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An efficient method for calculating the pair distribution functions of a ternary hard-sphere system in r space within the Percus–Yevick approximation

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We present a direct method which allows an accurate and—at the same time—economical calculation of the pair distribution functions (PDFs) $g_{ij}(r)$ of an additive ternary hard-sphere system within the Percus–Yevick approximation. The approach is based on the fact that for this approximation the Laplace transforms $[\hat{g}_{ij}(s)]$ of the PDFs are known analytically, so that the inversion of the $\hat{g}_{ij}(s)$ into r space can be performed exactly. The expressions presented here allow the determination of the $g_{ij}(r)$ for r values up to $8R_1$, R_1 being the diameter of the smallest species; this range in r space should be sufficient for applications in standard algorithms of liquid state theory, such as thermodynamic perturbation theories or integral-equation approaches.

1. Introduction

Ever since the presentation of the analytic solution of the Ornstein–Zernike (OZ) equations within the Percus–Yevick (PY) approximation for hard spheres (HS) [1, 2] (and their mixtures [3]), this simple model system has played an important role in liquid state theory. This still remains valid nowadays, even though, for instance, recent investigations of the properties of HS in the framework of sophisticated liquid state theories have revealed a large variety of phenomena [4] that cannot be described within the PY concept. HS still represent *the* preferred reference system in integral-equation theories or perturbation methods for determining the structure and thermodynamics of liquids [5]. Such applications require numerical algorithms which guarantee an accurate, yet time consuming determination of the structure functions of the reference system (mostly in terms of the pair distribution functions (PDFs) $g_{ij}(r)$); limitations of computing time and memory are particularly crucial if the number of components of the system is two or larger.

In this contribution we propose an efficient and accurate method for calculating the PDFs of a ternary system of HS over a r range $[0, 7R_1]$, R_1 being the diameter of the smallest species of spheres. This method has already been pointed out by Wertheim [1] and is based on the fact that the Laplace transforms of the PDFs $[\hat{g}_{ij}(s)]$ are known analytically in terms of simple polynomials and exponentials. This simple form allows a shell-by-shell inversion back into r space, where a shell is defined as a semi-infinite interval $[R, \infty)$, R being an integer multiple of the HS diameter (in the one-component case) or an integer or half-integer linear combination of the HS diameters R_i (in the general case of multicomponent systems). This shell method has turned out to be very useful in practical applications. The formalism can easily be extended to those hard-core systems that can be treated analytically, such as HS Yukawa (HSY) [6] or adhesive HS (AHS) [7]. Furthermore, a generalization for the binary case has been given in [8–12].

The realization of the inverse Laplace transformation for the $\hat{g}_{ij}(s)$ back into r space relies on the theorem of residues and gives closed expressions for the $g_{ij}(r)$ in terms of analytic functions (i.e. products of exponentials, polynomials, and step functions, the latter ones leading to the shell structure of the resulting PDFs). Although these explicit expressions are rather complex, their derivation can be achieved mostly with the help of symbolic languages (such as MATHEMATICA), so that an efficient numerical implementation (using, e.g. the new attractive features of Fortran90) is feasible. Hints for a practical implementation have been summarized in Appendix B.

In principle, the generalization for systems with four or more components is straightforward, and presents no

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special problems, at least when using the tools mentioned above. Nevertheless, (i) the rapidly increasing complexity of the expressions and (ii) a rapidly increasing number of shells occurring in the summation at a given r value impose certain practical limitations on the use of the resulting expressions.

The paper is organized as follows: in the following section we present the method, we summarize the explicit expressions for the $\hat{g}_{ij}(s)$ and the $g_{ij}(r)$ resulting from the inverse Laplace transformation. In the subsequent section we discuss the efficiency and numerical accuracy of the method as such and present a few results, leading to a concluding summary. Appendix A contains those expressions that are too complex to be presented in the text. In the other Appendix we give hints for actual numerical implementations.

2. The method

2.1. *Solution of the PY equations for an N-component system of HS*

An N-component system of HS is characterized by the diameters $\{R_1, \ldots, R_N\}$, the concentrations $\{c_1, \ldots, c_N\}$, the number density ρ, and the usual HS interactions which are assumed to be additive, i.e. $R_{ij} = \frac{1}{2}(R_i + R_j)$ with $R_{ii} = R_i$. We furthermore define the $S_{ij} = \frac{1}{2}(R_i - R_j)$, the partial number densities $\rho_i = c_i\rho$, and parameters ξ_n to be

$$\xi_n = \frac{\pi}{6}\sum_{k=1}^{N} \rho_k R_k^n. \tag{1}$$

In particular, $\xi_3 = \eta$, is the packing fraction and $\eta_i = (\pi/6)\rho_i$ are the partial packing fractions.

Following the work of Baxter [13], the Ornstein–Zernike (OZ) equations for a N-component system of HS

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

can be rewritten as two sets of integral equations, introducing the factor functions $Q_{ij}(r)$

$$rc_{ij}(r) = -Q'_{ij}(r) + 2\pi \sum_{k=1}^{N} \rho_k \times \int_{S_{ki}}^{\min[R_{ki}, R_{kj} - r]} \mathrm{d}t Q_{ki}(t) Q'_{kj}(t + r), \qquad S_{ij} < r < R_{ij}, \tag{3}$$

$$rh_{ij}(r) = -Q'_{ij}(r) + 2\pi \sum_{k=1}^{N} \rho_k \times \int_{S_{jk}}^{R_{jk}} \mathrm{d}t h_{ik}(|r - t|) Q_{kj}(t)(r - t), \qquad S_{ji} < r. \tag{4}$$

We should also like to mention that, in the present contribution, we follow the notation of [6, 14] that is slightly different from Baxter's original notation [13]. The $c_{ij}(r)$ and the $h_{ij}(r)$ are the direct and the total correlation functions, and the PDFs $g_{ij}(r)$ are defined as $g_{ij}(r) = h_{ij}(r) + 1$.

In combination with the PY closure relation [5], equations (3) and (4) can be solved *analytically* with the following solutions for the factor functions [14]

$$Q_{ij}(r) = \begin{cases} \frac{a_j}{2}(r^2 - R_{ij}^2) + b_j(r - R_{ij}), & S_{ji} < r < R_{ij}, \\ 0, & \text{elsewhere}, \end{cases} \tag{5}$$

and

$$a_i = \frac{1 - \xi_3 + 3R_i\xi_2}{(1 - \xi_3)^2}, \qquad b_i = -\frac{3}{2}\frac{R_i^2\xi_2}{(1 - \xi_3)^2}. \tag{6}$$

We now introduce the Laplace transforms of the pair distribution functions

$$\hat{g}_{ij}(s) = \int_0^\infty \mathrm{d}r\, r \exp(-sr) g_{ij}(r) \tag{7}$$

and the $\hat{Q}_{ij}(s)$, defined as

$$\hat{Q}_{ij}(s) = \int_{S_{ji}}^{R_{ij}} \mathrm{d}r \exp(-sr) Q_{ij}(r). \tag{8}$$

Using (5), we easily find

$$\hat{Q}_{ij}(s) = \frac{\exp(-sR_{ij})}{2s^3}\{f_{ij}^0(s) + \exp(sR_i)[-f_{ij}^0(s) + f_{ij}^1(s)]\} \tag{9}$$

with

$$f_{ij}^0(s) = -2a_j - 2s(a_jR_{ij} + b_j),$$
$$f_{ij}^1(s) = -2sa_jR_i - s^2(a_jR_iR_j + 2b_jR_i). \tag{10}$$

With all these definitions and after some algebra, equation (4) can be transformed into

$$\sum_{k=1}^{N} \hat{g}_{ik}(s)[\delta_{kj} - 2\pi\rho_k\hat{Q}_{kj}(s)] = -\frac{1}{2}\frac{\exp(-sR_{ij})}{s^2} f_{ij}^0(s). \tag{11}$$

2.2. *Explicit expressions for the $\hat{g}_{ij}(s)$*

The set of linear equations for the unknown $\hat{g}_{ij}(s)$ $(i,j = 1, \ldots, N)$ defined by (11) can—at least in principle—be solved for arbitrary N. For $N = 3$, in particu-

lar, we obtain using Cramer's rule for $i = j$

$$\hat{g}_{ii}(s) = \frac{1}{12\eta_i} s \frac{N_{ii}(s)}{D(s)} \tag{12}$$

and for $i \neq j$

$$\hat{g}_{ij}(s) = \hat{g}_{ji}(s) = s \frac{N_{ij}(s)}{2D(s)}. \tag{13}$$

The explicit expressions for $D(s)$ and the $N_{ij}(s)$ are found to be

$$\begin{aligned} D(s) = \mathcal{L}^{(0)}(s) &- \sum_{i=1}^{3} \exp(sR_i)\mathcal{L}_i^{(1)}(s) \\ &- \sum_{i<j}^{3} \exp[s(R_i + R_j)]\mathcal{L}_{ij}^{(2)}(s) \\ &+ \exp[s(R_1 + R_2 + R_3)]\mathcal{L}^{(3)}(s), \end{aligned} \tag{14}$$

$$\begin{aligned} N_{ii}(s) = \mathcal{L}^{(0)}(s) &- \sum_{l\neq i}^{3} \exp(sR_l)\mathcal{L}_l^{(1)}(s) \\ &- \exp[s(R_j + R_k)]\mathcal{L}_{jk}^{(2)}(s) \\ &\text{with } \{j,k\} = \{1,2,3\} \setminus \{i\} \quad \text{and } j < k, \end{aligned} \tag{15}$$

$$N_{ij}(s) = \exp[s(R_i + R_j)/2][\mathcal{M}_{ij}^{(0)}(s) + \exp(sR_k)\mathcal{M}_{ij}^{(1)}(s)]$$
$$\text{with } \{k\} = \{1,2,3\} \setminus \{i,j\}. \tag{16}$$

The $\mathcal{L}$'s and $\mathcal{M}$'s are polynomials in s that can be simplified according to the following rules, thereby introducing reduced polynomials $\bar{\mathcal{L}}$ and $\bar{\mathcal{M}}$

$$\mathcal{L}_i^{(1)}(s) = \mathcal{L}^{(0)}(s) + \bar{\mathcal{L}}_i^{(1)}(s), \tag{17}$$

$$\mathcal{L}_{ij}^{(2)}(s) = \mathcal{L}^{(0)}(s) - \bar{\mathcal{L}}_i^{(1)}(s) - \bar{\mathcal{L}}_j^{(1)}(s) + \bar{\mathcal{L}}_{ij}^{(2)}(s), \tag{18}$$

$$\begin{aligned} \mathcal{L}^{(3)}(s) = -\mathcal{L}^{(0)}(s) &+ \sum_{i=1}^{3} \mathcal{L}_i^{(1)}(s) \\ &+ \sum_{i<j}^{3} \mathcal{L}_{ij}^{(2)}(s) + \bar{\mathcal{L}}^{(3)}(s), \end{aligned} \tag{19}$$

$$\mathcal{M}_{ij}^{(1)}(s) = -\mathcal{M}_{ij}^{(0)}(s) + \bar{\mathcal{M}}_{ij}^{(1)}(s). \tag{20}$$

In particular, for the HS case one finds for $\mathcal{L}^{(0)}$ and the reduced polynomials:

$$\mathcal{L}^{(0)}(s) = 0, \tag{21}$$

$$\bar{\mathcal{L}}_i^{(1)}(s) = 288\eta_j\eta_k \frac{(R_j - R_k)^2}{(1-\xi_3)^2}$$
$$\text{with } \{j,k\} = \{1,2,3\} \setminus \{i\}, \tag{22}$$

$$\begin{aligned} \bar{\mathcal{L}}_{ij}^{(2)}(s) = 96\eta_k s &\frac{3R_k^2\xi_1 - 6R_k\xi_2 + \xi_3 - 1}{(1-\xi_3)^2} \\ &+ 48\eta_k s^2 \frac{R_k(2\xi_3 - 2 - 3R_k\xi_2)}{(1-\xi_3)^2} \\ &\text{with } \{k\} = \{1,2,3\} \setminus \{i,j\}, \end{aligned} \tag{23}$$

$$\begin{aligned} \bar{\mathcal{L}}^{(3)}(s) = 96\, s^2 &\frac{\xi_1(1-\xi_3) + 3\xi_2^2}{(1-\xi_3)^2} \\ &+ 48\, s^3 \frac{\xi_2}{(1-\xi_3)} + 8s^4, \end{aligned} \tag{24}$$

$$\mathcal{M}_{ij}^{(0)}(s) = 48\eta_k \frac{(R_i - R_k)(R_k - R_j)}{(1-\xi_3)^2}$$
$$\text{with } i \neq j \neq k, \tag{25}$$

$$\bar{\mathcal{M}}_{ij}^{(1)}(s) = 8s \frac{\begin{array}{r} 2 + 3\eta_k R_k(R_i - R_k)(R_k - R_j) - 3R_iR_j\xi_1 \\ + 3(R_i + R_j)\xi_2 + \xi_3 \end{array}}{(1-\xi_3)^2} + 8s^2 \frac{3R_iR_j\xi_2 + (R_i + R_j)(1-\xi_3)}{(1-\xi_3)^2}$$
$$\text{with } i \neq j \neq k. \tag{26}$$

$\mathcal{L}^{(0)}(s)$ being zero, we have been able to extract a common factor of s^5 in the above expressions for the reduced polynomials, but one should note that for the other analytically solvable models mentioned above—HSY and AHS—$\mathcal{L}^{(0)}$ will be non-vanishing.

2.3. *The inverse Laplace transformation back into r space*

Having obtained the $\hat{g}_{ij}(s)$ as presented in the preceding subsection, we can now analytically perform the inverse transformation back to r space. This method has been described in detail in previous papers [2,10]; therefore we restrict ourselves in the present contribution only to the peculiarities of the ternary case.

First we modify the common denominator of the $\hat{g}_{ij}(s)$

$$\frac{1}{D(s)} = \frac{\exp[-s(R_1 + R_2 + R_3)]}{\mathcal{L}^{(3)}(s)} \sum_{n=0}^{\infty} \left(\frac{\mathcal{I}(s)}{\mathcal{L}^{(3)}(s)} \right)^n, \tag{27}$$

thereby introducing

$$\mathcal{I}(s) = -\exp[-s(R_1+R_2+R_3)]\mathcal{L}^{(0)}(s) + \sum_{\substack{i=1 \\ \{j,k\}=\{1,2,3\}\setminus\{i\}}}^{3} \exp[-s(R_j+R_k)]\mathcal{L}_i^{(1)}(s) + \sum_{\substack{i<j \\ \{k\}=\{1,2,3\}\setminus\{i,j\}}}^{3} \exp(-sR_k)\mathcal{L}_{ij}^{(2)}(s). \quad (28)$$

We then obtain for the PDFs $g_{ij}(r)$ in r space for the case $i=j$

$$rg_{ii}(r) = \frac{1}{2\pi i}\frac{1}{12\eta_i}\sum_{n=0}^{\infty}\int_C \mathrm{d}s \; s\mathcal{I}^n(s)\frac{[\mathcal{L}^{(0)}(s) - \sum_{l\neq i}\exp(sR_l)\mathcal{L}_l^{(1)}(s) - \exp[s(R_j+R_k)]\mathcal{L}_{jk}^{(2)}(s)]}{[\mathcal{L}^{(3)}(s)]^{n+1}} \times \exp\{s[r-(R_1+R_2+R_3)]\} \quad \text{with } \{j,k\} = \{1,2,3\}\setminus\{i\}, \quad (29)$$

and for $i \neq j$

$$rg_{ij}(r) = \frac{1}{2\pi i}\sum_{n=0}^{\infty}\int_C \mathrm{d}s \; s\mathcal{I}^n(s)\exp[s(R_i+R_j)/2]\frac{\times\left[\mathcal{M}_{ij}^{(0)}(s) + \exp(sR_k)\mathcal{M}_{ij}^{(1)}(s)\right]}{2[\mathcal{L}^{(3)}(s)]^{n+1}} \times \exp\{s[r-(R_1+R_2+R_3)]\} \quad \text{with } \{k\} = \{1,2,3\}\setminus\{i,j\}. \quad (30)$$

Integration is to be carried out in these two expressions along a path C parallel to the imaginary s, axis and to the right of all poles of the integrand, i.e. the zeros of $\mathcal{L}^{(3)}(s)$.

Unifying (29) and (30), the $g_{ij}(r)$ can now be written as

$$rg_{ij}(r) = \frac{1}{2\pi i}\sum_{n=0}^{\infty}\sum_{\alpha}\int_C \mathrm{d}s \frac{sQ_{n,\alpha}^{ij}(s)}{[\mathcal{L}^{(3)}(s)]^{n+1}} \times \exp\{s[r-(\alpha_1R_1+\alpha_2R_2+\alpha_3R_3)]\}. \quad (31)$$

Since the $\mathcal{L}$'s and $\mathcal{M}$'s are polynomials in s, the $Q_{n,\alpha}^{ij}(s)$ are polynomials in s, too. A straightforward application of basic rules for multiplying polynomials easily yields their (rather complex) explicit expressions; these are collected in Appendix A. α stands for the set of the three non-negative integers or half-integers α_i; the possible values of the α_i (and hence the range of summation over α) in dependence of n, i, and j are also given in Appendix A.

The transformation of the $\hat{g}_{ij}(s)$ into r space by means of the explicit integration in (31) relies on the theorem of residues; again, we refer the reader for details to [2,10]. For a given set $\{i,j\}$ and fixed values of n and α one finds (with $R = \alpha_1R_1 + \alpha_2R_2 + \alpha_3R_3$) that

$$\int_C \mathrm{d}s \frac{sQ_{n,\alpha}^{ij}(s)}{[\mathcal{L}^{(3)}(s)]^{n+1}}\exp[s(r-R)] = \left[2\pi i\sum_{\tau=1}^{4}R_{n,\alpha}^{ij,\tau}\right]\Theta(r-R), \quad (32)$$

where $\Theta(x)$ is the usual Heaviside step function. Summation is extended over the four zeros s_τ of $\mathcal{L}^{(3)}(s)$, and the $R_{n,\alpha}^{ij,\tau}$ are the residues of the integrand in (32) for $s = s_\tau$, i.e.

$$R_{n,\alpha}^{ij,\tau} = \frac{1}{n!}\lim_{s\to s_\tau}\left\{\frac{\mathrm{d}^n}{\mathrm{d}s^n}\left((s-s_\tau)^{n+1}\frac{sQ_{n,\alpha}^{ij}(s)}{[\mathcal{L}^{(3)}(s)]^{n+1}} \times \exp[s(r-R)]\right)\right\}. \quad (33)$$

The expressions obtained by an explicit evaluation of the derivatives in (33) can be rearranged and simplified by introducing coefficients $a_n^{ij,\tau}$ and $b_{n,\alpha;m}^{ij,\tau}$, yielding the following, rather simple result for the PDFs in r space

$$rg_{ij}(r) = \sum_{n=0}^{\infty}rg_{ij}^n(r) = \sum_{n=0}^{\infty}\sum_{\alpha}\sum_{\tau=1}^{4}\left[a_n^{ij,\tau}\exp[s_\tau(r-R)] \times \left(\sum_{m=0}^{n}b_{n,\alpha;m}^{ij,\tau}(r-R)^m\Theta(r-R)\right)\right]. \quad (34)$$

To be more specific, the $a_n^{ij,\tau}$ are given by

$$a_n^{ij,\tau} = \frac{1}{n!}\frac{1}{\{[\mathcal{L}^{(3)}]'\}^{n+1}(s_\tau)},$$

correcting a typo in equation (A 3) of [10]; the $b_{n,\alpha;m}^{ij,\tau}$ are considerably more complex.

The structure of equation (33) being the same as in the binary case, we can use the expressions presented in equations (A 4)–(A 11) of [10] for the $b_{n,\alpha_1\alpha_2}^{m,\tau}$ by applying the following simple rules:

(a) rearrange upper and lower indices so that the $b_{n,\alpha_1\alpha_2}^{m,\tau}$ of the binary case match the $b_{n,\alpha;m}^{ij,\tau}$ of the ternary case;
(b) replace the $Q_{n,\alpha_1\alpha_2}(s)$ by the $Q_{n,\alpha}^{ij}(s)$;
(c) set $u(s) = 1$ in [10].

3. Discussion

The shell structure of the ternary case is substantially more complex than in the simple one-component or even

in the binary case. For a given n value we find subshells $S_{n,\alpha}$, characterized by the triple of α values, $\boldsymbol{\alpha}$, i.e.

$$S_{n,\alpha} = \{r | r \geq (\alpha_1 R_1 + \alpha_2 R_2 + \alpha_3 R_3)\}, \qquad (35)$$

where the ranges for the $\{\alpha_1, \alpha_2, \alpha_3\}$ for the different combinations of i and j are given in (A 2), (A 4), (A 6), and (A 8) of Appendix A. If we define the smallest left boundary of the n subshells (for a given pair of i and j) by

$$r_{0,n} = \min_{\alpha} \{\alpha_1 R_1 + \alpha_2 R_2 + \alpha_3 R_3\}, \qquad (36)$$

one can show that, if R_1 is the smallest diameter, $r_{0,n} = (n+1)R_1$. Then the expressions presented in *this* contribution in combination with those in [10] can be used for r values up to $r_{0,7}$. It should be added that an extension to higher values of n is in principle straightforward; however, a practical realization might be limited by the rapidly increasing complexity of the coefficients $a_n^{ij,\tau}$ and $b_{n,\alpha;m}^{ij,\tau}$ and a rapid increase in the number of subshells occurring in the summation of (34); in particular, the latter leads to a loss in numerical accuracy to be demonstrated in detail below. If the restriction $r < r_{0,7}$ is violated, contributions of subshells belonging to higher n values will be neglected, which, as a consequence, would lead to wrong results.

We demonstrate our method for a ternary system that is characterized by the set of $\{R_i\} = \{1, 1.2, 1.45\}$, the set of concentrations $\{c_i\} = \{0.2, 0.5, 0.3\}$, and a packing fraction $\eta = 0.4$. In figure 1 (*a*) we present the pair distribution function $g_{11}(r)$, in figure 1 (*b*) we display the corresponding shell structure $S_{n,\{\alpha_1,\alpha_2,\alpha_3\}}$. A closer analysis shows (i) that for $r = 7R_1$, $g_{11}(r)$ is made up of contributions of 140 subshells (cf. (34)) and (ii) that the largest and the smallest of these contributions are 27.64 and -50.36.

Large positive and negative contributions in equation (34) inevitably lead to numerical compensation errors and hence represent a drawback of this method, as already pointed out in [10]. Extensive numerical tests show that, in the case of HS, limitation of the r range to $r_{0,7}$ represents a reasonable compromise: even for high packing fractions the PDFs are practically unity at such distances. However, the situation might be different for other hard-core systems: for we know from the one-component case [11] that—depending on the choice of the system parameters—the PDFs for HSY fluids exhibit pronounced oscillations even for rather large distances. If in such a case the evaluation of the PDFs for $r > r_{0,7}$ is required we recommend to complement the shell method by implementing the asymptotic method, which is explained in detail in [11] and—using the expressions presented in this paper—can easily be generalized for the N-component case: for larger distances this method gives numerically more reliable results than the shell method.

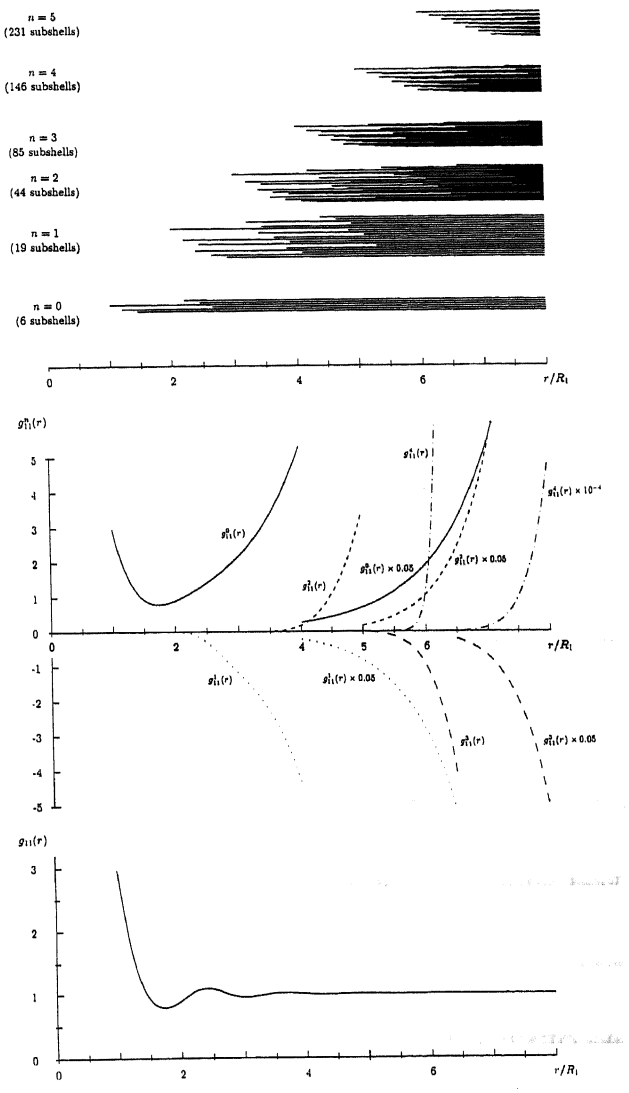

Figure 1. Shell structure (top), partial PDFs $g_{11}^n(r)$ (middle), and total PDF $g_{11}(r)$ (bottom) for a ternary HS system as defined in the text. r values are given in units of R_1, i.e. the smallest of the three HS diameters. Top panel: subshells $S_{n,\alpha}$ (as defined in equation (35)) for $n = 0, \ldots, 5$; total number of subshells for a given n are noted in brackets. Middle panel: partial PDFs $g_{11}^n(r)$ as defined in equation (34) for $n = 0, \ldots, 4$; the different functions are labelled by the respective multiplier, unless it is unity. Bottom panel: total PDF $g_{11}(r)$ as given in equation (34).

We have implemented the shell method in a Fortran90 code on a Linux-PC. Evaluation for the whole set of the $g_{ij}(r)$ over a range $[R_1, r_{0,7}]$ (R_1 being the smallest diameter) on a grid with a spacing of $0.05\,R_1$ typically takes 18 CPU seconds (on a Pentium processor of the first generation); a closer check shows that most of this time (i.e. 63%) goes into the calculation of the coefficients $b_{n,\alpha;m}^{ij,\tau}$. CPU times of this order of magnitude can be considered reasonable, hence the method is well

suited for practical applications such as perturbation theories, where the structure of the reference system must be calculated quite frequently for the determination of the system parameters of the reference system.

4. Conclusion

In this contribution we have presented an accurate, rapid, and efficient numerical method for calculating the pair distribution functions of a ternary hard-sphere system within the Percus–Yevick approximation over a representative range of r values; this range should be sufficiently large for most practical applications, and so the method represents a powerful tool in variational or perturbative calculations in liquid-state physics. It is based on the fact that the Laplace transforms of the PDFs are known analytically within the framework presented: this allows one to perform the transformation back into r space analytically using the theorem of residues. Although the expressions required for the actual calculation are rather complex, the method itself is numerically very stable and easy to use: all expressions required for a practical implementation (along with practical hints) have been given here (and in a previous publication). Furthermore, the expressions we present here are sufficiently general to allow an extension to other hard-core systems (such as hard-sphere Yukawa systems or adhesive hard spheres) that are similar to the hard-sphere case in that they can be treated fully analytically in one or the other liquid state approximation.

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Appendix A: Explicit expressions for the $Q^{ij}_{n,\alpha}(s)$

It is important to point out that the expressions for the $Q^{ij}_{n,\alpha}(s)$ presented in the following are by no means unique; other, equivalent formulations can easily be derived, which becomes particularly evident for the unlike case, since $g_{12}(r) = g_{21}(r)$. Furthermore, restricting ourselves in the present contribution to the HS case, we find $\mathcal{L}^{(0)}$ to be zero, so that we are able to neglect a number of terms involving positive powers of this function. For other hard core systems, such as HSY or AHS, this polynomial will be non-zero and the expressions for the $Q^{ij}_{n,\alpha}(s)$ must be readily generalized; the resulting expressions for the $Q^{ij}_{n,\alpha}(s)$ are considerably more complex but can be calculated in a straightforward manner using symbolic languages.

In the following we give the explicit expressions for the $Q^{ij}_{n,\alpha}(s)$ introduced in (31) along with the ranges for the indices (which follow from the fact that '$1/N! = 0$' for negative integer N).

One finds:

for $i = j$

$$
\begin{aligned}
Q^{ii}_{n,\alpha}(s) = -\frac{1}{12\eta_i} n! \alpha_i \sum_{n_1=\lambda_1}^{\Lambda-\lambda_2} \sum_{n_2=\lambda_2}^{\Lambda-n_1} & \\
\times \frac{[\mathcal{L}^{(2)}_{23}(s)]^{n_1}}{n_1!} \frac{[\mathcal{L}^{(2)}_{13}(s)]^{n_2}}{n_2!} & \\
\times \frac{[\mathcal{L}^{(2)}_{12}(s)]^{2+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3}}{(2+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3)!} & \\
\times \frac{[\mathcal{L}^{(1)}_{1}(s)]^{-1-n+n_1+\alpha_2+\alpha_3}}{(-1-n+n_1+\alpha_2+\alpha_3)!} & \\
\times \frac{[\mathcal{L}^{(1)}_{2}(s)]^{-1-n+n_2+\alpha_1+\alpha_3}}{(-1-n+n_2+\alpha_1+\alpha_3)!} & \\
\times \frac{\left[\mathcal{L}^{(1)}_{3}(s)\right]^{1+n-n_1-n_2-\alpha_3}}{(1+n-n_1-n_2-\alpha_3)!} & \qquad \text{(A 1)}
\end{aligned}
$$

with

$$
\begin{aligned}
\Lambda &= \min(1+n-\alpha_3, 2+2n-\alpha_1-\alpha_2-\alpha_3), \\
\lambda_1 &= \max(0, 1+n-\alpha_2-\alpha_3), \\
\lambda_2 &= \max(0, 1+n-\alpha_1-\alpha_3), \\
\alpha_1 &= 0, \ldots, 1+n, \\
\alpha_2 &= 0, \ldots, 1+n, \\
\alpha_3 &= \max(0, 1+n-\alpha_1-\alpha_2), \ldots, \\
&\quad \min(1+n, 2+2n-\alpha_1-\alpha_2). \qquad \text{(A 2)}
\end{aligned}
$$

For $i = 1$ and $j = 2$

$$
\begin{aligned}
Q^{12}_{n,\alpha}(s) = \frac{n!}{2} \sum_{n_1=\lambda_1}^{\Lambda-\lambda_2} \sum_{n_2=\lambda_2}^{\Lambda-n_1} & \frac{[\mathcal{L}^{(2)}_{23}(s)]^{n_2}}{n_2!} \\
\times \frac{[\mathcal{L}^{(2)}_{13}(s)]^{1+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3}}{(2+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3)!} & \\
\times \frac{[\mathcal{L}^{(2)}_{12}(s)]^{n_1}}{n_1!} \frac{[\mathcal{L}^{(1)}_{1}(s)]^{-\frac{3}{2}-n+n_2+\alpha_2+\alpha_3}}{(-\frac{1}{2}-n+n_2+\alpha_2+\alpha_3)!} & \\
\times \frac{[\mathcal{L}^{(1)}_{2}(s)]^{\frac{1}{2}+n-n_1-n_2-\alpha_2}}{(\frac{1}{2}+n-n_1-n_2-\alpha_2)!} & \\
\times \frac{[\mathcal{L}^{(1)}_{3}(s)]^{-1-n+n_1+\alpha_1+\alpha_2}}{(-1-n+n_1+\alpha_1+\alpha_2)!} & \\
\times [(-\tfrac{1}{2}-n+n_2+\alpha_2+\alpha_3)\mathcal{L}^{(2)}_{13}(s)\mathcal{M}^{(0)}_{12}(s) & \\
+ (2+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3) & \\
\times \mathcal{L}^{(1)}_{1}(s)\mathcal{M}^{(1)}_{12}(s)] & \qquad \text{(A 3)}
\end{aligned}
$$

with

$$\Lambda = \min(\tfrac{1}{2}+n-\alpha_2, 2+2n-\alpha_1-\alpha_2-\alpha_3),$$
$$\lambda_1 = \max(0, 1+n-\alpha_1-\alpha_2),$$
$$\lambda_2 = \max(0, \tfrac{1}{2}+n-\alpha_2-\alpha_3),$$
$$\alpha_1 = \tfrac{1}{2}, \ldots, \tfrac{3}{2}+n,$$
$$\alpha_2 = -\tfrac{1}{2}, \ldots, \tfrac{1}{2}+n,$$
$$\alpha_3 = \max(0, 1+n-\alpha_1-\alpha_2), \ldots, \min(1+n, 2+2n-\alpha_1-\alpha_2). \quad (A\,4)$$

For $i=1$ and $j=3$

$$Q^{13}_{n,\alpha}(s) = \frac{n!}{2}\sum_{n_1=\lambda_1}^{\Lambda-\lambda_2}\sum_{n_2=\lambda_2}^{\Lambda-n_1}\frac{[\mathcal{L}^{(2)}_{23}(s)]^{n_1}}{n_1!} \times \frac{[\mathcal{L}^{(2)}_{12}(s)]^{1+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3}}{(2+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3)!} \times \frac{[\mathcal{L}^{(2)}_{13}(s)]^{n_2}}{n_2!}\frac{[\mathcal{L}^{(1)}_{1}(s)]^{-\frac{3}{2}-n+n_1+\alpha_2+\alpha_3}}{(-\frac{1}{2}-n+n_1+\alpha_2+\alpha_3)!} \times \frac{[\mathcal{L}^{(1)}_{3}(s)]^{\frac{1}{2}+n-n_1-n_2-\alpha_3}}{(\frac{1}{2}+n-n_1-n_2-\alpha_3)!} \times \frac{[\mathcal{L}^{(1)}_{2}(s)]^{-1-n+n_2+\alpha_1+\alpha_3}}{(-1-n+n_2+\alpha_1+\alpha_3)!} \times [(-\tfrac{1}{2}-n+n_1+\alpha_2+\alpha_3)\mathcal{L}^{(2)}_{12}(s)\mathcal{M}^{(0)}_{13}(s) + (2+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3) \times \mathcal{L}^{(1)}_{1}(s)\mathcal{M}^{(1)}_{13}(s)] \quad (A\,5)$$

with

$$\Lambda = \min(\tfrac{1}{2}+n-\alpha_3, 2+2n-\alpha_1-\alpha_2-\alpha_3),$$
$$\lambda_1 = \max(0, \tfrac{1}{2}+n-\alpha_2-\alpha_3),$$
$$\lambda_2 = \max(0, 1+n-\alpha_1-\alpha_3),$$
$$\alpha_1 = \tfrac{1}{2}, \ldots, \tfrac{3}{2}+n,$$
$$\alpha_2 = 0, \ldots, 1+n,$$
$$\alpha_3 = \max(-\tfrac{1}{2}, 1+n-\alpha_1-\alpha_2), \ldots, \min(\tfrac{1}{2}+n, 2+2n-\alpha_1-\alpha_2). \quad (A\,6)$$

For $i=2$ and $j=3$

$$Q^{23}_{n,\alpha}(s) = \frac{n!}{2}\sum_{n_1=\lambda_1}^{\Lambda-\lambda_2}\sum_{n_2=\lambda_2}^{\Lambda-n_1}\frac{[\mathcal{L}^{(2)}_{23}(s)]^{n_1}}{n_1!} \times \frac{[\mathcal{L}^{(2)}_{12}(s)]^{1+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3}}{(2+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3)!} \times \frac{[\mathcal{L}^{(2)}_{13}(s)]^{n_2}}{n_2!}\frac{[\mathcal{L}^{(1)}_{1}(s)]^{-1-n+n_1+\alpha_2+\alpha_3}}{(-1-n+n_1+\alpha_2+\alpha_3)!} \times \frac{[\mathcal{L}^{(1)}_{3}(s)]^{\frac{1}{2}+n-n_1-n_2-\alpha_3}}{(\frac{1}{2}+n-n_1-n_2-\alpha_3)!} \times \frac{[\mathcal{L}^{(1)}_{2}(s)]^{-\frac{3}{2}-n+n_2+\alpha_1+\alpha_3}}{(-\frac{1}{2}-n+n_2+\alpha_1+\alpha_3)!} \times [(-\tfrac{1}{2}-n+n_2+\alpha_1+\alpha_3)\mathcal{L}^{(2)}_{12}(s)\mathcal{M}^{(0)}_{23}(s) + (2+2n-n_1-n_2-\alpha_1-\alpha_2-\alpha_3) \times \mathcal{L}^{(1)}_{2}(s)\mathcal{M}^{(1)}_{23}(s)] \quad (A\,7)$$

with

$$\Lambda = \min(\tfrac{1}{2}+n-\alpha_3, 2+2n-\alpha_1-\alpha_2-\alpha_3),$$
$$\lambda_1 = \max(0, 1+n-\alpha_2-\alpha_3),$$
$$\lambda_2 = \max(0, \tfrac{1}{2}+n-\alpha_1-\alpha_3),$$
$$\alpha_1 = 0, \ldots, 1+n,$$
$$\alpha_1 = \tfrac{1}{2}, \ldots, \tfrac{3}{2}+n,$$
$$\alpha_3 = \max(-\tfrac{1}{2}, 1+n-\alpha_1-\alpha_2), \ldots, \min(\tfrac{1}{2}+n, 2+2n-\alpha_1-\alpha_2). \quad (A\,8)$$

Special care must be taken when implementing equations (A 3), (A 5), and (A 7) for the unlike case: the factor in square brackets (last two lines) *must* be split up in order to avoid negative exponents of the $\mathcal{L}$'s in the nominators and negative arguments in the factorials in the denominators.

Appendix B: Hints for a numerical implementation

We have implemented this method in a Fortran90 program. The central problem here was the calculation of the coefficients $a_n^{ij,\tau}$ and $b^{ij,\tau}_{n,\alpha;m}$. These coefficients are introduced in (33) and can be calculated from the $Q^{ij}_{n,\alpha}(s)$ and the basic polynomials $\mathcal{L}$ and $\mathcal{M}$ and their derivatives with respect to s. However, since the explicit determination of the polynomials $Q^{ij}_{n,\alpha}(s)$ is too cumbersome we found it more convenient to proceed as follows (i.e. a route which is, in addition, less prone to errors): using the new features of Fortran90 we have created for a polynomial $p(x) = \sum_{i=0}^{n} p_i x^i$ a new data type (POLYNOMIAL), which contains the degree of the polynomial, n, and the array of coefficients $(p_i, i = 0, \ldots, n)$. For this derived data type we have defined

the usual polynomial operations, such as the sum and the product of two polynomials, the derivative of a polynomial and the evaluation of a polynomial $p(x)$ for a given x.

For the actual evaluation of the $Q^{ij}_{n,\alpha}(s)$ at the zeros s_τ further considerations can substantially reduce computing time and memory requirements: as is obvious from equation (A 1), the $Q^{ii}_{n,\alpha}(s)$ for like cases differ only in a prefactor, so that all three of them can be evaluated in one step.

For the calculation of the PDFs in the unlike case it is more economical (in particular with respect to memory requirements) to implement the expressions for the $b^{12,\tau}_{n,\alpha;m}$ and the $Q^{12}_{n,\alpha}(s)$, and to obtain the corresponding expressions for the other two cases by systematic permutation of the radii, i.e. $R_1 \to R_2$, $R_2 \to R_3$, and $R_3 \to R_1$.

Finally, when evaluating the PDFs via (34) the like and the unlike cases can be merged: for instance, by shifting the indices α_1 and α_2 for the unlike case $i = 1$ and $j = 2$ in (A 3) and (A 4) according to

$$\alpha_1 - \tfrac{1}{2} \to \bar{\alpha}_1 \qquad \text{and} \qquad \alpha_2 + \tfrac{1}{2} \to \bar{\alpha}_2 \qquad \text{(B 1)}$$

we find exactly the same range for $\bar{\alpha}_1$, $\bar{\alpha}_2$, and $\bar{\alpha}_3$ as for the α_1, α_2, and α_3 in the like case, which makes a common implementation possible.

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