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Generalized mean-spherical-approximation description of highly asymmetric hard-sphere mixtures

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Abstract. We use thermodynamically self-consistent integral equation theories to determine the structure of binary hard-sphere mixtures in a regime of moderate to high size asymmetry, and for low concentration of the species with bigger particle size. Calculations are performed by applying the generalized mean-spherical approximation (GMSA) and the Rogers–Young (RY) approximation. The thermodynamic consistency of the GMSA is implemented in terms of adjustable parameters which are used in order to reproduce the Mansoori–Carnahan–Starling–Leland equation of state, and to impose the equality of the osmotic isothermal compressibilities estimated through the virial and fluctuation routes. The structural results obtained for a moderate size asymmetry of the particle species compare rather satisfactorily with the available Monte Carlo (MC) data and their parametrizations, and with previously reported modified hypernetted-chain results. The relative performances of the GMSA and of the RY approximations are also examined for strongly asymmetric mixtures. A regime of semi-dilute concentration for which no simulation data are available is investigated first and a very close agreement emerges between the RY and GMSA radial distribution functions. The case of very high dilution of the component with bigger particle size, for which RY and MC results already exist, is then considered, but it appears impossible to achieve a thermodynamically consistent solution for the GMSA according to the consistency prescriptions adopted. Other possible implementations of the thermodynamic consistency of the GMSA for HSMs and other multicomponent fluids are discussed.

1. Introduction

Recent developments of simulation techniques and of theoretical approaches [1–4] have improved our knowledge of the phase diagram of binary hard-sphere mixtures (HSMs) and led to new and decisive contributions to the highly controversial debate about the occurrence and nature of phase separation in these fluid systems [2–9]. Further advances in this same field concern the prediction of the equation of state (EOS). The well-known semi-empirical Mansoori–Carnahan–Starling–Leland (MCSL) [10] EOS, together with more recent schemes based either on virial expansions exact up to the fifth virial coefficient [11–13], or on exact conditions satisfied by the mixture in the special limit where one of the components corresponds to point particles [14], constitute a remarkable body of information in this respect.

However, an accurate and complete description of HSMs at the level of structural distribution functions seems still to be lacking. Such knowledge would be of considerable

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interest both as regards the reference role played by HSMs in perturbation theory descriptions of many model fluids [15] and for helping us to achieve a general understanding of packing properties of multicomponent systems. In particular, it would be worthwhile to fill this information gap for HSMs characterized by strong size asymmetries and high dilutions of the bigger-sized species; actually, such a parameter regime is appropriate to model colloidal suspensions, a class of systems whose phase behaviour and microscopic structure have been objects of intense investigation in recent years [16]. Unfortunately, the simulation structural data hitherto published for such regimes of HSMs are somewhat sparse [4,17,18], basically due to the great difficulties arising in the statistical sampling of the phase space for such mixtures; this same circumstance has hampered rigorous and extensive tests of fluid-state theories. Moreover, it is known that some of the most refined theories applied to highly asymmetric HSMs do not even possess solutions beyond a certain instability line in the parameter space, usually identified as the spinodal of the theory [4,6].

In this paper we focus our attention on the application of integral equation theories of the fluid state to HSMs. We consider, in particular, the generalized mean-spherical approximation (GMSA [19]) and the Rogers–Young (RY [20]) approximation. As is known from previous studies [4, 21, 22], the RY approximation yields reasonably accurate structural and thermodynamic properties even in rather extreme parameter regimes for HSMs; in contrast, such an extensive test of the GMSA performances seems still to be lacking.

Our interest in assessing the accuracy of the GMSA is justified by several circumstances. First, the theory is solvable by algebraic means and provides explicit analytical expressions for a number of thermodynamic quantities. It thus should allow an efficient investigation of those portions of the phase diagram amenable to description in terms of a fluid-state theory (supplemented by some one-phase freezing criterion [9, 21, 23, 24] for the prediction of the freezing line). Second, an analytic solution scheme should not encounter the stability problems frequently met by the iterative procedures employed in the RY and other integral equation theories of the fluid state [15,21,25]. It is worth observing however that, as we shall comment on further later, in the GMSA case also there are regions of the parameter space where it turns out to be impossible to achieve a physical solution, or any solution at all [26].

Our solution for the GMSA is obtained through the scheme reported in the work by Arrieta *et al* [26], which we implement in a thermodynamically self-consistent framework. Specifically, we impose the equality of the virial and fluctuation route estimates of the osmotic isothermal compressibilities by introducing in the theory two internal consistency constraints [21,22]. We further impose one external consistency condition by fitting the GMSA EOS to the MCSL value for all of the states investigated. A somewhat similar application of the GMSA to charged hard spheres of equal size has been recently reported by other authors [27]; we are not aware, however, of other attempts to impose a partially internal thermodynamic consistency of the GMSA for hard-sphere mixtures [28].

The paper is organized as follows. In section 2 we present the model and the theories. Results and a discussion are reported in section 3. The conclusions follow in section 4.

2. Model and theories

We consider a binary system of hard-sphere particles interacting through the pair potential

$$v_{ij}(r) = \begin{cases} \infty & r < \sigma_{ij} \\ 0 & r > \sigma_{ij} \end{cases} \tag{1}$$

where σ_i is the diameter of particles of the ith species, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $i, j = 1, 2$. We describe our mixture in terms of the size asymmetry ratio $\Lambda = \sigma_1/\sigma_2$, the partial and

total number densities of particles ρ_i and ρ, respectively, and the concentration of particles of species i, $\chi_i = \rho_i/\rho$. The Ornstein–Zernike (OZ) equation for the homogeneous mixture is [15]

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^{2} \rho_k \int c_{ik}(|\boldsymbol{r} - \boldsymbol{r}'|) h_{kj}(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}' \tag{2}$$

where $h_{ij}(r) = g_{ij}(r) - 1$ and $c_{ij}(r)$ are the pair and the direct correlation function, respectively, and $g_{ij}(r)$ is the radial distribution function. We first observe that, because of the form (1) of the potential,

$$h_{ij}(r) = -1 \qquad r < \sigma_{ij}. \tag{3}$$

Then, the GMSA closure to the OZ equation is written in terms of a Yukawa '*ansatz*' for $c_{ij}(r)$:

$$c_{ij}(r) = K_{ij} \frac{\exp[-z(r - \sigma_{ij})]}{r/\sigma_{ij}} \qquad r > \sigma_{ij}. \tag{4}$$

The solution of the OZ equation (2) under the closure (4) is obtained in a semi-analytical form by solving numerically a non-linear system of eight algebraic equations. We refer the reader to the previously quoted paper by Arrieta *et al* for a detailed description of the solution procedure.

As observed in the introduction, in the GMSA various thermodynamic quantities of interest turn out to be written as explicit functions of the solution variables [26]. This happens, for instance, for the contact values of the radial distribution functions (rdfs) entering the virial EOS expression

$$\left(\frac{\beta P}{\rho}\right)^{vir} = \frac{2\pi}{3} \rho \sum_{ij} \chi_i \chi_j \sigma_{ij}^3 g_{ij}(\sigma_{ij}) \tag{5}$$

($\beta = 1/k_B T$ with k_B the Boltzmann constant) which we set equal to the MCSL pressure; that is,

$$\left(\frac{\beta P}{\rho}\right)^{vir} = \frac{6}{\pi\rho} \left\{ \frac{\xi_0}{(1-\xi_3)} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{\xi_2^3(3-\xi_3)}{(1-\xi_3)^3} \right\} \tag{6}$$

with

$$\xi_k = \frac{\pi\rho}{6} \left(\chi_1 \sigma_1^k + \chi_2 \sigma_2^k\right) = \frac{\pi}{6} \left(\rho_1 \sigma_1^k + \rho_2 \sigma_2^k\right). \tag{7}$$

(Note that $\xi_3 = \sum_i (\pi/6)\rho_i \sigma_i^3$ is the total packing fraction. In what follows we shall adopt for this same quantity the notation $\eta = \sum_i \eta_i$ with $\eta_i = (\pi/6)\rho_i\sigma_i^3$ the partial packing fraction of species i.) Equation (6) acts as an external consistency constraint of the GMSA. We then force the theory to satisfy two internal consistency constraints by imposing the equality of the two osmotic compressibilities as evaluated from the virial and fluctuation routes [6, 21]. We thus obtain the two equations

$$1 - \sum_j \rho_j \tilde{c}_{ij}(q = 0) = \left(\beta \frac{\partial P}{\partial \rho_i}\right)^{vir}_{T, \rho_{j\,(j \neq i)}} \tag{8}$$

where $\tilde{c}_{ij}(q)$ is the Fourier transform of the direct correlation function $c_{ij}(r)$

In order to satisfy conditions (6) and (8) we use as adjustable parameters K_{11}, K_{22} and z appearing in equation (4); the remaining fourth parameter K_{12} is fixed according to the Lorentz–Berthelot rule [15] $K_{12} = \sqrt{K_{11}K_{22}}$. The values of K_{ij} and z for which the thermodynamic consistency is obtained for the various mixtures examined are reported in table 1.

Table 1. Yukawa parameters yielding thermodynamic consistency of the GMSA solution for the different HSMs investigated (see section 3).

Λ	η	χ_2	MC	LL[a]	MHNC[b]	RY	GMSA	PY
$g_{11}(\sigma_{11})$								
0.333	0.45	0.01978	4.60[c]	3.89	3.81	3.78	3.83	3.53
	0.45	0.0625	3.30[c]	3.30	3.25	3.18	3.24	3.10
0.3	0.3	0.0625	1.92[d]		1.93	1.91	1.91	1.89
	0.49	0.0625	3.57[d]	3.60	3.68	3.44	3.53	3.37
0.1	0.3	0.05				1.55	1.54	1.54
	0.5	0.05				2.44	2.35	2.33
$g_{12}(\sigma_{12})$								
0.333	0.45	0.01978	5.60[c]	5.20	5.07	5.04	5.30	4.39
	0.45	0.0625	4.20[c]	4.19	4.11	4.10	4.20	3.74
0.3	0.3	0.0625	2.22[d]		2.19	2.22	2.26	2.14
	0.49	0.0625	4.70[d]	4.68	4.54	4.55	4.69	4.13
0.1	0.3	0.05				1.62	1.63	1.62
	0.5	0.05				2.62	2.67	2.66
$g_{12}(\sigma_{12})$								
0.333	0.45	0.01978	6.70[c]	10.2	10.4	10.5	10.6	6.96
	0.45	0.0625	8.00[c]	7.47	7.45	7.73	7.67	5.66
0.3	0.3	0.0625	3.55[d]		3.02	3.42	3.56	2.96
	0.49	0.0625	10.18[d]	9.21	7.64	9.67	9.49	6.66
0.1	0.3	0.05				2.56	2.69	2.50
	0.5	0.05				5.98	6.92	5.47

[a] Lee–Levesque data from references [17, 29].
[b] MHNC data from reference [22].
[c] MC data from reference [17].
[d] MC data from reference [18].

We have also solved the OZ equation in the RY approximation. As is well known, in this theory one assumes

$$g_{ij}(r) = \exp[-\beta v_{ij}(r)] \left\{ 1 + \frac{\exp\{f_{ij}(r)[h_{ij}(r) - c_{ij}(r)]\} - 1}{f_{ij}(r)} \right\} \tag{9}$$

where $f_{ij}(r) = 1 - \exp[\xi_{ij} r]$ and the ξ_{ij} are adjusted in such a way as to satisfy the thermodynamic consistency of the theory. In the present implementation of the RY approximation we assume all $\xi_{ij} = \xi$ and we fix this parameter by requesting the equality of the fluctuation and virial bulk isothermal compressibilities, a condition easily obtained by summing both sides of (8) over the two component species. RY results for HSMs with two consistency parameters have also been obtained by us in a previous work [22]; we find however that they do not differ significantly from those obtained with one parameter.

The solution for the RY approximation is obtained numerically by employing the well-known Gillan algorithm [25] on a spatial grid of 4096 points spanning over $42\sigma_1$ in r-space.

3. Results and discussion

All the results reported in this section will concern HSMs characterized by an intermediate-to-high size asymmetry and by a high dilution of the bigger-sized component. We first consider the $\Lambda = 0.3$, $\chi_2 = 0.0625$ case and compare the GMSA and RY results with MC data [18] and with the MHNC results obtained by us in a previous paper [22]. The rdfs are shown in figure 1, while the EOS and the contact rdfs are reported in tables 2 and 3, respectively.

Table 2. Equations of state of the HSMs at different state points (see the text for the meaning of the symbols).

Λ	η	χ_2	MC	MCSL	MHNC[a]	RY	GMSA[b]	PY
$\beta P/\rho$								
0.333	0.45	0.01978	8.40[c]	7.47	7.35	7.31	7.46	6.74
	0.45	0.0625	6.27[c]	6.21	6.14	6.11	6.21	5.68
0.3	0.3	0.0625	2.79[d]	2.78	2.75	2.78	2.80	2.71
	0.49	0.0625	7.15[d]	7.08	6.88	6.93	7.07	6.33
0.1	0.3	0.05		1.80		1.79	1.80	1.80
	0.5	0.05		3.42		3.30	3.42	3.27

[a] MHNC data from reference [22].
[b] GMSA data: the best fit obtained to the MCSL equation of state.
[c] MC data from reference [17].
[d] MC data from reference [18].

Table 3. Contact values of the radial distribution functions for the HSMs examined in table 1.

Λ	η	χ_2	z	K_{11}	K_{22}
0.333	0.45	0.01978	6.56	0.90	21.80
	0.45	0.0625	4.84	0.49	13.08
0.3	0.3	0.0625	2.54	0.06	2.74
	0.49	0.0625	4.85	0.57	20.87
0.1	0.3	0.05	0.62	0.001	4.05
	0.5	0.05	1.23	0.02	34.92

The RY $g_{i,j}(r)$ appear to be in almost quantitative agreement with the MC patterns [18] at both low and high packing fractions, and are only slightly less accurate than the MHNC ones [22]. The positions of the main features of the rdfs are fairly well predicted by the GMSA, but the amplitudes are only qualitatively reproduced. In particular, the main GMSA deficiency is the tendency to overestimate the emptying zone of g_{22} and g_{12} between the first and the second coordination shell. Something similar has been observed to happen in the so-called rational function approximation to HSMs, an approach that according to the authors of [30] yields results substantially equivalent to those from the GMSA scheme.

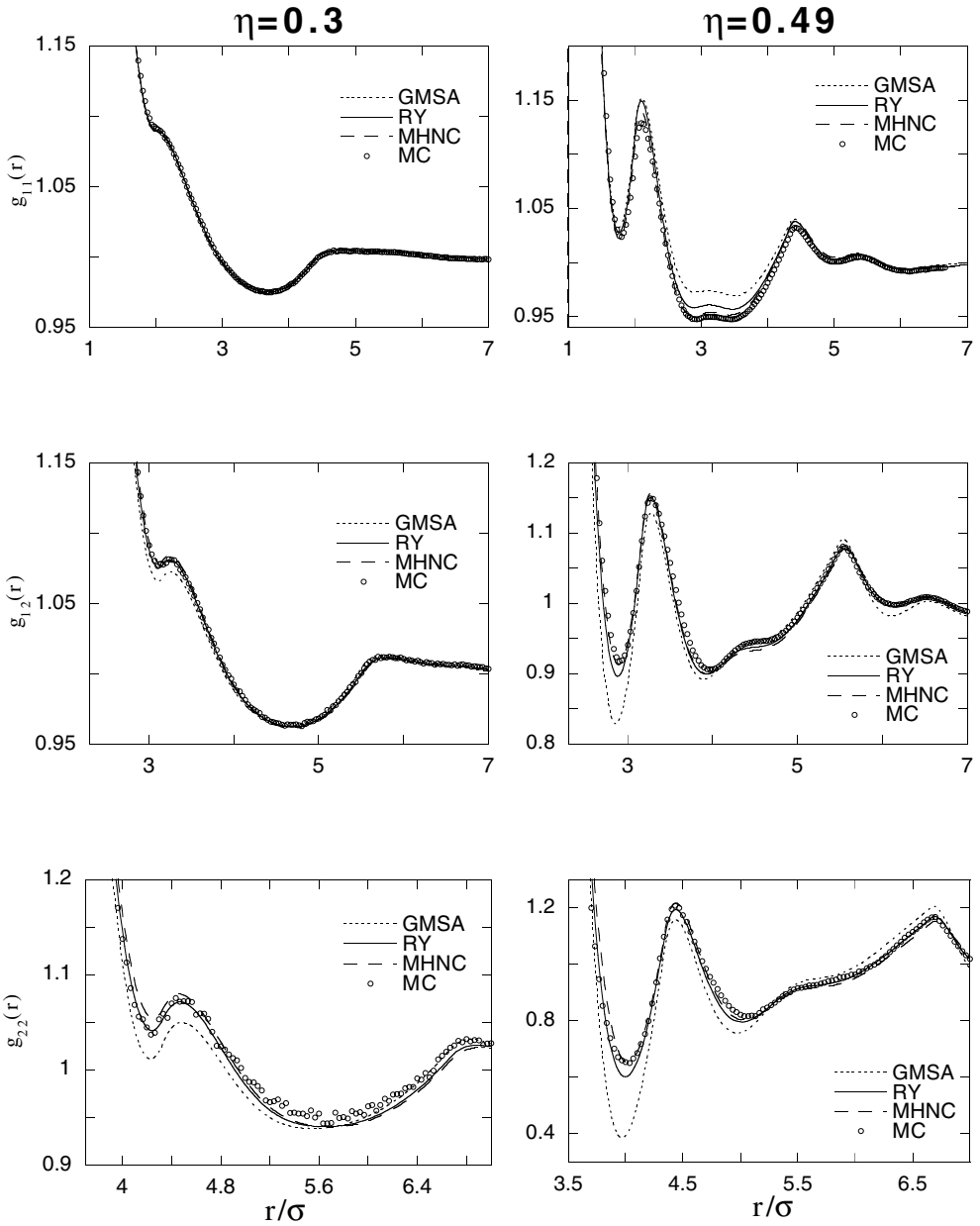

Figure 1. Radial distribution functions at $\Lambda = 0.3$, $\chi_2 = 0.0625$, for two different total packing fractions. $\sigma_1 = \sigma$ is the unit of length. MHNC data from reference [22]; MC data from reference [18]; RY and GMSA data: this work.

We do not report in figure 1 a comparison with the Percus–Yevick (PY) rdfs; these have been calculated and compared with MC data in reference [18]. On the basis of that study it appears that in the first-minimum region the PY functions are more accurate than the GMSA ones; however, as documented in table 3, the PY contact rdfs are definitely poorer than the GMSA estimates, while the latter are fairly close to the MC values with the exception of

$g_{22}(\sigma_{22})$ at $\eta = 0.49$. It also appears that the RY contacts are almost always slightly smaller than the MC and GMSA counterparts.

We also report in table 3 the comparison of the contact rdfs for the slightly less asymmetric case of $\Lambda = 0.333$ and $\eta = 0.45$ previously investigated in reference [17]. The results at $\chi_2 = 0.0625$ confirm for both the RY approximation and the GMSA a level of accuracy comparable to that for the $\Lambda = 0.3$ case. At the lower value $\chi_2 = 0.0198$, the comparison with the MC data is apparently less favourable; in fact the RY, the MHNC and the Lee–Levesque [29] $g_{ij}(\sigma_{ij})$ are all fairly close to each other (again with the RY results generally smaller than the GMSA ones) but they are appreciably different from the simulation values; on the other hand, the theoretical estimates of the EOS (which involve the $g_{ij}(\sigma_{ij})$ through equation (5)) reproduce the MCSL value well, as is apparent from table 2. It is worth noting at this stage that, as explicitly pointed out in reference [17], the MC $g_{ij}(r)$ at $\Lambda = 0.1$ and $\chi_2 = 0.0198$ were obtained with only a limited statistics; such a circumstance can explain the particularly low value of the MC $g_{22}(\sigma_{22})$ and the above-described discrepancy between theory and simulation.

We now consider the high-size-asymmetry case with $\Lambda = 0.1$ at concentration $\chi_2 = 0.05$ (see figure 2). No simulation data are available here for an assessment of the theoretical predictions. The RY and GMSA $g_{ij}(r)$ appear here to be in quite good agreement with each other and considerably less structured than in the $\Lambda = 0.3$ case at the two packing fractions investigated. This can be explained if one considers that at $\Lambda = 0.3$ and $\eta = 0.49$, the partial packing fraction of the bigger spheres, $\eta_2 = 0.349$, is of the same order of magnitude as that of the smaller spheres, $\eta_1 = 0.141$, whereas at $\Lambda = 0.1$ and $\eta = 0.5$ one has $\eta_2 = 0.491 \gg \eta_1 = 0.009$. It follows that in the more asymmetric case the structure of the system is entirely dominated by the arrangement of the large spheres despite their relatively smaller concentration. In the $\Lambda = 0.3$ case, however, the rdfs indicate the presence of different ordering length scales related to the sizes of the component particles. A good overall reciprocal agreement between the GMSA and the RY approximation is also found for the contact rdfs, as documented in table 3, but, similarly to what was found at the higher Λs, the RY $g_{12}(\sigma_{12})$ and $g_{22}(\sigma_{22})$ are definitely smaller than the GMSA ones. The PY values are also fairly good, except for $g_{22}(\sigma_{22})$.

As far as the EOS is concerned, the RY and the GMSA results are in close agreement with each other and with the MCSL results (see table 2). We recall that, as recently shown in reference [31], the RY approximation for this Λ reproduces fairly accurately the MCSL EOS at the higher value $\chi_2 = 0.1$ also. The PY prediction is also quite good in this case.

We finally examined the very dilute case with $\Lambda = 0.1$, $\chi_2 = 0.003$ (corresponding to $\eta_1 = 0.072$, $\eta_2 = 0.244$) previously investigated in reference [4] through both RY approximation and simulation. It was shown in [4] that the RY rdfs are on the whole in good agreement with simulation but the theory appears to significantly underestimate the MC contact rdfs. On the basis of this and the other comparisons with MC data just reported, it appears that the tendency of the RY approximation to underestimate the contact rdfs is systematic in the low-concentration regime. Since our GMSA contact rdfs are generally somewhat higher than the RY ones, it seems possible to conclude that the former theory should predict the $g_{ij}(\sigma_{ij})$ reasonably well in the previously considered case of $\Lambda = 0.1$, $\chi_2 = 0.05$.

It would be interesting to verify whether such accuracy also holds in the very dilute $\chi_2 = 0.003$ regime, where comparison with MC data [4] is possible. Unfortunately, we could not find a thermodynamically consistent solution for the GMSA in this case. What we find, in fact, is that the lower χ_2 is, the smaller the parameters K_{11} and z become (in terms of which conditions (6) and (8) are satisfied). This trend, already visible in table 1 at the lowest packing fractions considered there, is confirmed with χ_2 decreasing below 0.02,

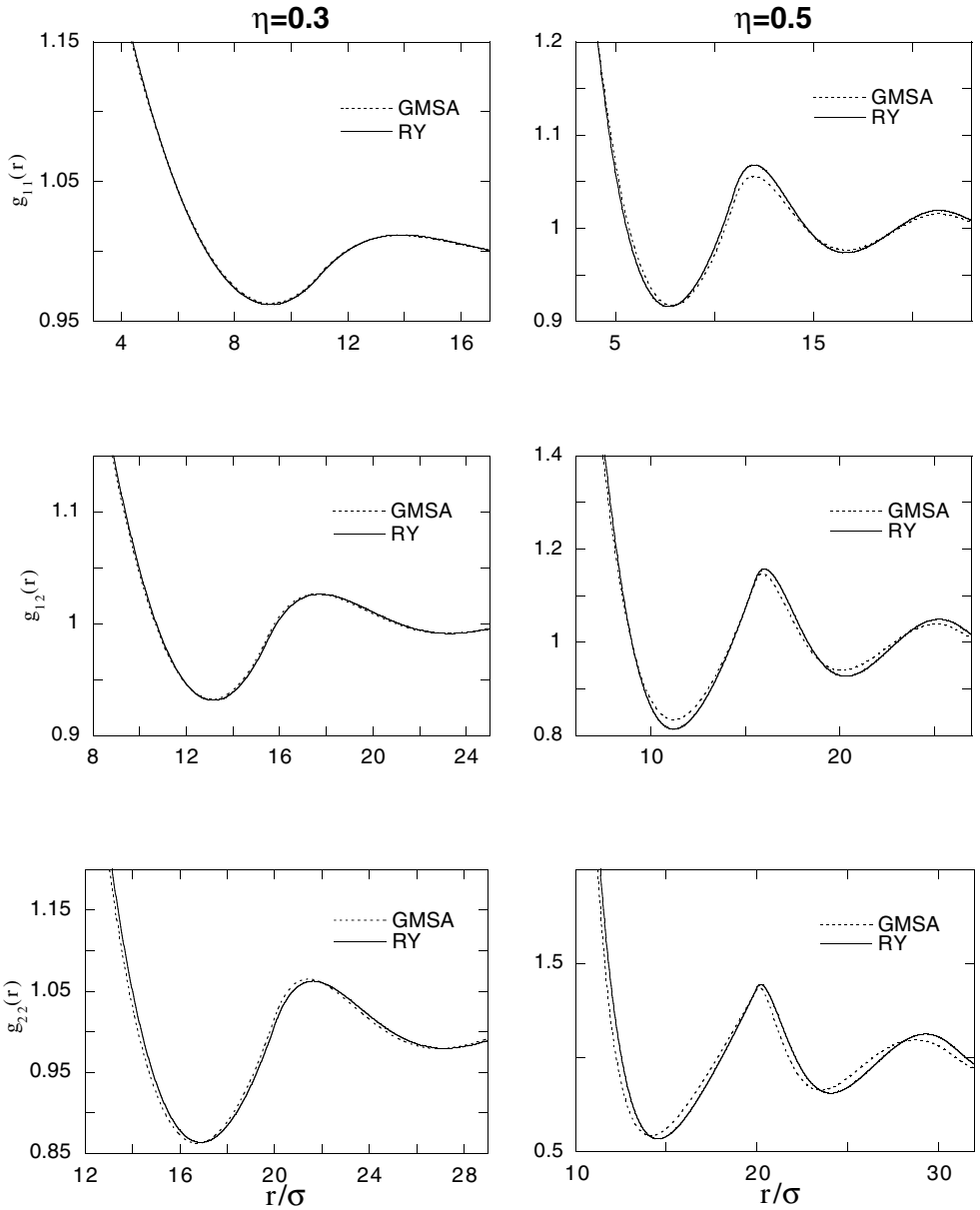

Figure 2. Radial distribution functions at $\Lambda = 0.1$, $\chi_2 = 0.05$, for two different total packing fractions. See figure 1 for the notation.

where we find that K_{11} tends to attain values of the order of 10^{-4}, and z approaches 0.2, until the Newton–Raphson algorithm for the solution for the GMSA fails to converge. Now, as mentioned in the introduction and shown by Arrieta *et al* [26], there are regions of the (K_{ij}, z) parameter space for which it turns out to be impossible to obtain a solution for the GMSA; the present failure to obtain thermodynamic consistency might then be due to the fact that, in imposing the latter, we are actually forcing the theory to work in a forbidden parameter region.

4. Conclusions

We have studied the structure of size-asymmetric semi-dilute hard-sphere mixtures in the framework of the thermodynamically self-consistent RY and GMSA theories. In particular, we have presented a new implementation of the thermodynamic consistency of the GMSA, in which both internal and external consistency constraints are imposed.

For moderate asymmetries, the GMSA structural functions turn out to be in qualitative agreement with simulation and with the RY predictions.

The semi-dilute regime of the bigger-sized particles has also been studied in a highly asymmetric configuration: the GMSA and RY rdfs obtained compare quite well with each other but no simulation data are available in this case for an assessment of the theoretical predictions.

Finally, attempts have been made to obtain a solution for the GMSA for a highly asymmetric mixture in a regime of concentration of the big particles so dilute that the partial packing fractions of the two component species become roughly of the same order of magnitude. Both RY and MC results would be available in this case for comparison; unfortunately, it turns out to be impossible to obtain a thermodynamically consistent solution for the GMSA in such a regime. This failure seems to be related to the tendency exhibited by two of the consistency parameters (one of which is the Yukawa decay inverse length z) to attain too-small values when the concentration of the bigger particles dramatically decreases. It would be interesting to verify to what extent these difficulties depend on the specific implementation of thermodynamic consistency that we have chosen. In particular, one could ascertain what the effect is of varying the prescription which fixes the cross Yukawa amplitude K_{12} in terms of K_{11} and K_{22}; alternatively, one could adopt an easier consistency scheme employing only two parameters, namely z and one of the K_{ij} (K_{22}, say) with the other Ks appropriately scaled on the basis of the results obtained for less extreme asymmetry and concentration regimes. Calculations in this direction are in progress.

Despite these limitations, the good overall performance of the GMSA might be of interest in view of the semi-analyticity of this theory. For instance, a GMSA investigation of the spinodal line of HSMs could prove useful, since iterative theories do yield considerably different predictions for that phase stability boundary [4].

The experience gained with HSMs could also prove useful in generalizing our GMSA consistency scheme to hard-core Yukawa mixtures (HCYM) (that is, hard spheres interacting through a Yukawa tail). A two-Yukawa-function *ansatz* for the direct correlation function [32] generalizing the closure (4) of the Ornstein–Zernike equation would be appropriate for this purpose: in such a scheme one of the Yukawa functions could be equated to the potential in a MSA-like closure, and the parameters of the second Yukawa function could serve to impose the thermodynamic consistency. A supplementary (with respect to the hard-sphere system) consistency condition would be provided in this case by the energy route to the equation of state. As is well known, hard-core plus Yukawa tail interactions are currently used to roughly model protein solutions [33] and the GMSA approach could be useful in order to study, at a qualitative level, the phase diagram of these systems, especially since their computer simulation investigation is seriously hampered by the strong size asymmetry and the deep potential wells characterizing the model potentials adopted.

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