

Corresponding-states approach to small-angle scattering from polydisperse ionic colloidal fluids

Domenico Gazzillo and Achille Giacometti

INFN Unità di Venezia and Facoltà di Scienze, Università di Venezia, S. Marta DD 2137, I-30123 Venezia, Italy

Flavio Carsughi

INFN Unità di Ancona and Facoltà di Agraria, Università di Ancona, Via Brezze Bianche, I-60131 Ancona, Italy

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Approximate scattering functions for polydisperse ionic colloidal fluids are obtained by a corresponding-states approach. This assumes that all pair correlation functions $g_{\alpha\beta}(r)$ of a polydisperse fluid are conformal to those of an appropriate monodisperse binary fluid (reference system) and can be generated from them by scaling transformations. The correspondence law extends to ionic fluids a scaling approximation (SA) successfully proposed for nonionic colloids in a recent paper. For the primitive model of charged hard spheres in a continuum solvent, the partial structure factors of the monodisperse binary reference system are evaluated by solving the Ornstein-Zernike (OZ) integral equations coupled with an approximate closure. The SA is first tested within the mean spherical approximation (MSA) closure, which allows analytical solutions. The results are found in good overall agreement with exact MSA predictions up to relevant polydispersity. The SA is shown to be an improvement over the “decoupling approximation” extended to the ionic case. The simplicity of the SA scheme allows its application also when the OZ equations can be solved only numerically. An example is then given by using the hypernetted chain closure. Shortcomings of the SA approach, its possible use in the analysis of experimental scattering data and other related points are also briefly addressed.

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I. INTRODUCTION

Colloidal suspensions of charged particles represent a special class of ionic fluids [1–3]. Unlike solutions of simple electrolytes such as NaCl, charged colloidal suspensions are highly asymmetric mixtures, containing both macroions and microions with large size and charge differences. Moreover, macroions often exhibit “polydispersity,” which means that particles of a same chemical species are not necessarily identical, because their size, charge or other properties may be spread over a large spectrum of values (chemical species whose particles are all identical are then referred as “monodisperse”). The presence of only one polydisperse macroion species is sufficient to make the colloidal suspension a mixture with a very large number p of components. The peculiar features of this “colloidal regime,” namely, asymmetry and polydispersity, give rise to a variety of phenomena concerning microscopic ordering, phase behavior, diffusion, and so on.

Experimental information on the structure of such fluids can be obtained from small-angle scattering (SAS) techniques, by using light, neutrons or x rays. However, when a significant degree of polydispersity is present in the sample, the interpretation of experimental data for scattering intensity is hardly a simple task. In fact, polydispersity and large size-charge differences represent a serious challenge to the available theoretical tools. Monte Carlo or molecular dynamics simulations for polydisperse colloidal fluids involve very large numbers of particles. Moreover, large size asymmetries at high densities may cause ergodicity problems. On the other hand, integral equations (IEs) of the liquid state theory are analytically solvable only under special conditions, whereas their numerical solution for mixtures with large

numbers p of components, such as the polydisperse ones, would require large systems of nonlinear equations. As a consequence, apart from very few peculiar cases [4], IE numerical studies on multicomponent fluids are usually restricted to $p \ll 10$. Finally, under the highly demanding conditions of colloidal suspensions nonconvergence problems of the algorithms may often arise.

The present paper will focus on the effects of polydispersity in SAS from ionic colloidal mixtures, in the framework of IE theories based upon the Ornstein-Zernike (OZ) equations with approximate closures. Our study refers to the simplest polydisperse case with only two ionic species: monodisperse microions and macroions with both size and charge polydispersity. We shall refer to this system as *polydisperse binary* (two-species) ionic mixture.

To overcome the impossibility of investigating polydisperse systems when IEs have to be solved numerically, one has to reduce the number of components and replace the study of a polydisperse fluid with that of a nearly equivalent but much simpler system. One possibility, not adopted in this paper, is to neglect microions altogether and approximate the fluid as a system of macroions interacting through a repulsive screened Coulomb potential, which implicitly takes into account the contribution of the neglected particles [3]. A further refinement of this viewpoint [3,5] is to build up an equivalent *effective mixture* with $p' \ll p$ new components, whose molar fractions and diameters are determined by replacing a continuous distribution of macroion sizes with an appropriate p' -component histogram. Usually, $p' = 3$ is already sufficient and therefore the problem is reduced to get a numerical solution of IEs for a three-component macroion mixture. This procedure could be easily extended to include monodisperse microions and its counterpart would involve a

four-component mixture (three for the macroions plus one for the microions). This method can be expected to be quite accurate, but it would demand a sizeable amount of numerical work.

In this paper we present an even simpler approach, which requires the solution of only two-component IEs. We shall show that the problem of a polydisperse binary ionic mixture can be reduced to the study of a *monodisperse binary* ionic mixture, with microions and all identical macroions. The solution for such a reference system is the “starting” point for several approximations of increasing accuracy. Our main purpose is to show that, at the end of this hierarchy, accurate approximate scattering functions for a polydisperse binary mixture can be easily calculated with moderate numerical work upon using a corresponding states theory. Our method hinges on a *conformality* [6] argument, which assumes that all pair correlation functions of the polydisperse fluid have essentially the same “shape” of their monodisperse binary counterparts and can be generated from them by means of simple scaling transformations. This correspondence law is the extension to ionic mixtures of a scaling approximation (SA) successfully proposed for nonionic colloids in a recent paper [7]. This is a nontrivial extension, since the good performance of the SA for the *short-range* potentials of non-ionic colloidal fluids examined in Ref. [7] (uncharged hard sphere and Lennard-Jones interactions) does not automatically ensure the same success in the presence of *long-range* Coulomb attractions and repulsions.

To properly treat both macroions and microions on the same footing, the colloidal suspension will be described by the primitive model (PM) of electrolyte solutions, which depicts all ions as charged hard spheres embedded in a dielectric continuum representing the solvent. The new SA will be tested, for the PM, against results from an analytic treatment of polydispersity, which is exact within the mean spherical approximation (MSA) closure for the OZ integral equations. In the PM-MSA case, the OZ equations were solved analytically many years ago [8–11], and, more recently, a closed analytical formula was obtained for the scattering intensity from charged hard sphere fluids with any arbitrary number of components [12]. An essential feature of the SA is that, because of its simplicity, this scheme can be applied equally well to combinations of potential models and closures for which only a numerical solution of IEs is possible. It is therefore possible for instance, as we shall explicitly show, to couple the SA with the hypernetted chain (HNC) closure, which is more accurate than the MSA one for ionic fluids. In these cases the SA becomes a valuable new tool to predict properties of polydisperse colloidal suspensions in a very simple way.

The paper is organized as follows. In the next section the basic formalism of the small angle scattering and integral equation theory is briefly recalled along with the primitive model for polydisperse ionic fluid in Sec. III. In Sec. IV our corresponding states treatment of scattering functions is presented in detail, together with two simpler approximations. The exact MSA analytical expression for the scattering intensity from charged hard spheres is also reviewed and some of its predictions for polydisperse fluids will be reported. In Sec. V numerical results from the proposed approximations are compared in detail within the MSA. The performance of

the SA with the HNC closure will then be addressed and few remarks will be included in the conclusive Sec. VI.

II. SMALL ANGLE SCATTERING AND INTEGRAL EQUATION THEORY

A. Scattering intensity and structure factors

An ionic colloidal solution is formed by macroions and microions suspended in a homogeneous solvent. Usually, this suspending fluid is formed by very small particles (with respect to the macroions) and is then modelled as a continuum, characterized by a given dielectric constant and an uniform density of scattering matter.

According to the scattering theory, the intensity of the scattered radiation (light, neutrons, or x rays) is proportional to the ensemble or time average of $|\tilde{n}(\mathbf{q})|^2$ over all possible equilibrium configurations of the sample particles. Here \mathbf{q} is the exchanged wave vector and $\tilde{n}(\mathbf{q})$ is the three-dimensional Fourier transform of $n(\mathbf{r})$, a quantity related to the density of scattering matter at the position \mathbf{r} inside the sample. For neutrons $n(\mathbf{r})$ is the scattering length density $n(\mathbf{r}) = \sum_k b_k \delta(\mathbf{r} - \mathbf{r}_k)$, where b_k is the scattering length of the k th nucleus located at \mathbf{r}_k and δ denotes the Dirac delta function. For x rays $n(\mathbf{r})$ coincides with the electron density, whereas for light it becomes the refractive index. In the continuum solvent, $n(\mathbf{r})$ has an uniform value n_0 .

In addition to the continuum solvent hypothesis, we assume that inside each ion (macroion or microion, indifferently) the scattering matter has a well defined boundary, i.e., there is a *scattering core* with a well-defined *scattering volume*, not necessarily coincident with the particle volume. While the former depends on the particle-radiation interaction, the latter is determined by the interparticle repulsions and is well-defined only in the presence of *hard* body repulsions. The definition of a volume for particles with soft repulsions (e.g., Lennard-Jones particles) requires in fact some arbitrary and nonuniversal convention.

In the case of suspended particles with spherically symmetric interactions (homogeneous and isotropic fluid) and spherical homogeneous scattering cores, the SAS theory yields the following expression for the total scattering intensity $I(q)$ of a p -component solution in a volume V [3]:

$$R(q) \equiv I(q)/V = \rho \sum_{\alpha=1}^p \sum_{\beta=1}^p \sqrt{x_{\alpha} x_{\beta}} F_{\alpha}(q) F_{\beta}(q) S_{\alpha\beta}(q), \quad (1)$$

as a function of the magnitude of the exchanged wave vector $q \equiv (4\pi/\lambda)\sin(\theta/2)$, with λ being the wavelength of the incident radiation and θ the scattering angle. The Rayleigh ratio $R(q)$ is the total scattering intensity per unit volume [also called the differential scattering cross section and often denoted by $(d\Sigma/d\Omega)(q)$]. In Eq. (1) ρ is the total number density, while x_{ν} and $F_{\nu}(q)$ are the molar fraction and the form factor of species ν , respectively. $F_{\nu}(q)$ is related to the distribution $n(\mathbf{r})$ of scattering matter inside particles of species ν and we can express it as

$$F_{\nu}(q) = V_{\nu}^{\text{scatt}} (n_{\nu} - n_0) \frac{3j_1(q\sigma_{\nu}^{\text{scatt}}/2)}{q\sigma_{\nu}^{\text{scatt}}/2}, \quad (2)$$

$\sigma_\nu^{\text{scatt}}$ being the diameter of the scattering core, $V_\nu^{\text{scatt}} = (\pi/6)(\sigma_\nu^{\text{scatt}})^3$ its volume, n_ν the uniform scattering density of species ν , and the difference $n_\nu - n_0$ its ‘‘contrast,’’ while $j_1(x) = (\sin x - x \cos x)/x^2$ is the first-order spherical Bessel function. Finally, the functions $S_{\alpha\beta}(q)$ are the Ashcroft-Langreth partial structure factors [13]

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + \rho \sqrt{x_\alpha x_\beta} \tilde{h}_{\alpha\beta}(q), \quad (3)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta and $\tilde{h}_{\alpha\beta}(q)$ is the three-dimensional Fourier transform of the total correlation function $h_{\alpha\beta}(r) \equiv g_{\alpha\beta}(r) - 1$. Here, $g_{\alpha\beta}(r)$ is the radial distribution function (RDF) between two particles of species α and β at a distance r .

In addition to the scattering intensity, it is then convenient to define a ‘‘measurable’’ structure factor [3] as

$$S_M(q) = \sum_{\alpha=1}^p \sum_{\beta=1}^p \sqrt{x_\alpha x_\beta} w_\alpha(q) w_\beta(q) S_{\alpha\beta}(q), \quad (4)$$

with weights

$$w_\nu(q) = \frac{F_\nu(q)}{\sqrt{\langle F^2(q) \rangle}}, \quad (5)$$

the brackets meaning $\langle F^2(q) \rangle \equiv \sum_\alpha x_\alpha F_\alpha^2(q)$. The relationship between $R(q)$ and $S_M(q)$ is

$$R(q) = \rho \langle F^2(q) \rangle S_M(q). \quad (6)$$

From the theoretical point of view, we will obtain the partial structure factors $S_{\alpha\beta}(q)$ by solving IEs for the $h_{\alpha\beta}(r)$.

B. Integral equations

The OZ integral equations of the liquid state theory for p -component mixtures with spherically symmetric interparticle potentials are [14,15]

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\nu=1}^p \rho_\nu \int d\mathbf{r}' c_{\alpha\nu}(r') h_{\nu\beta}(|\mathbf{r} - \mathbf{r}'|), \quad (7)$$

where the $c_{\alpha\beta}(r)$ are the direct correlation functions and $\rho_\nu \equiv x_\nu \rho$ is the number density of species ν . These equations can be solved only in combination with a further relationship between $h_{\alpha\beta}(r)$ and $c_{\alpha\beta}(r)$. The formally exact expression of this ‘‘closure’’ is

$$c_{\alpha\beta}(r) = \exp[-(k_B T)^{-1} u_{\alpha\beta}(r) + \gamma_{\alpha\beta}(r) + B_{\alpha\beta}(r)] - 1 - \gamma_{\alpha\beta}(r), \quad (8)$$

where $u_{\alpha\beta}(r)$ is the interparticle potential, k_B is Boltzmann’s constant, T the absolute temperature, $\gamma_{\alpha\beta}(r) \equiv h_{\alpha\beta}(r) - c_{\alpha\beta}(r)$ and the ‘‘bridge’’ functions $B_{\alpha\beta}(r)$ are functionals of $h_{\alpha\beta}(r)$ and higher order correlation functions. In practice, however, the exact $B_{\alpha\beta}(r)$ cannot be calculated, and several approximations proposed for these functions define a corresponding series of approximate closures [14,15].

The possibility of solving analytically the OZ equations depends on both the potential model $u_{\alpha\beta}(r)$ and the chosen

closure. Once that the IEs have been analytically or numerically solved, the partial structure factors $S_{\alpha\beta}(q)$ can be obtained from Eq. (3).

III. PRIMITIVE MODEL FOR POLYDISPERSE IONIC FLUIDS

We are interested in studying polydispersity effects by properly considering both macroions and microions on an equal footing. The simplest possibility is the primitive model (PM), well known in the theory of electrolyte solutions. It consists of an electroneutral mixture of p different components, represented by charged hard spheres embedded in a continuum solvent of dielectric constant ϵ . The species α , with diameter σ_α , has molar fraction x_α and electric charge $z_\alpha e$ (e is the proton charge and z_α the valency). The interparticle potential $u_{\alpha\beta}(r)$ is defined by

$$(k_B T)^{-1} u_{\alpha\beta}(r) = \begin{cases} +\infty & \text{for } r < \sigma_{\alpha\beta} \equiv \frac{1}{2}(\sigma_\alpha + \sigma_\beta), \\ z_\alpha z_\beta L_B / r & \text{for } r > \sigma_{\alpha\beta}, \end{cases} \quad (9)$$

where $L_B \equiv e^2 / (\epsilon k_B T)$ is the Bjerrum length. The electroneutrality condition requires that $\langle z \rangle \equiv \sum_{\nu=1}^p x_\nu z_\nu = 0$.

The PM can also be used for polydisperse colloidal suspensions. In a ‘‘discrete representation’’ of polydispersity, a polydisperse two-species fluid is described by a p -component mixture ($p \gg 1$), in which the monodisperse microions (chemical species 1) are the first component, with diameter σ_1 , charge z_1 and molar fraction x_1 , while the remaining $p - 1$ components correspond to different varieties of the single macroion species (chemical species 2). It is often convenient to adopt a ‘‘continuous representation’’ of polydispersity, with $p \rightarrow \infty$ and a continuous spectrum of values for the macroion ‘‘disperse’’ properties (size, charge, etc.). In such a *continuous-mixture* formalism, we assume that macroions have a continuous distribution of diameters σ around an average one, denoted by $\langle \sigma \rangle_2$. For simplicity, we make the further reasonable assumption that the charge polydispersity of macroions is fully correlated to the size polydispersity. This can be easily accomplished [3,4] by choosing the charge (or valency) of each macroion to be proportional to its surface area, i.e.,

$$z_2(\sigma) = z_{\langle \sigma \rangle_2} \left(\frac{\sigma}{\langle \sigma \rangle_2} \right)^2, \quad (10)$$

where $z_{\langle \sigma \rangle_2}$ is the valency of the macroions having diameter $\langle \sigma \rangle_2$. Both size and charge distributions of the macroions are therefore governed by a single independent variable, namely, the macroion diameter. The polydispersity of the macroions can then be expressed by a *molar fraction density function*, $p_2(\sigma) = x_2^{\text{tot}} f_2(\sigma)$, where $f_2(\sigma)$ is an appropriate distribution normalized to unit, while $x_2^{\text{tot}} = 1 - x_1$ is the ‘‘amplitude’’ of $p_2(\sigma)$.

In the passage from a discrete to a continuous representation of polydispersity, the molar fractions x_ν are replaced by $dx = p_2(\sigma) d\sigma$, the fraction of macroions having diameter in the range $(\sigma, \sigma + d\sigma)$, and the sums $\sum_\nu x_\nu \cdots$ become inte-

grals $\int d\sigma p_2(\sigma) \dots$. The average of a quantity Y over the macroion distribution is therefore written as

$$\begin{aligned} \langle Y \rangle_2 &\equiv \frac{1}{x_2^{\text{tot}}} \sum_{\nu \in \mathcal{E}_2} x_\nu Y_{\nu \rightarrow} \frac{1}{x_2^{\text{tot}}} \int d\sigma p_2(\sigma) Y(\sigma) \\ &= \int d\sigma f_2(\sigma) Y(\sigma), \end{aligned} \quad (11)$$

where \mathcal{E}_2 denotes the set of indices corresponding to the macroion components. The average of Y over the whole set of suspended particles is then: $\langle Y \rangle \equiv \sum_{\nu=1}^p x_\nu Y_{\nu \rightarrow} = x_1 Y_1 + x_2^{\text{tot}} \langle Y \rangle_2$.

For $f_2(\sigma) \equiv f(\sigma; \langle \sigma \rangle_2, s)$, we use the Schulz or gamma distribution

$$f(\sigma; \langle \sigma \rangle, s) = \frac{b^a}{\Gamma(a)} \sigma^{a-1} e^{-b\sigma} \quad (a > 1), \quad (12)$$

where Γ is the gamma function [16], while $a = 1/s^2$, $b = a/\langle \sigma \rangle$ are related to the mean value $\langle \sigma \rangle$ and the relative standard deviation $s \equiv \sqrt{\langle \sigma^2 \rangle - \langle \sigma \rangle^2} / \langle \sigma \rangle$, which measures the degree of polydispersity ($0 < s < 1$). The choice of the Schulz distribution is a popular one in colloidal theory because of its mathematical properties. For $s \rightarrow 0$, it reduces to a Dirac delta function centered at $\langle \sigma \rangle$ (monodisperse limit). For small values of s , $f(\sigma)$ is similar to a Gaussian distribution, while for larger polydispersity it becomes rather skewed [17]. Unlike the Gaussian function, the Schulz distribution is defined for positive values of σ only. Moreover, this distribution allows a straightforward analytical evaluation of simple averages of the kind displayed in Eq. (11). In particular, the first three moments of the distribution $f_2(\sigma)$ are $\langle \sigma \rangle_2, \langle \sigma^2 \rangle_2 = (1 + s^2) \langle \sigma \rangle_2^2$, and $\langle \sigma^3 \rangle_2 = (1 + s^2)(1 + 2s^2) \langle \sigma \rangle_2^3$, while use of Eq. (10) yields $\langle z \rangle_2 = z_{(\sigma)_2} (1 + s^2)$. These analytical results can be conveniently inserted into the expressions for the electroneutrality and the packing fraction η , i.e.,

$$x_1 z_1 + x_2^{\text{tot}} \langle z \rangle_2 = 0, \quad (13)$$

$$\eta = (\pi/6) \rho (x_1 \sigma_1^3 + x_2^{\text{tot}} \langle \sigma^3 \rangle_2). \quad (14)$$

The microion packing fraction is $\eta_1 \equiv (\pi/6) \rho_1 \sigma_1^3$, while its macroion counterpart is $\eta_2 \equiv (\pi/6) \rho_2^{\text{tot}} \langle \sigma^3 \rangle_2$, with $\rho_2^{\text{tot}} = \rho x_2^{\text{tot}}$. From Eq. (13) and $x_2^{\text{tot}} = 1 - x_1$, one then gets

$$x_1 = \left(1 - \frac{z_1}{\langle z \rangle_2} \right)^{-1} = \left[1 - \frac{z_1}{z_{(\sigma)_2} (1 + s^2)} \right]^{-1}, \quad (15)$$

which shows that x_1 is fully determined by z_1 and $\langle z \rangle_2$ (or equivalently $z_1, z_{(\sigma)_2}$, and s).

A final remark is in order. In evaluating the averages of more complex quantities any analytical integration becomes a formidable or impossible task and numerical integration brings back to discrete expressions. For this reason, in the following we shall continue to employ the discrete notation

under the implicit convention that $x_\alpha = x_2^{\text{tot}} f_2(\sigma_\alpha) \Delta \sigma$ for the macroion molar fraction ($\Delta \sigma$ is the grid size in the numerical integration).

IV. APPROXIMATIONS AND EXACT EXPRESSIONS

A. Corresponding states and scaling approximation

Interparticle potentials are said to be conformal when they have the same ‘‘shape,’’ and systems with conformal interactions are called conformal substances [6]. Analytically, the conformality of a set of potentials means that all their expressions can be generated from a single functional form by appropriate scaling of distances and potential parameters (particle sizes, energies, charges, etc.).

The simplest example refers to pure fluids, when the potential u_α of any species α , in a set of substances, depends on only two parameters and can be written as $u_\alpha(r) = \varepsilon_\alpha \hat{u}(r/\sigma_\alpha)$, where σ_α and ε_α are a characteristic length and energy respectively, while \hat{u} is a dimensionless function of the dimensionless ratio r/σ_α . The form of $u_\alpha(r)$ implies that all properties of that set of conformal fluids can be written in terms of dimensionless reduced variables, and it leads to the ‘‘corresponding states principle’’ commonly found in textbooks [6]: all conformal pure fluids at the same dimensionless density and temperature have identical dimensionless pressure. The RDF of a pure fluid of species α in a group of conformal substances can be written as

$$g_\alpha(r; \rho, T; \sigma_\alpha, \varepsilon_\alpha) = \hat{g} \left(\frac{r}{\sigma_\alpha}; \rho \sigma_\alpha^3, \frac{k_B T}{\varepsilon_\alpha} \right), \quad (16)$$

where \hat{g} is a universal function for such a group. If one among these fluids is arbitrarily chosen as reference system and its properties are labeled with the subscript 0, then its potential is $u_0(r) = \varepsilon_0 \hat{u}(r/\sigma_0)$ and its RDF is given by $g_0(r; \rho, T; \sigma_0, \varepsilon_0) = \hat{g}(r/\sigma_0; \rho \sigma_0^3, k_B T/\varepsilon_0)$. From Eq. (16) one then gets

$$g_\alpha(r; \rho, T; \sigma_\alpha, \varepsilon_\alpha) = g_0(\lambda_\alpha r; \rho/\lambda_\alpha^3, T/\xi_\alpha; \sigma_0, \varepsilon_0), \quad (17)$$

where we have introduced dimensionless scaling factors $\lambda_\alpha \equiv \sigma_0/\sigma_\alpha$ and $\xi_\alpha \equiv \varepsilon_\alpha/\varepsilon_0$. This result is tantamount to saying that if one knows the RDF of a reference fluid characterized by potential parameters σ_0, ε_0 , then it is possible to derive the RDF of any conformal fluid of species α , with potential parameters $\sigma_\alpha, \varepsilon_\alpha$. The value of g_α at r in a thermodynamic state (ρ, T) is equal to the value of g_0 at the *scaled* distance $\lambda_\alpha r$, in the *corresponding state* $(\rho/\lambda_\alpha^3, T/\xi_\alpha)$ with *scaled* density and temperature. For instance, if $\sigma_\alpha > \sigma_0$ and $\varepsilon_\alpha > \varepsilon_0$, then the corresponding state has a greater density and a lower temperature. Using the definition of the potential of mean force, $W \equiv -k_B T \ln g$, Eq. (17) could also be cast in the form

$$W_\alpha(r; \rho, T; \sigma_\alpha, \varepsilon_\alpha) = W_0(\lambda_\alpha r; \rho/\lambda_\alpha^3, T/\xi_\alpha; \sigma_0, \varepsilon_0). \quad (18)$$

For pure fluids then conformality of the potentials implies conformality of the potentials of mean force and hence of the RDFs. The potential of mean force between two particles is the sum of the direct pair potential plus an indirect interac-

tion, due to all the remaining fluid particles and averaged over all their possible equilibrium configurations. Finally, a similar property holds true for the structure factors as well

$$S_\alpha(q; \rho, T; \sigma_\alpha, \varepsilon_\alpha) = S_0(\lambda_\alpha^{-1} q; \rho/\lambda_\alpha^3, T/\xi_\alpha; \sigma_0, \varepsilon_0). \quad (19)$$

The scaling correspondence in q space is that the value of S_α at q is equal to the value of S_0 at $\lambda_\alpha^{-1} q$ (in a different thermodynamic state).

On the other hand, for mixtures conformality of potentials does not necessarily ensure conformality of RDFs in the same simple way. Nevertheless corresponding-states arguments have often been exploited in the liquid state theory, to postulate approximate conformality relations between mixture and pure RDFs [18,19]. Only recently, however, this kind of approach has been applied to polydisperse fluids and a scaling approximation (SA) has been proposed for non-ionic colloidal suspensions [7]. In the SA theory is possible to obtain rather accurate structure factors for a ‘‘polydisperse one-species’’ fluid of uncharged spherical particles, by first evaluating the RDF g_0 of an appropriate ‘‘monodisperse one-species’’ (pure) reference fluid and then generating all the $p(p+1)/2$ different RDFs of the mixture by taking the values of the single g_0 at suitably scaled distances. The present work is aimed at extending this SA scheme to polydisperse ionic colloidal suspensions. It employs two-species fluids with both positive and negative ions, in order to satisfy the electroneutrality condition. As a reference system for the ‘‘polydisperse binary’’ fluid a suitable ‘‘monodisperse binary’’ (M2) mixture is required, where species 1 coincides with the microions and has their density, size, and charge $(\rho_1^{\text{bin}}, \sigma_1^{\text{bin}}, z_1^{\text{bin}}) = (\rho_1, \sigma_1, z_1)$, while the distribution of macroions is replaced by a single ‘‘average’’ component (species 2) with parameters $(\rho_2^{\text{bin}}, \sigma_2^{\text{bin}}, z_2^{\text{bin}})$. The choice of this reference fluid will be discussed later. Note that the set of parameters $(\rho_1^{\text{bin}}, \rho_2^{\text{bin}}, T; \sigma_1^{\text{bin}}, z_1^{\text{bin}}, \sigma_2^{\text{bin}}, z_2^{\text{bin}})$ can be reduced to $(\rho^{\text{bin}}, T; \sigma_1, z_1, \sigma_2^{\text{bin}}, z_2^{\text{bin}})$, since x_1^{bin} is automatically fixed by the charge ratio through the electroneutrality condition as $x_1^{\text{bin}} = (1 - z_1/z_2^{\text{bin}})^{-1}$.

Our approximation consists in assuming that all RDFs of the polydisperse ionic mixture are conformal with the RDFs of the monodisperse binary fluid, which means that

$$g_{\alpha\beta}(r; \rho, \mathbf{x}, T; \{\sigma_{\gamma\delta}\}, \{z_{\gamma\delta}\}) \simeq g_{m_\alpha m_\beta}^{\text{bin}}(\lambda_{\alpha\beta} r; \rho, T; \sigma_1, z_1, \sigma_2^{\text{bin}}, z_2^{\text{bin}}), \quad (20)$$

where \mathbf{x} , $\{\sigma_{\gamma\delta}\}, \{z_{\gamma\delta}\}$ represent the complete set of molar fractions and potential parameters, $\rho^{\text{bin}} = \rho$, $\lambda_{\alpha\beta} \equiv \sigma_{m_\alpha m_\beta}^{\text{bin}} / \sigma_{\alpha\beta}$, with $\sigma_{m_\alpha m_\beta}^{\text{bin}} \equiv (\sigma_{m_\alpha}^{\text{bin}} + \sigma_{m_\beta}^{\text{bin}}) / 2$, $\alpha, \beta = 1, \dots, p$, and

$$m_\nu = \begin{cases} 1 & \text{when } \nu = 1, \\ 2 & \text{when } \nu \in \mathcal{E}_2 \end{cases} \quad (21)$$

[\mathcal{E}_2 was already defined in Eq. (11)]. The correspondence law (20) provides the recipe for generating all the $p(p+1)/2$ independent RDFs of the polydisperse fluid starting from the three RDFs of the monodisperse binary mixture. It explicitly reads $g_{11}(r) \simeq g_{11}^{\text{bin}}(r)$ for microion-microion pairs,

$g_{1\beta}(r) \simeq g_{12}^{\text{bin}}(\sigma_{12}^{\text{bin}} r / \sigma_{1\beta})$, $\beta \in \mathcal{E}_2$ for microions-macroions, $g_{\alpha\beta}(r) \simeq g_{22}^{\text{bin}}(\sigma_{22}^{\text{bin}} r / \sigma_{\alpha\beta})$, $\alpha, \beta \in \mathcal{E}_2$ for macroions-macroions.

Our choice of $\lambda_{\alpha\beta}$ for scaling the distances implies that, when $r < \sigma_{\alpha\beta}$, one gets $r'_{\alpha\beta} \equiv \lambda_{\alpha\beta} r < \sigma_{m_\alpha m_\beta}^{\text{bin}}$ and consequently ensures the correct hard core conditions, $g_{\alpha\beta}(r) = 0$ for $r < \sigma_{\alpha\beta}$. The excluded volume effects, very important for the structure of condensed phases, are thus properly taken into account by the SA.

Since the Fourier transform of $h_{m_\alpha m_\beta}^{\text{bin}}(\lambda_{\alpha\beta} r)$ is $\lambda_{\alpha\beta}^{-3} \tilde{h}_{m_\alpha m_\beta}^{\text{bin}}(\lambda_{\alpha\beta}^{-1} q)$, it is clear that $S_{m_\alpha m_\beta}^{\text{bin}} = \delta_{m_\alpha m_\beta} + \rho^{\text{bin}} \sqrt{x_{m_\alpha}^{\text{bin}} x_{m_\beta}^{\text{bin}}} \tilde{h}_{m_\alpha m_\beta}^{\text{bin}}$. Under the assumption that $\rho^{\text{bin}} = \rho$ and upon using Eqs. (3) and (20) one then obtains

$$S_{\alpha\beta}(q)^{\text{SA}} = \delta_{\alpha\beta} + \sqrt{\frac{x_\alpha x_\beta}{x_{m_\alpha}^{\text{bin}} x_{m_\beta}^{\text{bin}}}} \lambda_{\alpha\beta}^{-3} [S_{m_\alpha m_\beta}^{\text{bin}}(\lambda_{\alpha\beta}^{-1} q) - \delta_{m_\alpha m_\beta}], \quad (22)$$

where $S_{m_\alpha m_\beta}^{\text{bin}}(q)$ is a shorthand notation for $S_{m_\alpha m_\beta}^{\text{bin}}(q; \rho, T; \sigma_1, z_1, \sigma_2^{\text{bin}}, z_2^{\text{bin}})$, which will be exploited hereafter unless otherwise specified. Equation (4), within this approximation, takes the form

$$\begin{aligned} S_M(q)^{\text{SA}} &= 1 + x_1 w_1^2(q) [S_{11}^{\text{bin}}(q) - 1] \\ &+ x_2^{\text{tot}} \sum_{\alpha \in \mathcal{E}_2} \sum_{\beta \in \mathcal{E}_2} \frac{x_\alpha}{x_2^{\text{tot}}} \frac{x_\beta}{x_2^{\text{tot}}} w_\alpha(q) w_\beta(q) \\ &\times \left(\frac{\sigma_{\alpha\beta}}{\sigma_2^{\text{bin}}} \right)^3 \left[S_{22}^{\text{bin}} \left(\frac{\sigma_{\alpha\beta}}{\sigma_2^{\text{bin}}} q \right) - 1 \right] \\ &+ 2 \sqrt{x_1 x_2^{\text{tot}}} w_1(q) \sum_{\beta \in \mathcal{E}_2} \frac{x_\beta}{x_2^{\text{tot}}} w_\beta(q) \\ &\times \left(\frac{\sigma_{1\beta}}{\sigma_{12}^{\text{bin}}} \right)^3 S_{12}^{\text{bin}} \left(\frac{\sigma_{1\beta}}{\sigma_{12}^{\text{bin}}} q \right). \end{aligned} \quad (23)$$

Equation (23) is the basic result of the paper. It provides an expression for the measurable structure factor of the original polydisperse binary mixture, once that the partial structure factors of the reference monodisperse binary mixture are known. In the limit of vanishing charges and no microions it reduces to the one found in Ref. [7]. The scattering intensity per unit volume $R(q)^{\text{SA}}$ is then obtained by multiplying $S_M(q)^{\text{SA}}$ by $\rho \langle F^2(q) \rangle$.

B. Choice of the monodisperse binary mixture

As reference system, we select a monodisperse two-component (M2) mixture which mimics the polydisperse p -component fluid. We assume that species 1 coincides with the microions and hence $(\rho_1^{\text{bin}}, \sigma_1^{\text{bin}}, z_1^{\text{bin}}) = (\rho_1, \sigma_1, z_1)$, which implies the equality of the microion packing fraction, i.e., $\eta_1^{\text{bin}} = \eta_1$. Then we replace the polydisperse macroion species, containing $p-1$ components, with a monodisperse

macroion species 2, containing a single ‘‘averaged’’ component. To determine its parameters ($\rho_2^{\text{bin}}, \sigma_2^{\text{bin}}, z_2^{\text{bin}}$), we require that

$$\begin{aligned}\rho_2^{\text{bin}} &= \rho_2^{\text{tot}}, \\ \rho_2^{\text{bin}} (\sigma_2^{\text{bin}})^3 &= \rho_2^{\text{tot}} \langle \sigma^3 \rangle_2, \\ \rho_1 z_1 + \rho_2^{\text{bin}} z_2^{\text{bin}} &= 0.\end{aligned}\quad (24)$$

The first two equations guarantee that the total number of macroions and their packing fraction in the M2 mixture are the same as in the polydisperse fluid ($\eta_2^{\text{bin}} = \eta_2$); the third one is the electroneutrality condition for M2 mixture. Combining Eq. (24) with $\rho_1^{\text{bin}} = \rho_1$, one finds the solution

$$\begin{aligned}\rho^{\text{bin}} &= \rho \quad \text{and} \quad x_1^{\text{bin}} = x_1, \\ \sigma_2^{\text{bin}} &= \langle \sigma \rangle_2^{1/3}, \\ z_2^{\text{bin}} &= \langle z \rangle_2.\end{aligned}\quad (25)$$

In this way, the definition of the set of M2 mixture parameters ($\rho^{\text{bin}}, T; \sigma_1, z_1, \sigma_2^{\text{bin}}, z_2^{\text{bin}}$) is complete.

Choices other than Eq. (25) are clearly possible. We have explicitly worked out few of them and found that they do not significantly alter the final numerical results. Equation (25) has then been privileged on the basis of its simplicity and natural physical interpretation.

In addition to being used as a reference system for SA, the M2 mixture may itself be regarded as the simplest approximation to the polydisperse p -component fluid. The corresponding measurable structure factor would then be

$$\begin{aligned}S_M(q)^{\text{M2}} &= 1 + x_1 w_1^2(q) [S_{11}^{\text{bin}}(q) - 1] + x_2^{\text{tot}} [w_2^{\text{bin}}(q)]^2 \\ &\quad \times [S_{22}^{\text{bin}}(q) - 1] + 2 \sqrt{x_1 x_2^{\text{tot}}} w_1(q) w_2^{\text{bin}}(q) S_{12}^{\text{bin}}(q).\end{aligned}\quad (26)$$

which simply corresponds to approximate the original polydisperse binary mixture with a plain monodisperse binary mixture.

C. Extended decoupling approximation

To emphasize the role played by the scaling of distances in the SA, let us consider the simpler case of no scaling. This can be obtained from the SA expressions by setting $\lambda_{\alpha\beta} = 1$ everywhere. The result corresponds to an approximation which provides an exact evaluation of all form factors of the polydisperse system but assumes that the RDFs can be replaced by a set of only three effective RDFs of a monodisperse binary ionic fluid. Hence, in the previous language we have $g_{11}(r) \approx g_{11}^{\text{bin}}(r)$, $g_{1\beta}(r) \approx g_{12}^{\text{bin}}(r)$, and $g_{\alpha\beta}(r) \approx g_{22}^{\text{bin}}(r)$ for micro-micro, micro-macro, and macro-macro ionic pairs, respectively. Equation (23) simplifies to

$$\begin{aligned}S_M(q)^{\text{EDA}} &= 1 + x_1 w_1^2(q) [S_{11}^{\text{bin}}(q) - 1] + x_2^{\text{tot}} \langle w(q) \rangle_2^2 \\ &\quad \times [S_{22}^{\text{bin}}(q) - 1] + 2 \sqrt{x_1 x_2^{\text{tot}}} w_1(q) \\ &\quad \times \langle w(q) \rangle_2 S_{12}^{\text{bin}}(q).\end{aligned}\quad (27)$$

The superscript EDA means extended decoupling approximation, since this approximation may be reckoned as an ex-

pression to polydisperse ionic colloids of the ‘‘decoupling approximation’’ (DA), proposed by Kotlarchyk and Chen [20] for nonionic fluids and well known to the small angle scattering experimentalists. The EDA may also be regarded as a special limiting case of the binary substitutional model proposed by Nagele *et al.* [21] for a different colloidal model with two polydisperse macroion species and no microions.

D. MSA closure and analytic expressions

The expressions we have previously derived for SA, EDA, and M2 are clearly independent of the approximate ‘‘closure’’ chosen for solving the OZ equations. One then expects that an improvement in the selection of the closure would provide increasingly accurate results for the polydisperse colloidal suspension. In the present paper we shall focus mainly on the MSA closure, to take advantage of its analytical properties. Another example will be considered in Sec. V C.

For the PM, the MSA consists in adding to the exact hard sphere condition $g_{\alpha\beta}(r) = 0$ or $h_{\alpha\beta}(r) = -1$ when $r < \sigma_{\alpha\beta}$, the approximate relationship (closure)

$$c_{\alpha\beta}(r) = -(k_B T)^{-1} u_{\alpha\beta}(r) \quad \text{for } r > \sigma_{\alpha\beta}, \quad (28)$$

which is asymptotically correct for $r \rightarrow \infty$. The advantage of the MSA closure is that the corresponding OZ equations for the PM were solved analytically some times ago [8]. Senatore and Blum [22] employed MSA expressions for the partial structure factors $S_{\alpha\beta}(q)$ to calculate numerically $S_M(q)$ for charged hard spheres with *either* size polydispersity *or* charge polydispersity. More recently, a *closed* MSA formula for $S_M(q)$ by-passing the explicit calculation of the partial structure factors was obtained in Ref. [12]. This was the extension to ionic systems of an analogous expression for polydisperse uncharged hard spheres in the PY approximation [23]. For the sake of completeness, the MSA analytic expression for the scattering intensity is reported in the Appendix where some misprints appearing in Ref. [12] are also corrected. The MSA closure yields analytic expressions for both $S_{m\alpha\beta}^{\text{bin}}(q)$ and $S_M(q)$ depending on a single screening parameter 2Γ , which in turn has to be determined self-consistently.

A well known drawback of the MSA is that, for dilute solutions of highly charged particles, it may predict unphysical negative values for $g_{\alpha\beta}(r)$ near the contact distance $\sigma_{\alpha\beta}$ or in a neighborhood of the first minimum. Some proposal have been advanced to heal this restriction [24–26]. For simplicity, however, the emphasis of the present work will be mainly on concentrated suspensions of weakly charged particles. In this regime the MSA is reasonably accurate, with the Coulomb part of the potential being only a perturbation with respect to the hard sphere one. The above remark is nevertheless by no means a limit to our method which could be easily associated to more accurate closures such as the ‘‘hypernetted chain approximation’’ (HNC), corresponding to take $B_{\alpha\beta}(r) = 0$ in Eq. (8), or the self-consistent mixing scheme (HMSA) proposed by Zerah and Hansen for potentials with attractive terms [14,15]. Clearly, in the HNC or HMSA integral equations the monodisperse binary reference fluid can be treated only numerically. This point will be fur-

ther discussed in Sec. VC where an example of such calculation will be provided for the HNC.

V. NUMERICAL CALCULATIONS

In order to display the behavior of the scattering functions under some typical polydisperse conditions, we numerically reproduced a realistic experimental environment. The microions were given a valency $z_1 = +1$ and a diameter $\sigma_1 = 5 \text{ \AA}$ (solvated counterions), while we used an average macroion size $\langle \sigma \rangle_2 = 100 \text{ \AA}$ with relatively small charges $z_{\langle \sigma \rangle_2}$ in the range -20 to 0 (in e units) to ensure meaningful MSA results as previously discussed. We will increase this value up to $z_{\langle \sigma \rangle_2} = -50$ later on using HNC. The scattering due to the microions is in principle not completely negligible and it might be also characterized by a different contrast with respect to the macroions. Nevertheless both contrasts were here fixed to the same value $\Delta n = 4 \times 10^{10} \text{ cm}^{-2}$, which is typically found in neutron scattering from silica particles suspended in water [27]. In evaluating the form factors we further assumed $\sigma_{\nu}^{\text{scatt}} = \sigma_{\nu}$ for all particles. A room temperature $T = 298 \text{ K}$ and the dielectric constant $\epsilon = 78$ of water result into a value $L_B = 7.189 \text{ \AA}$ for the Bjerrum length. All numerical calculations were performed for packing fractions $\eta = 0.1, 0.3$, and polydispersity $s = 0, 0.1, 0.2$, and 0.3 (the first value corresponding to the monodisperse binary mixture). We note that when $s = 0$, it is necessary to take $|z_2^{\text{bin}}| \lesssim 30$ for $\eta = 0.3$ and $|z_2^{\text{bin}}| \lesssim 10$ for $\eta = 0.1$, to avoid unphysical negative values of the MSA g_{22}^{bin} at contact.

The three Schulz distributions, with polydispersity $s = 0.1, 0.2$, and 0.3 , were discretized with a grid size $\Delta\sigma/\langle \sigma \rangle_2 = 0.02$, and truncated at $\sigma_{\text{cut}}/\langle \sigma \rangle_2 = 1.56, 2.22$, and 2.96 , respectively. These σ_{cut} values correspond to polydisperse mixtures with a number of macroion components equal to 79, 112, and 149, practically intractable with the available algorithms for solving IEs numerically.

A. Polydispersity and charge effects in exact MSA results

Before analyzing the performance of the SA and other approximations, it is useful to recall how size and charges polydispersity affect the measurable scattering structure factor. This is achieved by using the closed analytical expression for $S_M(q)$ which is given in the Appendix which is exact within the MSA.

Figure 1 depicts the effects of polydispersity on the measurable structure factor. $S_M(q)^{\text{MSA}}$ is plotted as a function of the dimensionless variable $q\langle \sigma \rangle_2$ for increasing values of s and fixed $\eta = 0.3$ and $z_{\langle \sigma \rangle_2} = -20$. We note that as s increases at fixed η , ρ decreases. As expected, the effect of increasing polydispersity is threefold: (i) the oscillations on the tail of the curves are greatly reduced as a consequence of the destructive interference stemming from the several length scales involved, (ii) the first peak is lowered, broadened and shifted to smaller q values corresponding to a larger typical distance between macroions-macroions nearest-pairs, and (iii) the $q \rightarrow 0$ limit is increased since highly dispersed particles can be more efficiently packed. All these effects parallel those observed in polydisperse nonionic fluids [7,17] as well as in mixtures constituted of only macroions interacting

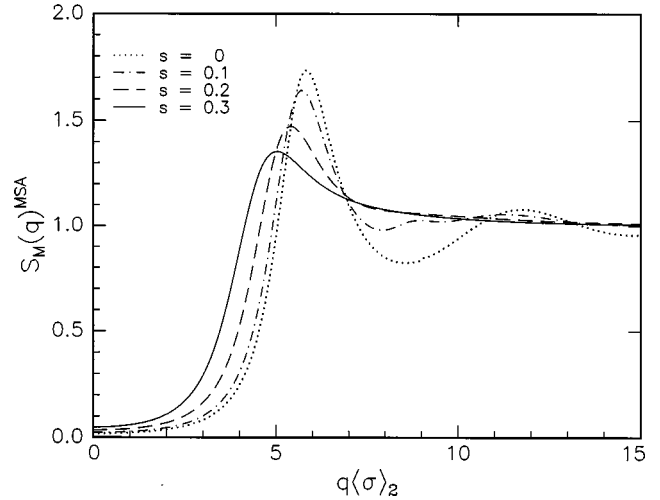


FIG. 1. Polydispersity effects. Exact MSA structure factor $S_M(q)$ of polydisperse charged hard spheres, at fixed packing fraction $\eta = 0.3$, for different degrees of polydispersity s ($s = 0$ corresponds to the monodisperse binary case). Other parameters: $\sigma_1 = 5 \text{ \AA}$, $z_1 = +1$ (e units) for microions; $\langle \sigma \rangle_2 = 100 \text{ \AA}$, $z_{\langle \sigma \rangle_2} = -20$ for macroions.

through a repulsive screened Coulomb interactions [28], and they were already recorded even in the PM [22].

Next we check the effect of the charge. This is reported in Fig. 2, where the $S_M(q)^{\text{MSA}}$ corresponding to $\eta = 0.3$, $z_{\langle \sigma \rangle_2} = -20$, $s = 0.3$ is compared with that of the polydisperse mixture of neutral hard spheres which results from “switching off” all charges and leaving all other parameters unchanged. As the charge increases, the main peak becomes higher and shifts to smaller q values, since its position is essentially determined by the macroion-macroion equilibrium distance which becomes larger in the presence of electrostatic repulsions. The difference in the $q \rightarrow 0$ behavior is also evident: the charges lower the $S_M(q)$ values near the

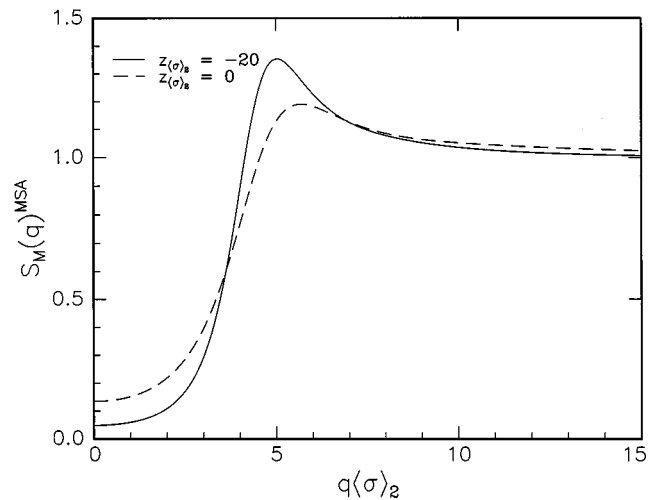


FIG. 2. Charge effects. The exact MSA structure factor $S_M(q)$ for polydisperse charged hard spheres with $\eta = 0.3$, $z_{\langle \sigma \rangle_2} = -20$, $s = 0.3$ (other parameters as in Fig. 1) is compared with its exact PY counterpart for the corresponding polydisperse mixture of neutral hard spheres.

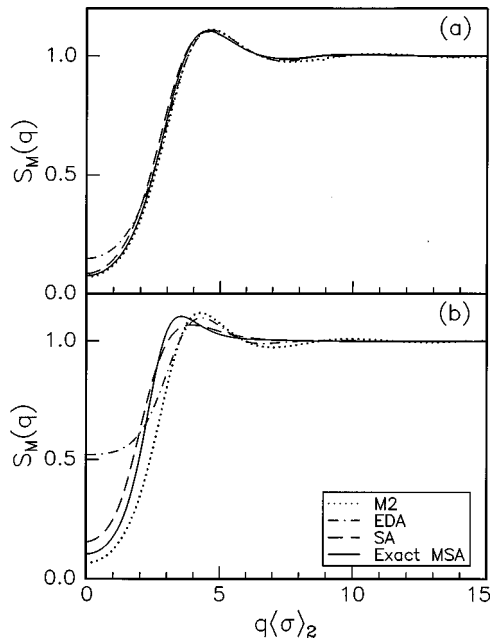


FIG. 3. (a) Structure factor $S_M(q)$ for $\eta=0.1$, $z_{\langle\sigma\rangle_2} = -10$, $s=0.1$ (other parameters as in Fig. 1). Comparison of M2-MSA, EDA-MSA, SA-MSA, and exact MSA results. (b) Same as (a), but for $s=0.3$.

origin, as a consequence of the long-range nature of the Coulomb potential.

B. Scaling approximation plus MSA

Our aim is now to display the performance of the SA when the partial structure factors $S_{m_\alpha m_\beta}^{\text{bin}}(q)$ of the reference M2 mixture are evaluated using the MSA closure. These SA-MSA results are compared with the exact MSA solution for polydisperse charged hard spheres previously discussed. We shall comment in the next subsection on a method we envisaged to avoid unnecessary repetitions in the IE calculations for the M2 mixture.

In Fig. 3 the structure factor $S_M(q)^{\text{SA-MSA}}$ is shown for two different degrees of polydispersity ($s=0.1$ and 0.3) at low concentration and under weak charge conditions ($\eta=0.1$ and $z_{\langle\sigma\rangle_2} = -10$). The corresponding results from the M2-MSA and EDA-MSA approximations are also reported for comparison. As expected, at small polydispersity [Fig. 3(a)] there are very little differences among all these curves, although the EDA yields a somewhat larger value for $S_M(q=0)$. This overestimation of the low- q scattering in the EDA becomes much larger as polydispersity increases [Fig. 3(b)]. This is the same qualitative trend resulted in the DA for neutral systems [1,3,7,29]. At $s=0.3$ it is apparent that the position of the first peak in the EDA follows that of the M2, whose maximum is shifted to larger q values with respect to the MSA result. On the other hand, the SA reproduces more accurately the position of the first peak and follows very closely the correct curve for $q\langle\sigma\rangle_2 \geq 6$.

The discrepancy in the low- q region, which is in fact the most interesting from the SAS point of view, can be more clearly seen in Fig. 4, where the scattering intensity per unit volume $R(q)$, calculated for the same parameters of Fig. 3 is displayed on a log-log scale. Nevertheless the SA performs

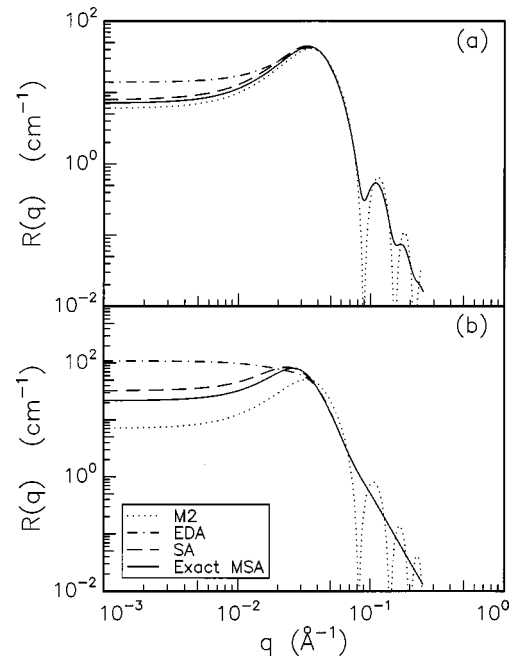


FIG. 4. Scattering intensity per unit volume, $R(q)$, using a log-log scale. Comparison of M2-MSA, EDA-MSA, SA-MSA, and exact MSA results. The systems are the same as in Fig. 3: (a) $\eta=0.1$, $z_{\langle\sigma\rangle_2} = -10$, $s=0.1$. (b) Same as (a), but for $s=0.3$.

overall rather well in all regions.

In Fig. 5 the same functions of Fig. 3 are then plotted for a more concentrated suspension and higher macroion charges ($\eta=0.3$ and $z_{\langle\sigma\rangle_2} = -20$), again for $s=0.1$ and 0.3 , while the corresponding results for $R(q)$ are displayed in Fig. 6. Figures 5(a) and 5(b) yield compelling evidence of the potentiality of the SA confirming the previous remarks. It is

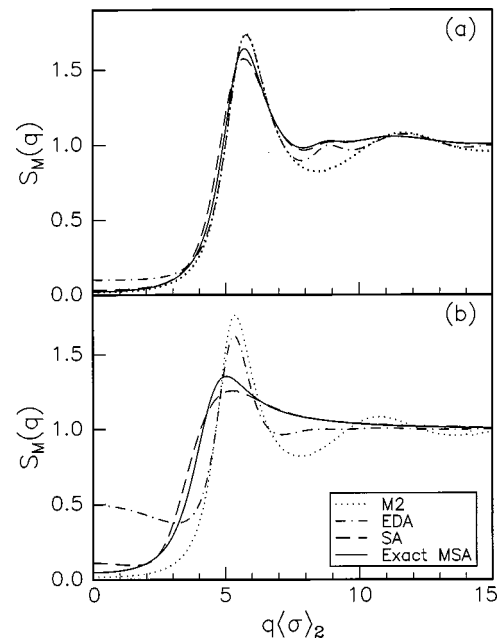


FIG. 5. (a) Structure factor $S_M(q)$ for $\eta=0.3$, $z_{\langle\sigma\rangle_2} = -20$, $s=0.1$ (other parameters as in Fig. 1). Comparison of M2-MSA, EDA-MSA, SA-MSA, and exact MSA results. (b) Same as (a), but for $s=0.3$.

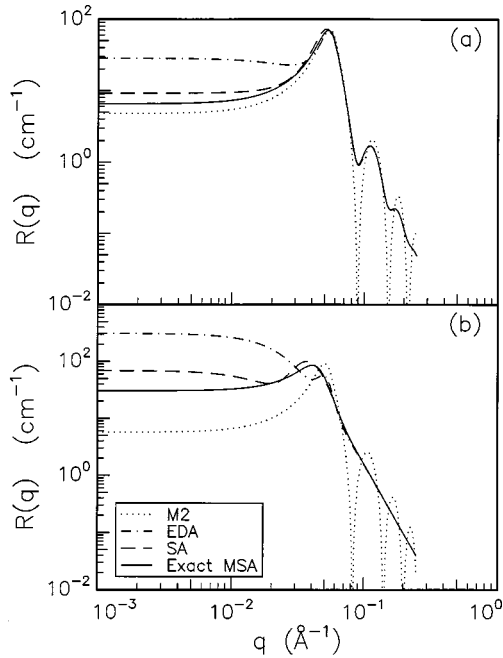


FIG. 6. Scattering intensity per unit volume, $R(q)$, using a log-log scale. Comparison of M2-MSA, EDA-MSA, SA-MSA, and exact MSA results. The systems are the same as in Fig. 5: (a) $\eta = 0.3$, $z_{\langle\sigma\rangle_2} = -20$, $s = 0.1$. (b) Same as (a), but for $s = 0.3$.

useful to analyze these results in the sequence $M2 \rightarrow EDA \rightarrow SA$. In Fig. 5(a) $S_M(q)^{EDA}$ exactly coincides with $S_M(q)^{M2}$ in the first peak region, but differs from it at the locations of the M2 minima and at small q values. On the contrary, the SA curve is close to the exact MSA one everywhere. In Fig. 5(b) the M2 approximation largely disagrees with the MSA one. The EDA improves here on the M2 since it takes all form factors of the polydisperse fluid correctly into account. It exhibits a lower peak height and practically no subsequent oscillations. Nevertheless, the EDA has a dramatic low- q overestimate and it behaves poorly in essentially all regions. On the contrary, the SA is fairly accurate in the whole experimentally accessible q range. Its performance at $\eta = 0.3$ appears to be even more accurate than at $\eta = 0.1$. All these features are quite remarkable if we recall that the SA, EDA, and M2 curves have been obtained starting from the same partial structure factors $S_{m_\alpha m_\beta}^{bin}(q)$. This fact clearly shows the crucial role played by the scaling of the distances. Its effect is to shift the first peak position to the right location and to dump all oscillations after the first peak. Physically it confirms the soundness of our “conformality” hypothesis as expressed by Eq. (20) and it shows that overlooking differences among macroion-macroion RDFs at contact (as it is done in the SA) is a reasonable assumption.

C. Scaling approximation plus HNC

To illustrate the possibility of applying the SA scheme even when the OZ equations admit only numerical solutions, we investigated SA with the HNC closure and analyzed two cases $\eta = 0.1$, $s = 0.3$ with $z_{\langle\sigma\rangle_2} = -10$ and $z_{\langle\sigma\rangle_2} = -50$, respectively (all other parameters were fixed as before). While the first case was already studied with the SA-MSA, the second one represents a situation, of low concentration and

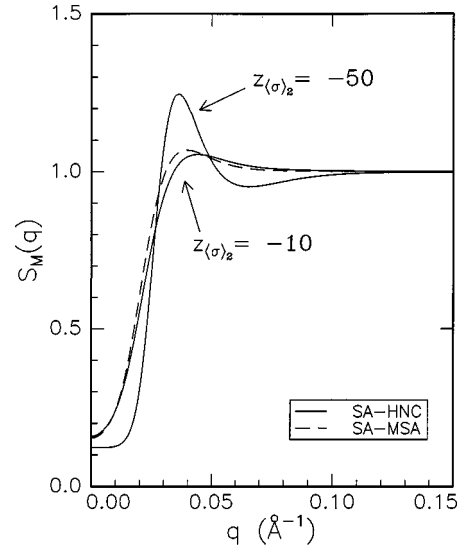


FIG. 7. SA-HNC predictions for the structure factor $S_M(q)$ at $\eta = 0.1$, $s = 0.3$, with $z_{\langle\sigma\rangle_2} = -10$ and $z_{\langle\sigma\rangle_2} = -50$ (other parameters as in Fig. 1). In the $z_{\langle\sigma\rangle_2} = -10$ case the corresponding SA-MSA curve is also plotted for comparison.

high charges, in which the MSA yields negative values of the macroion-macroion RDF at contact and hence cannot be utilized. This drawback is avoided by using the HNC closure.

In both cases we solved the HNC equations for the parameter values of the corresponding M2 reference mixture, using an r -space grid size $\Delta r / \langle\sigma\rangle_2 = 0.02$ and a number of grid points $\mathcal{N} = 4096$. This choice implies that $q_{\max} \langle\sigma\rangle_2 = 50\pi$, with a small enough grid size in q space, $\Delta q = q_{\max} / \mathcal{N}$, allowing the implementation of a “trick” proposed in Ref. [7]. In fact, the expression for $S_M(q)^{SA}$, Eq. (23), would require, at each q , the evaluation of one term $S_{11}^{bin}(q)$, $p-1$ terms $S_{12}^{bin}(q\sigma_{1\beta}/\sigma_{12}^{bin})$ and $(p-1)p/2$ terms $S_{22}^{bin}(q\sigma_{\alpha\beta}/\sigma_2^{bin})$ (recall that $p-1$ is the number of macroion components). These cumbersome repeated calculations can be avoided. We calculated S_{11}^{bin} , S_{12}^{bin} , and S_{22}^{bin} at the grid points $q_i = i\Delta q$ ($i = 0, \dots, \mathcal{N}-1$) only once, storing all these values in arrays. Although the grid points q_i do not exhaust the whole set of $q\sigma_{1\beta}/\sigma_{12}^{bin}$ and $q\sigma_{\alpha\beta}/\sigma_2^{bin}$ values required in Eq. (23), the stored structure factors represent a fine sampling of these continuous functions. Therefore, if the Δq is small enough, the value of S_{12}^{bin} (or S_{22}^{bin}) at a certain point can be approximated with that at the nearest grid point with a negligible error. In this way the sums of Eq. (23) can be quickly performed.

Figure 7 shows the $S_M(q)^{SA-HNC}$ curves, along with the SA-MSA one for $z_{\langle\sigma\rangle_2} = -10$. As expected, in the lower charge case the SA-HNC prediction is very close to the SA-MSA one, with only a slight shift in the first peak position. The SA-HNC structure factor with $z_{\langle\sigma\rangle_2} = -50$ is not a trivial result: it refers to a polydisperse colloidal system with mean size ratio $\sigma_1 : \langle\sigma\rangle_2 = 1:20$ and mean (absolute) charge ratio $|z_1| : |z_{\langle\sigma\rangle_2}| = 1:50$. Unfortunately, in this case we cannot make a comparison with “exact” data. On the other hand, the lack of these data and the difficulty of generating them in a very asymmetric regime is just the strongest motivation for introducing approximate theories such as the SA.

VI. CONCLUDING REMARKS

In this paper the problem of computing scattering functions for polydisperse ionic colloidal fluids has been addressed by integral equation methods. In the framework of the primitive model we have shown that, despite the complexity of these systems, surprisingly accurate predictions can be obtained with a limited numerical effort. We have successfully extended the *scaling approximation* introduced in Ref. [7] for polydisperse fluids of neutral particles. The SA still works well when Coulombic (both repulsive and attractive) interactions are present, notwithstanding the strong charge-size asymmetries of the polydisperse colloidal regime. Only the study of an appropriate monodisperse binary mixture (the M2 reference system) is required for a complete characterization of the polydisperse system.

Our corresponding states theory is based on the simple physical idea of conformality of all RDFs in the polydisperse mixture. All partial structure factors are generated by scaling their three counterparts of the M2 fluid. In the liquid state theory similar ideas have been widely exploited in the past [18,19] but, to our knowledge, Ref. [7] and this paper are the first application to polydisperse fluids.

Clearly, the SA theory is accurate only in the average. In fact, the scaling is hardly accurate for each individual pair correlation $g_{\alpha\beta}(r)$. In particular, it incorrectly assumes the equality of the RDFs at contact for all macroion-macroion pairs as well as for the microion-macroion ones. However, an essential feature of our SA is that it correctly ensures $g_{\alpha\beta}(r)=0$ inside the hard cores. These excluded volume conditions are crucial, as it is shown by the failure of the ‘‘extended decoupling approximation’’ which neglects them. The structure factors $S_M(q)^{SA}$ turn out to be accurate in the first peak region and beyond; some inaccuracy, due to the harsh approximations of our theory, is found at low q values. Since the $q \rightarrow 0$ limit is related to thermodynamics, this means that the SA can be meaningfully exploited to extract structural but not thermodynamical predictions.

Because of its simplicity, the SA can be safely employed also when the OZ integral equations have to be solved numerically since its application to both different closures and different potential for ionic colloids is feasible. These features are indicative that SA is a useful theoretical tool to investigate, to first approximation, the structure of polydisperse (nonionic and ionic) colloids under highly demanding conditions. The existence of a good approximation which reduces the study of polydisperse fluids to that of an effective monodisperse one should not be underestimated. Real life colloids are always polydisperse to a certain degree and polydispersity always represents a challenge in the interpretation of experimental data. We hope that the SA will result particularly useful in the analysis of small angle scattering data, since it considerably outperforms the ‘‘decoupling approximation,’’ popular in this context, at the cost of a minimal additional effort.

It would be interesting to compare our theory with the approach proposed by D’Aguanno and Klein [5]. As already mentioned in the Introduction, these authors followed a different point of view and replaced the continuous Schulz distribution with an histogram containing a finite number of well-chosen diameters, thus reducing the polydisperse fluid

to an effective mixture with a very small number p' of components. In this case, however, we expect a nontrivial increase in the numerical effort involved. In fact, to avoid the rapid increase in computational cost with increasing p' in the D’Aguanno-Klein mixtures, that approach was recently modified by Lado and co-workers by adding an orthogonal polynomial expansion technique [30], and afterwards by merging this with a thermodynamic perturbation scheme [31]. A comparison of the SA with these alternative theories is left to future work.

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APPENDIX: MSA EXPRESSION FOR THE SCATTERING INTENSITY

In this appendix we report the basic formulas involved in the MSA calculation of the scattering intensity from charged hard sphere fluids, as described in Ref. [12]. Let us introduce the following short-hand notations:

$$\{Y\}_0 \equiv \sum_{\nu=1}^p \rho_{\nu} Y_{\nu} = \rho \langle Y \rangle, \quad (A1)$$

$$\{Y\} \equiv \sum_{\nu=1}^p \rho_{\nu} Y_{\nu} e^{iX_{\nu}} = \rho \langle Y e^{iX} \rangle, \quad (A2)$$

where $X_{\nu} \equiv q \sigma_{\nu}/2$. The MSA analytical solution depends on the screening parameter 2Γ , which must be determined numerically by solving the consistency equation

$$(2\Gamma)^2 = 4 \pi L_B \sum_{\nu=1}^p \rho_{\nu} \left(\frac{z_{\nu} - P_z \sigma_{\nu}^2/2}{1 + \Gamma \sigma_{\nu}} \right)^2, \quad (A3)$$

where

$$P_z = \frac{\pi}{\Omega} \left\{ \frac{\sigma z}{1 + \Gamma \sigma} \right\}_0, \quad (A4)$$

$$\Omega = \Delta + \frac{\pi}{2} \left\{ \frac{\sigma^3}{1 + \Gamma \sigma} \right\}_0, \quad (A5)$$

with $\Delta = 1 - \eta$. These quantities are also required to compute

$$A_{\nu} = \frac{L_B z_{\nu} - P_z \sigma_{\nu}^2/2}{\Gamma (1 + \Gamma \sigma_{\nu})}. \quad (A6)$$

In the limit of point ions (all $\sigma_{\nu} \rightarrow 0$), 2Γ becomes the Debye inverse shielding length κ_D of the Debye-Hückel theory for electrolyte solutions, while for finite size ions it is always a lower bound (i.e., $2\Gamma \leq \kappa_D$). We also need

$$\alpha_\nu = \frac{\pi \sigma_\nu^3 \phi_\nu}{6\Delta}, \quad (\text{A7})$$

$$\beta_\nu = \frac{\pi \sigma_\nu^2 \psi_\nu}{2\Delta}, \quad (\text{A8})$$

$$\gamma_\nu^{(0)} = \frac{2\pi i}{q} \frac{\Gamma^2}{L_B} A_\nu \sigma_\nu \psi_\nu, \quad (\text{A9})$$

$$\gamma_\nu^{(1)} = \frac{2\pi i}{q} \frac{\Gamma}{L_B} A_\nu e^{-iX_\nu}, \quad (\text{A10})$$

$$\gamma_\nu = \gamma_\nu^{(0)} + \gamma_\nu^{(1)}, \quad (\text{A11})$$

where $\psi_\nu = j_0(X_\nu)$ and $\phi_\nu = 3j_1(X_\nu)/X_\nu$, with $j_0(x) = \sin x/x$ and $j_1(x) = (\cos x - x \sin x)/x^2$ being Bessel functions.

The final expression for the scattering intensity per unit of volume is

$$R(q) = R_1(q) + R_2(q), \quad (\text{A12})$$

where

$$R_1 = \{F^2\}_0 + \{\alpha^2\}_0 |c_1|^2 + \{\beta^2\}_0 |c_2|^2 + 2 \operatorname{Re}[\{F\alpha\}_0 c_1 + \{F\beta\}_0 c_2 + \{\alpha\beta\}_0 c_1 c_2^*], \quad (\text{A13})$$

$$R_2 = \{q\gamma^2\}_0 |c_3|^2 + 2 \operatorname{Re}[\{q\gamma F\}_0 c_3 + \{q\gamma\alpha\}_0 c_3 c_1^* + \{q\gamma\beta\}_0 c_3 c_2^*]. \quad (\text{A14})$$

Here, F_ν is the form factor given by Eq. (2), $\operatorname{Re}[\dots]$ the real part of a complex number, and the asterisk denotes complex conjugation. Other necessary quantities appearing in these equations are

$$c_1 = \frac{t_2}{t_1}, \quad c_2 = \frac{t_3}{t_1}, \quad c_3 = \frac{t_4}{t_1}, \quad (\text{A15})$$

$t_m (m=1, \dots, 4)$ being the cofactor of the $(1, m)$ th element of the first row in the following determinant:

$$\begin{vmatrix} \rho_\nu^{1/2} F_\nu & \rho_\nu^{1/2} \alpha_\nu & \rho_\nu^{1/2} \beta_\nu & \rho_\nu^{1/2} q \gamma_\nu \\ \{F\} & 1 + \{\alpha\} & \{\beta\} - 3\xi_2/\Delta + iq/2 & \{q\gamma^{(0)}\} - 2i\Gamma P_z \Delta \\ \{\sigma F\} & \{\sigma\alpha\} & 1 + \{\sigma\beta\} & \{\sigma q\gamma^{(0)}\} \\ \{AF\} & \{A\alpha\} & \{A\beta\} & q + \{Aq\gamma^{(0)}\} + 2i\Gamma \end{vmatrix}, \quad (\text{A16})$$

and where $\xi_2 = (\pi/6)\{\sigma^2\}_0$.

Equations (A4) and (A16) correct the misprints appearing in the corresponding equations of Ref. [12]. In the expression of P_z given by Eq. (48) of that paper the factor π was omitted. We also note that our definition of P_z and Ω differs from Blum's original one [8].

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