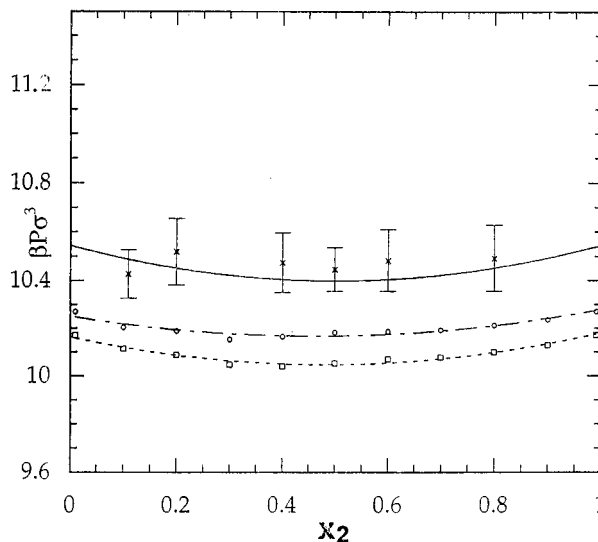


FIG. 1. Pressure in $k_B T / \sigma^3$ units [$\sigma^3 = x_2 \sigma_2^3 + (1 - x_2) \sigma_1^3$] for a mixture with $\alpha = 1.176$, $\eta = 0.4817$. Crosses with error bars, and full line: MD results and best fit, respectively (Kranendonk and Frenkel [35]); long dashed–short dashed line with circles: MHNC; short dashed line with circles: RY2.

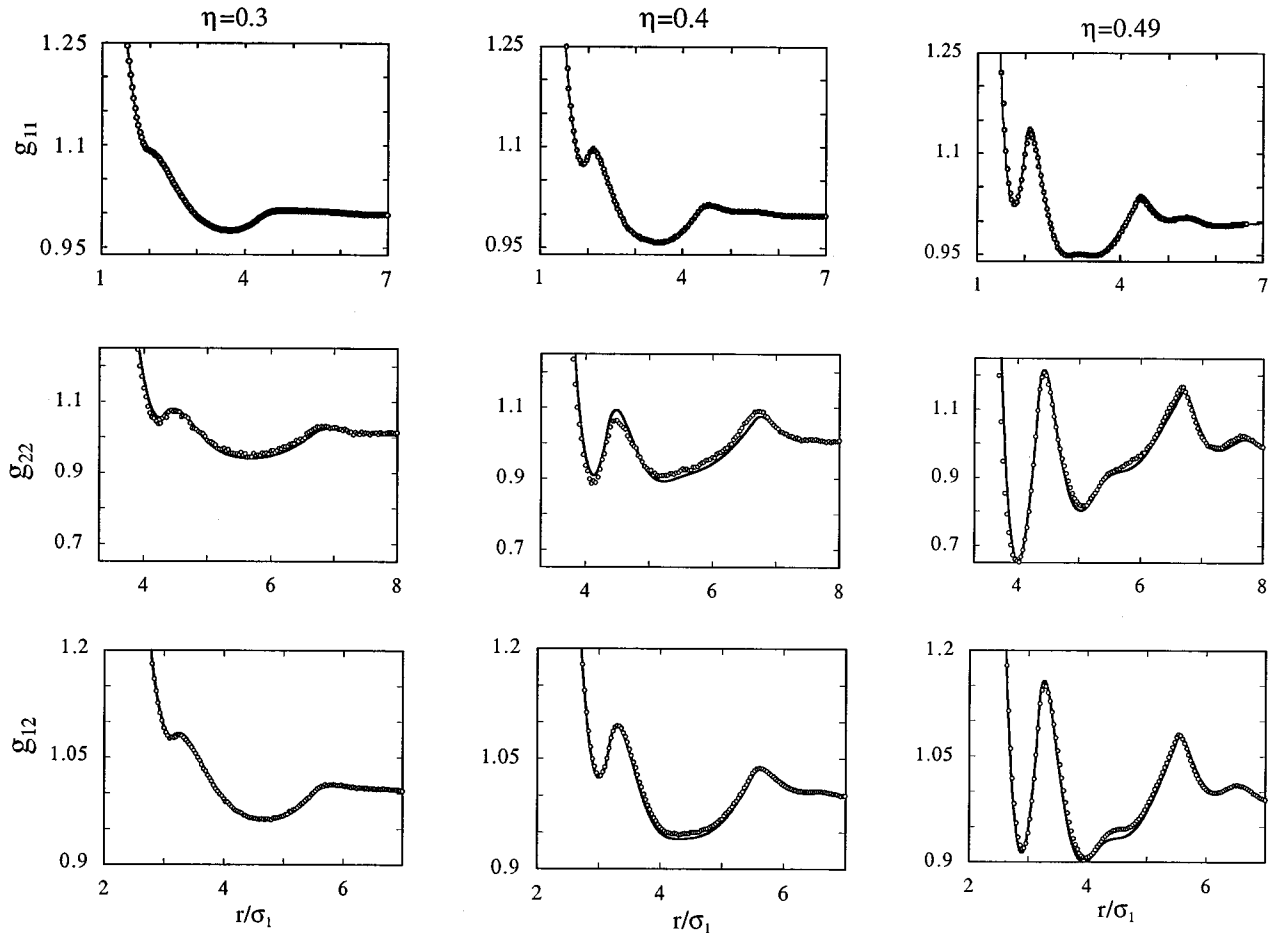


FIG. 2. Radial distribution functions for hard sphere mixtures with diameter ratio $\alpha = 3.333$ and concentration $x_2 = 0.0625$, at different packing fractions. Open circles: MC results (from Ref. [37]); full line: MHNC.

Zero separation theorems and approximate expressions for $y_{ij}(r)$ [22,27] are also available for two component hard sphere mixtures, but empirical equations of state (EOS) [28–30], such as the one due to Mansoori, Carnahan, Starling, and Leland [28] and Boublik [30] (henceforth termed BMCSL), and well known parametrizations of structural data due to Lee and Levesque (LL) [24] and Verlet and Weis (VW) [23], have been obtained from simulations only for not too large size asymmetries and dilutions of the bigger-sized hard spheres [30–38].

In order to apply the MHNC to multicomponent fluids we need therefore to resort to some approximate expression for the bridge functions. We do this according to an approach already adopted for one component fluids [21]; namely, we assume that the true bridge functions of the system can be represented by their Percus-Yevick (PY) counterparts, easily obtained from the analytic solution of this theory [39]; the hard sphere diameter entering the PY bridge functions are then used as adjustable parameters in order to enforce the thermodynamic self-consistency of the theory [40]. Such a type of investigation has been considered feasible since the MHNC has been devised [21,41]; we are not aware, however, of any published calculation for mixtures in which the PY bridge functions have been adopted within a thermodynamically self-consistent approach.

We consider hard sphere mixtures with various size asym-

metries of the components, and examine in detail the high dilution regime of the bigger-sized spheres. We also perform similarly self-consistent calculations in the well known Rogers-Young (RY) [42,43,7] approximation in which the consistency is imposed through the use of two adjustable parameters.

The theoretical predictions for thermodynamic and structural properties are first compared with simulations [33,35]. The PY bridge functions that yield the thermodynamic consistency are then compared with those of the actual mixture as estimated on the basis of parametrized simulation data.

In Sec. II we recall some basic relations of the MHNC and RY theories and describe the thermodynamic consistency procedure. Results are reported in Sec. III. Section IV contains the conclusions.

II. THEORETICAL APPROACH

We briefly recall the basic equations of the MHNC theory [21] for multicomponent fluids.

The exact relationship obtained through cluster expansion techniques,

$$g_{ij}(r) = \exp[-\beta V_{ij}(r) + h_{ij}(r) - c_{ij}(r) + B_{ij}(r)] \quad (1)$$

[where $h_{ij}(r) = g_{ij}(r) - 1$ is the pair correlation function,

$c_{ij}(r)$ is the direct correlation function, $B_{ij}(r)$ is the bridge function, and $V_{ij}(r)$ is the interparticle potential], and the Ornstein-Zernike equation

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^n \rho_k \int h_{ik}(r') c_{kj}(|\mathbf{r}-\mathbf{r}'|) d\mathbf{r}' \quad (2)$$

with ρ_k the number density of particles in the k th component, form a closed set of equations in the unknown $h_{ij}(r)$ and $c_{ij}(r)$ provided some prescription is available for $B_{ij}(r)$ (only formally known in terms of the infinite series of ‘‘bridge’’ diagrams).

Now for hard sphere mixtures we have

$$V_{ij}(r) = \begin{cases} \infty, & r < \sigma_{ij} \\ 0, & r > \sigma_{ij}, \end{cases} \quad (3)$$

with

$$\sigma_{ij} \equiv \frac{\sigma_i + \sigma_j}{2} \quad (4)$$

and σ_i the hard sphere diameter in the i th component.

As anticipated in the Introduction, our MHNC approach for particles interacting through potential (3) will consist in assuming that the true bridge function of the system can be represented in terms of PY bridge functions [21]

$$B_{ij}^{\text{PY}}(r; \sigma_{ij}^*) = \ln y_{ij}(r) - y_{ij}(r) + 1, \quad (5)$$

where $y_{ij}(r) = g_{ij}(r) \exp[\beta V_{ij}(r)]$ is the cavity distribution function and σ_{ij}^* are the adjustable diameters.

Thermodynamic consistency can then be imposed in two different manners:

(a) We can require that the virial and the compressibility equation of state (EOS) be equal. This can be obtained by taking the isothermal derivative of the virial pressure with respect to the density and equating it to the isothermal compressibility κ_T [44], namely, by setting

$$\left(\frac{\beta \partial P}{\partial \rho} \right)_T^{\text{vir}} = (\rho k_B T \kappa_T)^{-1} = 1 - \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j \rho \tilde{c}_{ij}(q=0); \quad (6)$$

here ρ is the total number density of particles, $x_i = \rho_i / \rho$ is the concentration of the i th species, and $\tilde{c}_{ij}(q)$ is the Fourier transform of $c_{ij}(r)$.

The left-hand side (lhs) of Eq. (6) is estimated from the virial EOS, which for hard sphere mixtures reads

$$\left(\frac{\beta P}{\rho} \right)^{\text{vir}} = 1 + \frac{2\pi\rho}{3} \sum_i \sum_j x_i x_j \sigma_{ij}^3 g_{ij}(\sigma_{ij}) \quad (7)$$

with $g_{ij}(\sigma_{ij})$ the contact values of the radial distribution functions (RDF’s).

(b) As discussed in previous works [8,43], we can also require consistency between the derivatives of the virial pressure and the osmotic compressibilities as estimated from fluctuation theory, that is,

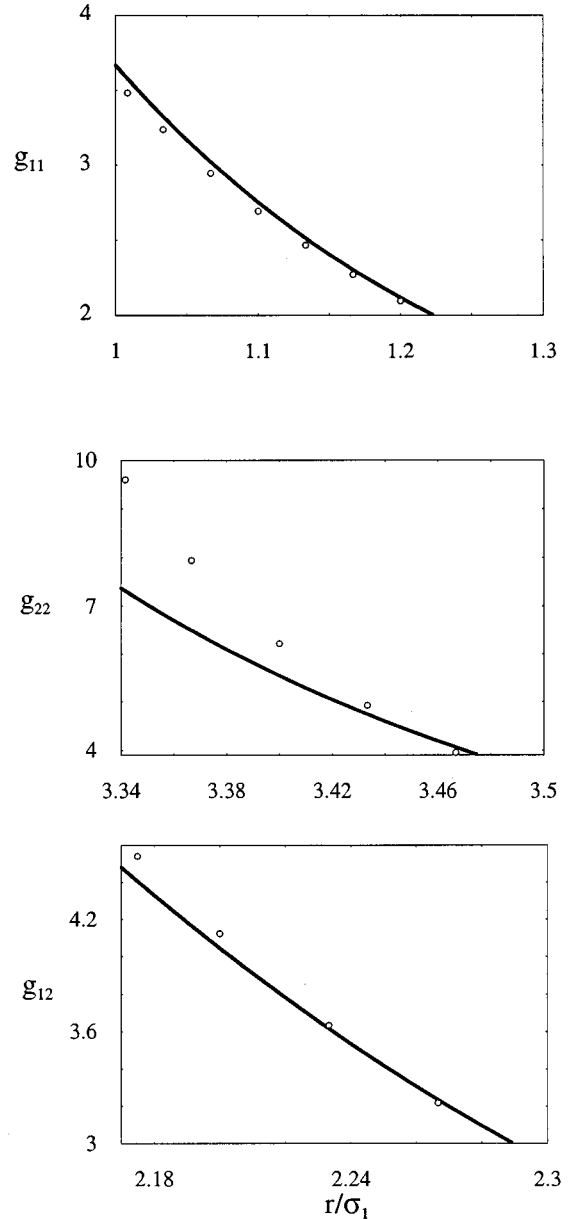


FIG. 3. Same as Fig. 2 near the hard sphere contact points (note the expanded distance scale).

$$\left(\frac{\beta \partial P}{\partial \rho_i} \right)_{T, \rho_i^-}^{\text{vir}} = 1 - \sum_{j=1}^2 \rho_j \tilde{c}_{ij}(q=0). \quad (8)$$

Obviously, the sum of conditions (8) yields Eq. (6), as is easy to verify.

Whether we adopt the single equation (6), or the two equations (8), we do not have yet enough conditions to fix the three σ_{ij}^* . We then assume that the additivity condition (4) for the cross diameter of the hard sphere mixture also holds for σ_{12}^* , namely, that

$$\sigma_{12}^* = \frac{1}{2}(\sigma_1^* + \sigma_2^*). \quad (9)$$

At this stage, if consistency is to be imposed through the unique condition (6), we further set

$$\frac{\sigma_2^*}{\sigma_1^*} = \frac{\sigma_2}{\sigma_1}, \quad (10)$$

so that we are left with only one free parameter to fit, say σ_1^* .

If conditions are adopted instead, we can work with two adjustable parameters, σ_1^* and σ_2^* , and fix σ_{12}^* according to prescription (9).

A consistency scheme similar to the one just described is also adopted for the other closure of the Ornstein-Zernike (OZ) equation that we have considered, namely, the Rogers-Young [42] approximation; this is written as

$$g_{ij}(r) = \exp[-\beta V_{ij}(r)] \times \left(1 + \frac{\exp(f_{ij}(r)[h_{ij}(r) - c_{ij}(r)] - 1)}{f_{ij}(r)} \right), \quad (11)$$

where $f_{ij}(r) = 1 - \exp[-\xi_{ij}r]$ and the ξ_{ij} are parameters that serve to enforce the thermodynamic consistency. Note that by means of Eqs. (1) and (11) one can determine the $B_{ij}(r)$ that correspond to any RY calculation.

The RY for hard sphere mixtures has been previously investigated by Biben and Hansen [8]. In the simplest version of this theory one can use a single consistency parameter either by setting $\xi_{ij} = \xi$ or by imposing relationships similar to Eqs. (9) and (10) for the ξ_{ij} . In the more sophisticated version two ξ parameters are used with different prescriptions for ξ_{12} (RY2) [8,43].

As already experienced by Biben and Hansen, [8] the results obtained in the two cases do not differ significantly from each other. In what follows we shall report only the results we obtained with two consistency parameters, which are slightly more accurate.

III. RESULTS

We first report MHNC and RY2 selfconsistent calculations of the EOS for a slightly asymmetric mixture with $\alpha \equiv \sigma_2/\sigma_1 = 1.176$ ($\sigma_1/\sigma_2 = 0.85$) at packing $\eta = (\pi/6)(\rho_1\sigma_1^3 + \rho_2\sigma_2^3) = 0.4817$. Results are reported in Fig. 1 and compared with computer simulation data [35]. It can be seen that the MHNC systematically improves over RY2; both theories, however, underestimate the pressure by 3–4% over the entire concentration range.

Results for the EOS and $g_{ij}(\sigma_{ij})$ of more asymmetric mixtures and in different concentration regimes are shown in Tables I and II.

It appears that the MHNC and RY2 provide very similar estimates of both $\beta P/\rho$ and $g_{ij}(\sigma_{ij})$, but the MHNC is systematically, albeit slightly, better than the RY2. The order of the discrepancy between the theoretical results and LL-VW parametrizations does not seem to depend significantly on α , x_2 , or η , and is at most 4%. The agreement between theory and Monte Carlo (MC) data is also generally good with the exception of $g_{22}(\sigma_{22})$, which seems poorly estimated in the more asymmetric case $\alpha = 3.333$, at the lowest concentration. It is worth observing that in such extreme regimes neither the BMCSL equation of state nor the LL-VW parametrizations are particularly accurate in comparison to simulation (see Tables I and II); note, however, that the simulation data

TABLE I. Values of $\beta P/\rho$ for various hard sphere mixtures as obtained from simulation, parametrizations of computer simulation data, and different theories.

α ($1/\alpha$)	η	x_2	MC	LL-VW	MHNC	RY2	PY
1.666 ^a	0.3	0.125	3.73		3.688		
[0.6]	0.4	0.125	6.396		6.277		
	0.49	0.125	11.102		10.723		
	0.3	0.25	3.648		3.617		
	0.4	0.25	6.241		6.119		
	0.49	0.25	10.767		10.423		
2 ^b	0.5	0.05	11.5	11.5	11.2	11.09	9.86
[0.5]	0.5	0.101	10.7	10.8	10.54	10.44	9.32
	0.5	0.199	10.1	10.4	10.09	9.99	8.93
3 ^b	0.45	0.0198	8.42	7.50	7.35	7.31	6.75
[0.333]	0.45	0.0625	6.27	6.22	6.14	6.11	5.68
	0.5	0.0625	8.47	8.32	8.15	8.08	7.34
3.333 ^c	0.3	0.0625	2.79		2.749		
[0.3]	0.4	0.0625	4.410		4.306		
	0.49	0.0625	7.158	7.07 ^d	6.862		
	0.3	0.125	2.687		2.650		
	0.4	0.125	4.204		4.101		
	0.49	0.125	6.77		6.49		
	0.49	0.5	8.81 ^e	8.65 ^e	8.37	8.34	8.18 ^e
5.0 ^f	0.1729	0.064	1.516		1.502		
[0.2]	0.1891	0.064	1.583		1.570		
	0.2039	0.064	1.652		1.637		
	0.2425	0.064	1.852		1.832		
	0.3006	0.064	2.241		2.202		

^aMC data from Ref. [36].

^bMC, LL, and PY data from Ref. [33].

^cMC data at $x_2 = 0.0625$ and 0.125 from Ref. [36].

^dEstimated from the BMCSL equation of state.

^eData from Ref. [1].

^fMC data from Ref. [38].

might be significantly affected by statistical problems for very low concentrations as, for instance, in the $x_2 = 0.02$ case [33].

We now show in Figs. 2 and 3 a detailed comparison between radial distribution functions obtained in the MHNC for $\alpha = 3.333$ and $x_2 = 0.0625$, with MC results.

The agreement between theory and simulation is generally very satisfactory except at very small distances; the failure of the MHNC to reproduce the MC $g_{22}(\sigma_{22})$ in this case, already quantified in Table II, is visible in Fig. 3. The theory confirms the existence in the rdfs of two extrema (a minimum and a maximum) above 1 at $r/\sigma_1 \approx 2$, first noticed in MC calculations by Malijevsky *et al.* [37]; the evolution with the packing fractions of such features, from the shoulder visible at $\eta = 0.3$ to the well defined minimum and peak, respectively, at $\eta = 0.49$, are also quite well reproduced.

We finally show the comparison of the PY bridge functions, which yield the thermodynamic self-consistency of the MHNC, with those obtained from parametrizations of computer simulation results.

TABLE II. Contact values or radial distribution functions. Same legend as Table I.

α (1/a)	η	x_2	MC	LL-VW	MHNC	RY2	PY
$g_{11}(\sigma_{11})$							
2 ^a [0.5]	0.5	0.05	5.40	5.28	5.11	5.05	4.55
	0.5	0.101	4.80	4.87	4.74	4.67	4.29
	0.5	0.199	4.20	4.45	4.34	4.27	4.00
3 ^a [0.333]	0.45	0.0198	4.70	3.89	3.81	3.78	3.53
	0.45	0.0625	3.30	3.30	3.25	3.18	3.10
	0.5	0.0625	4.20	4.05	3.97	3.91	3.72
3.333 ^b [0.3]	0.3	0.0625	1.92		1.93		
	0.4	0.0625	2.59		2.63		
	0.49	0.0625	3.57	3.60 ^c	3.68		
	0.3	0.125	1.83		1.84		
	0.4	0.125	2.40		2.44		
	0.49	0.125	3.26		3.34		
	0.49	0.5	3.06 ^d	2.96 ^d	2.9	2.8	2.86 ^d
$g_{12}(\sigma_{12})$							
2 ^a [0.5]	0.5	0.05	6.10	6.70	6.47	6.41	5.41
	0.5	0.101	5.70	6.08	5.89	5.82	5.05
	0.5	0.199	5.10	5.46	5.31	5.24	4.67
3 ^a [0.333]	0.45	0.0198	5.60	5.20	5.07	5.04	4.39
	0.45	0.062	4.20	4.19	4.11	4.10	3.74
	0.5	0.062	5.40	5.32	5.18	5.11	4.58
3.333 ^b [0.3]	0.3	0.0625	2.22		2.19		
	0.4	0.0625	3.19		3.12		
	0.49	0.0625	4.70	4.68 ^c	4.54		
	0.3	0.125	2.06		2.05		
	0.4	0.125	2.85		2.85		
	0.49	0.125	4.05		4.04		
	0.49	0.5	3.50 ^d	3.56 ^d	3.48	3.47	3.34 ^d
$g_{22}(\sigma_{22})$							
2 ^a [0.5]	0.5	0.05	12.4	10.0	9.84	9.89	7.11
	0.5	0.101	11.1	8.90	8.64	8.66	6.58
	0.5	0.199	8.6	7.78	7.52	7.52	6.00
3 ^a [0.333]	0.45	0.0198	6.70	10.2	10.4	10.5	6.96
	0.45	0.0625	8.00	7.47	7.45	7.73	5.66
	0.5	0.0625	10.0	10.1	9.98	10.1	7.16
3.333 ^b [0.3]	0.3	0.0625	3.55		3.02		
	0.4	0.0625	5.93		4.85		
	0.49	0.0625	10.18	9.21 ^c	7.64		
	0.3	0.125	3.03		2.78		
	0.4	0.125	4.89		4.31		
	0.49	0.125	8.14		6.74		
	0.49	0.5	6.18 ^d	5.98 ^d	5.74	5.74	4.96 ^d

^aMC, LL, and PY data from Ref. [33].

^bMC data at $x_2=0.0625$ and 0.125 from Ref. [37].

^cEstimated from the BMCSI equation of state.

^dData from Ref. [1].

In Fig. 4 we report the case of a hard sphere mixture with $\alpha=3.333$ and $x_2=0.5$ investigated by Enciso *et al.* [1].

It can be seen that the $B_{ij}^{\text{PY}}(r)$, considerably discrepant from the parametrized results when estimated at the proper

diameters of the mixture, become much more accurate when considered at the rescaled σ_{ij}^* yielding the thermodynamic consistency. It also appears that the RY2 bridge functions, though obtained through a similarly consistent calculation,

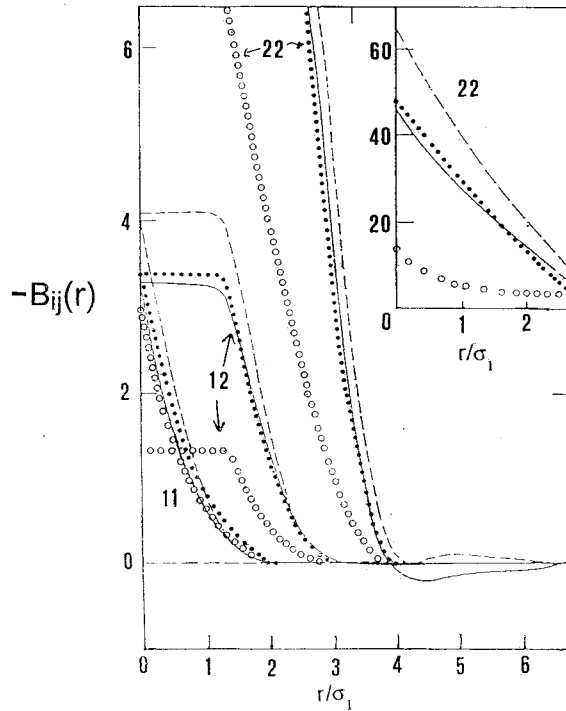


FIG. 4. Bridge functions for a hard sphere mixture with $\alpha = 3.333$, $\eta = 0.49$, and equimolar concentration ($x_2 = 0.5$). Full line: parametrized simulation results [1]; dashed line: PY estimated with hard sphere mixture diameters σ_{ij} ; black dots: PY, estimated at consistency diameters σ_{ij}^* ; open circles: RY2 results (see Sec. II).

are much less accurate than the PY ones.

The ability of the PY bridge function to faithfully map onto the parametrized ones is further documented in Fig. 5, where a much more diluted mixture having $x_2 = 0.0198$ and the same α as in Fig. 4 is considered.

We finally note that the flat behavior of $B_{12}^{\text{PY}}(r)$ in the region

$$0 \leq r \leq \Lambda_{12} = \frac{1}{\sigma_1} \left(\frac{\sigma_2 - \sigma_1}{2} \right) = \frac{\alpha - 1}{2}$$

is a consequence of the fact that in the PY for hard sphere mixtures one has [39]

$$-c_{12}(r) = y_{12}(r) = \text{const}, \quad r \leq \Lambda_{12}$$

so that, because of Eq. (5), also $B_{12}^{\text{PY}}(r)$ must be constant over the same range of distances. We note that this specific prediction of the PY turns out to be more than qualitatively accurate in comparison to the parametrized bridge functions, as visible in Figs. 4 and 5. Also note that the second zero separation theorem of Zhou and Stell [29] for hard sphere mixture bridge functions [Eqs. (2.12a) of Ref. [29]].

$$B'_{12}(0) = \frac{y'_{12}(0)}{y_{12}(0)},$$

combined with the first separation theorem for the cavity distribution function [22]

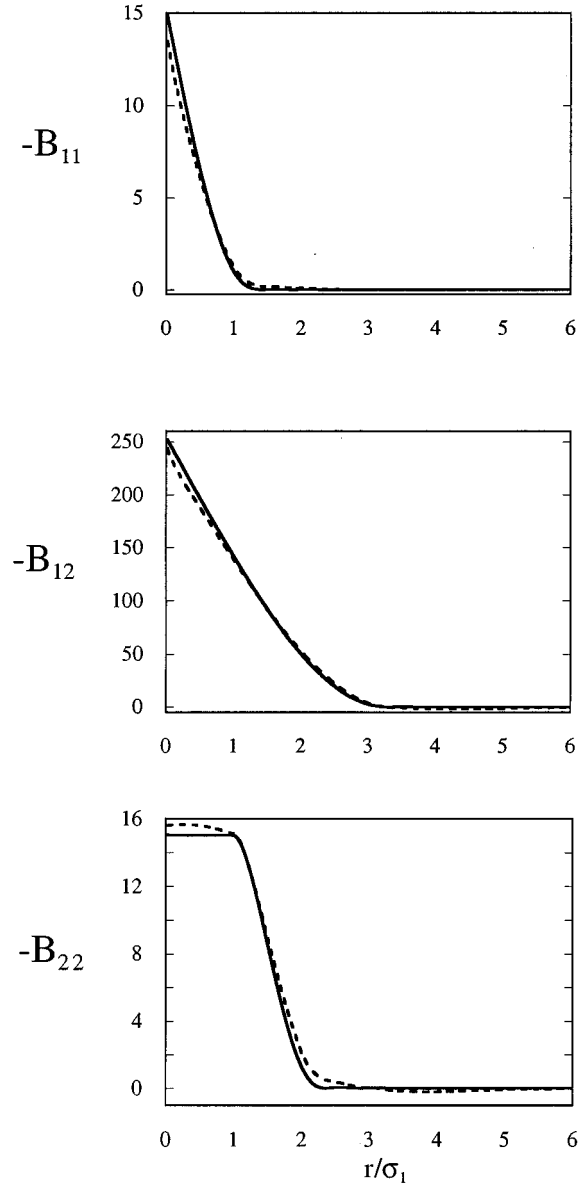


FIG. 5. Bridge functions for a mixture with $\alpha = 3.333$, $x_2 = 0.0198$, $\eta = 0.45$. Dashed line: parametrized bridge functions; full line: PY bridge functions at thermodynamic consistency.

$$y_{12}(r < \Lambda_{12}) = \frac{\exp(\beta\mu_1)}{\rho_1 \lambda_1^3} = \text{const}$$

(with μ and λ , the chemical potential and the thermal wavelength, respectively) implies zero slope for the true cross bridge function at $r=0$, and this limiting behavior is also satisfied by $B_{12}^{\text{PY}}(r)$.

We have verified, however, that for more extreme asymmetries, dilutions, and packing fractions, the PY representation of the bridge functions becomes poor, and unable to reproduce the marked oscillations that appear in the parametrized bridge functions.

IV. CONCLUSIONS

We have reported the results of MHNC calculations for hard sphere mixtures, performed on the basis of PY bridge

functions in which the hard sphere diameters are chosen in such a way as to impose the thermodynamic consistency of the theory. Parallel calculations in the RY approximation have been also performed, with the adoption of two free parameters.

For not too high asymmetries, the MHNC predictions turn out to be in general accurate, even for a concentration of the bigger-sized component as low as 2%, and up to packing fraction $\eta=0.49$. For higher asymmetries the theory seems unable to reproduce the simulation results, especially as far as the contact value of the radial distribution function of the bigger-sized hard spheres is concerned. The accuracy of the RY theory turns out to be slightly inferior to that of the MHNC for all the cases investigated.

We also find that the PY bridge functions map fairly accurately onto those obtained from parametrized computer simulation results, once thermodynamic self-consistency is imposed. Such an accuracy holds over the same wide range of diameter ratios, densities, and concentrations over which thermodynamic and structural properties are successfully reproduced by the MHNC.

We observe that our test of the PY bridge functions might deserve a further assessment since the parametrizations of computer simulation results used for the comparison are based on an approximate form for the cavity distribution function $y(r)$ [22,45]. It is also worth mentioning that recent studies [3] have documented the usually poor performances of various integral equation theories (PY included) for highly asymmetric hard sphere mixtures.

In conclusion, the present work allows one to get a quantitative estimate of the wide range of physical parameters over which the easily amenable PY information for hard sphere mixtures can be fruitfully employed, within the present MHNC approach, in order to predict thermodynamic and structural properties of hard sphere mixtures. In the absence of direct simulation information for mixtures more asymmetric than those here envisaged, and with the aim of further assessing the performances of liquid state theories in extreme regimes of the physical parameters, we think it would be also interesting to compare the present results with those obtainable through other closures of the OZ equation, as, for instance, the Verlet [44] approximation, recently reconsidered by Henderson *et al.* [5], or through the use of other bridge functions as, for instance, those obtained in the fundamental-measure free energy approach of Rosenfeld [15].

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