

A scaling approximation for structure factors in the integral equation theory of polydisperse nonionic colloidal fluids

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The integral equation theory of pure liquids, combined with a new “scaling approximation” based on a corresponding states treatment of pair correlation functions, is used to evaluate approximate structure factors for colloidal fluids constituted of uncharged particles with polydispersity in size and energy parameters. Both hard sphere and Lennard-Jones interactions are considered. For polydisperse hard spheres, the scaling approximation is compared to theories utilized by small angle scattering experimentalists (decoupling approximation and local monodisperse approximation) and to the van der Waals one-fluid theory. The results are tested against predictions from analytical expressions, exact within the Percus–Yevick approximation. For polydisperse Lennard-Jones particles, the scaling approximation, combined with a “modified hypernetted chain” integral equation, is tested against molecular dynamics data generated for the present work. Despite its simplicity, the scaling approximation exhibits a satisfactory performance for both potentials, and represents a considerable improvement over the above mentioned theories. Shortcomings of the proposed theory, its applicability to the analysis of experimental scattering data, and its possible extensions to different potentials are finally discussed. © 1999 American Institute of Physics. [S0021-9606(99)51138-0]

I. INTRODUCTION

Colloidal solutions consist of mesoscopic particles, with diameters between 10^{-8} and 10^{-4} m, suspended in a microscopic fluid. Colloidal particles of a same chemical species are not necessarily identical, but may differ in size, charge or other properties.^{1,2} This phenomenon is called “polydispersity,” and systems in which it does not occur are said to be “monodisperse.” A microscopic description of a fluid with a significant polydispersity is a difficult task, requiring a large number of independent variables. A great simplification is, however, possible by using the so-called *continuous-mixture*, or *polydisperse-mixture*, formalism. Such a model, adopted also in this paper, views the fluid as containing an infinite number of components ($p \rightarrow \infty$), with a continuous distribution of size and/or other properties. All molar fractions of the components are then replaced by a single distribution function, which describes the composition of the system.

Since polydispersity can significantly affect the microscopic ordering of colloidal suspensions, it must be taken into account in the analysis of experimental data on such fluids. In particular, we are interested in static structure factors obtainable from small angle scattering of light, neutrons or x rays.

In this paper we present integral equation (IE) calculations for the structure of polydisperse one-species fluids constituted of uncharged particles with hard sphere (HS) or Lennard-Jones (LJ) interactions, with polydispersity in size and, for LJ systems, also in energy parameters. IEs of statistical mechanics represent a powerful, although approximate, tool to determine both structures and thermodynamics of fluids in a simple way. However, while using IEs for pure fluids or binary mixtures is a rather common and successful practice, their application to multicomponent systems with large p or $p \rightarrow \infty$ is problematic and, consequently, less frequent in the literature.^{3,4} Only in special cases, when analytical solutions are available, IE calculations for polydisperse fluids can be performed in a rigorous and relatively easy way. For instance, a closed analytical formula for the scattering intensity of polydisperse hard spheres was obtained by Vrij⁵ from the solution of the Percus–Yevick (PY) IE. Similar expressions were derived for polydisperse charged hard spheres, by using the corresponding analytical solution in the mean spherical approximation.⁶

Unfortunately, for most “closures” and for most potentials, including the LJ one, the IEs must be solved numerically, requiring more and more computer memory and time with increasing p , so that the problem soon becomes practi-

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cally intractable (D'Aguanno and Klein⁷ reached $p=10$ for Yukawa plus HS interactions).

To overcome the impossibility of investigating polydisperse systems when IEs have to be solved numerically, alternative routes have been proposed. The common idea is to replace the polydisperse fluid with an appropriate system with very few components. A first method, not analyzed in this paper, builds up an equivalent *effective mixture* with $p' \ll p$ new components, whose molar fractions and diameters—in the case of size polydispersity—are determined by replacing the continuous size distribution with a p' -component histogram and requiring the equality of the first $2p'$ moments of the two distributions ($p'=2$ or 3 is usually sufficient).^{2,8} Other methods assume that the properties of polydisperse fluids can be obtained, to a good approximation, from those of *pure* fluids, if suitably averaged parameters and appropriate recipes are used. This same basic idea has often been employed, in several variants (van der Waals equation of state, perturbation theories, etc.), to predict thermodynamics of liquid mixtures with a small number of components.^{9–11} Some significant applications of these concepts have also been made to structural studies of polydisperse systems, mainly by experimentalists in the analysis of scattering data. Kotlarchyk and Chen¹² introduced the *decoupling approximation* (DA), which is perhaps the most famous of these approaches and involves an exact evaluation of the form factors for all components of the polydisperse system, but approximates every partial structure factor with that of a one-component fluid. A second approximation, suggested by Pedersen¹³ and known as *local monodisperse approximation* (LMA), replaces the polydisperse fluid not with a single pure system, but with a superposition of noninteracting pure fluids, whose number equals that of the species in the mixture.

The aim of the present paper is twofold. First, both DA and LMA are discussed in terms of pair correlation functions, to get some insight into their shortcomings. Second, we propose a simple *scaling approximation* (SA), which, with respect to DA and LMA, takes excluded volume effects more correctly into account and therefore yields significantly improved structure factors. By using corresponding states arguments the SA derives all pair correlation functions of a polydisperse mixture from an appropriate pure fluid counterpart, at the cost of *only one* IE computation. The performance of SA is tested on two typical potential models, namely polydisperse hard spheres and polydisperse Lennard-Jones particles. For HS systems, SA results for the “measurable” structure factor are compared to those obtained from Vrij’s analytical expression,⁵ which is exact within the PY approximation. For polydisperse LJ fluids, SA is tested against molecular dynamics (MD) data generated for this purpose.

II. INTEGRAL EQUATION THEORY

A. Basic equations

The Ornstein–Zernike (OZ) integral equations of the liquid state theory for p -component mixtures with spherically symmetric interparticle potentials are¹⁴

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

where $h_{\alpha\beta}(r) \equiv g_{\alpha\beta}(r) - 1$ is the total correlation function between two particles of species α and β at a distance r , $g_{\alpha\beta}(r)$ is the radial distribution function (RDF), $c_{\alpha\beta}(r)$ is the direct correlation function, $\rho \equiv N/V$ the total number density (N =total particle number, V =volume) and x_{γ} the molar fraction of species γ . These equations can be solved only when coupled with a *closure* relationship, given by the exact formula

$$c_{\alpha\beta}(r) = \exp[-u_{\alpha\beta}(r)/k_B T + \gamma_{\alpha\beta}(r) + B_{\alpha\beta}(r)] - 1 - \gamma_{\alpha\beta}(r) \quad (2)$$

plus an approximation to the “bridge” functions $B_{\alpha\beta}(r)$, which are functionals of $h_{\alpha\beta}(r)$ and higher order correlation functions^{14,15} [$u_{\alpha\beta}(r)$ is the interparticle potential, k_B is Boltzmann’s constant and T the absolute temperature; $\gamma_{\alpha\beta}(r) \equiv h_{\alpha\beta}(r) - c_{\alpha\beta}(r)$]. The OZ equations admit an analytical solution only in a relatively small class of cases, for some potentials and some peculiar closures.

In the first case considered in this paper, i.e., for HS particles with additive diameters¹⁶ σ_{α} , corresponding to the potential

$$u_{\alpha\beta}(r) = \begin{cases} +\infty, & r < \sigma_{\alpha\beta} \equiv (\sigma_{\alpha} + \sigma_{\beta})/2 \\ 0, & r \geq \sigma_{\alpha\beta} \end{cases} \quad (3)$$

an analytical solution is possible if one adds to the exact hard core condition, $h_{\alpha\beta}(r) = -1$ for $r < \sigma_{\alpha\beta}$, the PY approximation

$$B_{\alpha\beta}(r) = \ln[1 + \gamma_{\alpha\beta}(r)] - \gamma_{\alpha\beta}(r) \quad \text{for } r > \sigma_{\alpha\beta}, \quad (4)$$

which is equivalent to $c_{\alpha\beta}(r) = 0$ for $r > \sigma_{\alpha\beta}$.

Only a numerical solution is feasible in the second case of this paper, i.e., the LJ potential

$$u_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right], \quad (5)$$

where $\sigma_{\alpha\beta}$ are LJ diameters and $\epsilon_{\alpha\beta}$ energy parameters (well depths). The number of independent LJ parameters is reduced by assigning individual parameters ($\sigma_{\alpha}, \epsilon_{\alpha}$) to each species α and obtaining the cross interactions from combination rules

$$\sigma_{\alpha\beta} \equiv (\sigma_{\alpha} + \sigma_{\beta})/2 \quad (\text{Lorentz rule}), \quad (6)$$

$$\epsilon_{\alpha\beta} \equiv \sqrt{\epsilon_{\alpha}\epsilon_{\beta}} \quad (\text{Berthelot rule}). \quad (7)$$

The OZ equation is solved using the *modified hypernetted chain* (MHNC) closure described in Ref. 15, which is one of the best IE approximations for both structures and thermodynamics of LJ one-component fluids. All versions of the MHNC theory assume that the bridge function $B(r)$ has roughly the same functional form for all potentials and replace the unknown $B(r)$ of the system under study with that of a reference system whose properties are known. We approximate the LJ one-component bridge function with that of an appropriate HS fluid, i.e., $B_{\text{LJ}}(r; \sigma, \rho, T) \approx B_{\text{HS}}(r; d, \rho)$, where d is an equivalent HS diameter, which depends on ρ

and T . Our choice for B_{HS} is a slight modification of an empirical analytical approximation proposed by Malijevsky and Labik^{17,18} (ML), and d is selected by equating the second density derivative of the free energy of the LJ fluid with that of the HS reference, according to a prescription due to Rosenfeld and Blum.¹⁹ Further details can be found in the original paper.¹⁵

B. Structure factors

The Ashcroft–Langreth²⁰ *partial* structure factors $S_{\alpha\beta}(q)$ are defined as

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + \rho \sqrt{x_{\alpha} x_{\beta}} \tilde{h}_{\alpha\beta}(q), \quad (8)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta and $\tilde{h}_{\alpha\beta}(q)$ the three-dimensional Fourier transform of $h_{\alpha\beta}(r)$. Appropriate linear combinations of partial structure factors define *global* structure factors. A first example of these is the measurable structure factor²

$$S_M(q) = \sum_{\alpha=1}^p \sum_{\beta=1}^p w_{\alpha}(q) w_{\beta}(q) \sqrt{x_{\alpha} x_{\beta}} S_{\alpha\beta}(q) \quad (9)$$

with

$$w_{\nu}(q) \equiv \frac{F_{\nu}(q)}{\sqrt{\langle F^2(q) \rangle}}, \quad (10)$$

where $F_{\nu}(q)$ is the scattering form factor of species ν , and angular brackets, $\langle \dots \rangle$, denote, here and in the following, compositional averages over the distribution of particles, i.e., $\langle Y \rangle \equiv \sum_{\alpha=1}^p x_{\alpha} Y_{\alpha}$ for any property Y (note that $\langle w^2(q) \rangle = 1$).

We assume that 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. The former, in fact, depends on the particle-radiation interaction, whereas the latter is determined by the interparticle repulsions and may even not be well defined, as for LJ particles (only molecules with *hard* body repulsions possess a well-defined volume). For spherical homogeneous scattering cores, the form factors are

$$F_{\alpha}(q; \sigma_{\alpha}^{\text{scatt}}) \propto V_{\alpha}^{\text{scatt}} \frac{3j_1(q\sigma_{\alpha}^{\text{scatt}}/2)}{q\sigma_{\alpha}^{\text{scatt}}/2}, \quad (11)$$

where $\sigma_{\alpha}^{\text{scatt}} \leq \sigma_{\alpha}$ is the diameter of the scattering core of species α , $V_{\alpha}^{\text{scatt}} = \pi/6(\sigma_{\alpha}^{\text{scatt}})^3$ its volume, and $j_1(x) = (\sin x - x \cos x)/x^2$ is the first-order spherical Bessel function. The notation $F_{\alpha}(q; \sigma_{\alpha}^{\text{scatt}})$ emphasizes the dependence of the form factor on $\sigma_{\alpha}^{\text{scatt}}$, which in general may differ from σ_{α} . In this paper, for the sake of simplicity, $\sigma_{\alpha}^{\text{scatt}}$ is taken coincident with σ_{α} , for all species and for both HS and LJ potentials.

A second global structure factor of interest is the Bhatia–Thornton number–number structure factor,²¹ obtainable by taking all $w_{\nu} = 1$ in Eq. (9)

$$S_{\text{NN}}(q) = \sum_{\alpha=1}^p \sum_{\beta=1}^p \sqrt{x_{\alpha} x_{\beta}} S_{\alpha\beta}(q). \quad (12)$$

While $S_M(q)$ represents the structure factor measured in small angle scattering experiments, $S_{\text{NN}}(q)$ is related to the fluctuations in particle numbers.

C. Polydisperse continuous limit

All previous formulas, written in a discrete form, refer to a finite number p of components. On the other hand, theoretical treatments of polydispersity with continuous distributions refer to systems with an infinite number of components ($p \rightarrow \infty$).

For HS particles polydispersity of only one property—the diameter σ —is possible. For LJ particles both σ and ϵ might be polydisperse. In this paper, however, to simplify the LJ model, energy and size parameters will be correlated according to the law^{22,23}

$$\epsilon_{\alpha} = \epsilon_{\langle\sigma\rangle} \left(\frac{\sigma_{\alpha}}{\langle\sigma\rangle} \right)^z, \quad (13)$$

where $\langle\sigma\rangle$ is the average diameter, $\epsilon_{\langle\sigma\rangle}$ the corresponding well depth, and z is an adjustable exponent, for which we take the value $z=2$. Other choices will be discussed later.

The polydisperse continuous limit of the previous discrete expressions can therefore be obtained by simple *replacement rules*

$$x_{\alpha} \rightarrow dx = f(\sigma) d\sigma, \quad (14)$$

$$\sum_{\alpha} x_{\alpha} \dots \rightarrow \int d\sigma f(\sigma) \dots, \quad (15)$$

where $f(\sigma) d\sigma$ is the probability of finding a particle with diameter in the range $\sigma - \sigma + d\sigma$, and the distribution function $f(\sigma)$ (*molar fraction density function*) is normalized. Specifically, we shall use the Schulz (or gamma) distribution²⁴

$$f(\sigma) = \frac{b^a}{\Gamma(a)} \sigma^{a-1} e^{-b\sigma} \quad (a > 1), \quad (16)$$

where Γ is the gamma function,²⁵ and the two parameters a and b can be expressed as $a = 1/s^2$ and $b = a/\langle\sigma\rangle$, in terms of the mean value $\langle\sigma\rangle$ and the relative standard deviation $s \equiv \sqrt{\langle\sigma^2\rangle - \langle\sigma\rangle^2}/\langle\sigma\rangle$. The dispersion parameter s measures the degree of polydispersity, and varies in the range $0 < s < 1$. For $s \rightarrow 0$, the Schulz distribution reduces to a Dirac delta function centered at $\langle\sigma\rangle$ (monodisperse limit). For small s values $f(\sigma)$ is very similar to a Gaussian distribution (without its drawback of unphysically negative diameters). For s closer to one, $f(\sigma)$ becomes asymmetric, with a long tail at large diameters.²⁴ The first three moments of the Schulz distribution are: $\langle\sigma\rangle, \langle\sigma^2\rangle = (1+s^2)\langle\sigma\rangle^2$ and $\langle\sigma^3\rangle = (1+s^2)(1+2s^2)\langle\sigma\rangle^3$.

Whenever analytical integration is impossible, numerical integration brings back to discrete expressions (with large p , of order $10^2 - 10^3$), and therefore the replacement rule of Eq. (15) becomes unnecessary. Thus no integral is needed in the formulas and the discrete notation is always employed, implicitly assuming $x_{\alpha} = f(\sigma_{\alpha}) \Delta\sigma$, which is the discrete analogue of Eq. (14) ($\Delta\sigma$ is the grid size in the numerical integration).

III. CORRESPONDING STATES AND SCALING APPROXIMATION

To introduce our scaling approximation for global structure factors, a corresponding states^{26,27} approach will be used. The correspondence principle applies to systems which have *conformal* pair potentials, i.e., potentials of the same *shape*. The principle takes its simplest form when the potential u_α of each species α , in a set of conformal substances, depends on two parameters only and can be written as

$$u_\alpha(r) = \epsilon_\alpha u^* \left(\frac{r}{\sigma_\alpha} \right), \quad (17)$$

where σ_α and ϵ_α are a characteristic length and a characteristic energy, respectively, while u^* is a dimensionless function of the dimensionless distance $r^* \equiv r/\sigma$. Such a form of $u_\alpha(r)$ implies that all properties of a set of conformal fluids can be written in terms of dimensionless reduced variables, e.g., temperature $T_\alpha^* \equiv k_B T / \epsilon_\alpha$, number density $\rho_\alpha^* \equiv \rho \sigma_\alpha^3$, and pressure $p_\alpha^* \equiv p \sigma_\alpha^3 / \epsilon_\alpha$.

When written in terms of reduced distance $r_\alpha^* \equiv r/\sigma_\alpha$ and wave vector $q_\alpha^* \equiv q \sigma_\alpha$, the RDF and structure factor of any pure fluid of species α can be derived by scaling as

$$g_\alpha(r; \rho, T; \sigma_\alpha, \epsilon_\alpha) = \hat{g}(r_\alpha^*; \rho_\alpha^*, T_\alpha^*), \quad (18)$$

$$S_\alpha(q; \rho, T; \sigma_\alpha, \epsilon_\alpha) = \hat{S}(q_\alpha^*; \rho_\alpha^*, T_\alpha^*), \quad (19)$$

where \hat{g} and \hat{S} are functions common to the entire set of conformal substances. Equations (18) and (19) indicate that the scaling correspondence applies not only to thermodynamic variables, but also to ‘‘positions’’ in r and q space.²⁸ Both HS and LJ potentials satisfy the scaling condition given by Eq. (17) (in the HS case, since $\epsilon_\alpha = 1$, RDFs and structure factors do not depend on T).

Conformal mixtures are those in which all pair potentials are conformal to each other and to that of a pure (monodisperse one-species) reference fluid, according to the scaling relation

$$u_{\alpha\beta}(r) = \epsilon_{\alpha\beta} u_{\text{mono}}^* (\lambda_{\alpha\beta} r_{\text{mono}}^*), \quad (20)$$

where $r_{\text{mono}}^* \equiv r/\sigma_{\text{mono}}$, while $\epsilon_{\alpha\beta}$ and $\lambda_{\alpha\beta}$ are parameters characteristic of the pair α, β . For mixtures conformality of potentials does not imply conformality of RDFs in the same simple way as for pure fluids. Nevertheless, corresponding states arguments have sometimes been employed by postulating approximate conformality relations between mixture and pure RDFs.^{11,26} The same approach is also followed in the present paper.

We call *scaling approximations* (SA) those assuming approximate conformality of all RDFs of a mixture, according to the relation

$$g_{\alpha\beta}(r; \rho, \mathbf{x}, T; \{\sigma_{\gamma\delta}\}, \{\epsilon_{\gamma\delta}\}) \approx \hat{g}_{\text{mono}}(\lambda_{\alpha\beta} r_{\text{mono}}^*; \rho_{\text{mono}}^*, T_{\text{mono}}^*), \quad (21)$$

where \mathbf{x} , $\{\sigma_{\gamma\delta}\}, \{\epsilon_{\gamma\delta}\}$ represent the complete set of molar fractions and potential parameters,

$$\rho_{\text{mono}}^* \equiv \rho \sigma_{\text{mono}}^3, \quad T_{\text{mono}}^* \equiv \frac{k_B T}{\epsilon_{\text{mono}}}, \quad (22)$$

while σ_{mono} and ϵ_{mono} are suitably chosen average potential parameters. Generalizations with σ_{mono} and ϵ_{mono} replaced by pair-dependent parameters are possible,¹¹ but we will restrict ourselves to the simplest case. The value of each $g_{\alpha\beta}$ at r is obtained from a single functional form, appropriate to a pure HS fluid, by evaluating it at a *scaled* pair-dependent distance, $r'_{\alpha\beta} = \lambda_{\alpha\beta} r$, and at a *corresponding* thermodynamic state.

Since the Fourier transform of $h_{\text{mono}}(\lambda_{\alpha\beta} r)$ is $\lambda_{\alpha\beta}^{-3} \tilde{h}_{\text{mono}}(\lambda_{\alpha\beta}^{-1} q)$ and $S_{\text{mono}}(\lambda_{\alpha\beta}^{-1} q) = \hat{S}_{\text{mono}}(\lambda_{\alpha\beta}^{-1} q_{\text{mono}}^*)$, with $q_{\text{mono}}^* \equiv q \sigma_{\text{mono}}$,

the approximate partial structure factors become

$$S_{\alpha\beta}(q) \approx \delta_{\alpha\beta} + \sqrt{x_\alpha x_\beta} \lambda_{\alpha\beta}^{-3} \times [\hat{S}_{\text{mono}}(\lambda_{\alpha\beta}^{-1} q_{\text{mono}}^*; \rho_{\text{mono}}^*, T_{\text{mono}}^*) - 1]. \quad (24)$$

IV. HARD SPHERE POTENTIAL

For clarity, the various approximations examined in this paper are presented starting from a particular physical system, namely the HS potential. Both DA and LMA will be slightly reformulated, to point out the underlying approximations in terms of pair correlation functions $g_{\alpha\beta}(r)$.

A. Decoupling approximation

Kotlarchyk and Chen¹² proposed the *decoupling approximation* in a rather general form, to treat both polydisperse fluids and systems of nonspherical particles. They performed two basic approximations:

(a) First, they replaced orientation-dependent interparticle potentials with spherically symmetric ones. Strictly speaking, this is the actual ‘‘decoupling approximation,’’ which allows one to break the ensemble average present in the exact expression of the scattering intensity into two factors, neglecting correlations between particle orientations and positions. The result is the Fournet–Vrij expression for the scattering intensity,⁵ with form factors averaged over particle orientations. For spherical particles, this first approximation is unnecessary and hence will not be exploited in the present paper.

(b) Second, the partial structure factors $S_{\alpha\beta}(q)$ were approximated in terms of the structure factor of an appropriate *pure* fluid, as

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + \rho \sqrt{x_\alpha x_\beta} \tilde{h}_{\alpha\beta}(q) \approx \delta_{\alpha\beta} + \sqrt{x_\alpha x_\beta} [S_{\text{mono}}(q) - 1], \quad (25)$$

where the definition of the effective pure fluid must be completed suitably, depending on the particular physical system. In terms of correlation functions, this approximation is equivalent to assuming that: (i) all the RDF $g_{\alpha\beta}(r)$ have the same dependence on r , being equal to the RDF of the pure fluid, i.e., $g_{\alpha\beta}(r) \approx g_{\text{mono}}(r)$, or

$$h_{\alpha\beta}(r) \approx h_{\text{mono}}(r); \quad (26)$$

(ii) the number density of the pure fluid is equal to the total number density of the mixture, i.e., $\rho_{\text{mono}} = \rho$. With Eq. (26) and $S_{\text{mono}} = 1 + \rho_{\text{mono}} \tilde{h}_{\text{mono}}$, this implies Eq. (25).

For polydisperse HS, Kotlarchyk and Chen¹² defined the diameter of the effective HS fluid by choosing

$$\sigma_{\text{mono}} = \langle \sigma^3 \rangle^{1/3}, \quad (27)$$

ensuring that the volume fraction (or packing fraction) of the pure fluid $\eta_{\text{mono}} \equiv (\pi/6)\rho_{\text{mono}}\sigma_{\text{mono}}^3$ is equal to the total volume fraction of the mixture, $\eta \equiv (\pi/6)\rho\langle \sigma^3 \rangle$. The resulting DA structure factors are

$$S_{\alpha\beta}(q) \approx \delta_{\alpha\beta} + \sqrt{x_{\alpha}x_{\beta}}[\hat{S}_{\text{mono}}(q_{\text{mono}}^*; \eta) - 1], \quad (28)$$

$$S_M(q)^{\text{DA}} = 1 + \langle w(q) \rangle^2 [\hat{S}_{\text{mono}}(q_{\text{mono}}^*; \eta) - 1], \quad (29)$$

$$S_{\text{NN}}(q)^{\text{DA}} = \hat{S}_{\text{mono}}(q_{\text{mono}}^*; \eta). \quad (30)$$

On the left hand side of these equations the dependence on the thermodynamic state and the potential parameters of the mixture have been omitted for simplicity. Moreover, here and in the following, we simply write $\eta_{\text{mono}} = \eta$ instead of ρ_{mono}^* in \hat{S}_{mono} , since these quantities are proportional.

Before concluding this subsection, some remarks are appropriate. The first one is that the approximation expressed by Eq. (26) was already proposed in the theory of liquid mixtures: it is known as *random mixture*, or *random mixing*, approximation,^{9,10} and sometimes is also referred to as the *substitutional model*.² The weakness of this approach is evident from its RDF form, Eq. (26), because it ignores the ordering which takes place in the presence of different particle sizes. Therefore, the DA is expected to be a very poor approximation for moderate or even low size polydispersity. A second remark is that, for a given interparticle potential u_{mono} , it is possible to choose among several routes to evaluate S_{mono} from the pure fluid OZ integral equation, by changing the closure. In the luckiest cases an analytical solution may be available, but a numerical solution is always feasible. For polydisperse HS, Kotlarchyk and Chen¹² used the PY analytical solution for the monodisperse fluid, but other more accurate closures [as, for instance, the Ballone–Pastore–Galli–Gazzillo²⁹ (BPGG) or the Rogers–Young³⁰ (RY) approximations] could also be employed. A final remark is that DA may be regarded as a scaling approximation, obtained from Eq. (24) with the choice $\lambda_{\alpha\beta} = 1$ and $\sigma_{\text{mono}} = \langle \sigma^3 \rangle^{1/3}$.

B. Local monodisperse approximation

This approximation was originally formulated by Pedersen¹³ for polydisperse hard spheres, but can be easily extended to polydisperse fluids with different potentials. According to the original presentation, in LMA a p -component mixture is approximated by a set of p noninteracting pure subsystems (a subscript “mono- α ” will be used to characterize that of species α), and the scattering intensity is calculated as a superposition of the scattering intensities from the subsystems, weighted according to the size distribution of the mixture.

For HS, LMA may be expressed, in terms of partial structure factors, as

$$S_{\alpha\beta}(q) \approx \begin{cases} 0, & \alpha \neq \beta \\ \hat{S}_{\text{mono}}(q_{\alpha}^*; \eta), & \alpha = \beta, \end{cases} \quad (31)$$

which implies that

$$S_M(q)^{\text{LMA}} = \sum_{\alpha=1}^p x_{\alpha} w_{\alpha}^2(q) \hat{S}_{\text{mono}}(q_{\alpha}^*; \eta). \quad (32)$$

$S_{\text{NN}}(q)^{\text{LMA}}$ is obtained by putting all $w_{\alpha}(q) = 1$. The pure subsystem of species α consists of hard spheres with diameter $\sigma_{\text{mono-}\alpha} = \sigma_{\alpha}$ and at a number density $\rho_{\text{mono-}\alpha} = \rho\langle \sigma^3 \rangle / \sigma_{\alpha}^3$, which differs, in general, from the density $\rho_{\alpha} \equiv x_{\alpha}\rho$ of that species in the mixture. Such a choice for the $\rho_{\text{mono-}\alpha}$ values of the p subsystems ensures that the volume fraction of each of these pure fluids, $\eta_{\text{mono-}\alpha} \equiv (\pi/6)\rho_{\text{mono-}\alpha}\sigma_{\alpha}^3$, equals the total volume fraction η of the mixture. For S_{mono} Pedersen used the PY analytical expression.¹³

In terms of pair correlation functions, LMA may be written as

$$\rho \sqrt{x_{\alpha}x_{\beta}} h_{\alpha\beta}(r) \approx \delta_{\alpha\beta} \rho_{\text{mono-}\alpha} \hat{h}_{\text{mono}}(r_{\alpha}^*; \eta), \quad (33)$$

which shows that LMA neglects all interactions between particles with different diameters, i.e., $h_{\alpha\beta}(r) = 0$ if $\alpha \neq \beta$. Pedersen justified this approximation on the ground of a physical picture, in some sense complementary to DA, which assumes that particle sizes and positions are completely correlated. This means that particle size varies slowly with position, so that every particle is surrounded by particles of the same size and the system looks *locally monodisperse*. On the other hand, LMA may simply be regarded, in a corresponding states framework, as a conformality assumption not for $g_{\alpha\beta}$ but for $S_{\alpha\beta}$, done to reduce the double sum to a single sum in both structure factors.

C. Scaling approximation

After analyzing DA and LMA in terms of pair correlation functions, it becomes evident that *excluded volume* effects are not taken into account correctly by these approximations, since the exact hard core conditions, $g_{\alpha\beta}(r) = 0$ for $r < \sigma_{\alpha\beta}$, are not satisfied. To avoid this defect and obtain reasonably accurate RDFs of HS mixtures from pure fluid ones with a limited effort, we propose a *scaling approximation*, derived from Eq. (21) with the choice

$$\lambda_{\alpha\beta} = \sigma_{\text{mono}} / \sigma_{\alpha\beta} \quad \text{and} \quad \sigma_{\text{mono}} = \langle \sigma^3 \rangle^{1/3}. \quad (34)$$

Since $\lambda_{\alpha\beta} r_{\text{mono}}^* = r_{\alpha\beta}^*$, with the definition $r_{\alpha\beta}^* \equiv r / \sigma_{\alpha\beta}$, our SA for HS can be written as

$$g_{\alpha\beta}(r; \rho, \mathbf{x}; \{\sigma_{\gamma\delta}\}) \approx \hat{g}_{\text{mono}}(r_{\alpha\beta}^*; \eta). \quad (35)$$

Note that σ_{mono} is the same as in DA, while the choice for $\lambda_{\alpha\beta}$ ensures that, when $r < \sigma_{\alpha\beta}$, one gets $r_{\alpha\beta}^* < \sigma_{\text{mono}}$ and, consequently, $g_{\alpha\beta}(r) = 0$. Since excluded volume effects are very important for the structure of condensed fluids, it is therefore reasonable to expect that SA is better than both DA and LMA, although it incorrectly assumes that all RDF values at contact are equal: $g_{\alpha\beta}(\sigma_{\alpha\beta}) \approx g_{\text{mono}}(\sigma_{\text{mono}})$. Once

again the choice for σ_{mono} ensures that the RDF of the pure fluid is evaluated at the same packing fraction of the mixture. From Eqs. (9), (24) and (34) one then finds

$$S_M(q)^{\text{SA}} = 1 + \sum_{\alpha=1}^p \sum_{\beta=1}^p x_{\alpha} x_{\beta} w_{\alpha}(q) w_{\beta}(q) \times \frac{\sigma_{\alpha\beta}^3}{\langle \sigma^3 \rangle} [\hat{S}_{\text{mono}}(q_{\alpha\beta}^*; \eta) - 1] \quad (36)$$

with the definition $q_{\alpha\beta}^* \equiv q \sigma_{\alpha\beta}$. $S_{\text{NN}}(q)^{\text{SA}}$ is again obtained from the expression for $S_M(q)^{\text{SA}}$ by putting all $w_{\nu}(q) = 1$.

It should be noted that our SA closely resembles, albeit it is not identical to, the so-called *van der Waals one-fluid* (vdW1) *approximation*.⁹⁻¹¹ In vdW1 thermodynamics calculations the mixture is replaced by a single pure fluid, with averaged potential parameters σ_x, ϵ_x given by van der Waals rules

$$\begin{cases} \sigma_x^3 = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} \sigma_{\alpha\beta}^3, \\ \epsilon_x = \sigma_x^{-3} \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} \epsilon_{\alpha\beta} \sigma_{\alpha\beta}^3. \end{cases} \quad (37)$$

Of course, there is no ϵ_x and no dependence on T in the RDFs of HS fluids. Although often presented in the literature with a different notation, vdW1 may be regarded as a scaling approximation, obtainable from Eq. (21) with $\lambda_{\alpha\beta} = \sigma_{\text{mono}}/\sigma_{\alpha\beta}$ and $\sigma_{\text{mono}} = \sigma_x$. This choice for σ_{mono} implies that the vdW1 RDF of the pure fluid is evaluated at a packing fraction, $\eta_x \equiv (\pi/6)\rho\sigma_x^3$, which differs from that of the mixture, $\eta \equiv (\pi/6)\rho\langle\sigma^3\rangle$. As a consequence, for HS we can write

$$S_M(q)^{\text{vdW1}} = 1 + \sum_{\alpha=1}^p \sum_{\beta=1}^p x_{\alpha} x_{\beta} w_{\alpha}(q) w_{\beta}(q) \times \frac{\sigma_{\alpha\beta}^3}{\sigma_x^3} [\hat{S}_{\text{mono}}(q_{\alpha\beta}^*; \eta_x) - 1]. \quad (38)$$

D. Exact PY solution

The closed analytical expression for $S_M(q)$ of polydisperse HS in the PY approximation, $S_M(q)^{\text{PY}}$ can be found in Vrij's original paper⁵ or in Ref. 6 (with all charges set to zero). The corresponding expression for $S_{\text{NN}}(q)^{\text{PY}}$ is simply obtained by putting $F_{\nu}(q) = 1$ for all form factors in the $S_M(q)^{\text{PY}}$ formula.

E. Numerical results

We tested the results for $S_M(q)$ obtained from DA, LMA, SA and vdW1 against Vrij's $S_M(q)^{\text{PY}}$, which is exact within the PY approximation. Such a comparison requires the evaluation of $\hat{S}_{\text{mono}}(q_{\alpha\beta}^*; \eta_{\text{mono}})^{\text{PY}}$, for which a simple analytical expression is available.³¹

Using the Schulz distribution to represent the size polydispersity, the packing fraction of the HS mixture may be written as

$$\eta \equiv (\pi/6)\rho\langle\sigma^3\rangle = (\pi/6)\rho^*(1+s^2)(1+2s^2), \quad (39)$$

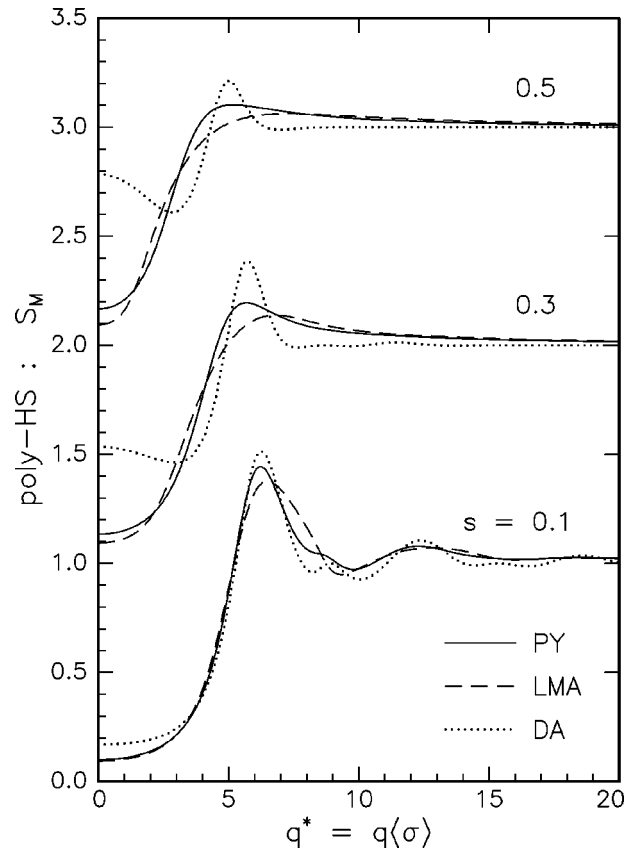


FIG. 1. Structure factor $S_M(q)$ of hard spheres, for different degrees of polydispersity s , at fixed packing fraction $\eta=0.3$ (here, and in all following figures, curves at different s are shifted upwards to avoid overlapping). Solid lines: Vrij's exact PY results. Dashed lines: local monodisperse approximation, LMA. Dotted lines: decoupling approximation, DA.

where we have chosen $\langle\sigma\rangle$ as the unit of length, and defined the dimensionless density $\rho^* \equiv \rho\langle\sigma\rangle^3$. Since working with dimensionless variables is very convenient, we also define $r^* \equiv r/\langle\sigma\rangle$, $\sigma^* \equiv \sigma/\langle\sigma\rangle$ and $q^* \equiv q\langle\sigma\rangle$.

The effect of polydispersity on structure factors may be studied by varying s with either η or ρ^* constant. Qualitatively, the results at a fixed total density and those at a fixed packing fraction are similar. In Figs. 1 and 2 we present some results for $S_M(q)$ at fixed packing fraction $\eta=0.3$, with varying polydispersity, $s=0.1, 0.3$ and 0.5 (most of the experimental s values lie in the range $0-0.3$). The three distributions of diameters were discretized with a grid size $\Delta\sigma^* = 0.02$, and truncated at $\sigma_{\text{cut}}^* = 1.68, 3.48$ and 5.90 (where $f(\sigma)\Delta\sigma \approx 10^{-8}$). These values of σ_{cut}^* correspond to polydisperse mixtures with a number of components $p = 85, 175$ and 296 , practically intractable with the available algorithms for solving IEs numerically.

At a fixed η , calculating $S_M(q)$ or $S_{\text{NN}}(q)$ in the DA, LMA and SA approximations requires the knowledge of $\hat{S}_{\text{mono}}(\hat{q}, \eta)^{\text{PY}}$ at $\hat{q} = q\langle\sigma^3\rangle^{1/3}$, $q\sigma_{\alpha}$ and $q\sigma_{\alpha\beta}$. In other words, for each q value, a single evaluation of \hat{S}_{mono} is needed for DA, a number p of evaluations is required for LMA, and $p(p+1)/2$ evaluations for SA and vdW1. For vdW1, \hat{S}_{mono} is computed at $\eta_{\text{mono}} = \eta_x$, rather than $\eta_{\text{mono}} = \eta$. To save computer time in LMA, SA and vdW1 calcu-

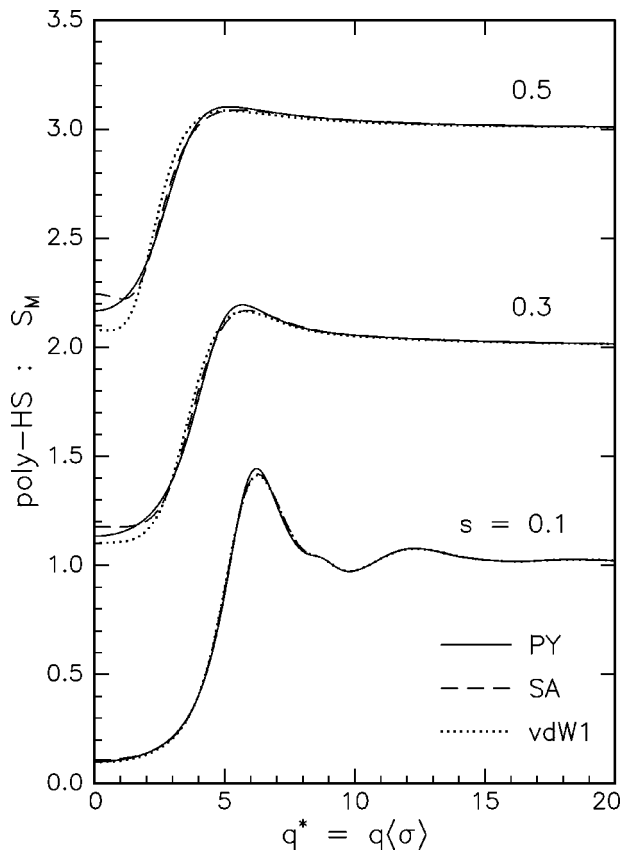


FIG. 2. Structure factor $S_M(q)$ of hard spheres, for different degrees of polydispersity s , at fixed packing fraction $\eta=0.3$. Solid lines: Vrij's exact PY results. Dashed lines: scaling approximation, SA. Dotted lines: van der Waals one-fluid approximation, vdW1.

lations, we avoid the repeated evaluations for each q by taking advantage of the fact that \hat{S}_{mono} does not depend on q and σ separately, but only on their product $\hat{q} = q\sigma_{\alpha\beta} = q^*\sigma_{\alpha\beta}^*$. Thus we can choose a suitable grid size Δq^* and a number of points \mathcal{N} , and calculate $\hat{S}_{\text{mono}}(\hat{q}_i, \eta)^{\text{PY}}$ at the grid points $\hat{q}_i = i\Delta q^*$ ($i=0, \dots, \mathcal{N}-1$) only once, storing all values in an array. Of course, the grid points \hat{q}_i do not exhaust all the required $q\sigma_{\alpha\beta}$ values. Nevertheless, if the grid size is small enough, the value of the continuous function \hat{S}_{mono} at $\hat{q} = q^*\sigma_{\alpha\beta}^*$ can be approximated with that at the nearest grid point, whose index in the array is simply determined from the ratio $q^*\sigma_{\alpha\beta}^*/\Delta q^*$. In the worst case, $s=0.5$, to get $S_M(q)$ in a range $0 \leq q^* \leq q_{\text{max}}^* \approx 20$ (a reasonable choice), $\hat{S}_{\text{mono}}(\hat{q})$ must be evaluated in a range $0 \leq \hat{q} \leq \max(q^*\sigma_{\text{cut}}^*) \approx 120$. To satisfy such a condition and get a good grid size in q^* space, $\Delta q^* = q_{\text{max}}^*/\mathcal{N}$, we choose $q_{\text{max}}^* = \pi/\Delta\sigma^* = 50\pi$ and $\mathcal{N} = 4096$.

Figure 1 shows DA and LMA results for $S_M(q)$ versus the exact PY ones. Similar plots are reported by Pedersen.¹³ With increasing polydispersity, $S_M(q)$ increases in the low- q region, its first peak is reduced and shifted to smaller q values, and the subsequent oscillations are progressively washed out. The failure of DA, even at low polydispersity, is evident not only at small q , but also in the first peak region. LMA is significantly better at small scattering vectors, but does not reproduce the shape of the first peak correctly.

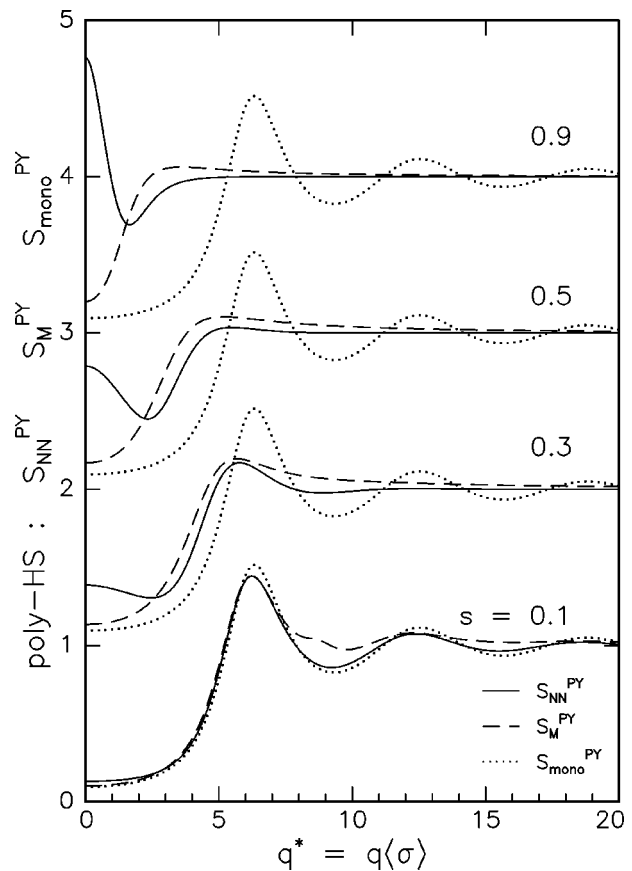


FIG. 3. Comparison of exact PY results for HS structure factors $S_M(q)$ and $S_{NN}(q)$, for different degrees of polydispersity s , at fixed packing fraction $\eta=0.3$. Solid lines: exact PY results for $S_{NN}(q)$. Dashed lines: exact PY results for $S_M(q)$. Dotted lines: monodisperse structure factor.

The corresponding SA and vdW1 results are plotted in Fig. 2. Now the agreement with the exact PY data is surprisingly good in both cases: the position of the first peak is well reproduced, and its height is only slightly underestimated. However, SA is globally superior: for $s=0.3$ and 0.5 its worst discrepancies are found near the origin, at $q^* \leq 2$, whereas the vdW1 curves are somewhat shifted with respect to the exact ones on the left side of the first peak. It should be recalled that, unlike vdW1, SA is evaluated at the true packing fraction of the mixture.

Finally, it is worth looking at the number-number structure factor $S_{NN}(q)$. In Fig. 3 a comparison is made among $S_{NN}(q)^{\text{PY}}$, $S_M(q)^{\text{PY}}$, and $S_{\text{mono}}(q)^{\text{PY}}$. The results for $S_{NN}(q)^{\text{PY}}$ were obtained from our closed analytical expression, which is exact within the PY approximation (Griffith, Triolo, and Compere³² presented similar data, calculated without using a closed formula³³). For $s=0$, all these structure factors coincide, but with increasing s the differences become larger and larger. In particular, $S_{NN}(q)^{\text{PY}}$ exhibits a more rapid flattening of the first peak than $S_M(q)^{\text{PY}}$, while its increase in the low- q region is much more dramatic (see the extreme case $s=0.9$, also included). Since $S_{NN}(0)$ measures the fluctuations in the total particle density (irrespective of the species), this behavior of $S_{NN}(q)$ provides more physical information than that provided by $S_M(q)$. Figure 4 then shows the $S_{NN}(q)$ predicted by SA, compared to

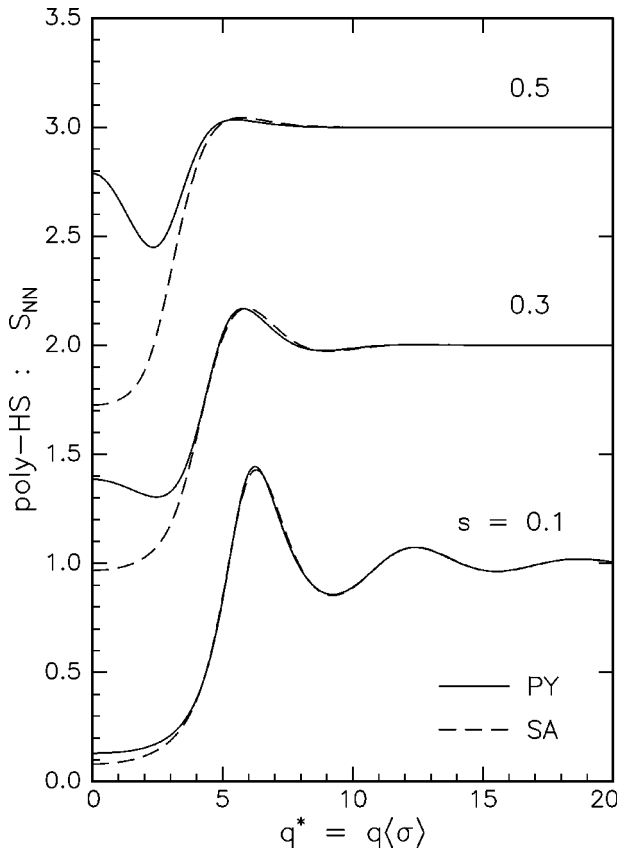


FIG. 4. Structure factor $S_{NN}(q)$ of hard spheres, for different degrees of polydispersity s , at fixed packing fraction $\eta=0.3$. Solid lines: exact PY results. Dashed lines: scaling approximation, SA.

$S_{NN}(q)^{PY}$. The performance of SA is good in the first peak region and beyond, but the approximation fails in the low- q region and is unable to reproduce the number density fluctuations correctly. This discrepancy is, however, less important in $S_M(q)$, which is the structure factor more directly comparable with small angle scattering data. In fact, multiplying $S_{\alpha\beta}(q)$ by the product of form factors $w_\alpha(q)w_\beta(q)$ reduces the mentioned defect (as already seen in Fig. 2); moreover, a significant part of the region near $q=0$ is experimentally inaccessible.

V. LENNARD-JONES POTENTIAL

From $\epsilon_\alpha = \epsilon_{\langle\sigma\rangle}(\sigma_\alpha/\langle\sigma\rangle)^z$ and the Berthelot rule, Eqs. (13) and (7), it follows that

$$\epsilon_{\alpha\beta}^* \equiv \frac{\epsilon_{\alpha\beta}}{k_B T} = \frac{1}{T^*} \left(\frac{\sqrt{\sigma_\alpha \sigma_\beta}}{\langle\sigma\rangle} \right)^z \quad (40)$$

with $T^* \equiv k_B T / \epsilon_{\langle\sigma\rangle}$.

As for HS mixtures, in addition to a density $\rho^* \equiv \rho \langle\sigma\rangle^3$, it is convenient to define a second dimensionless variable $\phi \equiv \rho \langle\sigma^3\rangle$, or $\eta_{LJ} \equiv \phi \pi/6$, which plays the same role as the HS packing fraction η (although, rigorously, a LJ particle has no definite boundary and volume). For the Schulz size distribution, $\phi = \rho^*(1+s^2)(1+2s^2)$.

We performed IE and MD calculations for LJ mixtures at fixed $T^*=1$, $\phi=0.8$ ($\eta_{LJ} \approx 0.42$) with $z=2$ and polydispersity parameter $s=0$ (monodisperse case), 0.1 and 0.3. For

$s=0$, one has $\phi = \rho^*$, and the corresponding thermodynamic state, $\rho^*=0.8$, $T^*=1$, is near the triple point in the LJ phase diagram.¹⁵ With increasing s at fixed ϕ , ρ^* decreases. Taking into account the superiority of SA with respect to DA, LMA and vdW1 approximation in the polydisperse HS case, our IE calculations for the LJ potential were restricted only to SA (some information about the performance of vdW1 for LJ potentials can be found in works by Hoheisel, Deiters, and Lucas,^{34,35} but only for binary mixtures).

Kofke and Glandt^{22,23} presented similar Monte Carlo results for a polydisperse LJ model of n paraffins. Unfortunately, since these authors started from an activity distribution, rather than a composition distribution, their simulations are not directly comparable with our IE calculations.

A. Molecular dynamics simulations

The MD simulations employed 1000 particles, in a cube with periodic boundary conditions, and, using Andersen's stochastic collision method,³⁶ described a fluid constrained at constant $\phi=0.8$ and maintained in contact with a heat bath. The equations of motion were integrated using the velocity Verlet algorithm.^{37,38} The atomic diameters σ were drawn from a Schulz distribution at the desired s , with well depths given by Eq. (40). To reduce the sampling noise, the distribution was periodically regenerated during the simulation. To avoid truncation effects in the Fourier transforms, $S_M(q)$ was evaluated in the simulation directly using the definition

$$S_M(q) = \frac{\langle |\sum_i F_i(q) \exp(i\mathbf{q} \cdot \mathbf{r}_i)|^2 \rangle}{\sum_i F_i^2(q)}, \quad (41)$$

where \mathbf{q} is the wave vector, $q=|\mathbf{q}|$, \mathbf{r}_i is the position of the i th particle and $F_i(q)$ its form factor, Eq. (11). A similar expression was used to obtain $S_{NN}(q)$, and we also calculated its r -space counterpart, the number-number correlation function³¹ $g_{NN}(r)$.

B. Scaling approximation and numerical results

The scaling approximation for the LJ potential is derived from Eq. (21) with the choice $\lambda_{\alpha\beta} = \sigma_{\text{mono}}/\sigma_{\alpha\beta}$ and $\sigma_{\text{mono}} = \langle\sigma^3\rangle^{1/3}$ [analogous to Eq. (34) for the HS potential], and

$$\epsilon_{\text{mono}} = \epsilon_{\langle\sigma\rangle} \left(\frac{\sigma_{\text{mono}}}{\langle\sigma\rangle} \right)^z, \quad (42)$$

which is consistent with Eqs. (13) and (40). The SA for LJ therefore reads

$$g_{\alpha\beta}(r; \rho, \mathbf{x}, T; \{\epsilon_{\gamma\delta}\}, \{\sigma_{\gamma\delta}\}) \approx \hat{g}_{\text{mono}}(r_{\alpha\beta}^*; \eta_{LJ}, T_{\text{mono}}^*). \quad (43)$$

Note that T_{mono}^* decreases with increasing s : with Eqs. (22), (42) and the Schulz distribution, $T_{\text{mono}}^* = T^*/[(1+s^2)(1+2s^2)]^{z/3}$.

To evaluate $\hat{g}_{\text{mono}}(q_{\alpha\beta}^*; \eta_{LJ}, T_{\text{mono}}^*)$, we solved numerically, for each T_{mono}^* value, the MHNC-ML integral equation with $\mathcal{N}=4096$ and $\Delta r^*=0.02$ (which corresponds to $q_{\text{max}}^* = \pi/\Delta r^* = 50\pi$, just as in the HS case). From the resulting \hat{S}_{mono} , the polydisperse structure factors $S_M(q)^{SA}$ and $S_{NN}(q)^{SA}$ were finally evaluated from the obvious analogue of Eq. (36), in the same manner presented in detail for the HS potential.

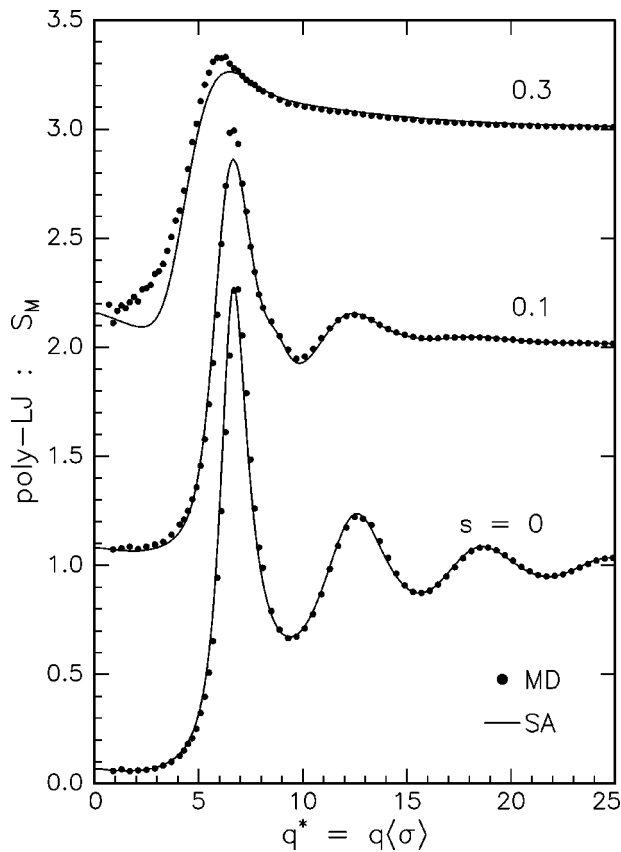


FIG. 5. Structure factor $S_M(q)$ of Lennard-Jones fluids, for different degrees of polydispersity s , at fixed $\phi=0.8$ and $T^*=1$. Points: molecular dynamics data. Lines: scaling approximation, SA.

In Figs. 5 and 6 the $S_M(q)^{SA}$ and $S_{NN}(q)^{SA}$ results are tested against the corresponding MD data. The overall agreement is good. For $s=0.1$ the positions of maxima and minima and the shape of both structure factors are correctly predicted; only the height of the first peak is slightly underestimated. For $s=0.3$ the first peak is well reproduced in $S_{NN}(q)^{SA}$, but not equally well in $S_M(q)^{SA}$. On the contrary, $S_{NN}(q)^{SA}$ is completely off in the region near the origin, where the discrepancy in $S_M(q)^{SA}$ is less dramatic. Finally, Fig. 7 shows the behavior of $g_{NN}(r)$: also in r space SA works quite well. In the IE calculations we employed the expression³¹

$$g_{NN}(r) = \sum_{\alpha=1}^P \sum_{\beta=1}^P x_{\alpha} x_{\beta} g_{\alpha\beta}(r). \quad (44)$$

The MD data for the monodisperse case, $s=0$, have been found to be in perfect agreement with the Monte Carlo results for $g(r)$ published by Llano-Restrepo and Chapman³⁹ (not reported in Fig. 7).

The slightly worse performance of SA in the LJ case with $s=0.3$, with respect to the HS one with the same polydispersity, depends only on the higher packing fraction ($\eta_{LJ}=0.42$, whereas $\eta=0.3$ for hard spheres).

Finally, it is worth mentioning that we also performed MD simulations with different z values ($z=1$ and 3), and tested variants of the SA with alternative choices for ϵ_{mono} (for instance, $\epsilon_{\text{mono}} = \epsilon_{\langle\sigma\rangle}$, or $\epsilon_{\text{mono}} = \epsilon_{\langle\sigma\rangle}(\sigma_{\text{mono}}/\langle\sigma\rangle)^3$).

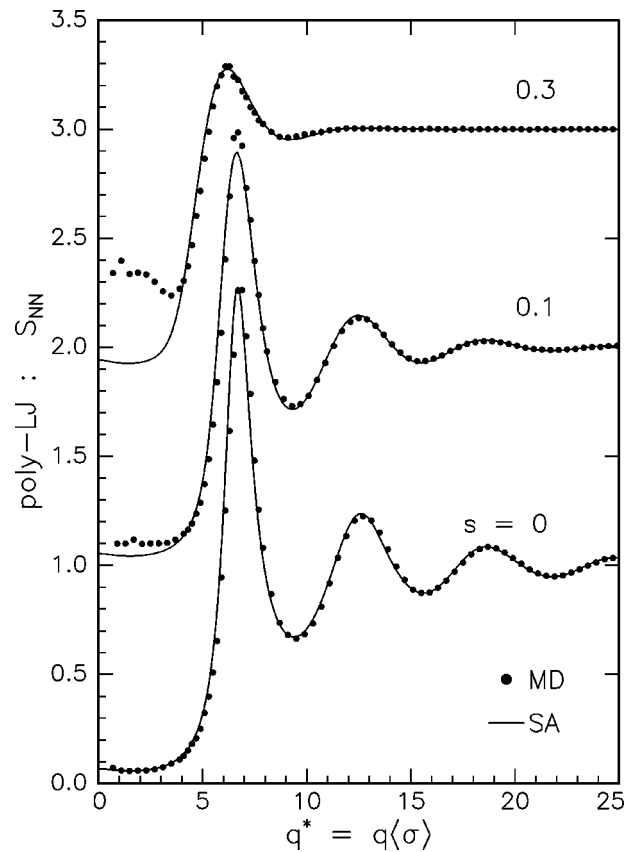


FIG. 6. Structure factor $S_{NN}(q)$ of Lennard-Jones fluids, for different degrees of polydispersity s , at fixed $\phi=0.8$ and $T^*=1$. Points: molecular dynamics data. Lines: scaling approximation, SA.

Only very small changes of peak heights were found in all cases. This relative insensitiveness to the well depths may perhaps be explained by the well known fact that at high packing fractions the structure depends essentially on the repulsive part of potentials, while the attractive forces sensibly affect only thermodynamics.

An improved SA could be obtained by replacing T_{mono}^* in Eq. (43) with $T_{\alpha\beta}^* \equiv k_B T / \epsilon_{\alpha\beta}$. This choice would be akin to the ‘‘mean density approximation,’’⁴⁰ used for binary LJ mixtures.^{34,35,41} However, we have not attempted its application to polydisperse fluids, since it would require the evaluation of \hat{g}_{mono} at many different reduced temperatures, which is inconvenient when IEs have to be solved numerically. In the particular case of the LJ potential one could take advantage of an explicit analytical parametrization for the RDF proposed by Goldman.⁴² This extension goes beyond the scope of the present paper and might be the subject of future work.

VI. CONCLUSIONS

In this paper we have shown that the structure of simple polydisperse fluids can be successfully predicted by integral equation methods, even when no analytical solution is available and a numerical one is impracticable because of the very large number of components. We have obtained rather accurate structure factors by solving IEs for appropriate pure fluids and applying a recipe based upon a corresponding states

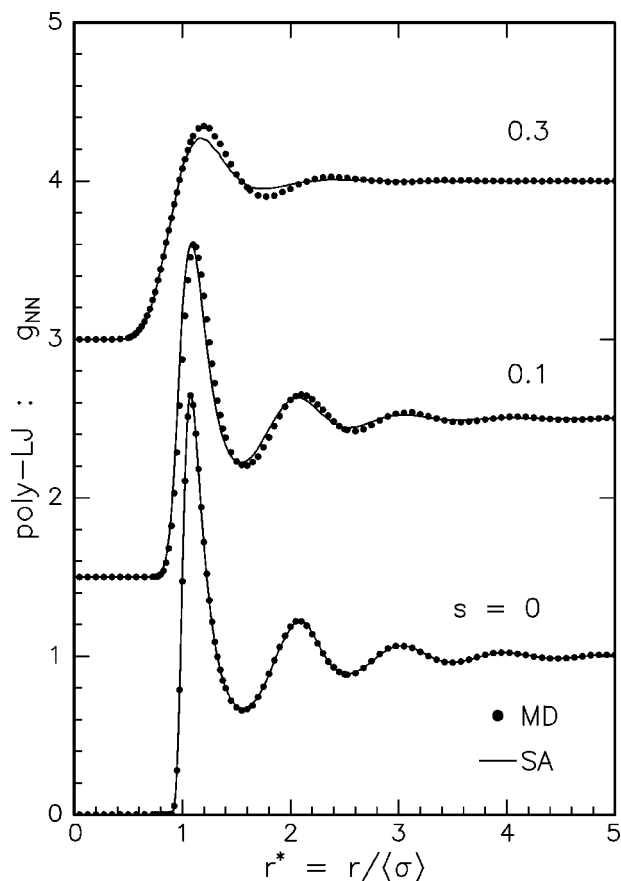


FIG. 7. Number-number correlation functions $g_{NN}(r)$ of Lennard-Jones fluids, for different degrees of polydispersity s , at fixed $\phi=0.8$ and $T^*=1$. Points: molecular dynamics data. Lines: scaling approximation, SA.

approach, which assumes conformality of all RDFs in the polydisperse mixture. Thus the hypothesis that all RDFs have essentially the same shape, but are scaled with respect to each other, turns out to be physically sound.

The good performance of the scaling approximation for rather concentrated systems is due to a correct treatment of excluded volumes. This feature appears to be lacking in both the decoupling approximation and the local monodisperse approximation, when these are reformulated in terms of pair correlation functions. The importance of evaluating the properties of the reference pure fluid at exactly the same packing fraction of the mixture is also to be emphasized. This condition is not satisfied by the very similar vdW1 approximation. A shortcoming of SA is certainly the equality of all RDFs at contact, but this error appears to be a higher order effect, at least at high packing fractions.

In conclusion, the proposed SA approximation offers to small angle scattering experimentalists a simple and valuable tool to predict structure factors or to fit data, and has proved superior to both DA and LMA. We have shown that the SA is applicable to different potentials for nonionic fluids. An extension of SA to polydisperse ionic mixtures will be presented in a forthcoming paper.

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