Structure factor for polydisperse fluids of particles with surface adhesion

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An exactly solvable model for polydisperse fluids of particles with surface adhesion is discussed. For this model, alternative to Baxter’s one and with factorized stickiness coefficients, all scattering functions can be computed analytically for an arbitrary number of components. An application to experimental small-angle scattering results on sterically stabilized colloidal particles interacting via an attractive short-ranged attraction shows the usefulness of this model. However, results on its thermodynamic properties reveal some intrinsic inconsistencies. A way out from this drawbacks is discussed in terms of a new potential.

Keywords: small-angle scattering: colloidal adhesive particles: polydisperse fluids.

1. Introduction

The interpretation of experimental small-angle scattering (SAS) data from colloidal or micellar solutions may become very difficult in the presence of a significant degree of ‘polydispersity’ in size, charge or other properties of the suspended macromolecules. In this context, the fluid is a mixture with a large number of components and strong asymmetries among particles, which represent a challenge for the most powerful tools of the statistical mechanical theory of liquids. In fact, Monte Carlo and molecular dynamics simulations for such systems require very large numbers of particles, while integral equations (IEs) must be solved numerically in most cases, and this is feasible in practice only when the number of components is very small.

Within the framework of IEs, size polydispersity has been included in calculations of structure factors in two different ways. In the first kind of approach, the basic idea is to reduce the study of a polydisperse fluid with that of a nearly equivalent system with very few components. Notable examples include the ‘decoupling approximation’ (Hayter & Penfold, 1983; Kotlarchyk & Chen, 1983), the ‘local monodisperse approximation’ (Pedersen, 1994), the ‘scaling approximation’ for both non-ionic and ionic systems (Gazzillo et al., 1999a, 1999b), and the ‘histogram method’ for the determination of an ‘effective mixture’ (D’Aguanno & Klein, 1992). A detailed comparison among the first three schemes has already been presented in previous papers (Gazzillo et al., 1999a, 1999b). All these approximations, albeit with different degrees of success, yield acceptable predictions only when the departure from monodispersity is not too strong.

A better approach hinges upon p-component models for which the Ornstein-Zernike (OZ) IEs are analytically solvable, when coupled with suitable approximations (‘closures’). Using these solutions, simple analytical expressions for the scattering intensity were obtained for polydisperse hard spheres (HS) within the Percus-Yevick (PY) closure (Vrij, 1978, 1979), and for polydisperse charged HS within the ‘mean spherical approximation’ (MSA) (Gazzillo et al., 1997). These formulas were implemented into a specialized computer program (FLAC) for SAS data analysis of dense polydisperse systems (Carsughi et al., 2000).

The present paper follows the second route in the context of polydisperse colloidal suspensions of neutral particles, interacting with a hard-core repulsion, plus a very short-ranged attraction.

A popular model for such fluids is Baxter’s one of ‘sticky hard spheres’ (SHS) (Baxter, 1968; Perram & Smith, 1975; Barboy & Tenne, 1979), where a surface adhesive term is included in the total potential \( \phi_{ij}(r) \) as a limit of an attractive square-well which becomes infinitely deep and narrow, but gives a finite non-zero contribution to the second virial coefficient (‘sticky limit’). A PY analytical solution for this model (which we call SHS1) is available, but its multi-component version is inapplicable to systems with significant polydispersity (i.e. large \( p \)), since it requires the computation of a set of parameters \( \{ \lambda_i \} \) through numerical solution of \( p(p+1)/2 \) coupled quadratic equations (Perram & Smith, 1975; Barboy & Tenne 1979). As a consequence, in the few applications of the SHS1-PY solution to SAS data (Robert et al., 1989; Duits et al., 1991), the representation of polydispersity was necessarily restricted to a small number of components (\( p \leq 9 \)).

Our paper thus focuses on an alternative SHS model (SHS2), proposed by (Brey et al., 1987; Mier-y-Teran et al., 1989) in the onecomponent case, and recently extended to mixtures (Tutschka & Kahl, 1998; Gazzillo & Giacometti, 2000). Here, the adhesive part of the potential is generated from an attractive Yukawa tail, whose amplitude and inverse range become infinite in the sticky limit, while their ratio remains constant. For SHS2, the OZ equations are analytically solvable within the MSA closure (Mier-y-Teran et al., 1989), and the SHS2-MSA solution is simpler than the SHS1-PY one. Using a version of the SHS2 model with factorized stickiness parameters, in previous papers (Gazzillo & Giacometti, 2000, 2002a) we derived a closed analytical expression for the average structure factor and discussed the effects of polydispersity on it, both theoretically and applied to experimental SAS data. Recently, we have also started an analysis (Gazzillo & Giacometti, 2002b) on the thermodynamical properties of this model.

Our aim in this paper is twofold. On the one hand, we shall review past results on the structure factor in a perspective useful for the SAS community. On the other hand, preliminary new results on thermodynamics will be presented. We shall see how an intrinsic inconsistency of the second virial coefficient of the SHS2 model can be resolved by the introduction of a new SHS3 model. All previous results on the structure factor remain still valid with a proper re-interpretation in terms of SHS3.

2. Scattering factor in terms of Baxter functions

The analytic solution of OZ-based IEs may be expressed in terms of Baxter functions \( q_{ij}(r) \), from which all correlation and scattering functions can be computed. The partial structure factors are given by (Gazzillo & Giacometti, 2000)

\[
S_{ij}(k) = \sum_{m=1}^{p} \hat{Q}_{im}^{-1}(k) \hat{Q}_{jm}^{-1}(-k),
\]

with \( \hat{Q}_{ij}(k) = \delta_{ij} - 2\pi(p\rho_i)^{1/2} q_{ij}(k) \), and \( q_{ij}(k) \) being the unidimensional Fourier transform of \( q_{ij}(r) \) (\( k \) is the magnitude of the exchanged wave vector, \( \delta_{ij} \) the Kronecker \( \delta \), \( \rho_i \) the number density of species \( i \)).

The measurable average structure factor is then

\[
S_M(k) = \sum_{i,j=1}^{p} (x_i x_j)^{1/2} F_i(k) F_j^*(k) S_{ij}(k) / \sum_{i=1}^{p} x_i |F_i(k)|^2,
\]

where \( x_i \) is the molar fraction of species \( i \), \( F_i(k) \) its form factor, and the asterisk denotes complex conjugation.

Both the SHS1-PY solution and the SHS2-MSA one have the form...


\[ q_{ij}(r) = \begin{cases} \frac{1}{2}a_{ij}(r^2 - \sigma_{ij}^2) + b_{ij}(r - \sigma_{ij}) + K_{ij}, & L_{ij} \leq r \leq \sigma_{ij}, \\ 0, & \text{elsewhere}, \end{cases} \tag{3} \]

with \( L_{ij} = (\sigma_i - \sigma_j)/2 \) and \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \) (\( \sigma_i \) being the HS diameter of species \( i \)), while the expressions of \( a_{ij} \) and \( b_{ij} \), which depend also on the parameters \( \{K_{ij}\} \), can be found in (Gazzillo & Giacometti, 2000; 2002b). Of course, \( K_{ij}^{\mathrm{SHS-1-PY}} \neq K_{ij}^{\mathrm{SHS-2-MSA}} \).

In the SHS1 model ( Perram & Smith, 1975), one starts adding to the HS potential the square-well tail

\[ \phi_{ij}^{\mathrm{SW1}}(r) = -k_BT \ln \left( \frac{R_{ij}}{12 \tau_{ij} R_{ij} - \sigma_{ij}} \right), \quad \sigma_{ij} \leq r \leq R_{ij}, \tag{4} \]

where \( R_{ij} - \sigma_{ij} \) denotes the well width, \( k_B \) is Boltzmann’s constant, \( T \) the temperature, and \( \sigma_{ij} \geq 0 \) is related to both the temperature and the stickiness between particles of species \( i \) and \( j \). From the general definition of second virial coefficient,

\[ B_2 = -2\pi \sum_{i=1}^{p} x_i x_j \int_0^\infty dr r^2 f_{ij}(r), \tag{5} \]

with \( f_{ij}(r) = \exp[-\beta \delta_{ij}(r)] - 1/\beta (=(k_BT)^{-1}) \), one can evaluate \( B_2^{\mathrm{SW1}} \). The sticky limit, \( \{R_{ij}\} \to \{\sigma_{ij}\} \), then yields

\[ B_2^{\mathrm{SHS1-1-PY}} = \lim_{\{\sigma_{ij}\} \to \{\sigma_{ij}\}} B_2^{\mathrm{SW1}} = \frac{2\pi}{3} \sum_{i=1}^{p} x_i x_j \sigma_{ij}^3 \left( 1 - \frac{1}{4\tau_{ij}} \right), \tag{6} \]

\[ K_{ij}^{\mathrm{SHS1-PY}} = \frac{1}{12 \tau_{ij}} Y_{ij} \sigma_{ij}^{-2}, \tag{7} \]

where \( y_{ij}(\sigma_{ij}) \) is the contact value of the cavity function.

In our SHS2 model, we start from a Yukawa tail,

\[ \phi_{ij}^{\mathrm{Y}}(r) = -z A_{ij} e^{-(r-r_{ij})/\rho}, \quad r \geq \sigma_{ij}, \tag{8} \]

with factorized coefficients \( A_{ij} = z_0 G_G \), where \( z \) is the inverse range, \( z_0 \) an energy, and \( G_G \) has dimensions of length. The MSA closure reads: \( c_{ij}(r) = -\beta \delta_{ij}(r) \) for \( r \geq \sigma_{ij} \) (\( c_{ij}(r) \) is the direct correlation function), and now the sticky limit corresponds to \( z \to +\infty \). The final result is

\[ K_{ij}^{\mathrm{SHS2-MSA}} = \frac{1}{12T}G_G \equiv YY_J, \tag{9} \]

with \( T^* \) being a reduced temperature, defined by \((12T^*)^{-1} = \beta z_0 = \gamma_0^2 \) (the factor 1/12 was absent in (Gazzillo & Giacometti, 2000; 2002a), and therefore: \( T^* = T_{\text{HS}}/(12) \). Low \( T^* \) (high \( \gamma_0 \)) values correspond to low temperature or strong attraction.

Note that \( K_{ij}^{\mathrm{SHS1-PY}} \) is non-factorized and density-dependent, whereas \( K_{ij}^{\mathrm{SHS2-MSA}} \) is factorized and density-independent.

3. The SHS2-MSA solution

Equation (1) shows that the computation of \( S_{ij}(k) \) requires the inversion of a \( p \times p \) matrix \( \mathbf{Q}(k) \), which usually is a difficult task when \( p \) is large. Nevertheless, when \( K_{ij} \) is factorized as in equation (9), \( \mathbf{Q}(k) \) has analytic inverse for any \( p \) (Gazzillo & Giacometti, 2000) (in general, this does not occur for the SHS1-PY solution). Another important property, again due to the factorized form of \( K_{ij}^{\mathrm{SHS2-MSA}} \), is that the sums in equation (2) can be performed analytically. In this way, the calculation of all individual \( S_{ij}(k) \)’s is bypassed, and one directly gets closed analytical expressions for \( S_{ij}(k) \) and the scattering intensity (Gazzillo & Giacometti, 2000), which represent a great advantage for the fit of experimental SAS data.

3.1. Polydispersity effects on SAS

We have investigated model systems with a Schulz distribution of diameters, where the degree of size polydispersity is measured by \( s_p = \left[ \langle \sigma^2 \rangle - \langle \sigma \rangle^2 \right]^{1/2} / \langle \sigma \rangle \) (\( \langle \cdot \rangle \) denotes a compositional average, i.e. \( \langle r \rangle \equiv \sum_m x_m r_m \)). As regards stickiness, two simple choices have been considered: i) all particles have the same stickiness, corresponding to the average diameter \( \langle \sigma \rangle \), i.e. \( Y = Y_0 \langle \sigma \rangle \) (Model I), or ii) the stickiness parameter is linearly related to the particle size, i.e. \( Y = Y_0 \sigma \) (Model II).

The structure of adhesive sphere fluids is, of course, determined by the competition between hard-core repulsions and surface attractions. Polydispersity acts as a further factor in this balance.

In the monodisperse case, \( s_p = 0 \), the presence of strong adhesive forces becomes apparent from the behaviour of the structure factor in the low-\( k \)-region, where SAS techniques can be employed. By lowering temperature, the system may undergo a first-order phase transition as signalled by a sudden increase of \( S_{\text{mono}}(k = 0) \), which is equal to the isothermal compressibility. This has in fact been experimentally observed in colloidal suspensions (de Kruif et al., 1989). On the other hand, the monodisperse SHS2-MSA solution predicts a critical temperature \( T_{\text{c}}^* \approx 0.13 \), and a Boyle temperature \( T_{\text{B}}^* \approx 0.25 \). When \( T^* > T_{\text{B}}^* \) (\( B_2 > 0 \)), repulsive forces are dominant, and the structure factor is similar to that of pure HS. When \( T^* < T_{\text{c}}^* \) (\( B_2 < 0 \)), the balance between attractive and repulsive forces becomes more complex: the attractions are dominant at low density, whereas repulsions again prevail at higher \( \rho \) (\( \rho = \sum_m \rho_m \) is the total number density). The remarkable point is that \( S_{\text{mono}}(k) \) may now cross over from the HS-like repulsive regime to the behaviour typical of the ‘strong-attraction regime’, where \( S_{\text{mono}}(k = 0) \) may even become higher than the first peak.

Figure 1

Structure factor of monodisperse sticky hard spheres at fixed packing fraction \( \eta = 0.2 \), for decreasing values of reduced temperature \( T^* \).

The behaviour of \( S_{\text{mono}}(k) \) with decreasing \( T^* \) is displayed in Fig. 1, while Figs. 2 and 3 refer to \( S_M(k) \) for polydisperse Models I and II, respectively (\( T^* = +\infty \) yields the corresponding HS limit).

When \( s_p \neq 0 \), the most evident effect of size polydispersity is that all oscillations of \( S_M(k) \) become damped, in the first peak region and
beyond (comparisons can be conveniently made at fixed packing fraction, \( \eta = (\pi/6) \rho (\sigma^2) \)). Even a small dispersion of diameters, with \( s_\sigma \simeq 0.1 \), can strongly modify the structure factor with respect to the monodisperse case. The importance of a proper treatment for polydispersity has been recently pointed out in the analysis of a set of SAS data (Duits et al., 1991) for silica particles coated with octadeyl chains and dispersed in benzene (Gazzillo & Giacometti, 2002a).

Even in the presence of polydispersity, there exist two ‘regimes’ in terms of a generalized Boyle temperature, \( T_{B}^* \), related to the crossover from ‘repulsive’ to ‘attractive’ regime of \( S_M(k) \) (Gazzillo & Giacometti, 2000). The novel feature of \( T_{B}^* \) is that it is a decreasing function of \( s_\sigma \) for both Models, I and II. Since larger \( s_\sigma \) values lead to lower \( T_{B}^* \), polydispersity can then stabilize the mixture against possible phase transitions, contrasting the attractive effects. This increase of stability is more sensible in Model I, where attractions seem to be, on the average, weaker (compare Figs. 2 and 3). However, the difference between the two stickiness distributions of Model I and II can be revealed only when size polydispersity is large and \( T^* \) is low (sufficiently strong adhesive forces and low temperature) (Gazzillo & Giacometti, 2000; 2002a). Unfortunately, no experimental data for such a regime are, to the best of our knowledge, available in the literature. As a consequence, although Model II appears to be more physically sound, no conclusive statements can be assessed on the relative applicability of the two models.

**Figure 2**  
Structure factor of polydisperse sticky hard spheres (Model I) at fixed \( \eta = 0.2 \), for two values of polydispersity degree, \( s_\sigma = 0.1, 0.3 \), and decreasing \( T^* \). All curves of part b) are shifted upwards for clarity.

**Figure 3**  
As in Fig. 2 but for Model II.

### 3.2. Thermodynamic pathologies

We have shown that the simple SHS2-MSA solution allows to get a physically significant insight into the structural properties of polydisperse fluids of adhesive colloidal particles. Next we turn to thermodynamic properties.

From \( q_{ij}(r) \), one can calculate, in principle, all thermodynamic quantities. The equation of state (EOS) can be derived, for instance, following the compressibility route, which provides two general relations in terms of Baxter functions, i.e.,

\[
\frac{\partial \beta P}{\partial \rho_i} \bigg|_{T, \rho_i} = a_i - 2\pi \sum_m \rho_i a_i q_{im}(0),
\]

\[
\frac{\partial \beta P}{\partial \rho} \bigg|_{T, \mathbf{x}} = \sum_j x_j \left( \frac{\partial \beta P}{\partial \rho_j} \right) \bigg|_{T, \rho_i} = \sum_j x_j a_i^2.
\]

Here, the pressure is regarded as a function of \((T, \rho_1, \ldots, \rho_p)\) in equation (10), and of \((T, \rho, \mathbf{x})\) in equation (11), where \( \mathbf{x} = (x_1, \ldots, x_{p-1}) \) represents the molar composition.

To obtain the compressibility pressure, one could integrate \((\partial \beta P/\partial \rho)_{T, \mathbf{x}}\), as given by of equation (11), with respect to \( \rho_j \) at fixed composition \( \mathbf{x} \). Unfortunately, this procedure is valid only if the differential \( \sum_j (\partial \beta P/\partial \rho_j) d\rho_j \), constructed with the partial derivatives given by equation (10), is exact, since \( P \) must be a state function. This requires that the Euler reciprocity relation, i.e.

\[
\frac{\partial}{\partial \rho_j} \left( \frac{\partial \beta P}{\partial \rho_j} \right) = \frac{\partial}{\partial \rho_i} \left( \frac{\partial \beta P}{\partial \rho_i} \right),
\]

is satisfied for any pair \( i \) and \( j \). This symmetry condition, obeyed by any exact theory, may break down for an approximate closure. In this case, no compressibility EOS can exist within that approximate theory.
We have demonstrated that, although a MSA compressibility EOS is known for pure SHS2 fluids (Mier-y-Teran et al., 1989), its extension to mixtures is not possible, since the condition (12) is violated by the SHS2-MSA solution (Gazzillo & Giacometti, 2002b). This inconsistency is due to the MSA closure, which is responsible for the density-independence of the coefficients $K_i^{SHS2}$\textsuperscript{--MSA}. More generally, we suspect that no compressibility EOS can exist for any solution $q_{ij}(r)$ of the kind given by equation (3) as long as the $K_i$'s are density-independent. To overcome such a deficiency, one should resort to density-dependent closures. A more detailed discussion, as well as an illustrative counterexample, can be found in (Gazzillo & Giacometti, 2002b).

On the other hand, there is another inconsistency, independent of the particular closure chosen to solve the OZ equations. It is easy to see that the exact second virial coefficient of our starting HS-Yukawa mixture,

$$B_{2}^{\text{HSY}} = 2\pi \sum_{i<j} \chi_{ij} \left\{ \frac{1}{3} \sigma_{ij}^{3} - \int_{0}^{\infty} \frac{d r}{\sigma_{ij}} \left[ \exp \left( \frac{z \beta \sigma_{ij} e^{-\left((r-\sigma_{ij})/r \right)}}{r} \right) - 1 \right] \right\},$$

is divergent in the $z \to \infty$ limit, and thus no EOS can exist. Unfortunately, this drawback is hidden in the MSA, where the integrand function, $\exp \left[ \frac{-\beta \phi_{ij}(r)}{r} \right] - 1$, is linearized, with the misleading consequence that $B_{2}^{\text{HSY-MSA}}$ remains finite in the sticky limit. We stress that the divergence of the exact $B_{2}^{\text{SHS2}}(\neq B_{2}^{\text{HSY-MSA}})$ means that the SHS2 model itself is ill-defined. Yet all previous results for the structure factor are still valid provided that an appropriate interpretation in terms of a new model is devised, as we shall see next.

4. The SHS3 model

As the simplest correct alternative to SHS2, we add to the HS potential the tail

$$\phi_{ij}^{Y3}(r) = -k_{B} T \ln \left[ 1 + z \beta \sigma_{ij} e^{-\left(r-\sigma_{ij} / r \right)} \right], \quad r \geq \sigma_{ij}, \quad (13)$$

in order to ensure that the second virial coefficient of the starting HS-Yukawa mixture, $B_{2}^{\text{HSY3}}$, tends, in the sticky limit, to the finite value:

$$B_{2}^{\text{HS3}} = B_{2}^{\text{HS}} - \frac{6}{6} \langle G \rangle \left( \sigma G \right) \frac{1}{\tau}, \quad (14)$$

where $\langle \sigma G \rangle \equiv \sum_{i} \chi_{i} \sigma_{i} G_{i}$. It is worth noting that this $B_{2}$-expression, exact for SHS3, is formally identical with $B_{2}^{\text{SHS2-MSA}}$, which is only approximate for SHS2.

Moreover, we replace the MSA closure, $c_{ij}^{\text{MSA}}(r) = -\beta \phi_{ij}(r)$ for $r \geq \sigma_{ij}$, with a modified mean spherical approximation (mMSA),

$$c_{ij}^{\text{mMSA}}(r) = f_{ij}(r), \quad r \geq \sigma_{ij}, \quad (15)$$

When applied to the HSY3 model, the mMSA becomes $c_{ij}^{\text{SY3-mMSA}}(r) = \beta \sigma_{ij} e^{-\left(r-\sigma_{ij} / r \right)}$ (outside the core), which coincides with the usual Yukawa closure. The solution $q_{ij}^{\text{SY3-mMSA}}(r)$ is thus formally identical to $q_{ij}^{\text{HSY-MSA}}(r)$, and in the sticky limit one obtains $q_{ij}^{\text{SY3-mMSA}}(r) = q_{ij}^{\text{HS2-MSA}}(r)$. The essential difference is that $q_{ij}^{\text{HS3-mMSA}}(r)$ now refers to a well-defined model. After this re-interpretation in terms of SHS3, all results previously found with SHS2, about structure and SAS, still apply.

Clearly, the impossibility of deriving a compressibility EOS, when $K_i$ is density-independent, remains true also for the SHS3-mMSA solution. However, we now know that this is certainly due to the closure, since the SHS3 model is well-defined. Future work will be necessary to improve in this direction.

5. Conclusion

In this manuscript we have presented, within a unified viewpoint, a simple SHS2 model for analyzing fluids of particles having two basic ingredients: an attractive short-ranged potential in addition to the hard-sphere repulsion, and a non-negligible polydispersity. We have discussed how this model can be solved exactly within the MSA closure, why it is interesting from a theoretical point of view, and to what extent it is expected to be useful in the analysis of SAS data on sterically stabilized colloidal fluids. On the other hand, a careful analysis of its thermodynamics indicates that the SHS2 potential is not well-defined. We have argued that the physical origin of this inconsistency originates from the particular sticky limit taken in the potential. Finally, we have indicated how one can resolve this difficulties in terms of a modified potential, SHS3, and how one can re-obtain the previous results about the structure factor in terms of a new closure (mMSA).

Although our findings are still far from being definitive, they provide a first step toward a useful tool which can be used in the best fit analysis of SAS data.

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