

# Average Correlation Functions of Hard Convex Body Mixtures

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The modification of the Ornstein–Zernike (OZ) equation for mixtures is derived and numerically solved for binary mixtures of hard spheres (HS) or hard spheres and hard prolate spherocylinders (HPS) with length-to-breadth ratio  $\gamma = 2.0$ . The solution method results in average pair correlation functions. To test the proposed theoretical approach, Monte Carlo (MC) simulations in *NVT* ensemble are employed. The HS binary systems with diameter ratios 0.4 and 0.7 and HS + HPS mixtures with spherocylinder thicknesses 1, 0.4, and 0.3 of sphere diameter were simulated, and the average correlation functions plus compressibility factors of studied mixtures are listed. The theoretical prediction of average correlation functions generally agrees well with the MC data; however, for some of the studied systems, the results are not so satisfactory.

## 1. Introduction

Modern theories of equilibrium fluids most often employ hard bodies as a reference system. For this purpose, a fair knowledge of the hard body equation of state and characterization of the hard body fluid structure is essential. For the characterization of the fluid structure in the case of simple fluids, the radial distribution function (rdf) is used (for its definition and methods of determination see, for example, ref 1); the solution of the Ornstein–Zernike<sup>2</sup> integral equation<sup>3–5</sup> is often used to get values of the rdf in a broad range of independent variables.

For molecular fluids, the interaction site (IS) model or Kihara<sup>6</sup> generalized pair potential is used to describe intermolecular interactions of nonspherical molecules. In the latter case, hard convex bodies (HCB)<sup>7</sup> are considered as the reference or representative systems in the perturbation approach. For two hard bodies, the pair potential is equal to infinity if they overlap or zero if not. [The simplest HCB fluid is the system of additive hard spheres (HS)]. The average correlation functions, as functions of the shortest core–core distance, are conveniently used to describe the structure of the Kihara fluids. Semiempirical expressions for average correlation functions can be found in the literature;<sup>8</sup> these are based on the simulation data obtained by Monte Carlo (MC) or molecular dynamics (MD) methods. (The details of the simulation techniques in fluid systems can be found, for example, in ref 9). One of the present authors proposed an empirical relation (e.g., see ref 10) between the HCB average correlation function and radial distribution function of the equivalent HS system.

From the a priori assumptions, closures to OZ, that proposed by Percus and Yevick (PY)<sup>11</sup> is usually used in the case of HS systems. This is because an analytic solution of the equation can be found and the numerical solution offers some simplifications. The study of further closures used for binary mixtures of hard spheres can be found in the work of Henderson et al.<sup>12</sup> Very precise study of HS mixtures, including the set of MC data, was published by Malijevský et al.<sup>13</sup>

Theoretical basis of our method was published in previous paper<sup>14</sup> dealing with the cluster integrals. The idea of separation

of the shape and force effect led to formulation of the modified OZ relation that was published<sup>15,16</sup> with first numerical results for pure hard prolate spherocylinders (HPS). In this paper, we will continue to test applicability of the modified OZ equation. We will introduce its extension to the mixtures of HCB, show a simple method of numerical solution, and present the new set of MC simulation data for average correlation functions of binary HS and HS + HPS mixtures.

In the first part of the paper, the refinement of the theory and its extension to mixtures of HCB is given. In the following part, we refer the used MC method and data obtained for the average correlation functions in the studied systems of HS mixtures and HS + HCB systems. The comparison of theoretical and simulation data is discussed in the third part.

## 2. Theory

**2.1. Basic Relations.** We assume that the pair interactions are described by the Kihara pair potential. If **1** and **2** denote generalized coordinates of convex cores of types *i* and *j*, the molecular pair interaction potential,  $u_{ij}$ , takes the form

$$u_{ij}(\mathbf{1}, \mathbf{2}) = u_{ij}(s_{ij}(\mathbf{1}, \mathbf{2}))$$

where  $s_{ij}(\mathbf{1}, \mathbf{2})$  denotes the distance between surfaces of hard convex cores. The Mayer function,  $f_{ij}$ , is defined as

$$f_{ij}(\mathbf{1}, \mathbf{2}) = f_{ij}(s_{ij}(\mathbf{1}, \mathbf{2})) = \exp[-\beta u_{ij}(s_{ij}(\mathbf{1}, \mathbf{2}))] - 1$$

The Mayer function depends, similarly to the pair potential, only on the distance,  $s_{ij}$ , of core surfaces. According to eq A2 in Appendix A, we can write

$$f_{ij}(s_{ij}(\mathbf{1}, \mathbf{2})) = \int_{-\infty}^{+\infty} f'_{ij}(r) F[r - s_{ij}(\mathbf{1}, \mathbf{2})] dr \quad (1)$$

where

$$F(z) = \begin{cases} 0, & z < 0 \\ -1, & z > 0 \end{cases}$$

The important observation is that  $F[r - s_{ij}(\mathbf{1}, \mathbf{2})]$  represents the Mayer function of particles the pair potential,  $u_{ij}$ , of which is

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given by prescription

$$u_{ij}(s_{ij}(\mathbf{1}, \mathbf{2})) = \begin{cases} +\infty, & s_{ij}(\mathbf{1}, \mathbf{2}) < r \\ 0, & s_{ij}(\mathbf{1}, \mathbf{2}) > r \end{cases} \quad (2)$$

It appears to be very useful for the further considerations to extend the notion of distance between core surfaces and introduce separation coordinate (or shortly separation),  $s_{ij}$ , that can possess negative values (characterizing average extent of pair overlap). Possible definition of  $s_{ij}$  takes the form

$$s_{ij}(\mathbf{1}, \mathbf{2}) = \bar{s}_{ij}(\mathbf{1}, \mathbf{2}) - \xi_i - \xi_j \quad (3)$$

where  $\bar{s}_{ij}$  denotes a distance between minimum convex cores inscribed into original cores so that original core of type  $l$  can be constructed by adding a layer of thickness  $\xi_l$  to the corresponding minimum core.

The important characteristic of molecular fluid structure is molecular pair correlation function,  $g_{ij}$ . For Kihara fluids, we define average pair correlation function,  $g_{ij}^{\text{av}}$ , depending only on the distance between hard convex cores. Performing the transformation  $\mathbf{1}, \mathbf{2} \rightarrow \mathbf{1}, r, \theta, \phi, \omega$ , we write

$$g_{ij}^{\text{av}}(r) = \frac{1}{S_{i+r+j}} \int \int_{r=\text{const}} g(r, \theta, \phi, \omega) dS_{i+r+j}(\omega) d\omega \quad (4)$$

where

$$dS_{i+r+j}(\omega) = \mathbf{v} \cdot \left( \frac{\partial \mathbf{r}_{12}}{\partial \theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \phi} \right) d\theta d\phi$$

denotes the surface element at the given mutual orientation  $\omega$ . The symbol  $\mathbf{r}_{12}$  means the vector tending from the center of the first core (fixed) to that of the second one. The above equation represents averaging of  $g_{ij}$  over all orientations  $\theta$  and  $\phi$  of the supporting plane normal vector,  $\mathbf{v}$ , and all mutual orientations  $\omega$  of convex cores, while core–core distance,  $r$ , is kept constant. Function  $S_{i+r+j}$  is the mean surface area of the pair of convex cores of types  $i$  and  $j$  at separation  $r$ . For convex bodies, it holds true that

$$S_{i+r+j} = \int \int_{r=\text{const}} dS_{i+r+j}(\omega) d\omega = S_{i+j} + 8\pi(R_i + R_j)r + 4\pi r^2 \quad (5)$$

where  $S_{i+j} = S_i + S_j + 8\pi R_i R_j$ . In eq 5,  $R_l$  stands for  $(4\pi)^{-1}$ -multiple of the mean curvature integral, while  $S_l$  denotes the surface area of the core of type  $l$ . These quantities, together with volume  $V_l$ , are called fundamental measures of a convex body. The average volume,  $V_{i+r+j}$ , of the pair of convex bodies at separation  $r$  is given by

$$V_{i+r+j} = \frac{1}{3} \int \int \int_{r=\text{const}} \mathbf{r}_{12} \cdot \left( \frac{\partial \mathbf{r}_{12}}{\partial \theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \phi} \right) d\theta d\phi d\omega = V_{i+j} + S_{i+j}r + 4\pi(R_i + R_j)r^2 + \frac{4}{3}\pi r^3 \quad (6)$$

where  $V_{i+j} = V_i + V_j + S_i R_j + S_j R_i$ . We will later appreciate following relations for the second virial coefficient,  $B_{ij}^{\text{hcb}}(r)$ , of hard convex bodies, parallel to the convex cores of types  $i$  and  $j$ , so that their pair potential is given by eq 2 or, in other words, they overlap when  $s_{ij}(\mathbf{1}, \mathbf{2}) < r$ .

$$B_{ij}^{\text{hcb}}(r) = -\frac{1}{2V} \int \int F[r - s_{ij}(\mathbf{1}, \mathbf{2})] d\mathbf{1} d\mathbf{2} \quad (7)$$

$$B_{ij}^{\text{hcb}}(r) = \frac{1}{2} V_{i+r+j} \quad (8)$$

$$\frac{d}{dr} V_{i+r+j} = S_{i+r+j} \quad (9)$$

Combination of relations 7 and 9 gives

$$S_{i+r+j} = -\frac{1}{V} \frac{d}{dr} \int \int F[r - s_{ij}(\mathbf{1}, \mathbf{2})] d\mathbf{1} d\mathbf{2} \quad (10)$$

Note that  $V$  stands for the total volume of the system. Finally, we write the expression for the third virial coefficient,  $G_{ijk}(r, t, v)$ , of three hard particles parallel to the cores of types  $i, j$ , and  $k$  with generalized coordinates  $\mathbf{1}, \mathbf{2}$ , and  $\mathbf{3}$  so that pair overlaps occur when corresponding inequalities  $s_{ij}(\mathbf{1}, \mathbf{2}) < r$ ,  $s_{ik}(\mathbf{1}, \mathbf{3}) < t$ , or  $s_{kj}(\mathbf{3}, \mathbf{2}) < v$  are satisfied.

$$G_{ijk}(r, t, v) = -\frac{1}{3V} \int \int \int F[r - s_{ij}(\mathbf{1}, \mathbf{2})] F[t - s_{ik}(\mathbf{1}, \mathbf{3})] F[v - s_{kj}(\mathbf{3}, \mathbf{2})] d\mathbf{1} d\mathbf{2} d\mathbf{3} \quad (11)$$

**2.2. Modification of the OZ Equation.** In this work, we will derive the extension of the formerly proposed<sup>15,16</sup> modified OZ relation to mixtures. A general form of the OZ equation for mixtures reads as

$$h_{ij}(\mathbf{1}, \mathbf{2}) = c_{ij}(\mathbf{1}, \mathbf{2}) + \rho \sum_k x_k \int c_{ik}(\mathbf{1}, \mathbf{3}) h_{kj}(\mathbf{3}, \mathbf{2}) d\mathbf{3} \quad (12)$$

where  $\rho$  is the number density,  $x_k$  is the molar fraction of the  $k$ th component, and indices  $i, j$  and  $k$  denote types of interacting particles with generalized coordinates  $\mathbf{1}, \mathbf{2}$ , and  $\mathbf{3}$ . The total correlation function,  $h_{ij}$ , is defined as  $h_{ij} = g_{ij} - 1$ . Equation 12 introduces the direct correlation function,  $c_{ij}$ . Using the Percus–Yevick (PY) closure, one can express  $c_{ij}$  as

$$c_{ij} = f_{ij} Y_{ij} \quad (13)$$

In the last equation, the background correlation function,  $Y_{ij}$ , is defined as

$$Y_{ij} = g_{ij} \exp(\beta u_{ij})$$

In the next step, we assume  $c_{ij}$  and  $h_{ij}$  to depend only on the separation  $s_{ij}$ . The considered functions can be expressed (using eq 2) as

$$c_{ik}(\mathbf{1}, \mathbf{3}) = \int_{-\infty}^{+\infty} c'_{ik}(t) F[t - s_{ik}(\mathbf{1}, \mathbf{3})] dt \quad (14)$$

$$h_{kj}(\mathbf{3}, \mathbf{2}) = \int_{-\infty}^{+\infty} h'_{kj}(v) F[v - s_{kj}(\mathbf{3}, \mathbf{2})] dv \quad (15)$$

Substitution of eqs 14 and 15 into eq 12 gives

$$\gamma_{ij}(r) = \rho \sum_k x_k \int \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} c'_{ik}(t) h'_{kj}(v) F[t - s_{ik}(\mathbf{1}, \mathbf{3})] F[v - s_{kj}(\mathbf{3}, \mathbf{2})] dv dt d\mathbf{3} \quad (16)$$

where  $\gamma_{ij}$  is the indirect correlation function defined as  $\gamma_{ij} = h_{ij} - c_{ij}$ .

It is important to realize that  $\gamma_{ij}(r) = \gamma_{ij}^{\text{av}}(r)$ . That is obvious from general definition of average functions (eq 4) where the integration is performed at constant  $r$ , which is the only independent (positional) variable of  $\gamma_{ij}(r)$ . Formal multiplication of  $\gamma_{ij}(r)$  by the unity in the form

$$\frac{\int \int dS_{i+r+j}(\omega) d\omega}{S_{i+r+j}}$$

gives

$$\gamma_{ij}(r) = \frac{1}{S_{i+r+j}} \int \int_{r=\text{const}} dS_{i+r+j}(\omega) d\omega = \frac{1}{S_{i+r+j}} \int \int_{r=\text{const}} \gamma_{ij}(r) dS_{i+r+j}(\omega) d\omega$$

But the right-hand side (rhs) is, within the used method, the definition of the average indirect correlation function,  $\gamma_{ij}^{\text{av}}(r)$ .

The similar formal multiplication can be applied on the rhs of eq 16. Employing eq 10, we find after rearrangement

$$\gamma_{ij}(r) = \frac{\rho}{S_{i+r+j}} \sum_k x_k \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} c'_{ik}(t) h'_{kj}(v) \frac{d}{dr} \left\{ -\frac{1}{V} \int \int F[r - s_{ij}(\mathbf{1}, \mathbf{2})] F[t - s_{ik}(\mathbf{1}, \mathbf{3})] F[v - s_{kj}(\mathbf{3}, \mathbf{2})] d\mathbf{1} d\mathbf{2} d\mathbf{3} \right\} dv dt$$

By using eq 11, we can write the last expression as

$$h_{ij}(r) = c_{ij}(r) + \frac{3\rho}{S_{i+r+j}} \sum_k x_k \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{\partial \mathcal{G}_{ijk}}{\partial r}(r, t, v) c'_{ik}(t) h'_{kj}(v) dv dt \quad (17)$$

Integration by parts results in a final expression

$$h_{ij}(r) = c_{ij}(r) + \frac{3\rho}{S_{i+r+j}} \sum_k x_k \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{\partial^3 \mathcal{G}_{ijk}}{\partial r \partial t \partial v}(r, t, v) c_{ik}(t) h_{kj}(v) dv dt \quad (18)$$

**2.3. Approximation of  $\mathcal{G}_{ijk}$ .** The applicability of eq 18 depends on our knowledge of the third virial coefficient,  $\mathcal{G}_{ijk}$ . For numerical solution, we use the approximate formula for the third virial coefficient  $\mathcal{G}_{ijk}^{\text{hcb}}$  for additive hard convex bodies (HCB) given<sup>17</sup> as

$$\mathcal{G}_{ijk}^{\text{hcb}} = \frac{1}{3} \left\{ [\mathcal{V}_i \mathcal{V}_j + \mathcal{V}_i \mathcal{V}_k + \mathcal{V}_j \mathcal{V}_k] + [\mathcal{V}_i (\mathcal{R}_j f_k + \mathcal{R}_k f_j) + \mathcal{V}_j (\mathcal{R}_i f_k + \mathcal{R}_k f_i) + \mathcal{V}_k (\mathcal{R}_i f_j + \mathcal{R}_j f_i)] + \frac{1}{3} [\mathcal{R}_i^2 f_j f_k + \mathcal{R}_j^2 f_i f_k + \mathcal{R}_k^2 f_i f_j] \right\} \quad (19)$$

where  $\mathcal{R}_l$ ,  $\mathcal{J}_l$ , and  $\mathcal{V}_l$  denote fundamental measures of the considered convex body. When we express them in terms of geometric quantities  $R_l$ ,  $S_l$ , and  $V_l$  of the corresponding convex cores, they are given by relations

$$\mathcal{R}_l = R_l + \xi_l$$

$$\mathcal{J}_l = S_l + 8\pi R_l \xi_l + 4\pi \xi_l^2$$

and

$$\mathcal{V}_l = V_l + S_l \xi_l + 4\pi R_l \xi_l^2 + \frac{3}{4} \pi \xi_l^3$$

Here  $\xi_l$  denotes the thickness added to convex core of type  $l$  to get parallel body “ $l + \xi$ ”. To satisfy eq 2, it must hold that

$$\xi_i + \xi_j = r, \quad \xi_i + \xi_k = t, \quad \text{and} \quad \xi_j + \xi_k = v$$

The differentiation of  $\mathcal{G}_{ijk}^{\text{hcb}}(r, t, v)$  with respect to  $r$ ,  $t$ , and  $v$  results in

$$\frac{\partial^3 \mathcal{G}_{ijk}^{\text{hcb}}}{\partial r \partial t \partial v}(r, t, v) = \frac{\pi^2}{3} \left\{ 8rtv + 8[R_i v(r+t) + R_j t(r+v) + R_k r(t+v)] + \frac{8}{3} [R_i^2 v + R_j^2 t + R_k^2 r] + 8[R_i R_j + R_i R_k + R_j R_k](r+t+v) + \frac{4}{3\pi} [S_i v + S_j t + S_k r] + 16R_i R_j R_k + \frac{4}{3\pi} [R_i(S_j + S_k) + R_j(S_i + S_k) + R_k(S_i + S_j)] + \frac{8}{3} [R_i^2(R_j + R_k) + R_j^2(R_i + R_k) + R_k^2(R_i + R_j)] \right\} \quad (20)$$

It is important to realize that  $\mathcal{G}_{ijk}$  in eq 18 is more general than  $\mathcal{G}_{ijk}^{\text{hcb}}$ . Mentioned quantities are identical only when constraints

$$r_{np} \leq r_{pq}, \quad r_{qn} \leq r_{pq}, \quad \text{and} \quad r_{pq} \leq r_{np} + r_{qn} + 2\xi_n \quad (21)$$

are satisfied for certain cyclic permutation ( $npq$ ) of indices (123). The symbol  $\xi_n$  denotes the minimum radius of curvature of the  $n$ th core,  $r_{12} = r$ ,  $r_{31} = t$ , and  $r_{23} = v$ .

### 3. Numerical Solution of Modified OZ Equation

**3.1. Formulation of the Problem.** We apply the proposed method to the following model of a HCB fluid: We consider a system consisting of  $m$  types (chemical species) of hard convex bodies. The shape of each body is described by the convex core of type  $l = 1, 2, \dots, m$  and thickness  $\xi_l \geq 0$  of parallel layer. In this paper, we analyze the situation in which all the bodies possess one universal thickness  $\xi$ . If we denote  $\sigma = 2\xi$ , then the pair interaction potential,  $u_{ij}$ , is given by

$$u_{ij}(r) = \begin{cases} +\infty, & r < \sigma \\ 0, & r > \sigma \end{cases}$$

Employing PY-closure (see eq 13), we can rewrite eq 18 using the background correlation function,  $Y_{ij}$ , as follows

$$Y_{ij}(r) = 1 + \frac{3\rho}{S_{i+r+j}} \sum_{k=1}^m x_k \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{\partial^3 \mathcal{G}_{ijk}}{\partial r \partial t \partial v}(r, t, v) c_{ik}(t) h_{kj}(v) dt dv \quad (22)$$

Note that PY-closure provides the following identities:

$$c_{ik}(t) = \begin{cases} -Y_{ik}(t), & t < \sigma \\ 0, & t > \sigma \end{cases} \quad h_{kj}(v) = \begin{cases} -1, & v < \sigma \\ Y_{kj}(v) - 1, & v > \sigma \end{cases} \quad (23)$$

We use the approximation

$$\frac{\partial^3 \mathcal{G}_{ijk}}{\partial r \partial t \partial v}(r, t, v) = \begin{cases} \frac{\partial^3 \mathcal{G}_{ijk}^{\text{hcb}}}{\partial r \partial t \partial v}(r, t, v), & (r, t, v) \in \Omega \\ 0, & \text{elsewhere} \end{cases} \quad (24)$$

where  $\Omega$  contains the region where conditions 21 are satisfied plus certain neighborhood. In other words, we use expression 20 in the domain extending the limits of its definition. The proper choice of bounds of  $\Omega$  must represent a compromise between generality (good results for large class of HCB systems) and efficiency (quantitative agreement with MC data in particular cases). For HS + HPS mixtures most ad hoc bounds working well for systems with equal thicknesses of both bodies failed to describe the systems with larger spheres and vice versa.

The problem of integration bounds is the most difficult task in our numerical study. See subsection 3.4 for details.

**3.2. The Decomposition of the Third Derivative of  $\mathcal{G}_{ijk}^{\text{hcb}}$ .** To evaluate the integral on the rhs of eq 22, it is suitable to rearrange the expression 20 to a form

$$\frac{\partial^3 \mathcal{G}_{ijk}^{\text{hcb}}}{\partial r \partial t \partial v}(r, t, v) = \frac{8}{3} \pi^2 \sum_{\alpha=0}^1 \sum_{\beta=0}^1 P_{ijk}^{\alpha\beta}(r) t^\alpha v^\beta \quad (25)$$

where

$$P_{ijk}^{\alpha\beta}(r) = a_{ijk}^{\alpha\beta} r + b_{ijk}^{\alpha\beta}$$

and  $\alpha, \beta = 0, 1$ . We list coefficients  $a_{ijk}^{\alpha\beta}$  and  $b_{ijk}^{\alpha\beta}$  in Appendix B.

**3.3. Algorithm of Solution.** Substituting eq 25 into eq 22 leads to the equation

$$Y_{ij}(r) = 1 + \frac{8\pi^2 \rho}{S_{i+r+j}} \sum_k x_k \sum_{\alpha, \beta} P_{ijk}^{\alpha\beta}(r) \int_{t_{ik}^\alpha}^\sigma t^\alpha c_{ik}(t) [E_{kj}^\beta(\eta_{kj}(r, t)) - E_{kj}^\beta(v_{kj}(r, t))] dt \quad (26)$$

where

$$E_{kj}^\beta(x) = \int_0^x v^\beta h_{kj}(v) dv$$

Functions  $\eta_{kj}(r, t)$  and  $v_{kj}(r, t)$  represent the maximum and minimum separation of molecules 2 and 3.

The main steps of solution algorithm (Picard method<sup>18</sup>) are as follows: (i) An initial guess is made. For the very first computation at low packing fractions (typically  $y = 0.1$ ), the background correlation functions of the corresponding hard sphere mixture are sufficient. Those functions are obtained by solution of the Percus–Yevick equation for the system at the same packing fraction as the studied mixture. Radii of spheres are chosen as the  $(4\pi)^{-1}$ -multiples of the mean curvature integrals of the corresponding bodies. In further computations, we proceed from lower to higher densities using the result of each run as an input for the next one until the desired density is reached. Note that  $Y_{ij}$  values are stored for separations  $r$  up to  $3-4M$  where  $M = 2R_1 + \sigma$ . For larger  $r$ , we assume that  $Y_{kj}(r) = 1$ . Note that  $R_1$  is always chosen so that  $R_1 \geq R_2$ . (ii) Evaluation of  $E_{kj}^\beta$  integrals is performed employing the trapezoidal rule. Functions  $h_{kj}$  are obtained from  $Y_{kj}$  using eq 23. (iii) Evaluation of the rhs of eq 26 is performed. Here the trapezoidal rule was employed, too. To get  $c_{ik}$ , we use eq 23 again. The function  $Y_{ij}^{[n]}$  is obtained as a result of the  $n$ th iteration. (iv) A convergence test is performed. A fixed  $\epsilon > 0$  small enough (typically 0.0001) is chosen. If  $|Y_{ij}^{[n]}(r) - Y_{ij}^{[n-1]}(r)| < \epsilon$ , for all  $r$ , computation is interrupted and  $Y_{ij}^{[n]}$  taken as a result. If the convergence is not reached yet, then the new  $Y_{ij}$  is constructed by the prescription

$$Y_{ij} = \lambda Y_{ij}^{[n]} + (1 - \lambda) Y_{ij}^{\text{old}}$$

where the relaxation parameter  $\lambda$  affects the stability of the convergence process. We used  $\lambda \in (0.03, 0.07)$ . The  $Y_{ij}$  obtained plays the role of a new guess. We repeat the iteration process from the second step. Starting from a good initial guess at  $y \approx 0.1$ , the computation of the state point at  $y \approx 0.3$  takes about 5 min on a PC with a 1 GHz CPU. Note that we obtain series of  $Y_{ij}$  for lower densities in addition. The speed of our program

was sufficient for the purpose of this study; no attempt was made to optimize.

**3.4. Integration Bounds.** As can be seen, the quantities in eq 26 are mostly well-defined and easy to evaluate. Unfortunately, there are three exceptions:  $t_{ik}^0$ ,  $\eta_{kj}$ , and  $v_{kj}$ . When finding their generic form, we meet some difficulties. It is not quite clear how to define “maximum” and “minimum” separation of molecules 2 and 3. In particular cases, it is possible to find those values by fitting methods. However, we made an effort to avoid the use of empirical parameters and construct expressions based on HCB geometry.

The necessary condition for accuracy of the chosen bounds is consistency with systems of hard spheres (HS) for which the following bounds can be found:

$$t_{ik}^0 = -d_{ik}, \quad \eta_{kj}(r, t) = r + t + d_{ii}$$

and

$$v_{kj}(r, t) = |r + d_{ij} - (t + d_{ik})| - d_{kj} \quad (27)$$

where  $d_{ij} = R_i + R_j$ . We make use of the following prescriptions:

$$t_{ik}^0 = r_{ik}^0, \quad \eta_{kj}(r, t) = r + t - \xi_i^0$$

and

$$v_{kj}(r, t) = \begin{cases} |r - t| + r_{kk}^0, & r > t \\ |r - t| + r_{jj}^0, & r \leq t \end{cases} \quad (28)$$

where

$$r_{ij}^0 = -d_{ij} + \sqrt{R_i^2 + R_j^2 - \frac{1}{4\pi}(S_i + S_j)}$$

and

$$\xi_i^0 = -R_i + \sqrt{R_i^2 - \frac{S_i}{4\pi}}$$

Those bounds are based on geometrical intuition together with some trends observed when changing the size ratio of considered convex bodies.

#### 4. Monte Carlo Simulation Study

All simulations were performed in  $NVT$  ensemble using a standard Metropolis algorithm. Two basic types of hard body systems were studied: a binary mixture of hard spheres and binary mixture of hard spheres and hard prolate spherocylinders (with length-to-breadth ratio  $\gamma = 2.0$ ).

The acceptance ratio,  $\chi \in (0.3, 0.6)$ , was chosen to be fixed for each simulation. To keep the value of  $\chi$  at a desired level, the maximum translational (respectively, rotational) displacements,  $\delta_t$  (respectively,  $\delta_r$ ), were adjusted during the simulation. In the case of hard spherocylinders, the translational and rotational moves were taken in separate steps. In each rotational move, we changed Euler angles  $\theta$  and  $\phi$ . To avoid the bottleneck effect, the uniform probability distribution in  $\cos \theta$  changes was employed.

To ensure relaxation the root-mean-square displacement,  $\langle |\Delta \mathbf{r}|^2 \rangle^{1/2}$ , translational order parameter,  $P_t(k)$ , and—in the case of spherocylinders—rotational order parameter,  $P_{\text{rot}}$ , were moni-



tored. Mentioned quantities are defined as follows:<sup>9</sup>

$$\langle |\Delta \mathbf{r}|^2 \rangle^{1/2} = \sqrt{\frac{1}{N} \sum_{i=1}^N |\mathbf{r}_i - \mathbf{r}_{0,i}|^2}$$

$$P_{\text{tr}}(k) = \frac{1}{N} \sum_{i=1}^N \cos(\mathbf{k} \cdot \mathbf{r}_i)$$

and

$$P_{\text{rot}} = \frac{1}{N} \sum_{i=1}^N \cos \psi_i$$

where  $N$  is the number of considered particles,  $\mathbf{r}_i$  is the position vector of the mass center of the  $i$ th particle,  $\mathbf{r}_{0,i}$  denotes its value in the initial lattice,  $\mathbf{k}$  is a reciprocal lattice vector of the initial lattice, and  $\psi_i$  is the angle between the molecular axis of molecule  $i$  and its initial direction.

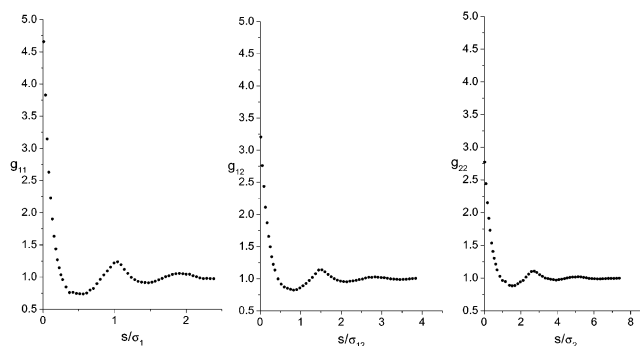
The root-mean-square displacement grows with the number of configurations up to a certain level where it fluctuates. Translational and rotational order parameters are on the order of unity in the initial lattice, while in liquid, they oscillate about zero. We were performing equilibration until the root-mean-square displacement reached at least the unit cell size of the initial lattice. Note that mentioned quantities were computed for each particle type separately (we additionally distinguished the translational and rotational changes in the case of  $\chi$ ).

The average correlation functions,  $g_{ij}^{\text{av}}$ , were evaluated from histograms of the shortest surface-to-surface distances,  $s$ , of pairs of considered convex bodies. Note that for hard spheres the radial distribution function,  $g_{ij}$ , when defined as a function of  $s = r - \sigma_{ij}$  (instead of the center-to-center distance,  $r$ ), is identical with  $g_{ij}^{\text{av}}$ . In mixtures with spherocylinders, the average projection,  $\langle \mathbf{r} \cdot \mathbf{v} \rangle_{ij}$ , of center-to-center distance on the direction of the supporting plane normal vector,  $\mathbf{v}$ , was computed, too.

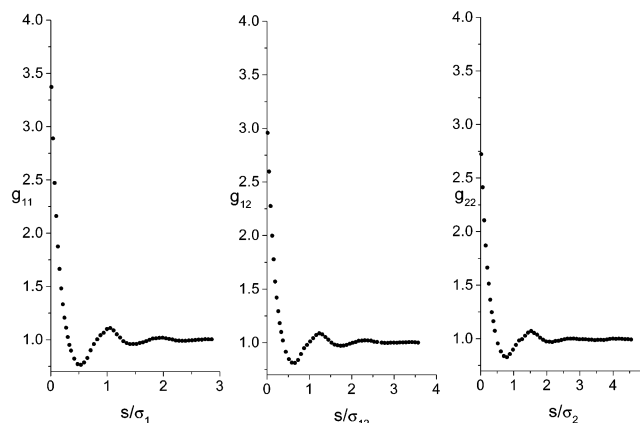
**4.1. Binary Mixtures of Hard Spheres.** To test the computational procedure for numerical solution, the MC simulations of HS binary mixtures were performed. Two binary mixtures with diameter ratios  $\sigma_2/\sigma_1 = 0.4$  and  $0.7$  were simulated in our laboratory; the data for diameter ratios  $0.3$  and  $0.9$  were taken from the work<sup>19</sup> of Lee and Levesque. For  $\sigma_2/\sigma_1 = 0.4$ , one state point at packing fraction  $y = 0.4536$  was measured; for  $\sigma_2/\sigma_1 = 0.7$ , the packing fraction was  $y = 0.3793$ . The total number of particles was  $N = 512$ , and molar fractions  $x_1 = x_2 = 0.5$  were used in both cases. The initial lattice was constructed by placing the smaller spheres into interstices of a fcc lattice of the larger ones. Typically  $5 \times 10^6$  configurations were generated to ensure equilibration and  $2 \times 10^6$  to compute ensemble averages.

**4.2. Binary Mixtures of Hard Spheres and Hard Prolate Spherocylinders.** Two basic geometrical types of HS+HPS systems were studied: the system with the HS diameter,  $\sigma_1$ , equal to the thickness of the HPS,  $\sigma_2$ , or the case when the diameter of the sphere was larger than the thickness of the spherocylinder. We always label spheres by index 1 and spherocylinders by index 2.

(i)  $\sigma_1 = \sigma_2$ . The system of 72 spheres and 72 spherocylinders with equal thicknesses was simulated at three packing fractions:  $0.3128$ ,  $0.3600$ , and  $0.4000$ . The initial lattice for equimolar mixtures was constructed from eight identical cells mixed from nine spheres and nine spherocylinders of three different orientations.



**Figure 1.** Radial distribution functions,  $g_{ij}$ , of binary mixture of hard spheres,  $y = 0.4536$ ,  $\sigma_2/\sigma_1 = 0.4$ ,  $x_1 = 0.5$ , MC data.



**Figure 2.** Radial distribution functions,  $g_{ij}$ , for binary mixture of hard spheres,  $y = 0.3793$ ,  $\sigma_2/\sigma_1 = 0.7$ ,  $x_1 = 0.5$ , MC data.

(ii)  $\sigma_1 > \sigma_2$ . The systems consisting of 125 spheres and 375 spherocylinders were used. For thickness-to-diameter ratio  $\sigma_2/\sigma_1 = 0.3$ , one state point at  $y = 0.2503$  was simulated. Two packing fractions,  $0.2824$  and  $0.3500$ , were chosen for  $\sigma_2/\sigma_1 = 0.4$ . The lattice of 500 particles was obtained by repeating of a unit cell containing one sphere placed in the center and three spherocylinders lying in the directions of Cartesian axes on the edges of the unit cell.

## 5. Results

**5.1. Overview of MC Data.** Radial distribution functions in binary mixtures of hard spheres at the highest packing fractions are plotted in Figures 1 and 2. For HS+HPS mixtures, the values of the average correlation functions,  $g_{ij}^{\text{av}}$ , at the highest packing fractions (for given geometry) are listed in Tables 1–3. Dependencies of  $g_{ij}^{\text{av}}$  are given in Figures 3–5. For consistency, all of the functions possess the shortest surface-to-surface distance,  $s$ , as an argument. In the mentioned tables, the values of  $s$  are reduced by the diameter (thickness),  $\sigma$ , of the considered sphere (prolate spherocylinder). In the case of unlike pairs, the cross parameters are given as  $\sigma_{12} = 1/2(\sigma_1 + \sigma_2)$ .

For systems of hard spheres, the compressibility factor,  $Z$ , was computed from contact values of radial distribution functions,  $g_{ij}(0+)$ , as follows

$$Z = 1 + \frac{2}{3} \pi \rho \sum_{i,j} x_i x_j \sigma_{ij}^3 g_{ij}(0+)$$

where  $\rho$  is the total number density and  $x_l$  is the molar fraction of the  $l$ th component. Contact values of  $g_{ij}$  were obtained by extrapolation of  $\ln g_{ij}$  using the least-squares quadratic poly-

**TABLE 1: Average Correlation Functions,  $g_{ij}^{\text{av}}$ , of Mixture of Hard Spheres (1) and Hard Prolate Spherocylinders (2),  $y = 0.2503$ ,  $\sigma_2/\sigma_1 = 0.3$ ,  $\gamma = 2.0$ ,  $x_1 = 0.25$ , MC Data<sup>a</sup>**

| $s/\sigma_1$ | $g_{11}^{\text{av}}$ | $s/\sigma_{12}$ | $g_{12}^{\text{av}}$ | $s/\sigma_2$ | $g_{22}^{\text{av}}$ | $s/\sigma_1$ | $g_{11}^{\text{av}}$ | $s/\sigma_{12}$ | $g_{12}^{\text{av}}$ | $s/\sigma_2$ | $g_{22}^{\text{av}}$ |
|--------------|----------------------|-----------------|----------------------|--------------|----------------------|--------------|----------------------|-----------------|----------------------|--------------|----------------------|
| 0.012        | 2.247                | 0.020           | 1.844                | 0.0467       | 1.675                | 1.020        | 1.007                | 1.780           | 1.016                | 4.1533       | 1.006                |
| 0.036        | 2.065                | 0.060           | 1.738                | 0.1400       | 1.583                | 1.068        | 1.014                | 1.860           | 1.016                | 4.3400       | 1.004                |
| 0.060        | 1.930                | 0.100           | 1.644                | 0.2333       | 1.514                | 1.116        | 1.021                | 1.940           | 1.015                | 4.5267       | 1.002                |
| 0.084        | 1.785                | 0.140           | 1.564                | 0.3267       | 1.441                | 1.164        | 1.024                | 2.020           | 1.012                | 4.7133       | 1.003                |
| 0.108        | 1.683                | 0.180           | 1.483                | 0.4200       | 1.387                | 1.212        | 1.019                | 2.100           | 1.008                | 4.9000       | 1.001                |
| 0.132        | 1.570                | 0.220           | 1.418                | 0.5133       | 1.321                | 1.260        | 1.017                | 2.180           | 1.007                | 5.0867       | 1.000                |
| 0.156        | 1.476                | 0.260           | 1.353                | 0.6067       | 1.276                | 1.308        | 1.011                | 2.260           | 1.005                | 5.2733       | 0.998                |
| 0.180        | 1.398                | 0.300           | 1.300                | 0.7000       | 1.230                | 1.356        | 1.007                | 2.340           | 1.003                | 5.4600       | 0.997                |
| 0.204        | 1.325                | 0.340           | 1.249                | 0.7933       | 1.190                | 1.404        | 1.006                | 2.420           | 1.000                | 5.6467       | 0.996                |
| 0.228        | 1.262                | 0.380           | 1.208                | 0.8867       | 1.156                | 1.452        | 1.003                | 2.500           | 0.999                | 5.8333       | 0.996                |
| 0.252        | 1.211                | 0.420           | 1.170                | 0.9800       | 1.131                | 1.500        | 0.999                | 2.580           | 0.998                | 6.0200       | 0.996                |
| 0.276        | 1.164                | 0.460           | 1.139                | 1.0733       | 1.108                | 1.548        | 0.996                | 2.660           | 0.999                | 6.2067       | 0.996                |
| 0.300        | 1.126                | 0.500           | 1.112                | 1.1667       | 1.087                | 1.596        | 0.995                | 2.740           | 0.998                | 6.3933       | 0.995                |
| 0.324        | 1.093                | 0.540           | 1.090                | 1.2600       | 1.068                | 1.644        | 0.997                | 2.820           | 0.999                | 6.5800       | 0.997                |
| 0.348        | 1.068                | 0.580           | 1.074                | 1.3533       | 1.054                | 1.692        | 0.999                | 2.900           | 0.999                | 6.7667       | 0.999                |
| 0.372        | 1.052                | 0.660           | 1.039                | 1.5400       | 1.025                | 1.740        | 0.996                | 2.980           | 0.999                | 6.9533       | 0.998                |
| 0.396        | 1.026                | 0.740           | 1.015                | 1.7267       | 1.007                | 1.788        | 0.994                | 3.060           | 1.000                | 7.1400       | 0.998                |
| 0.444        | 0.996                | 0.820           | 0.995                | 1.9133       | 0.989                | 1.836        | 0.997                | 3.140           | 1.001                | 7.3267       | 0.998                |
| 0.492        | 0.972                | 0.900           | 0.980                | 2.1000       | 0.978                | 1.884        | 0.994                | 3.220           | 1.001                | 7.5133       | 0.999                |
| 0.540        | 0.958                | 0.980           | 0.972                | 2.2867       | 0.969                | 1.932        | 0.997                | 3.300           | 1.000                | 7.7000       | 0.999                |
| 0.588        | 0.948                | 1.060           | 0.965                | 2.4733       | 0.964                | 1.980        | 0.998                | 3.380           | 1.002                | 7.8867       | 1.000                |
| 0.636        | 0.941                | 1.140           | 0.959                | 2.6600       | 0.962                | 2.028        | 0.998                | 3.460           | 1.001                | 8.0733       | 0.999                |
| 0.684        | 0.936                | 1.220           | 0.958                | 2.8467       | 0.964                | 2.076        | 1.000                | 3.540           | 1.001                | 8.2600       | 0.998                |
| 0.732        | 0.933                | 1.300           | 0.962                | 3.0333       | 0.968                | 2.124        | 1.003                | 3.620           | 1.001                | 8.4467       | 0.999                |
| 0.780        | 0.935                | 1.380           | 0.971                | 3.2200       | 0.979                | 2.172        | 0.998                | 3.700           | 1.001                | 8.6333       | 0.999                |
| 0.828        | 0.942                | 1.460           | 0.981                | 3.4067       | 0.989                | 2.220        | 0.999                | 3.780           | 1.001                | 8.8200       | 0.998                |
| 0.876        | 0.955                | 1.540           | 0.996                | 3.5933       | 1.000                | 2.268        | 0.999                | 3.860           | 1.001                | 9.0067       | 0.997                |
| 0.924        | 0.963                | 1.620           | 1.010                | 3.7800       | 1.005                | 2.316        | 1.001                | 3.940           | 1.001                | 9.1933       | 0.998                |
| 0.972        | 0.981                | 1.700           | 1.015                | 3.9667       | 1.006                |              |                      |                 |                      |              |                      |

<sup>a</sup>  $s$  denotes the shortest surface-to-surface distance.**TABLE 2: Average Correlation Functions,  $g_{ij}^{\text{av}}$ , of Mixture of Hard Spheres (1) and Hard Prolate Spherocylinders (2),  $y = 0.3500$ ,  $\sigma_2/\sigma_1 = 0.4$ ,  $\gamma = 2.0$ ,  $x_1 = 0.25$ , MC Data<sup>a</sup>**

| $s/\sigma_1$ | $g_{11}^{\text{av}}$ | $s/\sigma_{12}$ | $g_{12}^{\text{av}}$ | $s/\sigma_2$ | $g_{22}^{\text{av}}$ | $s/\sigma_1$ | $g_{11}^{\text{av}}$ | $s/\sigma_{12}$ | $g_{12}^{\text{av}}$ | $s/\sigma_2$ | $g_{22}^{\text{av}}$ |
|--------------|----------------------|-----------------|----------------------|--------------|----------------------|--------------|----------------------|-----------------|----------------------|--------------|----------------------|
| 0.0113       | 3.439                | 0.0168          | 2.780                | 0.0168       | 2.780                | 0.8921       | 0.998                | 1.4993          | 1.048                | 1.4993       | 1.048                |
| 0.0339       | 2.931                | 0.0505          | 2.469                | 0.0505       | 2.469                | 0.9372       | 1.013                | 1.5667          | 1.044                | 1.5667       | 1.044                |
| 0.0565       | 2.584                | 0.0842          | 2.223                | 0.0842       | 2.223                | 0.9824       | 1.043                | 1.6340          | 1.031                | 1.6340       | 1.031                |
| 0.0790       | 2.258                | 0.1179          | 2.012                | 0.1179       | 2.012                | 1.0276       | 1.057                | 1.7014          | 1.023                | 1.7014       | 1.023                |
| 0.1016       | 1.992                | 0.1516          | 1.818                | 0.1516       | 1.818                | 1.0727       | 1.055                | 1.7688          | 1.010                | 1.7688       | 1.010                |
| 0.1242       | 1.773                | 0.1853          | 1.662                | 0.1853       | 1.662                | 1.1179       | 1.053                | 1.8362          | 1.000                | 1.8362       | 1.000                |
| 0.1468       | 1.584                | 0.2190          | 1.521                | 0.2190       | 1.521                | 1.1631       | 1.041                | 1.9036          | 0.988                | 1.9036       | 0.988                |
| 0.1694       | 1.426                | 0.2527          | 1.409                | 0.2527       | 1.409                | 1.2082       | 1.016                | 1.9709          | 0.986                | 1.9709       | 0.986                |
| 0.1920       | 1.301                | 0.2864          | 1.312                | 0.2864       | 1.312                | 1.2534       | 1.002                | 2.0383          | 0.985                | 2.0383       | 0.985                |
| 0.2145       | 1.204                | 0.3201          | 1.221                | 0.3201       | 1.221                | 1.2986       | 1.002                | 2.1057          | 0.990                | 2.1057       | 0.990                |
| 0.2371       | 1.103                | 0.3538          | 1.152                | 0.3538       | 1.152                | 1.3437       | 0.995                | 2.1731          | 0.990                | 2.1731       | 0.990                |
| 0.2597       | 1.030                | 0.3875          | 1.095                | 0.3875       | 1.095                | 1.3889       | 0.994                | 2.2405          | 0.991                | 2.2405       | 0.991                |
| 0.2823       | 0.973                | 0.4211          | 1.044                | 0.4211       | 1.044                | 1.4341       | 0.986                | 2.3079          | 0.994                | 2.3079       | 0.994                |
| 0.3049       | 0.931                | 0.4885          | 0.979                | 0.4885       | 0.979                | 1.4793       | 0.996                | 2.3752          | 0.995                | 2.3752       | 0.995                |
| 0.3275       | 0.883                | 0.5559          | 0.942                | 0.5559       | 0.942                | 1.5244       | 0.984                | 2.4426          | 0.997                | 2.4426       | 0.997                |
| 0.3501       | 0.863                | 0.6233          | 0.933                | 0.6233       | 0.933                | 1.5696       | 0.988                | 2.5100          | 0.997                | 2.5100       | 0.997                |
| 0.3726       | 0.844                | 0.6907          | 0.940                | 0.6907       | 0.940                | 1.6148       | 0.989                | 2.5774          | 1.000                | 2.5774       | 1.000                |
| 0.3952       | 0.846                | 0.7581          | 0.939                | 0.7581       | 0.939                | 1.6599       | 0.992                | 2.6448          | 1.001                | 2.6448       | 1.001                |
| 0.4404       | 0.862                | 0.8254          | 0.936                | 0.8254       | 0.936                | 1.7051       | 0.995                | 2.7122          | 1.003                | 2.7122       | 1.003                |
| 0.4856       | 0.881                | 0.8928          | 0.944                | 0.8928       | 0.944                | 1.7503       | 0.993                | 2.7795          | 1.008                | 2.7795       | 1.008                |
| 0.5307       | 0.887                | 0.9602          | 0.952                | 0.9602       | 0.952                | 1.7954       | 0.999                | 2.8169          | 1.006                | 2.8169       | 1.006                |
| 0.5759       | 0.901                | 1.0276          | 0.957                | 1.0276       | 0.957                | 1.8406       | 0.999                | 2.9143          | 1.006                | 2.9143       | 1.006                |
| 0.6211       | 0.918                | 1.0950          | 0.968                | 1.0950       | 0.968                | 1.8858       | 0.993                | 2.9817          | 1.006                | 2.9817       | 1.006                |
| 0.6662       | 0.914                | 1.1624          | 0.981                | 1.1624       | 0.981                | 1.9309       | 0.994                | 3.0191          | 1.005                | 3.0191       | 1.005                |
| 0.7114       | 0.929                | 1.2297          | 0.994                | 1.2297       | 0.994                | 1.9761       | 0.997                | 3.1165          | 1.003                | 3.1165       | 1.003                |
| 0.7566       | 0.946                | 1.2971          | 1.005                | 1.2971       | 1.005                | 2.0213       | 0.999                | 3.1838          | 1.002                | 3.1838       | 1.002                |
| 0.8017       | 0.963                | 1.3645          | 1.022                | 1.3645       | 1.022                | 2.0664       | 0.998                | 3.2512          | 1.000                | 3.2512       | 1.000                |
| 0.8469       | 0.974                | 1.4319          | 1.041                | 1.4319       | 1.041                | 2.1116       | 0.992                | 3.3186          | 1.001                | 3.3186       | 1.001                |

<sup>a</sup>  $s$  denotes the shortest surface-to-surface distance.

nomial. The contact values of  $g_{ij}$  and compressibility factors are given in Table 4.

The same extrapolation was used in the case of hard spherocylinders. The compressibility factor was evaluated from

$$Z = 1 + \frac{1}{6} \rho \sum_{i,j} x_i x_j \langle \mathbf{r} \cdot \mathbf{v} \rangle_{ij}(0+) g_{ij}^{\text{av}}(0+) \mathcal{I}_{i+j}$$

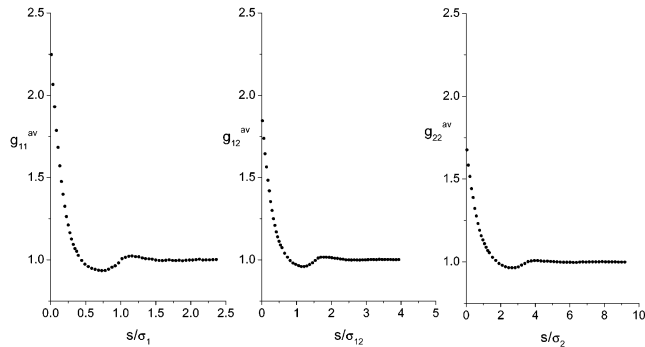
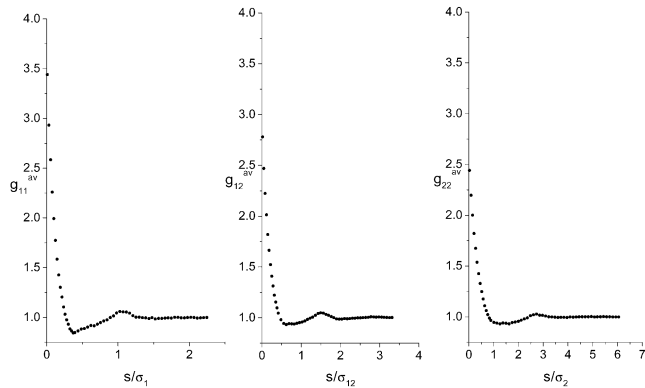
where  $\mathcal{I}_{i+j} = \mathcal{I}_i + \mathcal{I}_j + 8\pi \mathcal{R}_i \mathcal{R}_j$ . For hard spheres, it holds that

$\mathcal{R} = \sigma/2$  and  $\mathcal{I} = \pi\sigma^2$ ; for prolate spherocylinders, one gets  $\mathcal{R} = (\gamma + 1)\sigma/4$  and  $\mathcal{I} = \pi\gamma\sigma^2$ . The contact values of  $\langle \mathbf{r} \cdot \mathbf{v} \rangle_{ij}$  were estimated by linear fit. The values of  $g_{ij}^{\text{av}}(0+)$ , reduced projections  $p_{ij}(0+) = \langle \mathbf{r} \cdot \mathbf{v} \rangle_{ij}(0+)/\sigma_{ij}$ , and compressibility factors,  $Z$ , are given in Table 5.

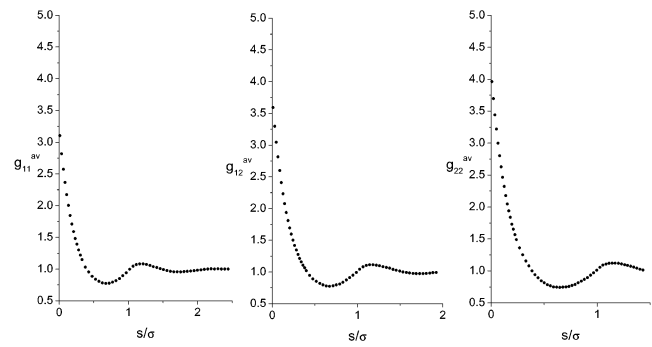
**5.2. Comparison with Theoretical Values.** Figures 6 and 7 show radial distribution functions in binary mixtures of hard spheres. Theoretical values were obtained by solution of eq 18 in which the smaller sphere had a pointlike core. Computed

**TABLE 3: Average Correlation Functions,  $g_{ij}^{\text{av}}$ , of Mixture of Hard Spheres (1) and Hard Prolate Spherocylinders (2),  $y = 0.4000$ ,  $\sigma_2/\sigma_1 = 1.0$ ,  $\gamma = 2.0$ ,  $x_1 = 0.5$ , MC Data<sup>a</sup>**

| $s/\sigma_1$ | $g_{11}^{\text{av}}$ | $s/\sigma_{12}$ | $g_{12}^{\text{av}}$ | $s/\sigma_2$ | $g_{22}^{\text{av}}$ | $s/\sigma_1$ | $g_{11}^{\text{av}}$ | $s/\sigma_{12}$ | $g_{12}^{\text{av}}$ | $s/\sigma_2$ | $g_{22}^{\text{av}}$ |
|--------------|----------------------|-----------------|----------------------|--------------|----------------------|--------------|----------------------|-----------------|----------------------|--------------|----------------------|
| 0.0123       | 3.103                | 0.0098          | 3.589                | 0.0073       | 3.962                | 1.1169       | 1.070                | 0.7526          | 0.793                | 0.6183       | 0.743                |
| 0.0368       | 2.817                | 0.0293          | 3.293                | 0.0218       | 3.694                | 1.1660       | 1.080                | 0.7917          | 0.809                | 0.6474       | 0.738                |
| 0.0614       | 2.569                | 0.0489          | 3.043                | 0.0364       | 3.440                | 1.2151       | 1.079                | 0.8308          | 0.835                | 0.6765       | 0.745                |
| 0.0859       | 2.363                | 0.0684          | 2.813                | 0.0509       | 3.216                | 1.2642       | 1.070                | 0.8699          | 0.871                | 0.7056       | 0.746                |
| 0.1105       | 2.172                | 0.0880          | 2.597                | 0.0655       | 2.999                | 1.3133       | 1.055                | 0.9090          | 0.909                | 0.7346       | 0.755                |
| 0.1350       | 2.001                | 0.1075          | 2.405                | 0.0800       | 2.799                | 1.3624       | 1.038                | 0.9481          | 0.947                | 0.7637       | 0.771                |
| 0.1596       | 1.842                | 0.1271          | 2.231                | 0.0946       | 2.625                | 1.4115       | 1.022                | 0.9871          | 0.991                | 0.7928       | 0.784                |
| 0.1841       | 1.707                | 0.1466          | 2.076                | 0.1091       | 2.463                | 1.4606       | 1.006                | 1.0262          | 1.041                | 0.8219       | 0.813                |
| 0.2087       | 1.589                | 0.1662          | 1.935                | 0.1237       | 2.320                | 1.5097       | 0.992                | 1.0653          | 1.080                | 0.8510       | 0.837                |
| 0.2332       | 1.479                | 0.1857          | 1.808                | 0.1382       | 2.175                | 1.5588       | 0.973                | 1.1044          | 1.102                | 0.8801       | 0.864                |
| 0.2577       | 1.391                | 0.2052          | 1.693                | 0.1527       | 2.046                | 1.6079       | 0.962                | 1.1435          | 1.112                | 0.9092       | 0.893                |
| 0.2823       | 1.299                | 0.2248          | 1.595                | 0.1673       | 1.938                | 1.6570       | 0.957                | 1.1826          | 1.113                | 0.9383       | 0.930                |
| 0.3068       | 1.218                | 0.2443          | 1.500                | 0.1818       | 1.836                | 1.7060       | 0.957                | 1.2217          | 1.103                | 0.9674       | 0.967                |
| 0.3314       | 1.147                | 0.2639          | 1.417                | 0.1964       | 1.730                | 1.7551       | 0.954                | 1.2608          | 1.096                | 0.9965       | 1.009                |
| 0.3805       | 1.030                | 0.2834          | 1.345                | 0.2109       | 1.651                | 1.8042       | 0.958                | 1.2999          | 1.082                | 1.0256       | 1.054                |
| 0.4296       | 0.954                | 0.3030          | 1.273                | 0.2255       | 1.567                | 1.8533       | 0.961                | 1.3390          | 1.069                | 1.0547       | 1.089                |
| 0.4787       | 0.882                | 0.3225          | 1.211                | 0.2400       | 1.487                | 1.9024       | 0.966                | 1.3781          | 1.058                | 1.0838       | 1.106                |
| 0.5278       | 0.838                | 0.3421          | 1.159                | 0.2691       | 1.361                | 1.9515       | 0.973                | 1.4172          | 1.039                | 1.1129       | 1.116                |
| 0.5769       | 0.804                | 0.3616          | 1.104                | 0.2982       | 1.250                | 2.0006       | 0.980                | 1.1563          | 1.025                | 1.1420       | 1.117                |
| 0.6260       | 0.779                | 0.3812          | 1.062                | 0.3273       | 1.153                | 2.0497       | 0.986                | 1.4954          | 1.011                | 1.1711       | 1.118                |
| 0.6751       | 0.772                | 0.4007          | 1.019                | 0.3564       | 1.076                | 2.0988       | 0.993                | 1.5345          | 1.000                | 1.2002       | 1.116                |
| 0.7242       | 0.776                | 0.4398          | 0.945                | 0.3855       | 0.997                | 2.1479       | 0.998                | 1.5736          | 0.991                | 1.2293       | 1.108                |
| 0.7732       | 0.792                | 0.4789          | 0.888                | 0.4146       | 0.940                | 2.1970       | 1.001                | 1.6127          | 0.984                | 1.2584       | 1.095                |
| 0.8223       | 0.816                | 0.5180          | 0.850                | 0.4437       | 0.890                | 2.2461       | 0.999                | 1.6518          | 0.975                | 1.2875       | 1.083                |
| 0.8714       | 0.849                | 0.5571          | 0.818                | 0.4728       | 0.843                | 2.2952       | 1.001                | 1.6909          | 0.972                | 1.3165       | 1.071                |
| 0.9205       | 0.893                | 0.5962          | 0.794                | 0.5019       | 0.813                | 2.3443       | 0.999                | 1.7300          | 0.972                | 1.3456       | 1.057                |
| 0.9696       | 0.939                | 0.6353          | 0.779                | 0.5310       | 0.782                | 2.3934       | 0.999                | 1.7690          | 0.973                | 1.3747       | 1.042                |
| 1.0187       | 0.996                | 0.6744          | 0.774                | 0.5601       | 0.766                | 2.4425       | 0.999                | 1.8081          | 0.974                | 1.4038       | 1.025                |
| 1.0678       | 1.042                | 0.7135          | 0.782                | 0.5892       | 0.748                |              |                      |                 |                      |              |                      |

<sup>a</sup>  $s$  denotes the shortest surface-to-surface distance.**Figure 3.** Average correlation functions,  $g_{ij}^{\text{av}}$ , of mixture of hard spheres (1) and hard prolate spherocylinders (2),  $y = 0.2503$ ,  $\sigma_2/\sigma_1 = 0.3$ ,  $\gamma = 2.0$ ,  $x_1 = 0.25$ , MC data**Figure 4.** Average correlation functions,  $g_{ij}^{\text{av}}$ , of mixture of hard spheres (1) and hard prolate spherocylinders (2),  $y = 0.3500$ ,  $\sigma_2/\sigma_1 = 0.4$ ,  $\gamma = 2.0$ ,  $x_1 = 0.25$ , MC data.

curves are plotted together with corresponding MC points. In other cases (diameter ratios 0.4 and 0.7), the situation is similar. For hard spheres, the numerical solution of eq 18 gives the same values as a simple Percus–Yevick approximation (PYA).

**Figure 5.** Average correlation functions,  $g_{ij}^{\text{av}}$ , of mixture of hard spheres (1) and hard prolate spherocylinders (2),  $y = 0.4000$ ,  $\sigma_2/\sigma_1 = 1.0$ ,  $\gamma = 2.0$ ,  $x_1 = 0.25$ , MC data.**TABLE 4: The Compressibility Factors ( $Z$ ), Packing Fraction ( $y$ ), Molar Fraction of Larger Spheres ( $x_1$ ), Diameter Ratio ( $\sigma_2/\sigma_1$ ), and Contact Value of Radial Distribution Function  $g_{ij}(0+)$  of Binary Systems of Hard Spheres**

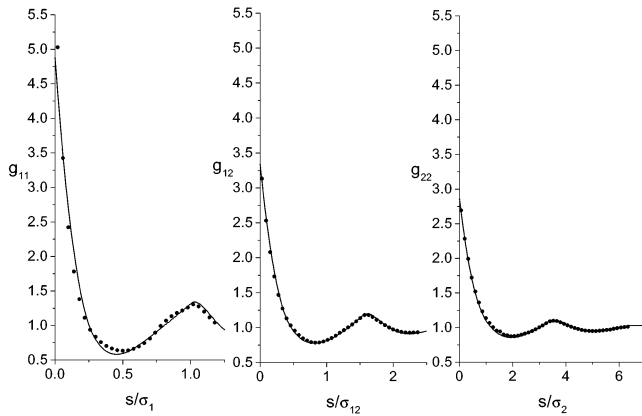
| $y$    | $x_1$ | $\sigma_2/\sigma_1$ | $g_{11}(0+)$ |       | $g_{12}(0+)$ |       | $g_{22}(0+)$ |       | $Z$   |       |
|--------|-------|---------------------|--------------|-------|--------------|-------|--------------|-------|-------|-------|
|        |       |                     | MC           | theor | MC           | theor | MC           | theor | MC    | theor |
| 0.4900 | 0.5   | 0.3                 | 6.16         | 4.88  | 3.54         | 3.34  | 2.94         | 2.86  | 8.81  | 7.48  |
| 0.4536 | 0.5   | 0.4                 | 5.21         | 4.25  | 3.48         | 3.23  | 2.98         | 2.83  | 7.64  | 6.67  |
| 0.3793 | 0.5   | 0.7                 | 3.68         | 3.11  | 3.21         | 2.98  | 2.94         | 2.75  | 5.87  | 5.36  |
| 0.4900 | 0.5   | 0.9                 | 6.02         | 4.76  | 5.84         | 7.74  | 5.43         | 5.83  | 12.33 | 10.23 |

Three plots of average correlation functions in system of hard spheres and hard prolate spherocylinders are also shown (see Figures 8, 9, and 10). For computation, the rodlike cores of spherocylinders were always chosen; the cores of hard spheres were either spheres (for  $\sigma_1 > \sigma_2$ ) or points (for  $\sigma_1 = \sigma_2$ ). Both theoretical and pseudoexperimental data are plotted as in the case of hard spheres.

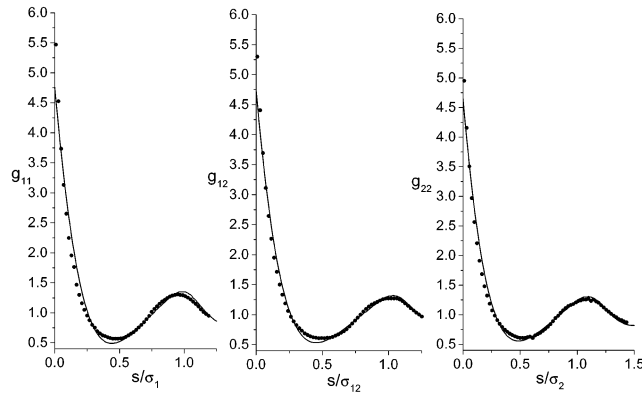
The theoretical contact values of  $g_{ij}$  and corresponding compressibility factors are included in Table 4. The proposed theoretical method does not provide  $p_{ij}$  values; therefore, only MC compressibility factors are available in Table 5.

**TABLE 5: The Compressibility Factors ( $Z$ ), Packing Fraction ( $y$ ), Molar Fraction of Spheres ( $x_1$ ), Thickness-to-Diameter Ratio ( $\sigma_2/\sigma_1$ ), Contact Value of Average Correlation Function  $g_{ij}^{av}$  ( $g_{ij}^{av}(0+)$ ) and Contact Value of Average Projection of Center-to-center Distance to the Direction of the Supporting Plane Normal ( $p_{ij}(0+)$ ) of Binary Systems of Hard Spheres (1) and Hard Prolate Spherocylinders (2)**

| $y$    | $x_1$ | $\sigma_2/\sigma_1$ | $\frac{g_{11}^{av}(0+)}{MC}$ | $\frac{g_{11}^{av}(0+)}{theor}$ | $\frac{p_{11}(0+)}{MC}$ | $\frac{g_{12}^{av}(0+)}{MC}$ | $\frac{g_{12}^{av}(0+)}{theor}$ | $\frac{p_{12}(0+)}{MC}$ | $\frac{g_{22}^{av}(0+)}{MC}$ | $\frac{g_{22}^{av}(0+)}{theor}$ | $\frac{p_{22}(0+)}{MC}$ | $Z$  |
|--------|-------|---------------------|------------------------------|---------------------------------|-------------------------|------------------------------|---------------------------------|-------------------------|------------------------------|---------------------------------|-------------------------|------|
| 0.3128 | 0.50  | 1.0                 | 2.40                         | 2.37                            | 1.00                    | 2.61                         | 2.59                            | 1.16                    | 2.84                         | 2.79                            | 1.33                    | 4.49 |
| 0.3600 | 0.50  | 1.0                 | 2.85                         | 2.85                            | 1.00                    | 3.13                         | 3.15                            | 1.16                    | 3.50                         | 3.43                            | 1.32                    | 5.85 |
| 0.4000 | 0.50  | 1.0                 | 3.25                         | 3.40                            | 1.00                    | 3.74                         | 3.77                            | 1.15                    | 4.12                         | 4.17                            | 1.31                    | 7.32 |
| 0.2503 | 0.25  | 0.3                 | 2.35                         | 2.10                            | 1.00                    | 1.91                         | 1.82                            | 1.09                    | 1.72                         | 1.67                            | 1.36                    | 2.62 |
| 0.2824 | 0.25  | 0.4                 | 2.75                         | 2.31                            | 1.00                    | 2.31                         | 2.07                            | 1.10                    | 2.05                         | 2.01                            | 1.34                    | 3.46 |
| 0.3500 | 0.25  | 0.4                 | 3.70                         | 2.89                            | 1.00                    | 2.96                         | 2.55                            | 1.10                    | 2.58                         | 2.48                            | 1.33                    | 4.91 |



**Figure 6.** Radial distribution functions,  $g_{ij}$ , of binary mixture of hard spheres,  $y = 0.4900$ ,  $\sigma_2/\sigma_1 = 0.3$ ,  $x_1 = 0.5$ : (●) MC data; (—) numerical solution of modified OZ.

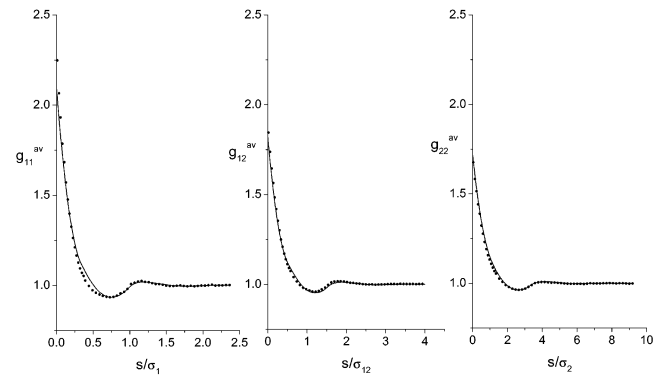


**Figure 7.** Radial distribution functions,  $g_{ij}$ , of binary mixture of hard spheres,  $y = 0.4900$ ,  $\sigma_2/\sigma_1 = 0.9$ ,  $x_1 = 0.5$ : (●) MC data; (—) numerical solution of modified OZ.

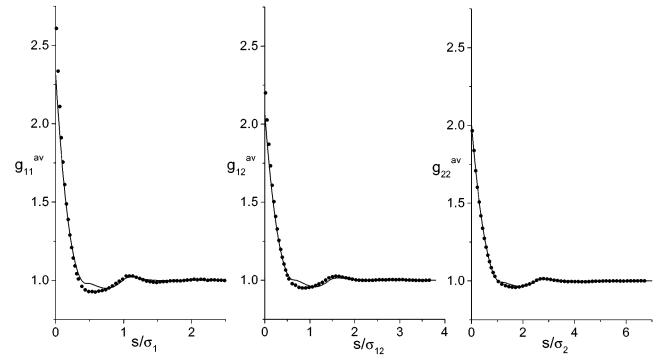
## 6. Conclusion

The Monte Carlo simulation study was performed for binary mixtures of (i) hard spheres having molar fraction  $x_1 = x_2 = 0.5$  and diameter ratios  $\sigma_2/\sigma_1 = 0.4$  or  $0.7$  and (ii) hard spheres and hard prolate spherocylinders ( $\gamma = 2.0$ ) having molar fractions  $x_1 = x_2 = 0.5$  for thickness-to-diameter ratio  $\sigma_2/\sigma_1 = 1$  or  $x_1 = 0.25$ ,  $x_2 = 0.75$  for  $\sigma_2/\sigma_1 = 0.4$  and  $0.3$ . The simulation data were used to verify the solution method of the OZ equation proposed in the theoretical part of this paper.

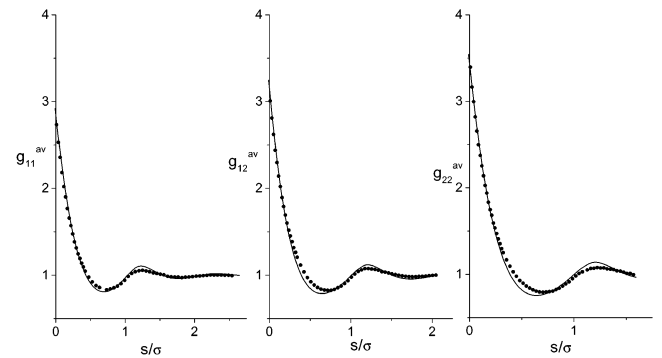
In the case of binary mixtures of hard spheres, the proposed theoretical method gives fair agreement with MC data. The values of the rdf obtained by our method agree with results of simple PYA. The situation is more complicated for mixtures of hard spheres and hard prolate spherocylinders. The agreement



**Figure 8.** Average correlation functions,  $g_{ij}^{av}$ , of mixture of hard spheres (1) and hard prolate spherocylinders (2),  $y = 0.2503$ ,  $\sigma_2/\sigma_1 = 0.3$ ,  $\gamma = 2.0$ ,  $x_1 = 0.25$ : (●) MC data; (—) numerical solution of modified OZ.



**Figure 9.** Average correlation functions,  $g_{ij}^{av}$ , of mixture of hard spheres (1) and hard prolate spherocylinders (2),  $y = 0.2824$ ,  $\sigma_2/\sigma_1 = 0.4$ ,  $\gamma = 2.0$ ,  $x_1 = 0.25$ : (●) MC data; (—) numerical solution of modified OZ.



**Figure 10.** Average correlation functions,  $g_{ij}^{av}$ , of mixture of hard spheres (1) and hard prolate spherocylinders (2),  $y = 0.3600$ ,  $\sigma_2/\sigma_1 = 1.0$ ,  $\gamma = 2.0$ ,  $x_1 = 0.5$ : (●) MC data; (—) numerical solution of modified OZ.

is good in the systems with  $\sigma_1 = \sigma_2$ , while for  $\sigma_1 > \sigma_2$ , we observe discrepancies growing with packing fraction. The curves differ even qualitatively from MC values at high densities, especially in the separations near to the first minimum of  $g_{ij}^{av}$  (see Figure 9).

The explanation of the above-mentioned deviations is probably insufficiency of approximations 14 and 15 combined with strong dependency of the resulting  $g_{ij}^{av}$  on integration bounds. Approximative expression for the third virial coefficient of hard convex bodies also plays an important role. The further improvement of the method should be focused to refinement of the expressions for the mentioned bounds and the third virial coefficient.



In comparison with formerly proposed empirical expression,<sup>10</sup> our theoretical method describes the correlation between spherocylinders ( $g_{22}^{\text{av}}$ ) better. While the mentioned empirical method, often used in the perturbation approach, works well from the contact point to the first minimum, the solution of the modified OZ is usable in a broad range of surface-to-surface distances. Note that because of the limited number of data these conclusions are only preliminary.

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## Appendix A. Derivation of Formula A2

Assume  $\varphi$  is a real function. Then one can write

$$\varphi(x) = \int_{-\infty}^{+\infty} \varphi(r) \delta(r - x) \, dr \quad (\text{A1})$$

where  $\delta$  denotes the Dirac distribution. Let us define a function  $F$  as a negatively taken Heaviside step function,  $H$ , also

$$F(y) = -H(y) = \begin{cases} 0, & y < 0 \\ -1, & y > 0 \end{cases}$$

The first derivative of  $F$  is  $F'(y) = -\delta(y)$ . Integrating eq A1 by parts and assuming  $\lim_{r \rightarrow +\infty} \varphi(r) = 0$ , we get

$$\varphi(x) = \int_{-\infty}^{+\infty} \varphi'(r) F(r - x) \, dr \quad (\text{A2})$$

## Appendix B. Coefficients of $P_{ijk}^{\alpha\beta}$

| $\alpha\beta$ | $a_{ijk}^{\alpha\beta}$  | $b_{ijk}^{\alpha\beta}$   |
|---------------|--|---|
| 11            | 1  | $R_i + R_j$   |
| 10            | $R_j + R_k$  | $R_i R_j + R_i R_k + R_j R_k + \frac{1}{3} R_j^2 + \frac{1}{6\pi} S_j$  |
| 01            | $R_i + R_k$  | $R_i R_j + R_i R_k + R_j R_k + R_j R_k + \frac{1}{3} R_i^2 + \frac{1}{6\pi} S_i$  |
| 00            | $\frac{1}{6\pi} S_k + \frac{1}{3} R_k^2 + R_i R_j + R_i R_k + R_j R_k$ | $\frac{1}{6\pi} [R_i(S_j + S_i)] + \frac{1}{3} [R_j^2(R_j + R_k) + R_k(S_i + S_j)] + \frac{1}{3} [R_i^2(R_j + R_k) + R_j(R_i + R_k) + R_k^2(R_i + R_j)] + 2R_j R_i R_k$ |

## References and Notes

- (1) Boublík, T.; Nezbeda, I.; Hlavate, K. *Statistical Thermodynamics of Simple Liquids and their Mixtures*; Elsevier: Amsterdam, 1980.
- (2) Ornstein, L. S.; Zernike, F. *Proc. Akad. Sci. (Amsterdam)* **1914**, 17, 793.
- (3) Thiele, E. *J. Chem. Phys.* **1963**, 39, 474.
- (4) Wertheim, M. S. *Phys. Rev. Lett.* **1963**, 10, 321.
- (5) Wertheim, M. S. *J. Math. Phys.* **1964**, 5, 643.
- (6) Kihara, T. *Adv. Chem. Phys.* **1963**, 5, 147.
- (7) Boublík, T.; Nezbeda, I. *Collect. Czech. Chem. Commun.* **1986**, 51, 2301.
- (8) Rickayzen, G. *Mol. Phys.* **1994**, 95, 393.
- (9) Allen, M. P.; Tildesley, D. J. *Computer Simulation in Liquids*; Oxford University Press: Oxford, U.K., 1987.
- (10) Boublík, T. *Mol. Phys.* **1984**, 51, 1429.
- (11) Percus, J. K.; Yevick, G. J. *Phys. Rev.* **1958**, 110, 1.
- (12) Henderson, D.; Malijevský, A.; Labík, S.; Chan, K. Y. *Mol. Phys.* **1996**, 87, 273.
- (13) Malijevský, A.; Barošová, M.; Smith, W. R. *Mol. Phys.* **1997**, 91, 65.
- (14) Šindelka, M.; Boublík, T. *Mol. Phys.* **1999**, 97, 1035.
- (15) Boublík, T.; Šindelka, M. *Phys. Chem. Chem. Phys.* **2001**, 3, 2411.
- (16) Boublík, T. *J. Chem. Phys.* **2001**, 115, 925.
- (17) Boublík, T. *Mol. Phys.* **1981**, 42, 209.
- (18) Lee, L. L. *Molecular Thermodynamics of Nonideal Fluids*; Butterworth: Boston, MA, 1988.
- (19) Lee, L. L.; Levesque, D. *Mol. Phys.* **1973**, 26, 1351.