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Integral-equation theory of polydisperse Yukawa systems

Bruno D'Aguanno* and Rudolf Klein
Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, Germany

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A discretization method is presented in order to describe structural properties of Yukawa-type fluids consisting of particles with a continuous size and charge distribution. The accuracy of the method is tested by comparing the results from the Rogers-Young closure scheme of the Ornstein-Zernike equation for the correlation functions with the corresponding Monte Carlo data. The relevance of this method for the interpretation of light- and neutron-scattering data of colloidal dispersions is also briefly discussed.

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I. INTRODUCTION

Complex liquids like colloidal dispersions are known to consist of a collection of macroparticles that exhibits a size distribution, a shape distribution, and, if the macroparticles are charged, also a charge distribution [1–5]. Whereas the shape polydispersity can often be avoided, the size and charge polydispersities are unavoidable, and they have to be considered as intrinsic characteristics of charge-stabilized colloidal dispersions. As a consequence, a statistical-mechanical description of the dispersions has to take into account the polydispersities and has to show how they influence measurable quantities like the structure factor $S(k)$, the diffusion coefficient D, and thermodynamic properties.

Here we show how to handle, in an (almost) exact way, the charge and size polydispersities of dispersions of spherical colloidal particles whose interactions can be described by Yukawa-type potentials. Despite their experimental importance, these charge- and size-polydisperse systems are theoretically less investigated as compared to size polydisperse hard-sphere systems, for which an analytical solution of the PY (Percus-Yevick) closure is known when the polydispersity is described by a continuous Schulz distribution [6]. The main reason is due to the fact that an accurate and quantitative description of Yukawa systems is possible through closure relations, i.e., HNC (hypernetted chain), MHNC (modified HNC), or RY (Rogers-Young) that have only numerical solutions. Analytic solutions of the MSA (mean spherical approximation) scheme for n-component mixtures of Yukawa particles have been recently published [7,8]. Although to solve MSA equations is in principle simpler than to solve HNC or RY equations, difficulties in selecting acceptable solutions from the manifold of solutions prevented the application of MSA to cases with continuous polydispersity. The only application to the microscopic structure concerns a case with $n=2$ [8]. It should also be recalled that MSA needs an *ad hoc* rescaling procedure when applied to a range of parameters characteristic of colloidal dispersions [9,8]. Another attempt to treat polydisperse colloidal suspensions has been made by Löwen, Roux, and Hansen [10]. When compared to MD (molecular-dynamics) data, the results show the same kind of drawbacks found from comparisons between one-component results and MD data on polydisperse systems. A satisfactory treatment of polydisperse Yukawa systems is, therefore, still lacking.

It is our aim to show how infinitely-many-component, or polydisperse, systems can be successfully described in the framework of the HNC and/or RY closures. We will present a methodology that is general and can be applied, with the necessary modifications, to cases in which polydispersities are described by a distribution different from the Schulz distribution, like the log-normal, the Gaussian, the exponential, etc. In addition, the method will give a comparable degree of accuracy also for cases in which the interparticle interactions are different from the Yukawa potential, since a large class of interactions is well treated by HNC and/or RY closures.

II. THEORY

We consider systems of N Yukawa particles whose size polydispersity is described by the Schulz distribution [11]

$$F(\sigma)=\left[\frac{t+1}{\langle\sigma\rangle}\right]^{t+1}\frac{\sigma^{t}}{\Gamma(t+1)}\exp\left[-\frac{t+1}{\langle\sigma\rangle}\sigma\right]\quad(t>0)\tag{1}$$

in which σ is the particle diameter, $\Gamma(t)$ is the gamma function, and t denotes a parameter controlling the width of the distribution. The normalized moments of this distribution are given by the recursion relations

$$\langle\sigma^{m}\rangle=\frac{1}{\langle\sigma\rangle^{m}}\int_{0}^{\infty}d\sigma\,\sigma^{m}F(\sigma)=\frac{t+m}{t+1}\langle\sigma^{m-1}\rangle\ ,\quad m=1,2\ldots\tag{2}$$

with $\langle\sigma^{0}\rangle=1$. We classify the different systems according to their standard deviations in size, $s_{\sigma}=(\langle\sigma^{2}\rangle-\langle\sigma\rangle^{2})^{1/2}/\langle\sigma\rangle$. The charge polydispersity is obtained by simply fixing the charge $Q_{\langle\sigma\rangle}$ on the particle of diameter $\langle\sigma\rangle$ and keeping the surface charge density constant, an assumption that can easily be replaced by a different scaling, if necessary.

The form of the interaction potential energy between particles σ and σ' is taken as [12]

$$\beta\varphi_{\sigma\sigma'}(r)=\frac{Z_\sigma L_B^{1/2}e^{\kappa\sigma/2}}{1+\kappa\sigma/2}\,\frac{Z_{\sigma'}L_B^{1/2}e^{\kappa\sigma'/2}}{1+\kappa\sigma'/2}\,\frac{e^{-\kappa r}}{r}$$
$$=A_\sigma A_{\sigma'}\frac{e^{-\kappa r}}{r}\ , \qquad (3)$$

where $L_B=e^2/(4\pi\epsilon_0\epsilon k_B T)$ is the Bjerrum length, Z_σ is the valence of the particle σ, $\beta=1/(k_B T)$, and $\kappa=(4\pi L_B\sum_\sigma n_\sigma Z_\sigma)^{1/2}$ denotes the inverse Debye-Hückel screening length, with n_σ the number density of species σ.

To show how to treat polydispersity in calculating various correlation functions, we consider the number-number pair-distribution function $g_{NN}(r)$, and the "measured" static structure factor $S^M(k)$. For a system with infinitely many components, $g_{NN}(r)$ is defined by

$$g_{NN}(r)=\int d\sigma\int d\sigma' F(\sigma)F(\sigma')g_{\sigma\sigma'}(r)\ , \qquad (4)$$

where

$$g_{\sigma\sigma'}=\frac{1}{NnF(\sigma)F(\sigma')}\left\langle\sum_{i=1}^{N_\sigma}\sum_{j=1}^{N_{\sigma'}}{}'\delta(\mathbf{r}+\mathbf{r}_j^{\sigma'}-\mathbf{r}_i^{\sigma})\right\rangle\ , \qquad (5)$$

with the prime on the summation indicating the emission of the $i=j$ terms when $\sigma=\sigma'$, and with $\mathbf{r}_i^\sigma$ denoting the position of the particle i belonging to the N_σ particles of diameter σ.

The "measured" static structure factor $S^M(k)$ is introduced in the context of static light-scattering experiments [13,14] and is defined by

$$S^M(k)=\frac{\int d\sigma\int d\sigma' F(\sigma)F(\sigma')b_\sigma(k)b_{\sigma'}(k)S_{\sigma\sigma'}(k)}{\int d\sigma F(\sigma)b_\sigma^2(k)}\ , \qquad (6)$$

in which, for the form amplitudes $b_\sigma(k)$, we take the expression obtained for spheres with a homogeneous distribution of scattering material

$$b_\sigma(k)\propto\sigma^2\frac{j_1(k\sigma/2)}{k}\ . \qquad (7)$$

Here j_1 is the spherical Bessel function of first order. The partial static-structure factors $S_{\sigma\sigma'}(k)$ are

$$S_{\sigma\sigma'}(k)=\frac{\delta_{\sigma\sigma'}}{F(\sigma)}+n\tilde{h}_{\sigma\sigma'}(k)\ , \qquad (8)$$

where $\tilde{h}_{\sigma\sigma'}(k)$ is the Fourier transform of $h_{\sigma\sigma'}(r)=g_{\sigma\sigma'}(r)-1$.

Equations (4) and (6) for $g_{NN}(r)$ and $S^M(k)$ are of no practical use in connection with integral-equation theories that require a numerical implementation for their solution, like the HNC and/or RY schemes. The only chance is to reduce the integrals appearing in these equations to summations over a small number of terms.

The problem of evaluating $g_{NN}(r)$ and $S^M(k)$ can be attacked from two different points of view. In the first one, which is more numerical by nature, we take advantage of the particular dependence of $F(\sigma)$ on the integration variable σ. Using Eq. (1), the integrals appearing in Eqs. (4) and (6) can be written in the form

$$I(x)=\int_0^\infty d\sigma\,\sigma^t\exp(-a\sigma)f(\sigma;x)\ , \qquad (9)$$

in which $f(\sigma;x)$ stays for a generic function of σ, and x is a parameter. As is well known, integrals of the same form as in Eq. (9) can be evaluated using the p-point Gauss-generalized Laguerre quadrature method [15], where the integration is replaced by the sum of the p quantities $w_i f(\sigma_i;x)$, with w_i and σ_i being weights and positions, respectively. The method is exact for functions $f(\sigma;x)$ that are polynomials of degree $2p-1$ in the variable σ. The method allows us to rewrite Eqs. (4) and (6) as

$$g_{NN}(r)\cong\sum_{\sigma=1}^{p}\sum_{\sigma'=1}^{p}w_\sigma w_{\sigma'}g_{\sigma\sigma'}(r)\ , \qquad (10)$$

$$S^M(k)\cong\frac{\sum_{\sigma=1}^{p}\sum_{\sigma'=1}^{p}w_\sigma w_{\sigma'}b_\sigma(k)b_{\sigma'}(k)S_{\sigma\sigma'}(k)}{\int d\sigma\,F(\sigma)b_\sigma^2(k)}\ . \qquad (11)$$

The integral in the denominator of this equation is not approximated by a sum since it can be evaluated analytically. A collection of analytical results for five different $F(\sigma)$, and for $b_\sigma(k)$ given in Eq. (7), has been recently reported by Sheu [16].

Even for polydispersities as large as $s_\sigma\approx0.3$, the various functions $f(\sigma;x)$ appearing in Eqs. (4) and (6) are expected to be slowly varying functions of σ, so that they are well represented by polynomials of low degree. Therefore p is a reasonable small number, and $g_{NN}(r)$ and $S^M(k)$ can be efficiently evaluated in the framework of the HNC and/or RY schemes.

From the second point of view, the integrals in Eqs. (4) and (6) are transformed by representing the continuous distribution $F(\sigma)$ by a histogram. The Schulz distribution is replaced by a p-component histogram whose positions σ_i and molar fractions w_i are obtained by solving the following system of $2p$ equations:

$$\sum_{i=1}^{p}w_i\sigma_i^m=\langle\sigma^m\rangle\ ,\quad m=0,1,\ldots,2p-1 \qquad (12)$$

with $\langle\sigma^m\rangle$ given by Eq. (2). With this reduction, the resulting expressions for $g_{NN}(r)$ and $S^M(k)$ are, once more, given by Eqs. (10) and (11). We expect also, in this case, that p will be a small number; this expectation is based on the experience with polydisperse hard-sphere systems [17,18]. In this case it has been shown that, within the PY approximation, the thermodynamics depends only on the first three moments of the size distribution, irrespective of the amount of polydispersity.

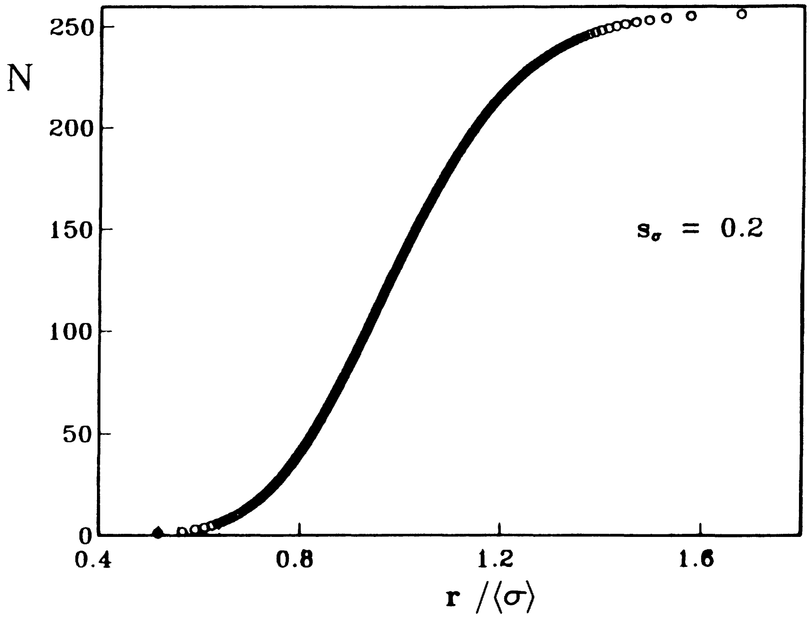

FIG. 1. Cumulative Schulz distribution of 256 Yukawa particles with $s_\sigma = 0.2$ vs reduced distance $r/\langle\sigma\rangle$.

Although the two different points of view both lead to Eqs. (10) and (11), it is so far unclear whether the molar fractions and positions determined from Eqs. (12) are the same as those in the Gauss-generalized Laguerre quadrature method. It is, however, easy to see that the two sets of $2p$ quantities w_i and σ_i, $i=1,\ldots,p$, obtained by both procedures are identical and that, therefore, both procedures are really two different points of view of the same method to take care of polydispersity. The solutions w_i and σ_i of Eqs. (12) determine the moments of $F(\sigma)$ exactly for $m \le 2p-1$. The mth moment is of the form of Eq. (9) with $f(\sigma,x) \propto \sigma^m$. Therefore, the quantities w_i and σ_i give the exact results of the integrals of the type of Eq. (9) for polynomials of degree $2p-1$, just as in the Gauss-generalized Laguerre quadrature method.

III. RESULTS AND DISCUSSION

The way to verify the reduction of the continuous distribution to a small number of components p, and to show how small p can be chosen in order to give satisfactory results, is to compare Monte Carlo simulation data for polydisperse systems with results from the RY scheme for p-component systems. To this purpose we performed standard Metropolis MC simulations on systems with standard deviation $s_\sigma = 0.0$, 0.1, 0.2, and 0.3. We used $N=256$ particles, which all have different diameters. The diameters are determined by the corresponding cumulative Schulz distribution, as in Fig. 1. The parameters of the one-component system ($s_\sigma = 0.0$) (which are kept constant for the system with $s_\sigma \neq 0.0$) are $\langle\sigma\rangle = 250$ Å, $Z_{\langle\sigma\rangle} = 200$, $n^* = n\langle\sigma\rangle^3 = 0.005$, and $L_B = 7.01$ Å. In Fig. 2 are shown the standard deviation of the charge s_Z, and the second and third moments of the size distribution (proportional, respectively, to the mean charge and to the total volume fraction), as a function of the standard deviation of the size. For the MC simulations, the particles of different size and charge are initially randomly distributed on a fcc lattice and equilibrated over $\approx 10^6$ configurations. The same number of configurations are generated to evaluate the block averages of the quantities of interest. To compute $S^M(k)$ we used the efficient procedure proposed by Frenkel *et al.* [19] in which

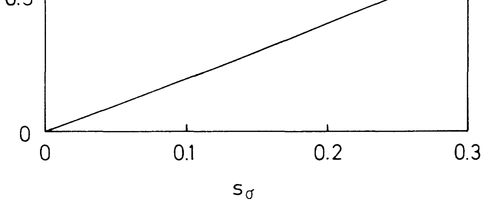

FIG. 2. Variation of the standard deviation of the charge s_Z, and of the second and third moments of the Schulz distribution (proportional, respectively, to the mean charge and to the volume fraction), as functions of s_σ.

$$S^M(k)=\frac{\left\langle \left|\sum_{i=1}^{N} b_i(k)\cos(\mathbf{k}\cdot\mathbf{r}_i)\right|^2+\left|\sum_{i=1}^{N} b_i(k)\sin(\mathbf{k}\cdot\mathbf{r}_i)\right|^2\right\rangle}{\sum_{i=1}^{N} b_i^2(k)} \tag{13}$$

The statistics of $S^M(k)$ is improved by taking the vector $\mathbf{k}$ along six independent directions, the permutations of [100] and [110].

The RY scheme [20], which consists of the following closed set of equations for a given interaction potential $\varphi_{\sigma\sigma'}(r)$,

$$\begin{aligned}
h_{\sigma\sigma'}(r)&=c_{\sigma\sigma'}(r)+n\sum_{\lambda=1}^{p} w_\lambda h_{\sigma\lambda}(r)*c_{\lambda\sigma'}(r)\ ,\\
h_{\sigma\sigma'}(r)&=-1+\exp[-\beta\varphi_{\sigma\sigma'}(r)]\left\{1+\frac{\exp\{f(r)[h_{\sigma\sigma'}(r)-c_{\sigma\sigma'}(r)]\}-1}{f(r)}\right\}\ ,\\
f(r)&=1-\exp(-\gamma r)\ ,
\end{aligned} \tag{14}$$

where γ is the parameter that ensures thermodynamic consistency and $*$ denotes the convolution integral, has been solved iteratively with the speeding procedure of Ng [21].

The MC and RY results for $g_{NN}(r)$ are shown in Fig. 3.

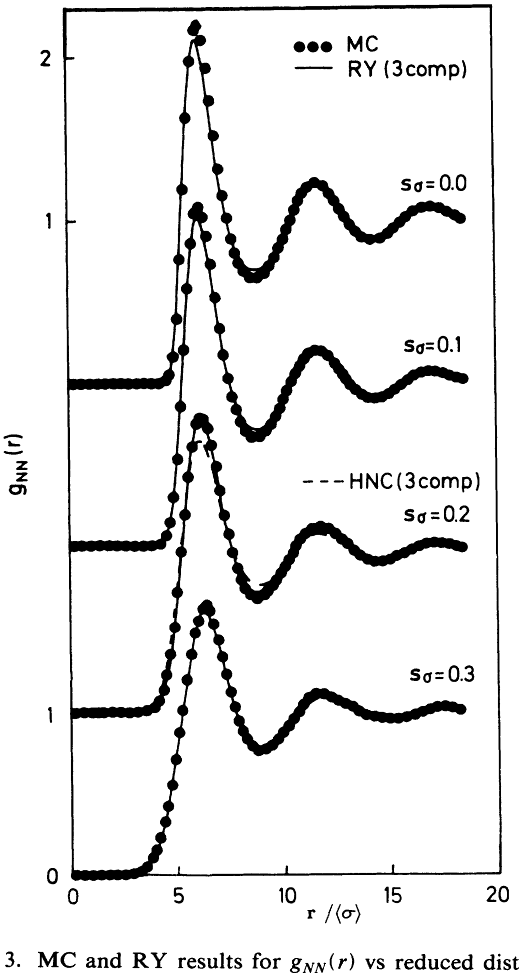

FIG. 3. MC and RY results for $g_{NN}(r)$ vs reduced distance $r/\langle\sigma\rangle$. Except for the case $s_\sigma=0.0$, the RY results come from the $p=3$ component model. A further increase in the number of components does not affect the RY results. For the system parameters, see the text.

For all cases, a quantitative agreement is obtained with $p=3$ components, proving that both the RY scheme and the discretization are surprisingly good approximations. Calculations have been performed also with five components, and the results are indistinguishable from those with $p=3$. For the particular case of $s_\sigma=0.2$, we present also the results of the HNC approximation; they clearly underestimate the structure. The underestimation has to be traced back to the HNC approximation itself and not to the reduction approximation involved in Eq. (10).

In Fig. 4, the "measured" static structure factor $S^M(k)$

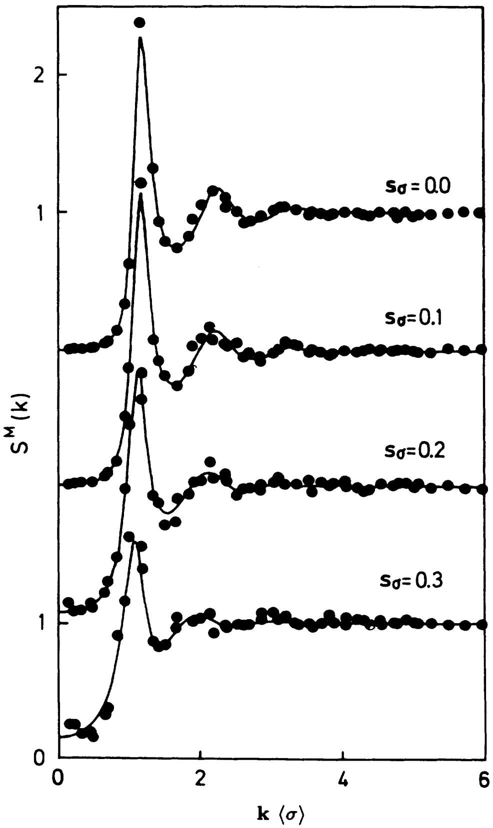

FIG. 4. "Measured" structure factors $S^M(k)$ for the four investigated systems of Fig. 2 as function of the reduced distance $k\langle\sigma\rangle$.

is shown. Once more, the three-component model gives quantitative agreement. When applied to fit small-angle-neutron-scattering (SANS) and static-light-scattering (SLS) data, the *quantitative* treatment of polydispersity leads to a different understanding of the underlying interparticle structure (microscopic level), and of the thermodynamic behavior (macroscopic level). A systematic study of such aspects has been given in Ref. [4].

This treatment of polydispersity can be applied to the inverse problem, namely the characterization of the colloidal particles and dispersions from scattering data. The full inverse problem requires, together with the study of the "measured" structure factor [Eq. (11)] and of the averaged form factor [denominator of Eq. (11)], the analysis of the Porod [22] and Guinier and Fournet [23] plots. The simultaneous fitting of all these experimentally accessible quantities with the results from the polydisperse model allows the exact determination of the density of the dispersion, the refractive index of the particles, and the shape and the moments of the size distribution. A successful application of our treatment of polydispersity to the full inverse problem has been given by Wagner *et al.* [24].

Parallel to the structural data, the excess internal energy U^{ex} and the excess pressure p^{ex} were obtained from both MC simulations and RY equations. As a function of s_σ, the relative percentage deviations of the two methods are, respectively, less than 1% for U^{ex}/N and less than 3% for $\beta p^{\mathrm{ex}}/n$. To understand the thermodynamic behavior of polydisperse systems as a function of s_σ and s_Z, we performed several computations moving in the parameter space spanned by Z, σ, n, and T. We did not find any systematic behavior, and more detailed calculations are presently in progress.

Summarizing, we have shown that size- and/or charge-polydisperse Yukawa systems can be well described by performing a reduction of the continuous distributions to a small number of components, thus reducing the complexity of the calculations to a very low level. In addition, the RY closure scheme has been found to be in quantitative agreement with MC simulation results. We also note that this methodology can be extended to situations in which the polydispersity is described by different distribution functions, and it can be used to achieve a successful fit of SLS and SANS data.

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[*] Present address: CRS4, Centro di Ricerca, Sviluppo e Studi Superiori in Sardegna, P.O. Box 488, I-09100 Cagliari, Italy.

[1] A. K. van Helden, J. W. Jansen, and A. Vrij, J. Colloid Interface Sci. **81**, 354 (1981).
[2] J. B. Hayter, in *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions,* edited by V. Degiorgio and M. Corti (North-Holland, Amsterdam, 1985), p. 59.
[3] C. G. de Kruif, W. J. Briels, R. P. May, and A. Vrij, Langmuir **4**, 668 (1988).
[4] B. D'Aguanno and R. Klein, J. Chem. Soc. Faraday Trans. **87**, 379 (1991).
[5] P. N. Pusey, in *Liquids, Freezing and the Glass Transition,* Proceedings of the Les Houches Session LI, 1989, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991).
[6] W. L. Griffith, R. Triolo, and A. L. Compere, Phys. Rev. A **33**, 2197 (1986).
[7] M. Ginoza, Mol. Phys. **71**, 145 (1990).
[8] H. Ruiz-Estrada, M. Medina-Noyola, and G. Nägele, Physica A **168**, 919 (1990).
[9] J. P. Hansen and J. B. Hayter, Mol. Phys. **46**, 651 (1982).
[10] H. Löwen, J. N. Roux, and J. P. Hansen, J. Phys.: Condens. Matter **3**, 997 (1991).
[11] G. V. Schulz, Z. Phys. Chem. Abt. B **43**, 25 (1939).
[12] E. J. W. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).
[13] L. Blum and G. Stell, J. Chem. Phys. **71**, 42 (1979).
[14] P. N. Pusey and R. J. A. Tough, in *Dynamic Light Scattering,* edited by R. Pecora (Plenum, New York, 1985).
[15] B. Carnahan, *Applied Numerical Methods* (Wiley, New York, 1969).
[16] E. Y. Sheu, Phys. Rev. A **45**, 2428 (1992).
[17] A. Vrij, J. Colloid Interface Sci. **90**, 110 (1982).
[18] J. J. Salacuse and G. Stell, J. Chem. Phys. **77**, 3714 (1982).
[19] D. Frenkel, R. J. Vos. C. G. de Kruif, and A. Vrij, J. Chem. Phys. **84**, 4625 (1986).
[20] F. J. Rogers and D. A. Young, Phys. Rev. **30A**, 999 (1984).
[21] J. C. Ng, J. Chem. Phys. **61**, 2680 (1974).
[22] G. Porod, Kolloidn Zh. **124**, 83 (1976).
[23] A. Guinier and G. Fournet, *Small Angle Scattering of X Rays* (Wiley, New York, 1955).
[24] N. J. Wagner, R. Krause, A. R. Rennie, B. D'Aguanno, and J. Goodwin, J. Chem. Phys. **95**, 494 (1991).