

# The mean spherical model for a Lorentz-Berthelot mixture of sticky hard spheres

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We have analyzed the Percus-Yevick (PY) and the mean spherical model (MSM) equation for an  $N$ -component system of sticky hard spheres. The PY approximation leads to a set of  $N(N+1)/2$  coupled quadratic equations for the unknown coefficients. While for this closure, the pair distribution functions have to be calculated *numerically*, we can proceed in the MSM one step further if we assume a Lorentz-Berthelot-type rule for the interactions: then the structure functions can be calculated *analytically*. We show that under these conditions in the limit  $N \rightarrow \infty$  (stochastic limit) the analyticity of the solution is preserved. General expressions both for the discrete and continuous (polydisperse) case are presented. © 1998 American Institute of Physics. [S0021-9606(98)51122-1]

## I. INTRODUCTION

In contrast to simple liquids,<sup>1</sup> colloidal systems<sup>2</sup> are—due to their production process—polydisperse<sup>3</sup> in size, i.e., every particle may be characterized by its diameter. As a consequence these particles will also be polydisperse with respect to their interactions. Such a system can be described essentially in two ways: (i) it can be considered either as an  $N$ -component system, where each component is characterized by its size (e.g., diameter) and its interaction (e.g., stickiness) parameter (to which we refer to as the discrete model). Such a description was probably first introduced by Vrij<sup>4</sup> and Blum and Stell<sup>3</sup> in the late 1970s, when investigating an  $N$ -component system of hard spheres (HS) with different size within the Percus-Yevick (PY) approximation. In their work, Blum and Stell<sup>3</sup> could show that—extending the basic solution<sup>5</sup>—the PY equations can be solved leading to *explicit* analytical expressions of the structure functions and—in a further step—to the scattering intensity of such a system; in this approach the crucial point is the special structure of an  $N$ -dimensional matrix  $\mathcal{M}$  which has to be inverted: only if  $\mathcal{M}$  can be cast into a special form one can write down a closed (and therefore exact) form of  $\mathcal{M}^{-1}$ . This inverse then helps to obtain explicit expressions for the structure function from the factorized Ornstein-Zernike (OZ) equations and finally the full structural information. (ii) As an alternative, however, it might be more convenient to consider the case  $N \rightarrow \infty$  where each particle is uniquely characterized by a value of some random variable  $X$ . In our case—and this was also done by Blum and Stell<sup>3</sup>—the most natural choice is  $X=R$ , i.e., we introduce the particle size as an independent parameter replacing thus the component index  $i$ .  $R$  is assumed to be distributed according to a probability distribution function  $f_R(R)$ . Blum and Stell<sup>3</sup> introduced for this transition the term “polydisperse.” In later work, Salacuse<sup>6</sup> has cast this formalism into a more rigid framework, introducing the concept of random (stochastic) sys-

tems. He also showed that expressions for both structural and thermodynamic quantities can be generalized from the discrete to the polydisperse case.<sup>6</sup>

In this contribution we show that it is in fact possible to extend the work of Blum and Stell from a system of HS to a system of sticky HS (SHS). Such a system—introduced by Baxter<sup>7</sup>—may be considered (*mathematically*) as the most simple extension of HS by adding a short-ranged strongly attractive interaction (representing the “stickiness”) to the hard core; *physically* it represents an appropriate model<sup>8</sup> to describe colloidal systems: their interaction has turned out to be very similar to those of SHS, i.e., strongly repulsive at short distances and attractive at the surface in a rather small range.<sup>2,8</sup> There is evidence that HS, SHS and charged hard spheres are the only systems where the polydisperse limit can be done explicitly.

In this paper we consider an  $N$ -component system of pure SHS. We first study the OZ equations for finite  $N$  both within the PY approximation and the mean spherical model (MSM). A Lorentz-rule (viz., additivity of the hard-core diameters  $R_{ij}$ ) is imposed per construction right from the beginning, while no restriction is made *a priori* for the stickiness parameters  $\gamma_{ij}$ . In the PY approximation we arrive at a set of  $N(N+1)/2$  coupled quadratic equations for the unknown coefficients of the structure functions. However, in this case the above mentioned matrix  $\mathcal{M}$  cannot be cast *a priori* into a special form which is required to allow an *analytic* inversion. Recently Herrera and Blum<sup>8</sup> considered—in a similar effort to go beyond simple HS—polydisperse charged particles with sticky interactions based on a PY/MSM approximation. They achieve factorization of  $\mathcal{M}$  *a posteriori* by assuming parameters of the species (which they call “stickiness probabilities”) to be independent.<sup>8</sup> In the MSM case (considering the SHS interaction as a limiting case of a HSY system<sup>9</sup>), however, such a transform for  $\mathcal{M}$  is possible *a priori* if we impose on the coupling (stickiness) parameters a Berthelot-type rule,<sup>1</sup> i.e.,  $\gamma_{ij}^2 = \gamma_{ii}\gamma_{jj}$ , i.e., an assumption which is physically sound and mathematically

convenient. Now, the matrix  $\mathcal{M}$  can be inverted exactly for arbitrary  $N$ , which allows us finally to proceed to the stochastic case where the Berthelot rule now reads  $\mathbf{G}^2([\mathbf{R} + \mathbf{R}']/2) = \mathbf{G}(\mathbf{R})\mathbf{G}(\mathbf{R}')$ ; this imposes some restrictions: if the size of the particles (i.e., the diameters) is distributed according to a probability distribution  $f_R(R)$ , then the Berthelot rule induces a probability distribution  $f_G(\gamma)$  for the stickiness; this means that their distribution can no longer be chosen independently. In contrast to the discrete case where the stickiness is characterized by the set of  $\{\gamma_{ij}\}$ , the distribution is now fixed by only two parameters (representing the strength and the variance of the stickiness). As an example we present results for the  $\Gamma$ -distribution (or frequently called Schulz distribution in this context<sup>10</sup>), i.e., a standard probability distribution used in this field. We furthermore present closed expressions for the structure functions for both the discrete and for the continuous (polydisperse) case.

The paper is organized as follows: in the subsequent section we present the model and the factorization of the OZ equations. In the subsequent section the PY equation and the MSM are introduced and results are presented for a finite number of components. We then discuss under which conditions the matrix  $\mathcal{M}$  can be inverted and how this can be achieved using the Lorentz-Berthelot rule. In Section IV we present the results after applying the stochastic limit; basic implications of the Lorentz-Berthelot rule on the relation between size and stickiness of the particles are deduced. The paper is closed with concluding remarks. Appendix A contains all formulas required for the discrete case (finite  $N$ ), while Appendix B presents all the expressions required for an implementation of a computer code for the continuous (polydisperse) case. Specialisation is done for the case where the diameters are distributed according to a  $\Gamma$ -distribution.

## II. THE MODEL

### A. Definition

We assume an  $N$ -component system of SHS, characterized by the number-density  $\rho$ , the concentrations  $c_i$  of species  $i$  ( $i = 1, \dots, N$ ) with partial number-densities  $\rho_i = c_i\rho$ . The set of interactions is defined by<sup>7,11</sup>

$$\beta\Phi_{ij}(x) = \begin{cases} \infty, & r < R_{ij}^-, \\ -\log\left[\gamma_{ij}\frac{R_{ij}}{(R_{ij}-R_{ij}^-)}\right], & R_{ij}^- \leq r \leq R_{ij}, \\ 0, & R_{ij} < r, \end{cases} \quad (1)$$

and taking the limit  $(R_{ij}-R_{ij}^-) \rightarrow 0$ ; the  $R_i = R_{ii}$  are the hard core diameter. We furthermore define  $R_{ij} = \frac{1}{2}(R_i + R_j)$  and  $S_{ij} = \frac{1}{2}(R_i - R_j)$ . For the Boltzmann-factor  $e_{ij}(r) = \exp[-\beta\Phi_{ij}(r)]$  we obtain<sup>7,11</sup>

$$e_{ij}(r) = \Theta(r - R_{ij}) + \gamma_{ij}R_{ij}\delta(r - R_{ij}^-). \quad (2)$$

$\Theta(x)$  is the usual Heaviside step-function, i.e.,  $\Theta(x) = 0$  for  $x < 0$  and  $\Theta(x) = 1$  for  $x > 0$ . The Mayer function  $f_{ij}(r)$  is then given by  $f_{ij}(r) = e_{ij}(r) - 1$ . The  $\gamma_{ij}$  are dimensionless positive parameters and represent thus a measure of the attraction (stickiness) between particles  $i$  and  $j$ : in the limit  $\gamma_{ij} = 0$  we recover the case of a mixture of simple HS,<sup>5</sup> while  $\gamma_{ij} \rightarrow \infty$  represents the case of an infinitely strong adhesion between the spheres.

The definition of the  $R_{ij}$  makes the spheres additive (Lorentz-rule), while no restriction has been made up to now for the  $\gamma_{ij}$ .

### B. Wiener-Hopf factorization

If we want to calculate the structure of the system [in terms of the partial pair distribution functions (PDFs)  $g_{ij}(r)$ ] we have to solve the OZ equations, generalized to the  $N$ -component case

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^N \rho_k \int d\mathbf{r}' c_{ik}(r') h_{kj}(|\mathbf{r} - \mathbf{r}'|) \quad (3)$$

along with a closure relation. In above equations the  $h_{ij}(r) = [g_{ij}(r) - 1]$  and the  $c_{ij}(r)$  are the total and direct correlation functions.

As done in Ref. 3 we use the Wiener-Hopf (Wertheim-Baxter) factorization<sup>5,12</sup> for the solution of the OZ equations which transform—under the assumption that  $c_{ij}(r) = 0$  for  $r > R_{ij}$ —into two sets of coupled matrix integral equations for the factor functions  $Q_{ij}(r)$ :<sup>5</sup>

$$rc_{ij}(r) = -Q'_{ij}(r) + 2\pi \sum_{k=1}^N \rho_k \int_{S_{ki}}^{\min[R_{ki}, R_{kj} - r]} dt \times Q_{ki}(t) Q'_{kj}(t+r), \quad S_{ij} < r < R_{ij}, \quad (4)$$

$$rh_{ij}(r) = -Q'_{ij}(r) + 2\pi \sum_{k=1}^N \rho_k \int_{S_{ik}}^{R_{ik}} dt Q_{ik}(t) h_{kj}(|r-t|) \times (r-t), \quad S_{ij} < r. \quad (5)$$

Drawing on parallels from the one component case<sup>7</sup> for SHS and from a study of an  $N$ -component system of HS<sup>5</sup> we start from the exact expression for the  $h_{ij}(r)$ :

$$h_{ij}(r) = -1 + \lambda_{ij}R_{ij}\delta(r - R_{ij}^-), \quad 0 \leq r \leq R_{ij}. \quad (6)$$

As a consequence the  $Q_{ij}(r)$  are found to be polynomials of second order for  $S_{ij} \leq r \leq R_{ij}$  and 0 elsewhere, introducing three unknown coefficients. Inserting the expressions for the  $h_{ij}(r)$  and the  $Q_{ij}(r)$  into Eq. (5) and taking special care at contact ( $R_{ij}$ ) we obtain for the factor functions<sup>5,11</sup>

$$Q_{ij}(r) = \begin{cases} \frac{a_i}{2}(r - R_{ij})^2 + (b_i + a_i R_{ij})(r - R_{ij}) + \lambda_{ij}R_{ij}^2, & S_{ij} < r < R_{ij}, \\ 0, & \text{elsewhere} \end{cases} \quad (7)$$

The coefficients are given in terms of

$$a_i = \frac{1 - \xi_3 + 3R_i\xi_2}{(1 - \xi_3)^2} - \frac{12\zeta_i}{1 - \xi_3}, \quad (8)$$

$$b_i = -\frac{3}{2}R_i^2\xi_2 \frac{1}{(1 - \xi_3)^2} + \frac{6\zeta_i R_i}{(1 - \xi_3)}, \quad (9)$$

where we have used the abbreviations

$$\xi_u = \frac{\pi}{6} \sum_{i=1}^N \rho_i R_i^u, \quad \zeta_i = \frac{\pi}{6} \sum_{j=1}^N \rho_j \lambda_{ij} R_{ij}^2 R_j. \quad (10)$$

We easily recover the case of hard spheres<sup>5</sup> by putting  $\lambda_{ij} = 0$  (and hence  $\zeta_i = 0$ ) in Eqs. (8) and (9).

The next step is concerned with the determination of the structure of the system in terms of the partial correlation functions. To this end we define  $\tilde{H}_{ij}(s)$  and  $\tilde{Q}_{ij}(s)$  via

$$\tilde{H}_{ij}(s) = \mathcal{L}[r h_{ij}(r)](s) = \int_0^\infty dr e^{-sr} r h_{ij}(r), \quad (11)$$

$$\tilde{Q}_{ij}(s) = \int_{s_{ij}}^{R_{ij}} dr e^{-sr} Q_{ij}(r). \quad (12)$$

The  $\tilde{Q}_{ij}(s)$  are found to be given by

$$\begin{aligned} \tilde{Q}_{ij}(s) = & e^{-s s_{ij}} [a_i \varphi_2(s; R_j) + (a_i R_{ij} + b_i) \varphi_1(s; R_j) \\ & + \lambda_{ij} R_{ij}^2 \varphi_0(s; R_j)] \end{aligned} \quad (13)$$

introducing the modified incomplete gamma functions  $\varphi_\alpha(s; x)$  ( $\alpha = 0, 1, 2$ ) that are listed in Appendix A.

A Laplace-transform of Eq. (5) yields after some lengthy algebra the following (matrix)-equation:

$$\begin{aligned} \sum_{l=1}^N [\delta_{il} - 2\pi\rho_l \tilde{Q}_{il}(s)] \left[ \tilde{H}_{lj}(s) + \frac{1}{s^2} \right] \\ = \frac{e^{-s R_{ij}}}{s^2} [a_i + (a_i R_{ij} + b_i)s + \lambda_{ij} R_{ij}^2 s^2]. \end{aligned} \quad (14)$$

In deriving the above equation, special care has to be taken for the terms containing the  $\delta$ -function introduced via the ansatz (6).

Furthermore, it must be pointed out that Pastore<sup>13</sup> has discussed (in a different context) the complete equivalence of the original problem [solution of Eq. (3)] and the above equation (14): this is only ensured if the function  $\Delta(s) = \det[\delta_{ij} - 2\pi\sqrt{\rho_i\rho_j} \tilde{Q}_{ij}(s)]$  has no zeros in the right half plane of the complex  $s$ -plane; it is possible to give a very simple local test to detect the presence of zeros in the right half plane: as already remarked by Baxter<sup>5</sup>  $\Delta(0) < 0$  is a sufficient condition to find at least one zero there.

The parameters  $\lambda_{ij}$  introduced in the ansatz (6) and the coefficients of the  $Q_{ij}(r)$  remain yet undetermined.

The ultimate goal of this paper is to calculate the PDFs: this is only possible if we are able to invert Eqs. (14) so that we can obtain *explicit* expressions for the  $\tilde{H}_{ij}(s)$  and from these the PDFs  $g_{ij}(r)$ . To this end we have inverted the matrix

$$(\mathcal{M})_{ij} = M_{ij} = [\delta_{ij} - 2\pi\rho_j \tilde{Q}_{ij}(s)]. \quad (15)$$

Possibilities to achieve this (under certain assumptions) will be discussed in the subsequent section.

### III. EXPLICIT SOLUTION

In fact, the OZ equations (4) and (5) can be solved for an  $N$ -component system of SHS *analytically* both within the PY approximation and an approximation based on the MSM. The solution of the OZ equation, along with one of these two approximations fixes the yet undetermined parameters  $\lambda_{ij}$ .

#### A. Percus-Yevick equation

The PY closure relation

$$c_{ij}(r) = [1 + h_{ij}(r)][1 - \exp\{\beta\Phi_{ij}(r)\}] \quad (16)$$

leads after some algebra to a set of  $N(N+1)/2$  coupled quadratic equations<sup>11</sup>

$$\lambda_{ij} R_{ij} = \gamma_{ij} \left[ a_i R_{ij} + b_i + 2\pi \sum_{k=1}^N \rho_k \lambda_{kj} R_{kj}^2 Q_{ik}(S_{ik}) \right]. \quad (17)$$

These equations have to be solved for the  $\lambda_{ij}$ , which are then inserted into Eq. (14) [both directly and via the  $Q_{ij}(s)$ ]. Due to the nonlinear structure of Eq. (17) the unknown parameters  $\lambda_{ij}$  are explicitly *density-dependent*.

#### B. Mean spherical model

Apart from Baxter's original definition (1), the interaction of SHS can be considered as a limiting case<sup>9</sup> of a HSY<sup>14</sup> interaction

$$\beta\Phi_{ij}(r) = -\gamma_{ij} z \frac{R_{ij}^2}{r} \exp[-z(r - R_{ij})] \quad \text{for } r > R_{ij} \quad (18)$$

and considering the limit  $z \rightarrow \infty$ .<sup>9</sup> Now, it is well known that the MSM, defined by the closure relations

$$h_{ij}(r) = -1 \quad r < R_{ij} \quad \text{and} \quad c_{ij}(r) = -\beta\Phi_{ij}(r) \quad R_{ij} \leq r \quad (19)$$

can be solved analytically for a multicomponent HSY potential for any finite  $z$ .<sup>14</sup> The unknown coefficients appearing in the factor functions are solutions of a set of rather complicated algebraic equations.<sup>14</sup> Similar to the one-component case<sup>9</sup> the above limit can be applied to these equations which leads to a MSM solution for SHS. In this paper we generalize this procedure to an  $N$ -component system and obtain the simple solution

$$\lambda_{ij} = \gamma_{ij}. \quad (20)$$

The  $\lambda_{ij}$  are now, of course, *density-independent*, a fact which will help us to proceed later to the polydisperse case.

#### C. Lorentz-Berthelot mixtures

We now come back to our previous problem, viz., to find the inverse of the matrix  $\mathcal{M}$  defined in Eq. (15). Using one of the analytic solutions (17) or (20) discussed above we are now able to calculate  $\mathcal{M}^{-1}$  for any *finite* number of components  $N$ ; in practice, however, numerical limits restrict actual

applications to  $N$ -values which are not too large: this holds both for the MSM and the PY approximation (for the latter see, e.g., Refs. 4 and 15).

However, it has been shown<sup>3</sup> that a matrix such as  $\mathcal{M}$  in Eq. (15) can be inverted exactly for *arbitrary*  $N$  under special conditions, viz., if the matrix can be cast into a form

$$M_{ij} = \delta_{ij} - \sum_{\nu=1}^{\bar{\nu}} A_i^\nu B_j^\nu, \quad i, j = 1, \dots, N; \quad (21)$$

then  $(\mathcal{M}^{-1})_{ij} = M_{ij}^{-1}$  is found to be<sup>3,8</sup>

$$M_{ij}^{-1} = \delta_{ij} + \frac{1}{D} \sum_{\mu, \nu} A_i^\mu B_j^\nu |m_{\mu\nu}| \quad (22)$$

with

$$(\mathcal{D})^{\mu\nu} = D^{\mu\nu} = \delta^{\mu\nu} - \sum_{i=1}^N A_i^\mu B_i^\nu, \quad \nu, \mu = 1, \dots, \bar{\nu}. \quad (23)$$

$D = \det \mathcal{D} = \det \mathcal{M}$  and  $|m_{\mu\nu}|$  is a cofactor of  $\mathcal{D}$ . All quantities used in the above equations are functions of  $s$ , which—for simplicity—has been omitted as an argument.

A closer analysis of the PY approximation shows that there is no hope to cast  $\mathcal{M}$  into the desired form (21): due to the structure of Eq. (17) a separation according to (21) into “ $i$ ”- and “ $j$ ”-components of  $\mathcal{M}$  is *a priori* impossible. For completeness it should be mentioned that Herrera and Blum<sup>8</sup> considered polydisperse charge particles with sticky interactions within the PY/MSM approximation. In order to make a matrix (which corresponds to our matrix  $\mathcal{M}$ ) invertible for an arbitrary number of components they make some *ad hoc* assumption on quantities they call stickiness probabilities which then makes a factorization in the above sense possible.

However, in the MSM it is *a priori* possible to obtain the special structure for  $\mathcal{M}$  if we assume some further approximation for the stickiness parameters  $\gamma_{ij}$ : we take the solution of the MSM equations for SHS (20) and introduce a Berthelot-type rule for the parameters  $\gamma_{ij}$ :

$$\gamma_{ij}^2 = \gamma_{ii} \gamma_{jj}. \quad (24)$$

Such an approximation is encountered frequently in binary (or multicomponent) liquid systems<sup>1</sup> and seems to us therefore to be not only a mathematically *convenient* but also a physically *sound* choice. It is now guaranteed that the matrix  $\mathcal{M}$  can be cast into the desired form (21) and therefore can be inverted analytically for an *arbitrary* number of components  $N$ . This, in turn, allows us to proceed to the continuous (polydisperse) case.

In our case  $\bar{\nu}$  turns out to be 5 (while in the HS case<sup>3</sup> it was 2); the rather lengthy expressions for the  $A_i^\mu$  and  $B_i^\nu$  which build up  $\mathcal{M}$  along with the elements of  $\mathcal{D}$  are compiled in Appendix A. In this context we also would like to point out that the decomposition into the  $A_i^\mu$  and the  $B_j^\nu$  is *not* unique.

Now that the explicit form of  $\mathcal{M}$  is available, Eq. (14) can be inverted. Interchanging the summation over  $\nu$  and  $\mu$  with the matrix multiplication we obtain an *explicit* expression for the Laplace-transforms of the total correlation functions:

$$\tilde{H}_{ij}(s) + \frac{1}{s^2} = \frac{e^{-sR_{ij}}}{s^2} \left[ \mathcal{E}_{ij} + \frac{1}{D} \sum_{\mu, \nu} A_i^\mu B_j^\nu |m_{\mu\nu}| \right], \quad (25)$$

where the elements  $\mathcal{A}_i^\mu$ ,  $\mathcal{B}_j^\nu$ , and  $\mathcal{E}_{ij}$  are given by

$$\mathcal{A}_i^\mu = A_i^\mu e^{sR_i/2}, \quad (26)$$

$$\mathcal{B}_i^\nu = \sum_{j=1}^N B_j^\nu \left[ a_j \left( 1 + s \frac{R_i}{2} \right) + s \frac{R_j}{2(1-\xi_3)} + \gamma_{ji} R_{ji}^2 s^2 \right] e^{-sR_j/2}, \quad (27)$$

$$\mathcal{E}_{ij} = a_i \left( 1 + s \frac{R_j}{2} \right) + s \frac{R_i}{2(1-\xi_3)} + \gamma_{ij} R_{ij}^2 s^2, \quad (28)$$

with  $\nu, \mu = 1, \dots, 5$  and  $i, j = 1, \dots, N$ . The explicit expressions for the  $\mathcal{B}_i^\nu, \nu = 1, \dots, 5$  in terms of the  $\xi$ -parameters appearing in the matrix  $\mathcal{M}$  are listed in Appendix A.

It is now straightforward to calculate the Fourier-transforms of the PDFs: via the general relation between Fourier- and Laplace-transforms [Ref. 3 (cf. errata) and Ref. 16] one then obtains

$$H_{ij}(q) = \frac{2\pi\sqrt{\rho_i\rho_j}}{iq} [\tilde{H}_{ij}(-iq) - \tilde{H}_{ij}(iq)] = S_{ij}(q) - \delta_{ij}, \quad (29)$$

where the  $S_{ij}(q)$  are the partial structure factors.

With these functions we can now proceed to calculate the scattering intensity  $I(q)$ , which—taking only the coherent contribution—is given for an  $N$ -particle system by<sup>4,17,10</sup> (and references quoted therein)

$$I(q) = \sum_{i,j=1}^N P_i(q) P_j(q) \sqrt{\rho_i\rho_j} [\delta_{ij} + H_{ij}(q)]. \quad (30)$$

This equation applies when multiple scattering is negligible.<sup>17</sup>  $P_i(q) = f_i B_i(q)$  is the scattering amplitude of species  $i$  and  $f_i$  is the excess zero-angle scattering amplitude. The interparticle interference function  $B_i(q)$  is—for the case of a spherosymmetric distribution of the scattering material  $\omega_i(R)$  inside a particle of species  $i$ —simply the Fourier-transform of  $\omega_i(R)$ .<sup>4</sup> Examples for different distributions  $\omega_i(R)$  are given in Ref. 17.

#### IV. THE STOCHASTIC LIMIT

In their work on an  $N$ -component system of HS Blum and Stell<sup>3</sup> performed the limit  $N \rightarrow \infty$ , introducing thus—what they call—the “continuous-distribution” limit. In subsequent years this generalization was cast into a rigorous framework (i.e., a statistical mechanical description of polydisperse systems) by Salacuse<sup>6</sup> and also by Briano and Glandt.<sup>18</sup> In Ref. 6, a polydisperse system is defined as a “system in which each particle is uniquely associated with a value of some characteristic parameter  $X$ , distributed according to a probability distribution function  $f_X(x)$ ;  $X$  is a continuous random variable.” It was demonstrated there (and in subsequent work) that several realistic systems can be described within this formalism very conveniently, as, e.g.,

when the number of discrete species of a fluid mixture becomes sufficiently large. This is for instance the case in colloidal systems<sup>2</sup> where—due to the production process—the size of the particles can be described more conveniently by a continuous distribution rather than a discrete number of particles.

Dealing with a hard-core system, the diameter  $R$  is of course the natural choice for the continuous random variable,  $X=R$ ,  $R$  being distributed according to a probability distribution function  $f_R(R)$ . The transition from a mixture with a *finite* number of components to a *polydisperse* system is most readily realized via the prescription (stochastic limit)<sup>6</sup>

$$c_i \rightarrow f_R(R) dR, \quad \rho_i \rightarrow \rho f_R(R) dR, \quad (31)$$

where  $c_i$  is the concentration of the particles with diameter  $R_i$ . Thus,  $f_R(R') dR'$  represents the fraction of particles in the system with diameter  $R$  in the range  $[R', R' + dR']$ . Summations over characteristic quantities  $X_i$  of species  $i$  now become integrals

$$\sum_{i=1}^N \rho_i X_i \rightarrow \rho \int_0^\infty dR f_R(R) X(R); \quad (32)$$

$f_R(R)$  has the usual features of a probability distribution function, i.e.,

$$f_R(R) > 0 \text{ for all } R; \quad \int_0^\infty dR f_R(R) = 1. \quad (33)$$

The formalism of polydisperse systems has been extended to structural and thermodynamic properties in Refs. 6, 18, and 19.

In the case of the MSM solution (along with the Lorentz-Berthelot assumption for the stickiness) the transition (31) can be performed by *fully* maintaining the analyticity of the expressions presented in Sec. III C (Appendix B 1). For instance, expression (30) for the scattering intensity now reads

$$\begin{aligned} I(q) = & \rho \int_0^\infty dR P^2(R; q) f_R(R) \\ & + \frac{2\pi}{iq} \rho^2 \int_0^\infty \int_0^\infty dR dR' P(R; q) P(R'; q) \\ & \times [\tilde{H}(R, R'; -iq) - \tilde{H}(R, R'; iq)] f_R(R) f_R(R'), \end{aligned} \quad (34)$$

with  $\tilde{H}_{ij}(s) \rightarrow \tilde{H}(R, R'; s)$  and  $P_i(q) \rightarrow P(R; q)$ .

Similar to the diameter  $R_i$  (which has become in the stochastic limit the random variable  $R$ ) the stickiness  $\gamma_{ii}$  turns into a random variable  $G=G(R)$ , which is—by definition of polydisperse systems—a function of the random variable  $R$ . At the level of  $G$  the Berthelot-rule (24) now becomes

$$G^2(\frac{1}{2}(R+R')) = G(R)G(R'), \quad (35)$$

which can be considered as a functional equation for  $G(R)$  with the continuous solution being

$$G(R) = \gamma_0 e^{zR}. \quad (36)$$

The  $N$  parameters  $\gamma_{ii}$  in the discrete case are now in the stochastic case reduced to two parameters  $\gamma_0$  and  $z$  which can be adjusted to experimental data.

Furthermore, if  $R$  is distributed according to some probability distribution function  $f_R(R)$  then

$$f_G(\gamma) = \frac{1}{z\gamma} f_R \left[ z^{-1} \ln \left( \frac{\gamma}{\gamma_0} \right) \right]. \quad (37)$$

This means that the distribution of the stickiness is now *induced* by the distribution of the particle-size,  $f_R(R)$ .

In addition  $\gamma_0$  and  $z$  *have* to be positive: the first one for physical reasons, i.e., to guarantee that the interaction is attractive, the latter one for mathematical and physical reasons, i.e., to guarantee that the mapping (36) is a monotonous one and that the stickiness increases with increasing size of the particles.

The following two limiting cases are direct consequences of the formalism developed above: (i) for  $z \rightarrow 0^+$  one finds

$$f_G(\gamma) = \delta(\gamma - \gamma_0) \quad (38)$$

for any distribution  $f_R(R)$  (i.e., polydisperse in size but monodisperse in coupling) and (ii) the case of a *finite* number  $N$  of components is recovered by choosing

$$f_R(R) \propto \sum_{i=1}^N \delta(R - R_i). \quad (39)$$

The advantage of the stochastic limit lies in the fact that the continuous case can be treated (numerically) with much less effort, than the discrete case with a larger number of components: given some probability distribution function for the size,  $f_R(R)$ , it is sufficient to evaluate integrals, such as

$$m_n(s) = \int_0^\infty dR f_R(R) R^n e^{sR}. \quad (40)$$

For several distributions these integrals can be evaluated *analytically*. These (general) expressions are summarized in Appendix B 1.

Finally we choose  $f_R(R)$  to be a  $\Gamma$ -distribution, i.e.,

$$f_R(R) = \frac{1}{D\Gamma(c)} \left( \frac{R}{D} \right)^{c-1} e^{-R/D}; \quad (41)$$

$D$  and  $c$  are positive parameters. Such a distribution for the size of the particles has been frequently used in colloidal sciences; there it is rather known as Schulz distribution.<sup>10</sup> It has the mathematically appealing feature that within the present model all quantities required to calculate the scattering intensity can be calculated analytically; these expressions are compiled in Appendix B 2.

## V. CONCLUSION

In this paper we have presented the solution of the OZ equations for an  $N$ -component system of sticky spheres, using the PY closure relation and the MSM. We have furthermore shown that the analyticity of the solution can be fully maintained in the case of the MSM if we perform the stochastic limit, i.e., if we consider a system of infinitely many

components which are characterized by a probability distribution function for the diameters. This extension is possible if we assume a Berthelot-type rule for the stickiness parameters. It then turns out that closed expressions can be given for the partial structure factor and hence for the scattering intensity. These appealing features have been demonstrated explicitly for the case that the particle size is distributed according to a  $\Gamma$ -distribution.

*Note added in proof.* We would like to point out that during the refereeing process for this manuscript a paper on a related problem has been published in *The Journal of Chemical Physics*:<sup>20</sup> the authors consider a multicomponent system of charged hard spheres (including the polydisperse limit) in the mean spherical approximation.

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## APPENDIX A: THE DISCRETE CASE

The explicit expressions for the quantities  $A_i^\nu$  and  $B_i^\nu$ ,  $\nu=1, \dots, 5$ ,  $i=1, \dots, N$  which build up  $\mathcal{M}$  according to Eq. (21) are as follows:

$$\begin{aligned}
 A_i^1 &= a_i e^{-sR_i/2}, & B_i^1 &= 2\pi\rho_i e^{sR_i/2} \left[ \varphi_2(s;R_i) + \frac{R_i}{2} \varphi_1(s;R_i) \right], \\
 A_i^2 &= \frac{R_i}{2(1-\xi_3)} e^{-sR_i/2}, & B_i^2 &= 2\pi\rho_i e^{sR_i/2} \varphi_1(s;R_i), \\
 A_i^3 &= \sqrt{\gamma_{ii}} \frac{1}{4} e^{-sR_i/2} R_i^2, & B_i^3 &= \sqrt{\gamma_{ii}} 2\pi\rho_i e^{sR_i/2} \varphi_0(s;R_i), \\
 A_i^4 &= \sqrt{\gamma_{ii}} \frac{1}{2} e^{-sR_i/2} R_i, & B_i^4 &= \sqrt{\gamma_{ii}} 2\pi\rho_i e^{sR_i/2} R_i \varphi_0(s;R_i), \\
 A_i^5 &= \sqrt{\gamma_{ii}} \frac{1}{4} e^{-sR_i/2}, & B_i^5 &= \sqrt{\gamma_{ii}} 2\pi\rho_i e^{sR_i/2} R_i^2 \varphi_0(s;R_i).
 \end{aligned} \tag{A1}$$

The  $\varphi_\alpha(s;x)$ 's ( $\alpha=0,1,2$ ) are the modified incomplete gamma functions

$$\varphi_0(s;x) = \frac{1}{s} (1 - e^{-sx}), \tag{A2}$$

$$\varphi_1(s;x) = \frac{1}{s^2} (1 - sx - e^{-sx}), \tag{A3}$$

$$\varphi_2(s;x) = \frac{1}{s^3} \left( 1 - sx + \frac{1}{2} s^2 x^2 - e^{-sx} \right). \tag{A4}$$

The elements  $\mathcal{S}^{\mu\nu}$  ( $\mu, \nu=1, \dots, 5$ ) of the matrix  $\mathcal{S}$  are calculated from these quantities via Eq. (23) and are found to be ( $\mathbf{1}$  is the unit matrix)

$$\mathcal{S} = \mathbf{1} - 3 \begin{pmatrix} 4 \left( \xi_{200}^a + \frac{1}{2} \xi_{110}^a \right) & 4 \xi_{100}^a & 4 \xi_{001}^a & 4 \xi_{011}^a & 4 \xi_{021}^a \\ 2 \left( \bar{\xi}_{210} + \frac{1}{2} \bar{\xi}_{120} \right) & 2 \bar{\xi}_{110} & 2 \bar{\xi}_{011} & 2 \bar{\xi}_{021} & 2 \bar{\xi}_{031} \\ \left( \xi_{221} + \frac{1}{2} \xi_{131} \right) & \xi_{121} & \xi_{022} & \xi_{032} & \xi_{042} \\ 2 \left( \xi_{211} + \frac{1}{2} \xi_{121} \right) & 2 \xi_{111} & 2 \xi_{012} & 2 \xi_{022} & 2 \xi_{032} \\ \left( \xi_{201} + \frac{1}{2} \xi_{111} \right) & \xi_{101} & \xi_{002} & \xi_{012} & \xi_{022} \end{pmatrix} \tag{A5}$$

with

$$\begin{aligned}\xi_{\alpha\beta\gamma} &= \frac{\pi}{6} \sum_i \rho_i \varphi_\alpha(s; R_i) R_i^\beta (\sqrt{\gamma_{ii}})^\gamma, \\ \xi_{\alpha\beta\gamma}^a &= \frac{\pi}{6} \sum_i \rho_i a_i \varphi_\alpha(s; R_i) R_i^\beta (\sqrt{\gamma_{ii}})^\gamma, \\ \bar{\xi}_{\alpha\beta\gamma} &= \frac{1}{(1-\xi_3)} \xi_{\alpha\beta\gamma}.\end{aligned}\quad (\text{A6})$$

The coefficients  $\mathcal{B}_i^\mu$ ,  $\mu=1, \dots, 5$  and  $i=1, \dots, N$  defined in Eq. (27) are given by

$$\begin{aligned}\mathcal{B}_i^1 &= 12 \left( 1 + s \frac{R_i}{2} \right) \left( \xi_{200}^a + \frac{1}{2} \xi_{110}^a \right) + 6 \left( \bar{\xi}_{210} \right. \\ &\quad \left. + \frac{1}{2} \bar{\xi}_{120} \right) s + 3 \left[ \left( \xi_{221} + \frac{1}{2} \xi_{131} \right) + 2 \left( \xi_{211} \right. \right. \\ &\quad \left. \left. + \frac{1}{2} \xi_{121} \right) R_i + \left( \xi_{201} + \frac{1}{2} \xi_{111} \right) R_i^2 \right] \sqrt{\gamma_{ii}} s^2, \quad (\text{A7})\end{aligned}$$

$$\begin{aligned}\mathcal{B}_i^2 &= 12 \left( 1 + s \frac{R_i}{2} \right) \xi_{100}^a + 6 \bar{\xi}_{110} s + 3 \left[ \xi_{121} + 2 \xi_{111} R_i \right. \\ &\quad \left. + \xi_{101} R_i^2 \right] \sqrt{\gamma_{ii}} s^2, \quad (\text{A8})\end{aligned}$$

$$\begin{aligned}\mathcal{B}_i^{3+\beta} &= 12 \left( 1 + s \frac{R_i}{2} \right) \xi_{0\beta 1}^a + 6 \bar{\xi}_{0(\beta+1)1} s + 3 \left[ \xi_{0(\beta+2)2} \right. \\ &\quad \left. + 2 \xi_{0(\beta+1)2} R_i + \xi_{0\beta 2} R_i^2 \right] \sqrt{\gamma_{ii}} s^2, \quad \beta=0,1,2. \quad (\text{A9})\end{aligned}$$

## APPENDIX B: THE CONTINUOUS CASE

In the polydisperse case the discrete quantities characterizing the component by the index  $i$  now become *continuous* functions of the diameter  $R$ , which now characterizes this species. Formally this transition will be specified, for instance, by  $a_i \rightarrow a(R)$ .

### 1. General expressions

In order to calculate the scattering intensity (34) one has to calculate the following expressions (where the integrals extend over the range  $[0, \infty]$ ):

$$\xi_u = \frac{\pi}{6} \rho \int dR f_R(R) R^u, \quad (\text{B1})$$

$$\zeta_i \rightarrow \zeta(R) = \frac{\pi}{24} \rho \gamma_0 e^{zR/2} \int dR' f_R(R') R' (R+R')^2 e^{zR'/2}, \quad (\text{B1})$$

$$a_i \rightarrow a(R) = \frac{1-\xi_3+3R\xi_2}{(1-\xi_3)^2} - \frac{12\zeta(R)}{1-\xi_3}, \quad (\text{B2})$$

$$b_i \rightarrow b(R) = -\frac{3}{2} R^2 \xi_2 \frac{1}{(1-\xi_3)^2} + \frac{6\zeta(R)R}{(1-\xi_3)}, \quad (\text{B3})$$

$$\xi_{\alpha\beta\gamma} = \frac{\pi}{6} \rho \gamma_0^{1/2} \int dR f_R(R) \varphi_\alpha(s; R) R^\beta e^{\gamma z R/2}, \quad (\text{B4})$$

$$\xi_{\alpha\beta\gamma}^a = \frac{\pi}{6} \rho \gamma_0^{1/2} \int dR f_R(R) a(R) \varphi_\alpha(s; R) R^\beta e^{\gamma z R/2},$$

$$\bar{\xi}_{\alpha,\beta,\gamma} = \frac{1}{(1-\xi_3)} \xi_{\alpha,\beta,\gamma},$$

$$\mathcal{A}_i^1 \rightarrow \mathcal{A}^1(R) = a(R), \quad \mathcal{A}_i^2 \rightarrow \mathcal{A}^2(R) = \frac{R}{2(1-\xi_3)}, \quad (\text{B5})$$

$$\mathcal{A}_i^3 \rightarrow \mathcal{A}^3(R) = \frac{1}{4} \sqrt{\gamma_0} e^{zR/2} R^2,$$

$$\mathcal{A}_i^4 \rightarrow \mathcal{A}^4(R) = \frac{1}{2} \sqrt{\gamma_0} e^{zR/2} R,$$

$$\mathcal{A}_i^5 \rightarrow \mathcal{A}^5(R) = \frac{1}{4} \sqrt{\gamma_0} e^{zR/2},$$

$$\begin{aligned}\mathcal{B}_i^1 \rightarrow \mathcal{B}^1(R) &= 12 \left( 1 + s \frac{R}{2} \right) \left( \xi_{200}^a + \frac{1}{2} \xi_{110}^a \right) \\ &\quad + 6 \left( \bar{\xi}_{210} + \frac{1}{2} \bar{\xi}_{120} \right) s + 3 \sqrt{\gamma_0} \left[ \left( \xi_{221} + \frac{1}{2} \xi_{131} \right) \right. \\ &\quad \left. + 2 \left( \xi_{211} + \frac{1}{2} \xi_{121} \right) R + \left( \xi_{201} + \frac{1}{2} \xi_{111} \right) R^2 \right] e^{zR/2} s^2, \quad (\text{B6})\end{aligned}$$

$$\begin{aligned}\mathcal{B}_i^2 \rightarrow \mathcal{B}^2(R) &= 12 \left( 1 + s \frac{R}{2} \right) \xi_{100}^a + 6 \bar{\xi}_{110} s \\ &\quad + 3 \sqrt{\gamma_0} \left[ \xi_{121} + 2 \xi_{111} R + \xi_{101} R^2 \right] e^{zR/2} s^2, \quad (\text{B7})\end{aligned}$$

$$\begin{aligned}\mathcal{B}_i^{3+\beta} \rightarrow \mathcal{B}^{3+\beta}(R) &= 12 \left( 1 + s \frac{R}{2} \right) \xi_{0\beta 1}^a + 6 \bar{\xi}_{0(\beta+1)1} s \\ &\quad + 3 \sqrt{\gamma_0} \left[ \xi_{0(\beta+2)2} + 2 \xi_{0(\beta+1)2} R \right. \\ &\quad \left. + \xi_{0\beta 2} R^2 \right] e^{zR/2} s^2, \quad \beta=0,1,2, \quad (\text{B8})\end{aligned}$$

$$\begin{aligned}\mathcal{C}_{ij} \rightarrow \mathcal{C}(R, R') &= a(R) \left( 1 + s \frac{R'}{2} \right) + \frac{R}{2(1-\xi_3)} s \\ &\quad + \frac{1}{4} \gamma_0 e^{z(R+R')/2} (R+R')^2 s^2. \quad (\text{B9})\end{aligned}$$

The calculation of  $\mathcal{D}$ ,  $D$  and of the cofactors  $\|m_{\mu\nu}\|$  follows Eq. (A5). Then

$$\begin{aligned}\left[ \tilde{H}_{ij}(s) + \frac{1}{s^2} \right] &\rightarrow \left[ \tilde{H}(R, R'; s) + \frac{1}{s^2} \right] \\ &= \frac{1}{s^2} e^{-s(R+R')/2} \left[ \mathcal{C}(R, R') \right. \\ &\quad \left. + \frac{1}{D} \sum_{\nu, \mu} \bar{\nu} \mathcal{A}^\nu(R) \mathcal{B}^\mu(R') \|m_{\nu\mu}\| \right]. \quad (\text{B10})\end{aligned}$$

Due to the fact that  $\mathcal{E}(R, R')$  can be split up into a product of  $R$ - and  $R'$ -dependent quantities the double-integral (34) can be *factorized*.

## 2. $\Gamma$ -distribution

In this subsection we specialize the expressions developed for the polydisperse case in the preceding subsection to the case that  $f_R(R)$  is a  $\Gamma$ -distribution (41).<sup>10</sup> To this end it is very convenient to describe quantities  $\bar{m}_\alpha(s)$  defined as

$$\bar{m}_n(s) = \int_0^\infty dR f_R(R) R^n e^{sR}. \quad (\text{B11})$$

They are found to be

$$\bar{m}_n(s) = c \cdot (c+1) \cdots (c+n-1) \left(\frac{1}{D}\right)^c \left(\frac{1}{D} - s\right)^{-n-c}. \quad (\text{B12})$$

For  $s=0$  the  $\bar{m}_n(s)$  become the moments  $m_n$  of the distribution  $f_R(R)$ , i.e.,

$$\bar{m}_n(0) = m_n = c \cdot (c+1) \cdots (c+n-1) D^n. \quad (\text{B13})$$

Hence

$$\xi_u = \frac{\pi}{6} \rho m_u, \quad u = 0, \dots, 3, \quad (\text{B14})$$

$$\zeta(R) = \frac{\pi}{24} \rho \gamma_0 e^{zR/2} [R^2 \bar{m}_1(z/2) + 2R \bar{m}_2(z/2) + \bar{m}_3(z/2)], \quad (\text{B15})$$

$a(R)$  and  $b(R)$  are then obtained from Eqs. (B2) and (B3). Furthermore,

$$\xi_{0,\beta,\gamma} = \frac{\pi}{6} \rho \gamma_0^{\gamma/2} \frac{1}{s} [\bar{m}_\beta(z\gamma/2) - \bar{m}_\beta(z\gamma/2 - s)], \quad (\text{B16})$$

$$\xi_{1,\beta,\gamma} = \frac{1}{s} \left[ \xi_{0,\beta,\gamma} - \frac{\pi}{6} \rho \gamma_0^{\gamma/2} \bar{m}_{\beta+1}(z\gamma/2) \right], \quad (\text{B17})$$

$$\xi_{2,\beta,\gamma} = \frac{1}{s} \left[ \xi_{1,\beta,\gamma} + \frac{\pi}{12} \rho \gamma_0^{\gamma/2} \bar{m}_{\beta+2}(z\gamma/2) \right], \quad (\text{B18})$$

$$\begin{aligned} \xi_{\alpha\beta\gamma}^a &= \frac{1}{1-\xi_3} \xi_{\alpha\beta\gamma} + \frac{3\xi_2}{(1-\xi_3)^2} \xi_{\alpha(\beta+1)\gamma} \\ &\quad - \frac{3}{1-\xi_2} \frac{\pi}{6} \rho \gamma_0^{1/2} [\xi_{\alpha(\beta+2)(\gamma+1)} \bar{m}_1(z/2) \\ &\quad + 2\xi_{\alpha(\beta+1)(\gamma+1)} \bar{m}_2(z/2) + \xi_{\alpha\beta(\gamma+1)} \bar{m}_3(z/2)]. \end{aligned} \quad (\text{B19})$$

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