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Analytic solution of the reference interaction site model equation for a mixture of hard spheres and symmetric rigid molecules

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Abstract. The analytic solution of the set of site–site Ornstein–Zernike equations within the Chandler–Andersen approximation for a mixture of hard spheres and symmetric rigid molecules is presented. Using the zero-pole approximation, the site–site radial distribution functions are calculated.

1. Introduction

Owing to the application of the site–site approach, great progress in the theory of molecular fluids has been achieved in recent years [1–3]. This approach is based on the use of site–site distribution functions. The site–site radial distribution functions (SSRDF) are usually calculated from the set of site–site Ornstein–Zernike (SSOZ) equations, introduced by Chandler and Andersen [4]. We may write them in the form

$$h(k) = S(k)c(k)S(k) + S(k)c(k)\rho h(k) \tag{1}$$

where the matrices $c(k)$, $h(k)$, $S(k)$ and ρ are

$$\begin{aligned} h^{ab}_{\alpha\beta}(k) &= (4\pi/k)\int_0^\infty r h^{ab}_{\alpha\beta}(r)\sin(kr)\,\mathrm{d}r \\ c^{ab}_{\alpha\beta}(k) &= (4\pi/k)\int_0^\infty r c^{ab}_{\alpha\beta}(r)\sin(kr)\,\mathrm{d}r \\ \rho^{ab}_{\alpha\beta} &= \rho_a\delta_{ab}\delta_{\alpha\beta} \\ S^{ab}_{\alpha\beta}(k) &= \delta_{ab}[\delta_{\alpha\beta} + (1-\delta_{\alpha\beta})\sin(kl^a_{\alpha\beta})/(kl^a_{\alpha\beta})]. \end{aligned} \tag{1a}$$

Here $c^{ab}_{\alpha\beta}(r)$ and $h^{ab}_{\alpha\beta}(r)$ are the direct and the total correlation functions, respectively, of the sites α and β, belonging to molecules a and b; $\rho_a = N_a/V$, where N_a is the number of molecules of sort a; and $l^a_{\alpha\beta}$ is the intra-molecular distance between sites α and β. In the case of symmetric homonuclear molecules the set of SSOZ equations reduces to one equation [5]

$$h_{ss}(k) = [1+(n_s-1)s(k)]^2 c_{ss}(k) + n_s\rho[1+(n_s-1)s(k)]c_{ss}(k)h_{ss}(k). \tag{2}$$

Here index s denotes the molecular site; $\rho = N/V$, where N is the number of molecules;

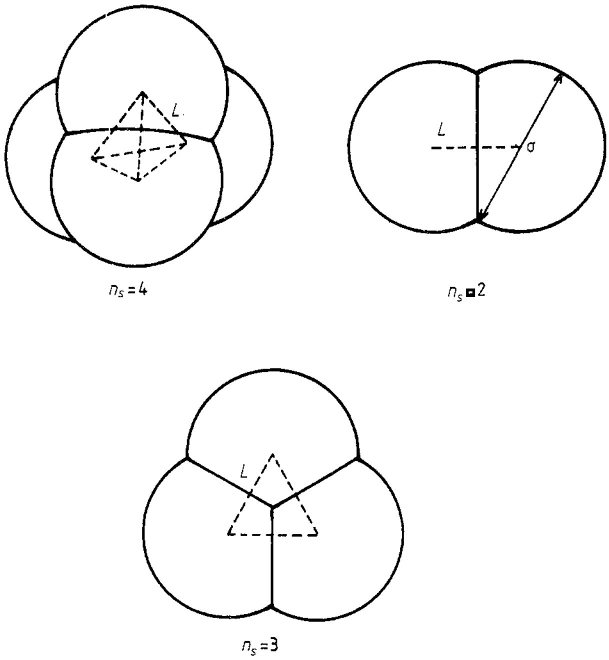

Figure 1. The models of the molecules.

$s(k) = \sin(kl_s)/(kl_s)$; and n_s is the number of sites in the molecule. Particularly $n_s = 2$ corresponds to dumb-bells, $n_s = 3$ to triangular triatomics and $n_s = 4$ to tetrahedral tetra-atomics (see figure 1).

The special class of site–site models with hard-sphere site–site interaction can be separated out. Such models are called the reference interaction site models (RISM) [1–5]. For RISM the total correlation function satisfies the exact condition

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

where σ_{ss} is the hard-sphere size. Similarly to the Percus–Yevick approximation for the hard-sphere model, the following closure for the SSOZ equation was introduced [3, 4]

$$c_{ss}(r) = 0 \qquad r > \sigma_{ss}. \tag{3b}$$

The analytic solution of equation (2) combined with the closure relation (3) for the system of dumb-bells was obtained recently [6–11]. The method of solution is based upon the Wiener–Hopf factorisation technique and generalises Baxter's method of solution of the usual Ornstein–Zernike equation for a hard-sphere system in the Percus–Yevick approximation [12, 13]. For the SSOZ equation (2), the Baxter function $Q(r)$ contains an infinite series of exponentially damped oscillating terms, which have their origin in the poles of the function $[1 + s(k)]^{-1}$. It was shown [8, 10], however, that for high densities one can neglect all these terms and obtain quantitatively good results. Such an approximation is called the zero-pole approximation (ZPA).

The above analytic solution was generalised for the system of symmetric n_s-atomic molecules [14]. The investigations carried out in [14] show that, in the case of triatomics and especially in the case of tetra-atomics, the results obtained in the ZPA become not so good and it is necessary to take into consideration the poles of the function $[1 + s(k)]^{-1}$.

The purpose of the present paper is to present the analytic solution of the set of SSOZ equations for a mixture of hard spheres and symmetric n_s-atomic molecules (figure 1). For such a two-component mixture we can write this set of equations in the following form [15, 16]

$$h^{(s)}(k) = w(k)c^{(s)}(k)w(k) + w(k)c^{(s)}(k)\rho h^{(s)}(k) \tag{4}$$

where

$$h^{(s)}(k) = \begin{pmatrix} h^{(s)}_{ii}(k) & h^{(s)}_{is}(k) \\ h^{(s)}_{si}(k) & h^{(s)}_{ss}(k) \end{pmatrix} \qquad c^{(s)}(k) = \begin{pmatrix} c^{(s)}_{ii}(k) & c^{(s)}_{is}(k) \\ c^{(s)}_{si}(k) & c^{(s)}_{ss}(k) \end{pmatrix}$$

$$w(k) = \begin{pmatrix} 1 & 0 \\ 0 & 1 + (n_s - 1)s(k) \end{pmatrix} \qquad \rho = \begin{pmatrix} \rho_i & 0 \\ 0 & n_s\rho_s \end{pmatrix} \tag{5}$$

$$\rho_s = N/V \qquad \rho_i = N_i/V.$$

Here, indices i and s denote the hard sphere and the molecular site, respectively; N_i and N are the number of hard spheres and molecules in the system.

The closure relation for the set of equations (4) in the case of equal size of hard spheres and molecular sites, $\sigma_{ii} = \sigma_{is} = \sigma_{ss} = \sigma$, is given by

$$\begin{aligned} h^{(s)}(r) &= -1 \qquad r < \sigma \\ c^{(s)}(r) &= 0 \qquad r > \sigma. \end{aligned} \tag{6}$$

The present analytic solution of the set of equations (4) coupled by closure relation (6) is based on the generalisation of the method introduced in [6–11].

The main results of the present paper were published in [16]. Recently for a mixture of hard spheres and dumb-bells with $l_s = \frac{1}{2}\sigma$ the set of SSOZ equations was solved in the ZPA by Cummings and Stell [17]. Using the numerical method of Lowden and Chandler [18] the SSRDF for a mixture of hard spheres and dumb-bells were considered in [19].

2. Wiener–Hopf factorisation

The set of equations (4) can be conveniently written in dimensionless form as

$$[w^{-1}(k) - c(k)][w(k) + h(k)] = 1 \tag{7}$$

where the matrices $c(k)$ and $h(k)$ are

$$\begin{aligned} c_{lm}(k) &= (6/\pi)(\eta_l\eta_m)^{1/2}c^{(s)}_{lm}(k) = 2\int_0^1 S_{lm}(r)\cos(kr)\,\mathrm{d}r \\ h_{lm}(k) &= (6/\pi)(\eta_l\eta_m)^{1/2}h^{(s)}_{lm}(k) = 2\int_0^\infty J_{lm}(r)\cos(kr)\,\mathrm{d}r. \end{aligned} \tag{8}$$

Here $l = (i, s)$, $m = (i, s)$, $\eta_i = \pi N_i\sigma^3/6V$, $\eta_s = \pi n_s N\sigma^3/6V$, and

$$\begin{aligned} S_{lm}(r) &= 12(\eta_l\eta_m)^{1/2}\int_r^1 tc^{(s)}_{lm}(t)\,\mathrm{d}t \\ J_{lm}(r) &= 12(\eta_l\eta_m)^{1/2}\int_r^\infty th^{(s)}_{lm}(t)\,\mathrm{d}t. \end{aligned} \tag{9}$$

Owing to the finiteness of the functions $w(k)$ and $h(k)$ for all real k, the symmetric matrix $w^{-1}(k) - c(k)$ can be expressed as

$$w^{-1}(k) - c(k) = Q^{\mathrm{T}}(-k)Q(k). \tag{10}$$

The elements of the matrix $Q(k)$ are analytic in the upper half-plane and the elements of the matrix $Q^{\mathrm{T}}(-k)$ are analytic in the lower half-plane. When $k \to \infty$ it follows from (10) that $Q(k) \to 1$. Thus the inverse Fourier transformation of the matrix elements $[1 - Q(k)]_{lm}$ can be represented by

$$12(\eta_l \eta_m)^{1/2} q_{lm}(r) = (2\pi)^{-1} \int_{-\infty}^{\infty} [\delta_{lm} - Q_{lm}(k)] \exp(-\mathrm{i}kr)\, \mathrm{d}k. \qquad (11)$$

For $r < 0$, closing the integration contour round the upper half-plane we have

$$q_{lm}(r) = 0 \qquad r < 0. \qquad (12)$$

Owing to the relation (10) the analytic continuation of the matrix $Q(k)$ into the lower half-plane is defined by

$$Q(k) = [Q^{\mathrm{T}}(-k)]^{-1}[w^{-1}(k) - c(k)]. \qquad (13)$$

Thus, the elements of the matrix $q(r)$ can be represented as

$$q_{lm}(r) = \mathrm{Re} \sum_{n=1}^{\infty} \xi_{lm}^{(n)} \exp(-\mathrm{i}\lambda_n r) \qquad r \geqslant 1 \qquad (14)$$

where λ_n are the roots of the equation

$$1 + (n_s - 1)s(k) = 0 \qquad (15)$$

and

$$\xi_{lm}^{(n)} = \mathrm{i}[Q^{\mathrm{T}}(-\lambda_n)]_{lm}^{-1} \delta_{ms} [6(\eta_l \eta_m)^{1/2} (n_s - 1) s'(\lambda_n)]^{-1} \qquad L = l_s/\sigma. \qquad (16)$$

From equations (7) and (10) we have

$$Q(k)[w(k) + h(k)] = [Q^{\mathrm{T}}(-k)]^{-1}. \qquad (17)$$

Considering equation (17) in real space we obtain the set of equations for the functions $J_{lm}(r)$

$$J_{lm}(r) = 12(\eta_l \eta_m)^{1/2} q_{lm}(r) + 12 \sum_p (\eta_l \eta_p)^{1/2} \times \left(\int_0^{\infty} q_{lp}(t) J_{pm}(|r - t|)\, \mathrm{d}t + \delta_{ps} \delta_{ms} \tilde{n}_s \int_{r-L}^{r+L} q_{lp}(t)\, \mathrm{d}t \right) - \delta_{ls} \delta_{ms} \tilde{n}_s \theta(L - r) \qquad (18)$$

where

$$\theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases} \qquad \tilde{n}_s = (n_s - 1)/2L.$$

Differentiating with respect to r gives the set of equations for the functions $h_{lm}^{(s)}(r)$

$$r h_{lm}^{(s)}(r) = -q'_{lm}(r) - [\tilde{n}_s (\delta_{ms} \delta_{ls})/12\eta_s] \delta(L - r) - \tilde{n}_s \delta_{ms} [q_{lm}(r + L) - q_{lm}(r - L)] + 12 \sum_p \eta_p \int_0^{\infty} q_{lp}(t)(r - t) h_{pm}^{(s)}(|r - t|)\, \mathrm{d}t. \qquad (19)$$

When $\eta_i \to 0$ it follows that (18) corresponds to a one-component molecular system [6–8], and when $\eta_s \to 0$ (18) corresponds to the Percus–Yevick approximation for a one-component hard-sphere system.

3. Derivation of the Baxter functions

Once the functions $q_{lm}(r)$ are known, the set of equations (19) may be used to derive the total correlation functions $h^{(s)}_{lm}(r)$. For this purpose let us use the set of equations (19) at $0<r<1$. Owing to the closure relation (6) and to (14) for the functions $q_{lm}(r)$ we have the set of differential equations

$$q'_{lm}(r)+\delta_{ms}\tilde{n}_s[q_{ls}(r+L)-q_{ls}(r-L)]+[\delta_{ms}\delta_{ls}\tilde{n}_s/12\eta_s]\delta(r-L)$$
$$=a_{lm}r+b_{lm}+\operatorname{Re}\sum_{n=1}^{\infty}d^{(n)}_{lm}\exp(-\mathrm{i}\lambda_n r)\equiv B_{lm}(r) \qquad (20)$$

where

$$a_{lm}=1-12\sum_p \eta_p\int q_{lp}(t)\,\mathrm{d}t-12\eta_s\operatorname{Re}\sum_{n=1}^{\infty}\xi^{(n)}_{ls}/(\mathrm{i}\lambda_n)\exp(-\mathrm{i}\lambda_n)$$
$$b_{lm}=12\sum_p \eta_p\int q_{lp}(t)t\,\mathrm{d}t-12\eta_s\operatorname{Re}\sum_{n=1}^{\infty}\xi^{(n)}_{ls}[\lambda_n^{-2}-1/(\mathrm{i}\lambda_n)]\exp(-\mathrm{i}\lambda_n) \qquad (21)$$
$$d^{(n)}_{lm}=-12\eta_s\xi^{(n)}_{ls}F_{sm}(\mathrm{i}\lambda_n).$$

The Laplace transform of the corresponding SSRDF is

$$F_{lm}(\mathrm{i}\lambda_n)=\int_0^{\infty}r\exp(-\mathrm{i}\lambda_n r)[h^{(s)}_{lm}(r)+1]\,\mathrm{d}r.$$

The boundary and discontinuity conditions on the functions $q_{lm}(r)$ are

$$q_{lm}(1)=\operatorname{Re}\sum_{n=1}^{\infty}\xi^{(n)}_{lm}\exp(-\mathrm{i}\lambda_n)$$
$$q_{ls}(L^-)-q_{ls}(L^+)=\delta_{ls}\tilde{n}_s/12\eta_s. \qquad (22)$$

To solve the set of equations (20) consider now two different cases: (*a*) $\frac{1}{2}\leqslant L<1$ and (*b*) $\frac{1}{3}\leqslant L<\frac{1}{2}$.

3.1. Case (a) $\frac{1}{2}\leqslant L<1$

Let us divide the interval $0<r\leqslant 1$ into three sub-intervals

$$\mathrm{I}=(0,1-L)\qquad \mathrm{II}=(1-L,L)\qquad \mathrm{III}=(L,1).$$

Consideration of the set of equations (20) in each of these sub-intervals gives

$$q'_{li}(r)=B_{li}(r)\qquad 0<r\leqslant 1 \qquad (23)$$

$$q'_{ls}(r)+\tilde{n}_s q_{ls}(r+L)=B_{ls}(r)\qquad r\in\mathrm{I}$$
$$q'_{ls}(r)=B_{ls}(r)-\tilde{n}_s q_{ls}(r+L)\qquad r\in\mathrm{II} \qquad (24)$$
$$q'_{ls}(r)-\tilde{n}_s q_{ls}(r-L)=B_{ls}(r)-\tilde{n}_s q_{ls}(r+L)\qquad r\in\mathrm{III}.$$

Using (23) and the second equation in (24) we have

$$q_{li}(r)=\tfrac{1}{2}(r^2-1)a_{li}+(r-1)b_{li}$$
$$-\operatorname{Re}\sum_{n=1}^{\infty}d^{(n)}_{li}/(\mathrm{i}\lambda_n)[\exp(-\mathrm{i}\lambda_n r)-\exp(-\mathrm{i}\lambda_n)]\qquad 0<r\leqslant 1 \qquad (25a)$$

$$q_{ls}(r) = \tfrac{1}{2}r^2 a_{ls} + b_{ls} r - \mathrm{Re} \sum_{n=1}^{\infty} 1/(\mathrm{i}\lambda_n)[d_{ls}^{(n)} - \tilde{n}_s \xi_{ls}^{(n)} \exp(-\mathrm{i}\lambda_n L)] \times \exp(-\mathrm{i}\lambda_n r) + e_{ls} \qquad r \in \mathrm{II}. \tag{25b}$$

From the last equations in (24) it follows that

$$q_{ls}''(r) + \tilde{n}_s^2 q_{ls}(r) = B_{ls}'(r) - \tilde{n}_s B_{ls}(r+L) + \tilde{n}_s^2 q_{ls}(r+2L) \qquad r \in \mathrm{I}. \tag{26}$$

Solution of this equation can be expressed in the form

$$q_{ls}(r) = \tilde{n}_s^{-1}(\tilde{n}_s^{-1} - r - L)a_{ls} - \tilde{n}_s^{-1} b_{ls} + \mathrm{Re} \sum_{n=1}^{\infty} \alpha_{ls}^{(n)} \exp(-\mathrm{i}\lambda_n r) + f_{ls} \cos(\tilde{n}_s r) - t_{ls} \sin(\tilde{n}_s r) \qquad r \in \mathrm{I} \tag{27}$$

where

$$\alpha_{ls}^{(n)} = [\xi_{ls}^{(n)} \tilde{n}_s^2 \exp(-\mathrm{i}\lambda_n 2L) - d_{ls}^{(n)}(\mathrm{i}\lambda_n + \tilde{n}_s \exp(-\mathrm{i}\lambda_n L))](\tilde{n}_s^2 - \lambda_n^2)^{-1}.$$

Now it is not difficult to obtain the expressions for the function $q_{lm}(r)$ when $r \in \mathrm{III}$

$$q_{ls}(r) = \tilde{n}_s^{-1}(r - L + \tilde{n}_s^{-1})a_{ls} + \tilde{n}_s^{-1} b_{ls} + \tilde{n}_s^{-1} \mathrm{Re} \sum_{n=1}^{\infty} \mu_{ls}^{(n)} \exp(-\mathrm{i}\lambda_n r) + f_{ls} \sin[\tilde{n}_s(r-L)] + t_{ls} \cos[\tilde{n}_s(r-L)] \qquad r \in \mathrm{III} \tag{28}$$

where

$$\mu_{ls} = (d_{ls}^{(n)} + \mathrm{i}\lambda_n \alpha_{ls}^{(n)}) \exp(\mathrm{i}\lambda_n L).$$

The constants f_{ls}, t_{ls} and e_{ls} can be evaluated using the boundary conditions (22) and continuity condition on the function $q_{ls}(r)$

$$q_{ls}(1 - L + \delta) = q_{ls}(1 - L - \delta) \qquad \delta \to 0.$$

3.2. Case (b) $\frac{1}{3} \leqslant L < \frac{1}{2}$

Following the method proposed in [10] let us divide the whole interval $0 \leqslant r < 1$ into five sub-intervals

$$\mathrm{I} = (0, 1-2L) \qquad \mathrm{II} = (1-2L, L) \qquad \mathrm{III} = (L, 1-L) \qquad \mathrm{IV} = (1-L, 2L) \qquad \mathrm{V} = (2L, 1). \tag{29}$$

In each of these sub-intervals the set of equations (20) have the following form

$$q_{li}'(r) = B_{li}(r) \qquad 0 < r \leqslant 1 \tag{30}$$

$$q_{ls}'(r) + \tilde{n}_s q_{ls}(r+L) = B_{ls}(r) \qquad r \in \mathrm{I} \tag{31}$$

$$q_{ls}'(r) + \tilde{n}_s q_{ls}(r+L) = B_{ls}(r) \qquad r \in \mathrm{II} \tag{32}$$

$$q_{ls}'(r) + \tilde{n}_s [q_{ls}(r+L) - q_{ls}(r-L)] = B_{ls}(r) \qquad r \in \mathrm{III} \tag{33}$$

$$q_{ls}'(r) - \tilde{n}_s q_{ls}(r-L) = B_{ls}(r) - \tilde{n}_s q_{ls}(r+L) \qquad r \in \mathrm{IV} \tag{34}$$

$$q'_{ls}(r) - \tilde{n}_s q_{ls}(r-L) = B_{ls}(r) - \tilde{n}_s q_{ls}(r+L) \qquad r \in \text{V}. \tag{35}$$

From (30) immediately follows the expression for $q_{li}(r)$

$$q_{li}(r) = \tfrac{1}{2}(r^2-1)a_{li} + (r-1)b_{li} - \text{Re}\sum_{n=1}^{\infty} d_{li}^{(n)}/(\text{i}\lambda_n)[\exp(-\text{i}\lambda_n r - \exp(\text{i}\lambda_n)]. \tag{36}$$

Considering equations (31), (33) and (35) and then (32) and (34) gives the following two independent differential equations

$$q'''_{ls}(r) + 2\tilde{n}_s^2 q'_{ls}(r) = B''_{ls}(r) - \tilde{n}_s B'_{ls}(r+L)$$
$$+ \tilde{n}_s^2[B_{ls}(r+2L) + B_{ls}(r) - \tilde{n}_s q_{ls}(r+3L)] \qquad r \in \text{I} \tag{37}$$

$$q''_{ls}(r) + \tilde{n}_s^2 q_{ls}(r) = B'_{ls}(r) - \tilde{n}_s[B_{ls}(r+L) + \tilde{n}_s q_{ls}(r+2L)] \qquad r \in \text{II}. \tag{38}$$

Solution of these equations determines the functions $q_{ls}(r)$ in the intervals I and II respectively

$$q_{ls}(r) = \tfrac{1}{2}r^2 a_{ls} + [L(n_s-2)/(n_s-1)a_{ls} + b_{ls}]r + \text{Re}\sum_{n=1}^{\infty}\beta_{ls}^{(n)}\exp(-\text{i}\lambda_n r)$$
$$+ v_{ls} + k_{ls}\sin(\sqrt{2}\tilde{n}_s r) + p_{ls}\cos(\sqrt{2}\tilde{n}_s r) \qquad r \in \text{I} \tag{39}$$

$$q_{ls}(r) = \tilde{n}_s^{-1}[(\tilde{n}_s^{-1} - r - L)a_{ls} - b_{ls}] + \text{Re}\sum_{n=1}^{\infty}\alpha_{ls}^{(n)}\exp(-\text{i}\lambda_n r)$$
$$+ u_{ls}\cos[\tilde{n}_s(r-1+2L)] + w_{ls}\sin[\tilde{n}_s(r-1+2L)] \qquad r \in \text{II} \tag{40}$$

where

$$\beta_{ls}^{(n)} = [\tilde{n}_s^3\xi_{ls}^{(n)}\exp(-3\text{i}\lambda_n L) - \tilde{n}_s^2 d_{ls}^{(n)}\exp(-2\text{i}\lambda_n L) - \tilde{n}_s d_{ls}^{(n)}\exp(-\text{i}\lambda_n L)$$
$$- d_{ls}^{(n)}(2\tilde{n}_s^2 - 2\lambda_n^2)][\text{i}\lambda_n(\tilde{n}_s^2 - \lambda_n^2)]^{-1}.$$

Now using equations (31)–(35), it is easy to obtain the functions $q_{ls}(r)$ for another three sub-intervals

$$q_{ls}(r) = -2L^2(n_s-2)/(n_s-1)^2 a_{ls} + \text{Re}\sum_{n=1}^{\infty}\gamma_{ls}^{(n)}\exp(-\text{i}\lambda_n r)$$
$$- \sqrt{2}k_{ls}\cos[\sqrt{2}\tilde{n}_s(r-L)] + \sqrt{2}p_{ls}\sin[\sqrt{2}\tilde{n}_s(r-L)] \qquad r \in \text{III} \tag{41}$$

$$q_{ls}(r) - \tilde{n}_s^{-1}[(r - L + \tilde{n}_s^{-1})a_{ls} + b_{ls}] + \tilde{n}_s^{-1}\,\text{Re}\sum_{n=1}^{\infty}\mu_{ls}^{(n)}\exp(-\text{i}\lambda_n r)$$
$$+ u_{ls}\sin[\tilde{n}_s(r-1+L)] - w_{ls}\cos[\tilde{n}_s(r-1+L)] \qquad r \in \text{IV} \tag{42}$$

$$q_{ls}(r) = \tfrac{1}{2}r^2 a_{ls} + [b_{ls} - La_{ls}(n_s-2)/(n_s-1)]r + 2Lb_{ls}(2-n_s)/(n_s-1)$$
$$+ \text{Re}\sum_{n=1}^{\infty}\chi_{ls}^{(n)}\exp(-\text{i}\lambda_n r) + v_{ls} - k_{ls}\sin[\sqrt{2}\tilde{n}_s(r-2L)]$$
$$- p_{ls}\cos[\sqrt{2}\tilde{n}_s(r-2L)] \qquad r \in \text{V} \tag{43}$$

where

$$\chi_{ls}^{(n)} = \tilde{n}_s^{-1}d_{ls}^{(n)}\exp(\text{i}\lambda_n L) + [\tilde{n}_s^{-1}\text{i}\lambda_n(d_{ls}^{(n)} + \text{i}\lambda_n\beta_{ls}^{(n)} + \beta_{ls}^{(n)}]\exp(2\text{i}\lambda_n L)$$

$$\gamma_{ls}^{(n)} = (d_{ls}^{(n)} - i\lambda_n \beta_{ls}^{(n)}) \exp(i\lambda_n L).$$

The expressions for $\alpha_{ls}^{(n)}$ and $\mu_{ls}^{(n)}$ are the same, as in case (*a*). To determine the constants of integration in (39)–(43) the boundary conditions (22) and continuity conditions on the function $q_{ls}(r)$

$$\begin{aligned} &q_{ls}(1-2L+\delta) = q_{ls}(1-2L-\delta) \qquad q_{ls}(1-L+\delta) = q_{ls}(1-L-\delta) \\ &q_{ls}(2L+\delta) = q_{ls}(2L-\delta) \qquad \delta \to 0 \end{aligned} \tag{44}$$

must be used.

Expressions for the functions $q_{lm}(r)$ also contain the constants a_{lm}, b_{lm} and $\xi_{lm}^{(n)}$, which can be evaluated from the equations, derived with the help of (21) and (11).

As follows from (14) the functions $q_{lm}(r)$ contain an infinite sum of terms, which is determined by $1 + (n_s - 1)s(k) = 0$. It can be shown that for large n

$$\lambda_n L \simeq (2n + \tfrac{3}{2})\pi - i \ln[(4n+3)\pi/(n_s - 1)]$$

and

$$Q^{\mathrm{T}}(\lambda_n) \to 1 \qquad n \to \infty.$$

Using these conditions it is not difficult to prove the convergence of the series in (14) when $\eta_s \neq 0$ and $r > L$.

4. Zero-pole approximation

In order to provide further calculations the infinite series for $q_{lm}(r)$ when $r > 1$ must be terminated. As in the case of a one-component molecular system [7–11] consideration of the whole series in (14) is important only when $\eta_s \to 0$. For sufficiently high values of η_s one need take into account only the first few terms of the infinite series for $q_{lm}(r)$ [8] or use the ZPA, due to which the whole series in (14) can be neglected [10].

In ZPA in view of (25), (27) and (28) for $\frac{1}{2} \leqslant L < 1$ we have

$$\begin{aligned} &q_{li}(r) = \tfrac{1}{2}(r^2 - 1)a_{li} + b_{li}(r-1) \qquad 0 < r \leqslant 1 \\ &q_{ls}(r) = (\tilde{n}_s^{-1} - r - L)\tilde{n}_s^{-1} a_{ls} - \tilde{n}_s^{-1} b_{ls} + f_{ls} \cos(\tilde{n}_s r) - t_{ls} \sin(\tilde{n}_s r) \qquad r \in \mathrm{I} \\ &q_{ls}(r) = \tfrac{1}{2} a_{ls} r^2 + b_{ls} r + e_{ls} \qquad r \in \mathrm{II} \end{aligned} \tag{45}$$

$$\begin{aligned} q_{ls}(r) &+ \tilde{n}_s^{-1}(r - L + \tilde{n}_s^{-1})a_{ls} + \tilde{n}_s^{-1} b_{ls} + f_{ls} \sin[\tilde{n}_s(r-L)] \\ &+ t_{ls} \cos[\tilde{n}_s(r-L)] \qquad r \in \mathrm{III}. \end{aligned}$$

Taking into consideration (21), boundary conditions (22) and continuity conditions on the function $q_{ls}(r)$ when $r = 1 - L$ we find the set of linear equations for the constants a_{lm}, b_{lm}, t_{ls}, f_{ls} and e_{ls}:

$$\begin{aligned} &X^{(1)} A^{(1)} = R^{(1)} \\ &a_{ls} = a_{li} \\ &b_{ls} = b_{li} \end{aligned} \tag{46}$$

where $X^{(1)} = (a_{ls}, b_{ls}, t_{ls}, f_{ls}, e_{ls})$ and the elements of the matrices $A^{(1)}$ and $R^{(1)}$ are presented in the Appendix.

Considering the case when $\frac{1}{3} \leq L < \frac{1}{2}$ and taking into account (36), (39)–(43) in the ZPA we find

$$
\begin{aligned}
q_{li}(r) &= \tfrac{1}{2}(r^2 - 1)a_{li} + b_{li}(r - 1) \qquad 0 < r \leq 1 \\
q_{ls}(r) &= \tfrac{1}{2}r^2 a_{ls} + [L(n_s - 2)/(n_s - 1)a_{ls} + b_{ls}]r + v_{ls} + k_{ls}\sin(\sqrt{2}\,\tilde{n}_s r) \\
&\quad + p_{ls}\cos(\sqrt{2}\,\tilde{n}_s r) \qquad r \in \mathrm{I} \\
q_{ls}(r) &= \tilde{n}_s^{-1}[(\tilde{n}_s^{-1} - r - L)a_{ls} - b_{ls}] + u_{ls}\cos[\tilde{n}_s(r - 1 + 2L)] \\
&\quad + w_{ls}\sin[\tilde{n}_s(r - 1 + 2L)] \qquad r \in \mathrm{II} \\
q_{ls}(r) &= -2L^2(n_s - 2)/(n_s - 1)^2 a_{ls} - \sqrt{2}\,k_{ls}\cos[\sqrt{2}\,\tilde{n}_s(r - L)] \\
&\quad + \sqrt{2}\,p_{ls}\sin[\sqrt{2}\,\tilde{n}_s(r - L)] \qquad r \in \mathrm{III} \\
q_{ls}(r) &= \tilde{n}_s^{-1}[(r - L + \tilde{n}_s^{-1})a_{ls} + b_{ls}] + u_{ls}\sin[\tilde{n}_s(r - 1 + L)] \\
&\quad - w_{ls}\cos[\tilde{n}_s(r - 1 + L)] \qquad r \in \mathrm{IV} \\
q_{ls}(r) &= \tfrac{1}{2}a_{ls}r^2 + [b_{ls} - L(n_s - 2)/(n_s - 1)a_{ls}]r + (2 - n_s)\tilde{n}_s^{-1}b_{ls} + v_{ls} \\
&\quad + k_{ls}\sin[\sqrt{2}\,\tilde{n}_s(r - 2L)] - p_{ls}\cos[\sqrt{2}\,\tilde{n}_s(r - 2L)] \qquad r \in \mathrm{V}
\end{aligned}
\tag{47}
$$

and the constants a_{lm}, b_{lm}, v_{lm}, k_{lm}, p_{lm}, u_{lm}, w_{lm} can be determined from the set of linear equations

$$
\begin{aligned}
&X^{(2)}A^{(2)} = R^{(2)} \\
&a_{ls} = a_{li} \\
&b_{ls} = b_{li}
\end{aligned}
\tag{48}
$$

where $X^{(2)} = (a_{ls}, b_{ls}, v_{ls}, k_{ls}, p_{ls}, u_{ls}, w_{ls})$ and the elements of the matrices $A^{(2)}$ and $R^{(2)}$ are presented in the Appendix.

Finally, considering (19) in the ZPA when $r = 1$ yields the contact values for the SSRDF $g_{lm}(r) = h_{lm}^{(s)}(r) + 1$

$$
\begin{aligned}
g_{lm}(1^+) &= \tilde{n}_s\delta_{ms}[(1 - L)^2/2a_{ls} + (1 - L)b_{ls} + e_{ls}] + a_{lm} + b_{lm} \qquad \tfrac{1}{2} < L < 1 \\
g_{lm}(1^+) &= (n_s - 1)\delta_{ms}\{1/(n_s - 1)[(1 - 2L + \tilde{n}_s^{-1})a_{ls} + b_{ls}] - w_{ls}/(2L)\} \\
&\quad + a_{lm} + b_{lm} \qquad \tfrac{1}{3} \leq L \leq \tfrac{1}{2}.
\end{aligned}
$$

5. Site–site radial distribution functions

Substituting into the set of equations (19) the expression for the SSRDF $g_{lm}(r) = h_{lm}^{(s)}(r) + 1$ yields

$$
\begin{aligned}
&q'_{lm}(r) + \tilde{n}_s\delta_{ms}[q_{lm}(r + L) - q_{lm}(r - L)] + \delta_{ms}\delta_{lm}\tilde{n}_s\delta(r - L)/12\eta_s - r \\
&\quad + 12\sum_p \eta_p \int_0^\infty q_{lp}(t)(r - t)\,\mathrm{d}t - 12\sum_p \eta_p \int_r^\infty q_{lp}(t)(r - t)g_{pm}(t - r)\,\mathrm{d}t \\
&\quad + rg_{lm}(r) - 12\sum_p \eta_p \int_0^r q_{lp}(t)(r - t)g_{pm}(r - t)\,\mathrm{d}t = 0.
\end{aligned}
\tag{49}
$$

With the help of the Laplace transformation the set of equations (49) can be written in the form

$$\hat{g}_{lm}(s) - 12\sum_p (\eta_p/\eta_l)^{1/2}\hat{Q}_{lp}(s)\hat{g}_{pm}(s) = -\hat{\Xi}_{lm}(s)/12(\eta_l\eta_m)^{1/2} \tag{50}$$

where

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

$$\hat{Q}_{lm}(s) = 12(\eta_l\eta_m)^{1/2}\int_0^\infty \exp(-sr)q_{lm}(r)\,\mathrm{d}r$$

$$\hat{\Xi}_{lm}(s)/12(\eta_l\eta_m)^{1/2} = \int_1^{1+L}\{q'_{lm}(r) + \delta_{ms}\tilde{n}_s[q_{ls}(r+L) - q_{ls}(r-L)]\}\exp(-sr)\,\mathrm{d}r - \int_1^\infty B_{lm}(r)\exp(-sr)\,\mathrm{d}r. \tag{51}$$

The set of equations (50) yields the following expression for the SSRDF

$$12(\eta_l\eta_m)^{1/2}g_{lm}(r) = (2\pi\mathrm{i}r)^{-1}\sum_p\int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty}[\hat{Q}(s)-1]^{-1}_{lp}\hat{\Xi}_{pm}(s)\exp(sr)\,\mathrm{d}s \tag{52}$$

and when $s = \mathrm{i}\lambda_n$ gives the relation between $F_{lm}(\mathrm{i}\lambda_n)$ and $\xi^{(n)}_{lm}$

$$-F_{lm}(\mathrm{i}\lambda_n) + 12\sum_p(\eta_p/\eta_l)^{1/2}\hat{Q}_{lp}(-\lambda_n)F_{pm}(\mathrm{i}\lambda_n) = \hat{\Xi}_{lm}(\mathrm{i}\lambda_n)/12(\eta_l\eta_m)^{1/2}.$$

This relation can be used for determination of the constants $d^{(n)}_{lm}$.

To illustrate the method of obtaining the SSRDF let us consider the case when $L = \frac{1}{2}$. Combining equations (45), (51) and (52) we find

$$12(\eta_l\eta_m)^{1/2}g_{lm}(r) = (2\pi\mathrm{i}r)^{-1}\int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty}N^{-1}(s)\sum_{j=1}^{4}\{K^{(j)}_{lm}(s) \times\exp[(j-6)s/2]\}\exp(sr)\,\mathrm{d}s \tag{53}$$

$$N(s) = \sum_{j=1}^{5}P_j(s)\exp[(j-5)s/2]$$

where expressions for the functions $K^{(j)}_{lm}(s)$ and $P_j(s)$ (where $j = 1, \ldots$) are presented in the Appendix.

Using the following form for $N(s)$ in (53)

$$N^{-1}(s) = \exp(s)\sum_{n\geqslant 0}(-1)^n/P_5^{n+1}(s)$$

$$\sum_{\{m_i\}} n!/(m_1!\,m_2!\,m_3!\,m_4!)P_4^{m_1}(s)P_3^{m_2}(s)P_2^{m_3}(s)P_1^{m_4}(s)\exp[-s(\alpha+1)]$$

we finally get the expressions for the SSRDF

$$12(\eta_l\eta_m)^{1/2}g_{lm}(r) = (r)^{-1}\sum_{n\geqslant 0}\sum_{l=1}^{5}\lim_{s\to s_l}\mathrm{d}^n/\mathrm{d}s^n \times\left[(s-s_l)^{n+1}(-1)^n/P_5^{n+1}(s)\sum_{\{m_i\}}\left(\prod_{j=1}^{4}P^{m_j}_{5-j}(s)\right)\Big/\left(\prod_{j=1}^{4}m_j!\right)\right.$$

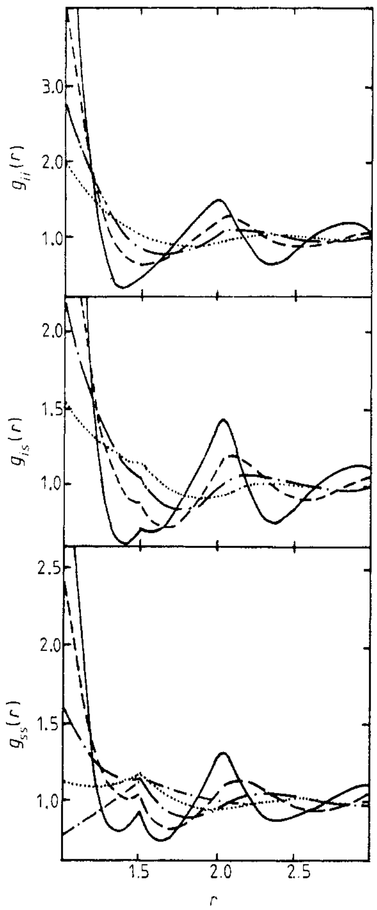

Figure 2. The site–site radial distribution functions of a mixture of hard spheres and dumb-bells ($L = \frac{1}{2}$) at $\eta_s = 0.2$ and $\eta_i = 0$ (–·–·–), $\eta_i = 0.1$ (····), $\eta_i = 0.2$ (——·——), $\eta_i = 0.3$ (– – –) and $\eta_i = 0.4$ (——). The contact values at $\eta_i = 0.4$ are $g_{ii}(1^+) = 6.2$, $g_{is}(1^+) = 5.0$ and $g_{ss}(1^+) = 3.9$; and at $\eta_i = 0.3$ is $g_{is}(1^+) = 3.2$.

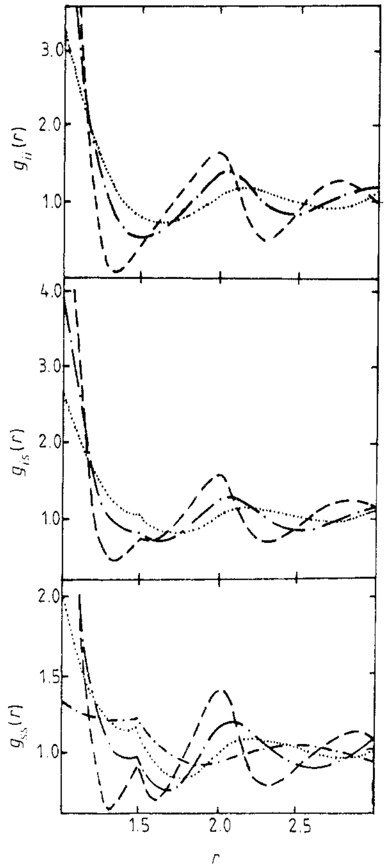

Figure 3. The site–site radial distribution functions of a mixture of hard spheres and dumb-bells ($L = \frac{1}{2}$) at $\eta_s = 0.4$. The legend for η_i is the same as that of figure 2. The contact values at $\eta_i = 0.3$ are $g_{ii}(1^+) = 8.0$, $g_{is}(1^+) = 6.4$ and $g_{ss}(1^+) = 5.1$; and at $\eta_i = 0.2$ are $g_{ii}(1^+) = 4.9$ and $g_{ss}(1^+) = 2.8$.

$$\times \sum_{j=1}^{4} K_{lm}^{(5-j)}(s)\theta[r-\alpha-(j+1)/2] \exp\{s[r-\alpha-(j+1)/2]\}\Bigg] \qquad (54)$$

where s_l are the roots of the equation $P_5(s) = 0$, $\alpha = \frac{1}{2}m_1 + m_2 + \frac{3}{2}m_3 + 2m_4$

$$\sum_{\{m_i\}} \rightarrow \sum_{m_1m_2m_3m_4>0} \quad \text{and} \quad \sum_{i=1}^{4} m_i = n.$$

6. Results

In figures 2–5 we present the SSRDF for a mixture of hard spheres with dumb-bells (figures 2 and 3) and for a mixture of hard spheres with tetrahedral tetra-atomics

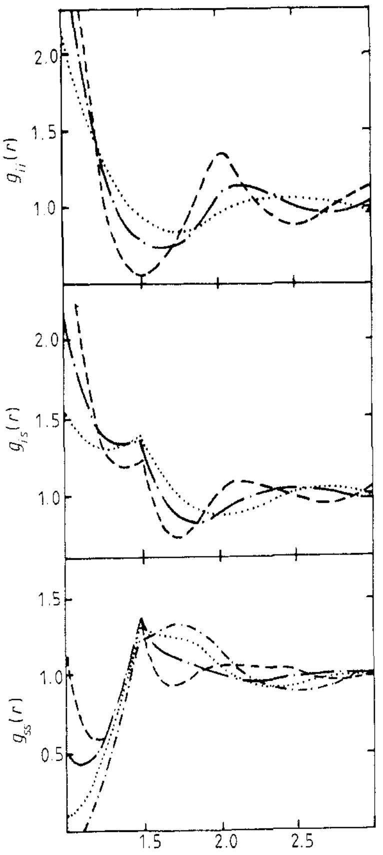

Figure 4. The site–site radial distribution functions of a mixture of hard spheres and tetra-atomics ($L = \frac{1}{2}$) at $\eta_s = 0.35$. The legend for η_i is the same as that of figure 2. The contact values at $\eta_i = 0.3$ are $g_{ii}(1^+) = 4.4$ and $g_{is}(1^-) = 3.2$; and at $\eta_i = 0.2$ is $g_{ii}(1^+) = 2.8$.

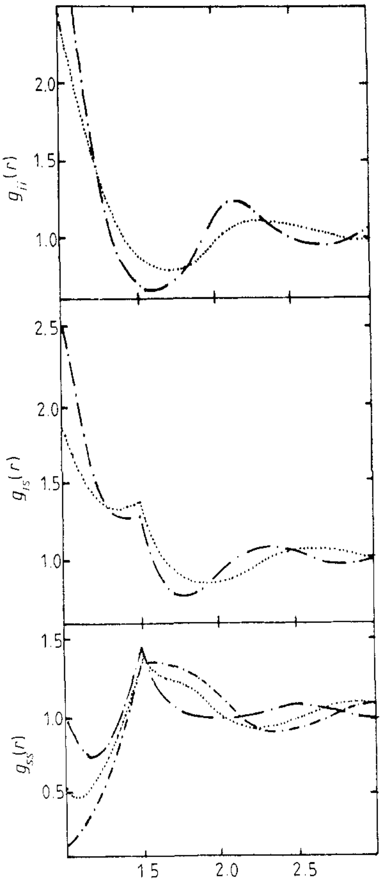

Figure 5. The site–site radial distribution functions of a mixture of hard spheres and tetra-atomics ($L = \frac{1}{2}$) at $\eta_s = 0.45$. The legend for η_i is the same as that of figure 2. The contact value of $g_{ii}(r)$ at $\eta_i = 0.2$ is 3.6.

(figures 4 and 5). The qualitative behaviour of the SSRDF $g_{ii}(r)$ and $g_{ss}(r)$ is the same as in the case of one-component hard-sphere or one-component molecular systems. The radial distribution function $g_{is}(r)$ has some characteristic features of $g_{ss}(r)$ as well as those of $g_{ii}(r)$. Particularly it has a cusp at $r = 1 + L$. The contact values of the SSRDF $g_{ss}(r)$ and $g_{is}(r)$ are lower than those of $g_{ii}(r)$. In the case presented in figure 4, the contact value of the function $g_{ss}(r)$ becomes less than zero. This fact illustrates that the ZPA for such values of densities is not good. As was shown in [14] for the triatomic and tetra-atomic molecules, the ZPA overestimates the structure of the system and gives the physically meaningless jump discontinuity of the SSRDF $g_{ss}(r)$ at $r = 2L$. The role of poles of the function $[1 + (n_s - 1)s(k)]$ increases with decrease in density and/or increase in the number of sites and/or increase in the molecular elongation L. Results of calculations of the above system SSRDF taking into account the poles will be published elsewhere. Finally, in figure 6 we present a comparison of the distribution

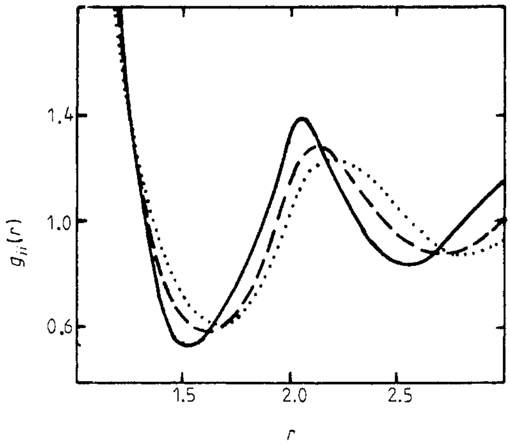

Figure 6. The radial distribution functions $g_{ii}(r)$ of a mixture of hard spheres and dumb-bells (——), hard spheres and triatomics (---) and hard spheres and tetra-atomics (···) at $\eta_s^0 = 0.5$ and $\eta_i = 0.05$. The intra-molecular distance L between sites is $\frac{1}{2}$. The contact values are $g_{ii}(1^+) = 4.7$ (——), $g_{ii}(1^+) = 3.9$ (----) and $g_{ii}(1^+) = 3.4$ (····).

functions $g_{ii}(r)$ for the systems with different shapes of the molecules at equal values of hard-sphere density ($\eta_i = 0.05$) and molecular packing parameter $\eta_s^0 = V_{n_s}\rho_s$ ($\eta_s^0 = 0.5$). Here V_{n_s} is the volume of the n_s-site molecule and $g_{ii}^{(n_s)}(r)$ is the sphere–sphere radial distribution function of a mixture of hard spheres and n_s-atomic molecules. Let us note that it is impossible to obtain coincidence of the curves for $g_{ii}^{(n_s)}(r)$ at arbitrary molecular density $\eta_s = 0$ for each system and equal values of hard-sphere densities. Such coincidence can be obtained only if $\eta_s^0 \to 0$. Thus the difference between these radial distribution functions shows the influence of molecular shape on the structure of the system. The following relations hold between the contact values and the values of the first maxima of the radial distribution functions $g_{ii}^{(n_s)}(r)$ for different n_s (figure 6)

$$g_{ii}^{(2)}(1^+) > g_{ii}^{(3)}(1^+) > g_{ii}^{(4)}(1^+)$$

$$g_{ii}^{(2)}(r_M) > g_{ii}^{(3)}(r_M) > g_{ii}^{(4)}(r_M)$$

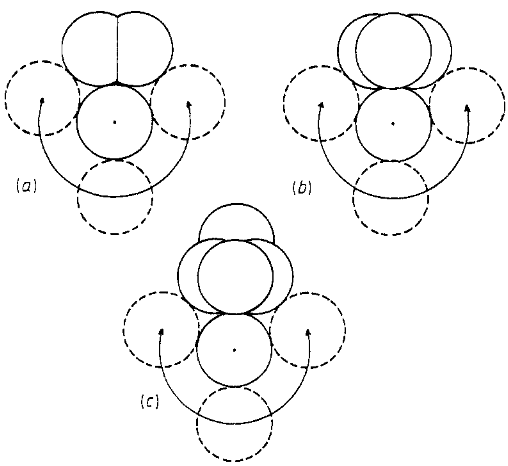

Figure 7. Possible positions of two spheres in contact: (*a*) for a mixture of hard spheres with dumb-bells, (*b*) for a mixture of hard spheres with triatomics and (*c*) for a mixture of hard spheres with tetra-atomics. The configurations in which three sites of the molecule are at the same time in contact with a sphere occur more often in (*c*) than in (*b*).

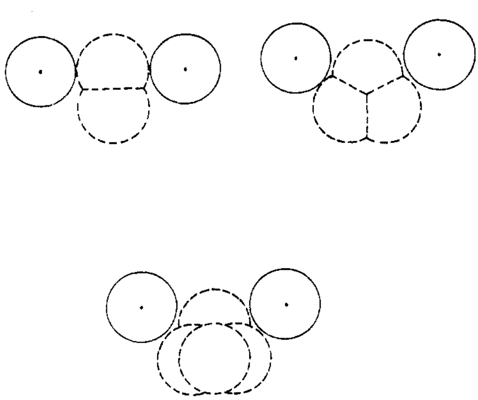

Figure 8. Configurations that give the main contribution to the first maximum of the functions $g_{ii}^{(2)}(r)$, $g_{ii}^{(3)}(r)$ and $g_{ii}^{(4)}(r)$ when $\eta_s^0 \gg \eta_i$. In this position the dumb-bells have the largest degree of freedom. The lowest degree of freedom is in the case of tetra-atomics.

where r_M is the position of the first maximum. These relations can be explained as follows. As is clear from figures 7 and 8 the largest average number of configurations which can be realised when the distance between two spheres is $r = 1$ (figure 7) or $r = r_M$ (figure 8) occurs for the mixture of hard spheres with dumb-bells and the lowest for the mixture of hard spheres with tetra-atomics.

Appendix

Expressions for the elements of the matrices $A^{(1)}$, $A^{(2)}$, $R^{(1)}$ and $R^{(2)}$, which are involved in equations (46) and (48):

$$A^{(1)}_{1,1} = 4\eta_i - 12\eta_s\{L(1-L)\tilde{n}_s^{-1}[4/(n_s-1)-1] + \tfrac{1}{6}(2L-1)(L^2-L+1)\} - 1$$

$$A^{(1)}_{2,1} = 6\eta_i - 6\eta_s(2L-1)$$

$$A^{(1)}_{3,1} = -12\eta_s\tilde{n}_s^{-1}\{\cos[\tilde{n}_s(1-L)] + \sin[\tilde{n}_s(1-L)] - 1\}$$

$$A^{(1)}_{4,1} = -12\eta_s\tilde{n}_s^{-1}\{\sin[\tilde{n}_s(1-L)] - \cos[\tilde{n}_s(1-L)] + 1\}$$

$$A^{(1)}_{5,1} = -12\eta_s(2L-1)$$

$$A^{(1)}_{1,2} = 12\eta_s\{L(1-L)^2/(n_s-1)[(2/(n_s-1)-\tfrac{1}{3})L - \tfrac{2}{3}] + \tfrac{1}{8}(2L-1)(2L^2-2L+1) + L/(n_s-1) \times [\tfrac{2}{3}(1-L^3) + L(2/(n_s-1)-1)(1-L^2)]\} - \tfrac{3}{2}\eta_i$$

$$A^{(1)}_{2,2} = 12\eta_s[L(1-L)\tilde{n}_s^{-1} + \tfrac{1}{8}(2L-1)(L^2-L+1)] - 2\eta_i - 1$$

$$A^{(1)}_{3,2} = -12\tilde{n}_s^{-2}\eta_s\{(1-\tilde{n}_s)\sin[\tilde{n}_s(1-L)] - [1+\tilde{n}_s(1-L)]\cos[\tilde{n}_s(1-L)] + 1\}$$

$$A^{(1)}_{4,2} = 12\tilde{n}_s^{-2}\eta_s\{[1+\tilde{n}_s(1-L)]\sin[\tilde{n}_s(1-L)] + (1-\tilde{n}_s)\cos[\tilde{n}_s(1-L)] + (n_s-1)/2 - 1\}$$

$$\mathrm{A}^{(1)}_{5,2} = 6\eta_s(2L-1)$$

$$A^{(1)}_{1,3} = L^2[4/(n_s-1)^2 - \tfrac{1}{2}] + L[1-2/(n_s-1)] - \tfrac{1}{2}$$

$$A^{(1)}_{2,3} = L - \tilde{n}_s^{-1} - 1 \qquad A^{(1)}_{3,3} = -\sin[\tilde{n}_s(1-L)]$$

$$A^{(1)}_{4,3} = \cos[\tilde{n}_s(1-L)] \qquad A^{(1)}_{5,3} = -1$$

$$A^{(1)}_{1,4} = \tilde{n}_s^{-1}(1+\tilde{n}_s^{-1}-L) \qquad A^{(1)}_{2,4} = \tilde{n}_s^{-1} \qquad A^{(1)}_{3,4} = \cos[\tilde{n}_s(1-L)]$$

$$A^{(1)}_{4,4} = \sin[\tilde{n}_s(1-L)] \qquad A^{(1)}_{5,4} = 0$$

$$A^{(1)}_{1,5} = \tilde{n}_s^{-2} - L^2/2 \qquad A^{(1)}_{2,5} = \tilde{n}_s^{-1} - L$$

$$A^{(1)}_{3,5} = 1 \qquad A^{(1)}_{4,5} = 0 \qquad A^{(1)}_{5,5} = -1$$

$$R^{(1)}_1 = -1 \qquad R^{(1)}_i = 0 \quad (i=2,3,4) \qquad R^{(1)}_5 = -\delta_{ls}\tilde{n}_s/12\eta_s$$

$$A^{(2)}_{1,1} = 4\eta_i - 12\eta_s\{L^3[24/(n_s-1)^2 - 6/(n_s-1) - \tfrac{8}{3}] + L^2[-8/(n_s-1)^2 + 2/(n_s-1) + 2] - L + \tfrac{1}{3} - 4L^2(n_s-2)$$

$$\times (1-2L)/(n_s-1)^2\} - 1$$

$$A^{(2)}_{2,1} = 6\eta_i - 12\eta_s[1 - 2L + (2-n_s)(1-2L)\tilde{n}_s^{-1}]$$

$$A^{(2)}_{3,1} = -24\eta_s(1-2L) \qquad A^{(2)}_{4,1} = 12\eta_s S_1 \tilde{n}_s^{-1}$$

$$A^{(2)}_{5,1} = -12\eta_s(1-C_1)\tilde{n}_s^{-1} \qquad A^{(2)}_{6,1} = -12\eta_s(S_2 - C_2 + 1)\tilde{n}_s^{-1}$$

$$A^{(2)}_{7,1} = -12\eta_s(1-S_2-C_2)\tilde{n}_s^{-1}$$

$$A^{(2)}_{1,2} = 12\eta_s\{L^3[12/(n_s-1)^2 - 4] + L^2[3 - 4/(n_s-1)^2] - L + \tfrac{1}{4} + \tfrac{1}{2}(n_s-2)(1-2L)n_s^{-1}[\tfrac{1}{3}(1-2L)^2 - L/(n_s-1)]\} - \tfrac{3}{2}\eta_i$$

$$A^{(2)}_{2,2} = 12\eta_s\{L^3[6/(n_s-1) - \tfrac{16}{3}] + L^2[4 - 2/(n_s-1)] - 2L + \tfrac{2}{3} + L(2-n_s)(1-4L^2)/(n_s-1)\} - 2\eta_i - 1$$

$$A^{(2)}_{3,2} = 12\eta_s(1-2L)$$

$$A^{(2)}_{4,2} = 12\eta_s[\sqrt{8}(n_s-2)L^2(C_1-1)/(n_s-1)^2 - 2(1-L)LS_1/(n_s-1)]$$

$$A^{(2)}_{5,2} = 12\eta_s[\sqrt{8}(2-n_s)S_1/(n_s-1)^2 + 2L^2/(n_s-1) - 2L(1-L)C_1/(n_s-1)]$$

$$A^{(2)}_{6,2} = 24\eta_s[(n_s+1)S_2L^2/(n_s-1)^2 + (2-n_s)2L^2C_2/(n_s-1)^2 + L(1-L)/(n_s-1) - 2L^2/(n_s-1)^2]$$

$$A^{(2)}_{7,2} = 24\eta_s[-L^2(n_s+1)C_2/(n_s-1)^2 + 2(2-n_s)L^2S_2/(n_s-1)^2 + (1-2L)L/(n_s-1) + 2L^2/(n_s-1)^2]$$

$$A^{(2)}_{1,3} = L^2[2 - 4/(n_s-1)^2 - 2/(n_s-1)] - (n_s-2)L(1+2L)/(n_s-1) + \tfrac{1}{2}$$

$$A^{(2)}_{2,3} = 1 + 2L(2-n_s)/(n_s-1) \qquad A^{(2)}_{3,3} = 1 \qquad A^{(2)}_{4,3} = S_1$$

$$A^{(2)}_{5,3} = C_1 \qquad A^{(2)}_{6,3} = -1 \qquad A^{(2)}_{7,3} = 0$$

$$A^{(2)}_{1,4} = 2L^2(n_s-2)/(n_s-1)^2 - \tilde{n}_s^{-1} \qquad A^{(2)}_{2,4} = -\tilde{n}_s^{-1} \qquad A^{(2)}_{3,4} = 0$$

$$A^{(2)}_{4,4} = -\sqrt{2}C_1 \qquad A^{(2)}_{5,4} = \sqrt{2}S_1 \qquad A^{(2)}_{6,4} = 0 \qquad A^{(2)}_{7,4} = 1$$

$$A^{(2)}_{1,5} = \tilde{n}_s^{-2} \qquad A^{(2)}_{2,5} = 0 \qquad A^{(2)}_{3,5} = -1 \qquad A^{(2)}_{4,5} = 0$$

$$A^{(2)}_{5,5} = 1 \qquad A^{(2)}_{6,5} = S_2 \qquad A^{(2)}_{7,5} = -C_2$$

$$A^{(2)}_{1,6} = \tfrac{1}{2} - (n_s-2)L/(n_s-1) \qquad A^{(2)}_{2,6} = 1 + 2L(2-n_s)/(n_s-1)$$

$$A^{(2)}_{3,6} = 1 \qquad A^{(2)}_{4,6} = -S_1 \qquad A^{(2)}_{5,6} = -C_1 \qquad A^{(2)}_{6,6} = 0 \qquad A^{(2)}_{7,6} = 0$$

$$A^{(2)}_{1,7} = 2L^2(2-n_s)/(n_s-1)^2 \qquad A^{(2)}_{2,7} = -\tilde{n}_s^{-1} \qquad A^{(2)}_{3,7} = 0$$

$$A^{(2)}_{4,7} = \sqrt{2} \qquad A^{(2)}_{5,7} = 0 \qquad A^{(2)}_{6,7} = C_2 \qquad A^{(2)}_{7,7} = S_2$$

$$S_1 = \sin[\sqrt{2}\tilde{n}_s(1-2L)] \qquad C_1 = \cos[\sqrt{2}\tilde{n}_s(1-2L)]$$

$$S_2 = \sin[\tilde{n}_s(3L-1)] \qquad C_2 = \cos[\tilde{n}_s(3L-1)]$$

$$R^{(2)}_1 = -1 \qquad R^{(2)}_i = 0 \quad (i = 2,3,4,5,6) \qquad R^{(2)}_7 = \delta_{ls}\tilde{n}_s/12\eta_s.$$

Expressions for the functions $P_j(s)$ and $K_{lm}^{(j)}(s)$ $(j = 1, 2, \ldots)$ which appear in the expressions for SSRDF (53) and (54):

$$P_j(s) = P_{j,j}s^j + P_{j,j-1}s^{j-1} + \ldots + P_{j,0}$$

$$P_j(s) = 0 \qquad \text{when } j > 5$$

$$K_{ii}^{(j)}(s) = s\exp(s/2)\{K_{ii}^{(j,j)}s^j + K_{ii}^{(j,j-1)}s^{j-1} + \ldots + K_{ii}^{(j,0)}\}$$

$$K_{ii}^{(j)}(s) = 0 \qquad \text{when } j > 3$$

$$K_{is}^{(1)}(s) = [(n_s - 1)^2 + s^2]s\exp(3s/2)\{K_{is}^{(1,1)}s + K_{is}^{(1,0)}\}$$

$$K_{is}^{(j)}(s) = 0 \qquad \text{when } j > 1$$

$$K_{ss}^{(j)}(s) = K_{ss}^{(j,j)}s^j + K_{ss}^{(j,j-1)}s^{j-1} + \ldots + K_{ss}^{(j,0)}$$

$$K_{ss}^{(j)}(s) = 0 \qquad \text{when } j > 4$$

$$P_{5,5} = 1 \qquad P_{5,4} = \sum_{n=0}^{1} (M_{ii}^{(3-n)} M_{ss}^{(3+n)})$$

$$P_{5,3} = \sum_{n=0}^{2} (M_{ii}^{(3-n)} M_{ss}^{(2+n)}) - M_{si}^{(2)} M_{is}^{(3)}$$

$$P_{5,2} = \sum_{n=0}^{3} (M_{ii}^{(3-n)} M_{ss}^{(1-n)}) - \sum_{n=0}^{1} (M_{si}^{(2-n)} M_{is}^{(2+n)})$$

$$P_{5,1} = \sum_{n=0}^{3} (M_{ii}^{(3-n)} M_{ss}^{(n)}) - \sum_{n=0}^{2} (M_{si}^{(2-n)} M_{is}^{(1+n)})$$

$$P_{5,0} = \sum_{n=0}^{2} (M_{ii}^{(2-n)} M_{ss}^{(n)} - M_{si}^{(2-n)} M_{is}^{(n)})$$

$$P_{4,4} = 1 \qquad P_{4,3} = \sum_{n=0}^{1} (M_{ii}^{(3-n)} S_{ss}^{(2+n)})$$

$$P_{4,2} = \sum_{n=0}^{2} (M_{ii}^{(3-n)} S_{ss}^{(1+n)}) - M_{si}^{(2)} S_{is}^{(2)} \qquad P_{4,1} = \sum_{n=0}^{3} (M_{ii}^{(3-n)} S_{ss}^{(n)}) - \sum_{n=0}^{1} (M_{si}^{(2-n)} S_{is}^{(1+n)})$$

$$P_{4,0} = \sum_{n=0}^{2} (M_{ii}^{(2-n)} S_{ss}^{(n)} - M_{si}^{(2-n)} S_{is}^{(n)})$$

$$P_{3,3} = M_{ss}^{(4)} L_{ii}^{(1)} + M_{ii}^{(3)} L_{ss}^{(2)}$$

$$P_{3,2} = \sum_{n=0}^{1} (L_{ii}^{(1-n)} M_{ss}^{(3+n)} + M_{ii}^{(3-n)} L_{ss}^{(1+n)} - M_{is}^{(3-n)} L_{is}^{(1+n)})$$

$$P_{3,1} = \sum_{n=0}^{1} (L_{ii}^{(1-n)} M_{ss}^{(2+n)} - L_{si}^{(1-n)} M_{is}^{(2+n)} - M_{si}^{(2-n)} L_{is}^{(1+n)}) + \sum_{n=0}^{2} (M_{ii}^{(3-n)} L_{ss}^{(n)})$$

$$P_{3,0} = \sum_{n=0}^{1} (L_{ii}^{(1-n)} M_{ss}^{(1+n)} - L_{si}^{(1-n)} M_{is}^{(1+n)}) + \sum_{n=0}^{2} (M_{ii}^{(2-n)} L_{ss}^{(n)} - M_{si}^{(2-n)} L_{is}^{(n)})$$

$$P_{2,2} = L_{ii}^{(1)} S_{ss}^{(3)} \qquad P_{2,1} = \sum_{n=0}^{1} (L_{ii}^{(1-n)} S_{ss}^{(2+n)}) - L_{si}^{(1)} S_{is}^{(2)}$$

$$P_{2,0} = \sum_{n=0}^{2} (L_{ii}^{(1-n)} S_{ss}^{(1+n)} - L_{si}^{(1-n)} S_{is}^{(1+n)})$$

$$P_{1,1} = L_{ii}^{(1)} L_{ss}^{(2)} - L_{si}^{(1)} L_{is}^{(2)} \qquad P_{1,0} = \sum_{n=0}^{1} (L_{ii}^{(1-n)} L_{ss}^{(1+n)} - L_{si}^{(1-n)} L_{ss}^{(1+n)})$$

$$K_{ii}^{(3,3)} = D_{ii}^{(1)} M_{ss}^{(4)} \qquad K_{ii}^{(3,2)} = \sum_{n=0}^{1} (D_{ii}^{(1-n)} M_{ss}^{(3+n)}) - D_{si}^{(1)} M_{is}^{(3)}$$

$$K_{ii}^{(3,1)} = \sum_{n=0}^{1} (D_{ii}^{(1-n)} M_{ss}^{(2+n)} - D_{si}^{(1-n)} M_{is}^{(2+n)})$$

$$K_{ii}^{(3,0)} = \sum_{n=0}^{1} (D_{ii}^{(1-n)} M_{ss}^{(1+n)} - D_{si}^{(1-n)} M_{is}^{(1+n)})$$

$$K_{ii}^{(2,2)} = D_{ii}^{(1)} S_{ss}^{(3)} \qquad K_{ii}^{(2,1)} = \sum_{n=0}^{1} (D_{ii}^{(1-n)} S_{ss}^{(2+n)}) - D_{si}^{(1)} S_{is}^{(2)}$$

$$K_{ii}^{(2,0)} = \sum_{n=0}^{1} (D_{ii}^{(1-n)} S_{ss}^{(1+n)} - D_{si}^{(1-n)} S_{is}^{(1+n)})$$

$$K_{ii}^{(1,1)} = D_{ii}^{(1)} L_{ss}^{(2)} - D_{si}^{(1)} L_{is}^{(2)} \qquad K_{ii}^{(1,0)} = \sum_{n=0}^{1} (D_{ii}^{(1-n)} L_{ss}^{(1+n)} - D_{si}^{(1-n)} L_{is}^{(1+n)})$$

$$K_{is}^{(1,1)} = M_{ii}^{(3)} D_{si}^{(1)} \qquad K_{is}^{(1,0)} = \sum_{n=0}^{1} (M_{ii}^{(3-n)} D_{si}^{(n)}) - M_{si}^{(2)} D_{ii}^{(1)}$$

$$K_{ss}^{(4,4)} = M_{ii}^{(3)} D_{ss}^{(3)} \qquad K_{ss}^{(4,3)} = \sum_{n=0}^{1} (M_{ii}^{(3-n)} D_{ss}^{(2+n)}) - M_{si}^{(2)} D_{is}^{(3)}$$

$$K_{ss}^{(4,2)} = \sum_{n=0}^{2} (M_{ii}^{(3-n)} D_{ss}^{(1+n)}) - \sum_{n=0}^{1} (M_{si}^{(2-n)} D_{is}^{(2+n)})$$

$$K_{ss}^{(4,1)} = \sum_{n=0}^{3} (M_{ii}^{(3-n)} D_{ss}^{(n)}) - \sum_{n=0}^{2} (M_{si}^{(2-n)} D_{is}^{(1+n)})$$

$$K_{ss}^{(4,0)} = \sum_{n=0}^{2} (M_{ii}^{(2+n)} D_{ss}^{(n)} - M_{si}^{(2+n)} D_{is}^{(n)})$$

$$K_{ss}^{(3,3)} = M_{ii}^{(3)} T_{ss}^{(2)} \qquad K_{ss}^{(3,2)} = \sum_{n=0}^{1} (M_{ii}^{(3-n)} T_{ss}^{(1+n)}) - M_{si}^{(2)} T_{is}^{(2)}$$

$$K_{ss}^{(3,1)} = \sum_{n=0}^{2} (M_{ii}^{(3-n)} T_{ss}^{(n)}) - \sum_{n=0}^{1} (M_{si}^{(2-n)} T_{is}^{(1-n)})$$

$$K_{ss}^{(3,0)} = \sum_{n=0}^{2} (M_{ii}^{(2-n)} T_{ss}^{(n)} - M_{si}^{(2-n)} T_{is}^{(n)})$$

$$K_{ss}^{(2,2)} = L_{ii}^{(1)} D_{ss}^{(3)} - L_{si}^{(1)} D_{is}^{(3)} \qquad K_{ss}^{(2,1)} = \sum_{n=0}^{1} (L_{ii}^{(1-n)} D_{ss}^{(2+n)} - L_{si}^{(1-n)} D_{is}^{(2+n)})$$

$$K_{ss}^{(2,0)} = \sum_{n=0}^{1} (L_{ii}^{(1-n)} D_{ss}^{(1+n)} - L_{si}^{(1-n)} D_{is}^{(1+n)})$$

$$K_{ss}^{(1,1)} = L_{ii}^{(1)} T_{ss}^{(2)} - L_{si}^{(1)} T_{is}^{(2)} \qquad K_{ss}^{(1,0)} = \sum_{n=0}^{1} (L_{ii}^{(1-n)} T_{ss}^{(1+n)} - L_{si}^{(1-n)} T_{is}^{(1+n)})$$

$$M_{ls}^{(4)} = -1 \qquad M_{ls}^{(3)} = [(n_s-1)^{-1} - \tfrac{1}{2}]a_{ls}/(n_s-1) + f_{ls} - b_{ls}/(n_s-1)$$
$$M_{ls}^{(2)} = -[(n_s-1)t_{ls} + a_{ls}/(n_s-1) + \delta_{ls}(n_s-1)^2]$$
$$M_{ls}^{(1)} = \{[(n_s-1)^{-1} - \tfrac{1}{2}]a_{ls} - b_{ls}\}(n_s-1) \qquad M_{ls}^{(0)} = -a_{ls}(n_s-1)$$

$$L_{ls}^{(2)} = (n_s-1)\{t_{ls}\sin[\tfrac{1}{2}(n_s-1)] - f_{ls}\cos[\tfrac{1}{2}(n_s-1)]\} - a_{ls}/(n_s-1)$$
$$L_{ls}^{(1)} = -(n_s-1)\{a_{ls}[(n_s-1)^{-1} + \tfrac{1}{2}] + b_{ls}\} \qquad L_{ls}^{(0)} = -(n_s-1)a_{ls}$$

$$S_{ls}^{(3)} = -\delta_{ls}(n_s-1)$$
$$S_{ls}^{(2)} = (n_s-1)\{f_{ls}\sin[(n_s-1)/2] + t_{ls}\cos[(n_s-1)/2] + f_{ls}\} + 2a_{ls}/(n_s-1)$$
$$S_{ls}^{(1)} = (n_s-1)(a_{ls} + 2b_{ls}) \qquad S_{ls}^{(0)} = 2(n_s-1)a_{ls}$$

$$T_{ls}^{(2)} = (n_s-1)^2\{f_{ls}\cos[(n_s-1)/2] - t_{ls}\sin[(n_s-1)/2]\} + a_{ls}$$
$$T_{ls}^{(1)} = (n_s-1)^2[1/(n_s-1) + \tfrac{1}{2}]a_{ls} + b_{ls} \qquad T_{ls}^{(0)} = a_{ls}(n_s-1)^2$$

$$D_{ls}^{(3)} = -\{a_{ls}[1 + 1/(n_s-1)] + 2b_{ls} + (n_s-1)t_{ls}\} \qquad D_{ls}^{(2)} = -[2a_{ls} + (n_s-1)^2 f_{ls}]$$
$$D_{ls}^{(1)} = -(n_s-1)^2\{a_{ls}[1 + 1/(n_s-1)] + 2b_{ls}\} \qquad D_{ls}^{(0)} = -2a_{ls}(n_s-1)^2$$

$$M_{li}^{(3)} = -1 \qquad M_{li}^{(2)} = -[\tfrac{1}{2}a_{li} + b_{li}] \qquad M_{li}^{(1)} = b_{li} \qquad M_{li}^{(0)} = a_{li}$$

$$L_{li}^{(1)} = -a_{li} - b_{li} \qquad L_{li}^{(0)} = -a_{li} \qquad D_{li}^{(1)} = -a_{li} - b_{li} \qquad D_{li}^{(0)} = -a_{li}$$

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