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Analytical scattering function of a polydisperse Percus-Yevick fluid with Schulz- (Γ-) distributed diameters

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Analytical expressions for the scattering function for a polydisperse Percus-Yevick fluid with Schulz- (Γ-) distributed particle diameters have been obtained. Results obtained with the expression for selected width factors and particle densities are presented. Comparisons have been made with approximations routinely used to model small-angle scattering curves. The expression derived is shown to yield the static structure function as a special case.

INTRODUCTION

Structural and thermodynamic properties of many high-density fluids are mainly determined by excluded volume contributions. Even for systems whose molecules are far from being hard or spheres, use of hard-sphere (HS) models has been successful. Among the liquid-state approximations used to model macromolecular- and colloid-system properties, the Percus-Yevick (PY) approximation has been solved for a variety of Hamiltonians corresponding to HS models. For a monodisperse HS fluid of indistinguishable particles, whose properties are dependent upon integrals over discontinuous (δ) functions, both rigorous and approximate thermodynamic and structure function expressions can be obtained. Real fluid particles are associated with properties with a non-δ function distribution. Such systems may be monodisperse for some properties and polydisperse for others. For example, a population can be polydisperse in size but not in scattering length or vice versa.

Vrij[1] and Blum and Stell[2] derived expressions for the scattering intensity of polydisperse systems (PHS). Salacuse and Stell[3] generalized the thermodynamic approximations of Mansoori *et al.*[4] to cover the statistical thermodynamics of polydisperse systems of particles, including hard spheres, hard spheres with Kac tails, and hard spheres polydisperse in size and permeability. Hayter,[5] and Kotlarchyk and Chen[6] outline a simple procedure using numerical integration over the size distribution function, for analyzing small-angle neutron scattering data from systems of interacting hard moderately polydisperse spheres with Schulz distributed diameters and no correlation of orientation.

In this paper, we present a fully analytic solution for the scattering intensity of a PHS fluid applicable to any degree of size polydispersity which can be represented by a Γ (Schulz) distribution. We chose the Γ distribution because of its widespread use to model polydisperse systems and its mathematical tractability. After considerable algebraic manipulations, we were able to cast this equation in a form particularly suitable to the least-squares applications characteristic of current computer analyses. Besides its obvious computational advantage, this analytical solution allows a rigorous evaluation of the scattered intensity while avoiding the approximations caused by factoring.[5,6] Additionally, the particular form used in Eq. (1), by its mathematical simplicity, improves on the method outlined by Vrij,[1] while providing results identical within our calculational accuracy.

THEORY

The scattering intensity from a medium containing a continuous distribution of particles with diameters σ_i and scattering amplitudes $P_i(k)$ is given by

$$I(k)=\rho \int_0^\infty P_i^2(k)f(\sigma_i)d\sigma_i + \rho \int_0^\infty \int_0^\infty P_i(k)P_j(k)H_{ij}(k)f(\sigma_i)f(\sigma_j)d\sigma_i d\sigma_j \ , \quad (1)$$

where ρ is the total particle number density, k is the modulus of the wave vector ($k=4\pi\sin(\theta)/\lambda$ with scattering angle 2θ and wavelength λ), $H_{ij}(k)$ is the pair structure function, and $f(\sigma_i)$ and $f(\sigma_j)$ are the distribution functions of particles i and j, respectively. For a Γ (Schulz) distribution, the probability density function is given by

$$f(\sigma)=(\sigma/b)^{c-1}e^{-\sigma/b}/[b\Gamma(c)]d\sigma = \sigma^{c-1}e^{-\sigma/b}/[b^c\Gamma(c)]d\sigma \ , \quad (2)$$

where the parameters b and c are given by $b=\sigma_{\text{mean}}/(z+1)$ and $c=z+1$, where z is the Schulz "width factor," $z>-1$. This distribution has a mean equal to bc and variance equal to b^2c.

For spheres with uniform scattering length density, the scattering amplitude $P_i(k)$ for a particle with diameter σ_i is given by

$$P_i(k)=4\pi p[\sin(k\sigma_i/2)-\tfrac{1}{2}k\sigma_i\cos(k\sigma_i/2)] \ , \quad (3)$$

where p is the contrast between the particle and the surrounding medium.

Expressions for the partial structure functions $H_{ij}(k)$ have been derived by Blum and Stell[2] within the Percus-Yevick approximation by

$$H_{ij}(k)=-2(\rho_i\rho_j)^{1/2}\frac{Z_2Z_3+Z_1Z_4}{k^3(X^2+Y^2)} \ , \quad (4)$$

where for $\sigma_{ij}=\frac{1}{2}(\sigma_i+\sigma_i)$

$$Z_1=Y\sin(k\sigma_{ij})-X\cos(k\sigma_{ij}) , \tag{5}$$

$$Z_2=X\sin(k\sigma_{ij})+Y\cos(k\sigma_{ij}) , \tag{6}$$

and

$$Z_3=Q''_{ij}-kT_3 , \tag{7}$$

where Q''_{ij} is redefined[7] with respect to the definition given for it in Ref. 2 by

$$Q''_{ij}=(2\pi/\Delta)(1+\tfrac{1}{2}\xi_3\pi/\Delta) ,$$

where $\Delta=1-\pi\xi_3/6$ and

$$Z_4=kQ'_{ij}+kR_4 . \tag{8}$$

Here Q'_{ij} is defined as

$$Q'_{ij}(\sigma_{ij})=(\pi/\Delta)(\sigma_i+\sigma_j+\tfrac{1}{2}\sigma_i\sigma_j\xi_2\pi/\Delta) ,$$

where ξ_i is the product of the total particle density and the ith moment of the Γ distribution about the origin which can be written in terms of the density and parameters b and c as

$$\xi_i=\rho b^i(c)_i , \tag{9}$$

where $(c)_n=\Gamma(c+n)/\Gamma(c)$.

Expressions for X, Y, R_3, and R_4 are given in terms of the x_1, x_2, y_1, and y_2, with the sign of y_2 different from that given in Ref. 2 (see footnote 7) by

$$x_1(\sigma)=k^{-2}[\cos(k\sigma)-1] , \tag{10}$$

$$y_1(\sigma)=k^{-2}[k\sigma-\sin(k\sigma)] , \tag{11}$$

$$x_2(\sigma)=k^{-3}[k\sigma-\sin(k\sigma)] , \tag{12}$$

$$y_2(\sigma)=-k^{-3}[\cos(k\sigma)+\tfrac{1}{2}k^2\sigma^2-1] , \tag{13}$$

$$R_3=(\pi/\Delta)^2\rho\int_0^\infty f(\sigma_k)(\sigma_k-\sigma_i)(\sigma_k-\sigma_j)y_1(\sigma_k)d\sigma_k , \tag{14}$$

$$R_4=(\pi/\Delta)^2\rho\int_0^\infty f(\sigma_k)(\sigma_k-\sigma_i)(\sigma_k-\sigma_j)x_1(\sigma_k)d\sigma_k , \tag{15}$$

$$\begin{aligned}X=1&-(2\pi/\Delta)(1+\tfrac{1}{2}\pi\xi_3/\Delta)\rho\int_0^\infty f(\sigma_k)x_2(\sigma_k)d\sigma_k-(2\pi/\Delta)\rho\int_0^\infty\sigma_k f(\sigma_k)x_1(\sigma_k)(1+\tfrac{1}{4}\pi\xi_2\sigma_k/\Delta)d\sigma_k\\&-\tfrac{1}{2}(\pi\rho/\Delta)^2\int_0^\infty f(\sigma_k)d\sigma_k\int_0^\infty f(\sigma_l)[x_1(\sigma_k)x_1(\sigma_l)-y_1(\sigma_k)y_1(\sigma_l)](\sigma_k-\sigma_l)^2d\sigma_l ,\end{aligned} \tag{16}$$

$$\begin{aligned}Y=&-(2\pi/\Delta)(1+\tfrac{1}{2}\pi\xi_3/\Delta)\rho\int_0^\infty f(\sigma_l)y_2(\sigma_l)d\sigma_l-(2\pi/\Delta)\rho\int_0^\infty\sigma_k f(\sigma_k)y_1(\sigma_k)(1+\tfrac{1}{4}\pi\xi_2\sigma_k/\Delta)d\sigma_k\\&-\tfrac{1}{2}(\pi\rho/\Delta)^2\int_0^\infty f(\sigma_k)d\sigma_k\int_0^\infty f(\sigma_l)[x_1(\sigma_k)y_1(\sigma_l)+y_1(\sigma_k)x_1(\sigma_l)](\sigma_k-\sigma_l)^2d\sigma_l .\end{aligned} \tag{17}$$

It turns out that the analytical solution for Eq. (1) for the Γ distribution is a function of 14 integrals which are well-known integral transforms of the form

$$\int_0^\infty f(\sigma)\sigma^n g(\sigma)d\sigma , \tag{18}$$

with $g(\sigma)=1$, $\sin(k\sigma)$, $\sin(k\sigma/2)$, or corresponding cosine arguments, and $f(\sigma)$ is the Γ density function. It is of considerable advantage to adopt the notation for these integrals listed in Table I, where the common term $G=b^c\Gamma(c)$ has

TABLE I. Integral transform notation.[a]

$g(\sigma)$	n	$G^{-1}\int_0^\infty f(\sigma)\sigma^n g(\sigma)d\sigma$	Notation
1	0	1	1
1	1	bc	ξ'
1	2	$b^2c(c+1)$	ξ''
1	3	$b^3c(c+1)(c+2)$	ξ'''
$\sin(k\sigma)$	0	$v_1^{c/2}\sin[c\tan^{-1}(bk)]$	ψ
$\sin(k\sigma)$	1	$bcv_1^{(c+1)/2}\sin[(c+1)\tan^{-1}(bk)]$	ψ'
$\sin(k\sigma)$	2	$b^2c(c+1)v_1^{(c+2)/2}\sin[(c+2)\tan^{-1}(bk)]$	ψ''
$\sin(k\sigma/2)$	0	$2^cv_2^{c/2}\sin[c\tan^{-1}(bk/2)]$	μ
$\sin(k\sigma/2)$	1	$2^{c+1}bcv_2^{(c+1)/2}\sin[(c+1)\tan^{-1}(bk/2)]$	μ'
$\cos(k\sigma)$	0	$v_1^{c/2}\cos[c\tan^{-1}(bk)]$	χ
$\cos(k\sigma)$	1	$bcv_1^{(c+1)/2}\cos[(c+1)\tan^{-1}(bk)]$	χ'
$\cos(k\sigma)$	2	$b^2c(c+1)v_1^{(c+2)/2}\cos[(c+2)\tan^{-1}(bk)]$	χ''
$\cos(k\sigma/2)$	0	$2^cv_2^{c/2}\cos[c\tan^{-1}(bk/2)]$	λ
$\cos(k\sigma/2)$	1	$2^{c+1}bcv_2^{(c+1)/2}\cos[(c+1)\tan^{-1}(bk/2)]$	λ'

[a] $v_m=[m^2+(bk)^2]^{-1}$

been factored to avoid calculating $\Gamma(c)$ for large arguments.

The analytical expression for the first integral I_1 in Eq. (1) was published by Aragón and Pecora.[8] In our notation we have for uniform particles, $P_i(k)=P_j(k)=P(k)$:

$$I_1(k)=8\pi^2\rho P^2(k)k^{-6}[1-\chi-k\psi'+\tfrac{1}{4}k^2(\zeta''+\chi'')] \ . \tag{19}$$

The integrated form of the second integral I_2 in Eq. (1) using this notation is

$$\begin{aligned} I_2(k)=-2\rho\{&\Lambda[\Lambda(Y\delta_1-X\delta_6)+\Lambda'(Y\delta_2-X\delta_4)+M(X\delta_1+Y\delta_6)+M'(X\delta_2+Y\delta_4)]\\ &+\Lambda'[\Lambda(Y\delta_2-X\delta_4)+\Lambda'(Y\delta_3-X\delta_5)+M(X\delta_2+Y\delta_4)+M'(X\delta_3+Y\delta_5)]\\ &+M[\Lambda(X\delta_1+Y\delta_6)+\Lambda'(X\delta_2+Y\delta_4)+M(X\delta_6-Y\delta_1)+M'(X\delta_4-Y\delta_2)]\\ &+M'[\Lambda(X\delta_2+Y\delta_4)+\Lambda'(X\delta_3+Y\delta_5)+M(X\delta_4-Y\delta_2)+M'(X\delta_5-Y\delta_3)]\}/[k^3(X^2+Y^2)] \ , \end{aligned} \tag{20}$$

where

$$\Lambda=\tfrac{2}{3}\pi\rho p k^{-3}[\psi-\tfrac{1}{2}k(\zeta'+\chi')] \ , \tag{21}$$

$$\Lambda'=\tfrac{2}{3}\pi\rho p k^{-3}[\psi'-\tfrac{1}{2}k(\zeta''+\chi'')] \ , \tag{22}$$

$$M=\tfrac{2}{3}\pi\rho p k^{-3}(1-\chi-\tfrac{1}{2}k\psi') \ , \tag{23}$$

$$M'=\tfrac{2}{3}\pi\rho p k^{-3}(\zeta'-\chi'-\tfrac{1}{2}k\psi'') \ , \tag{24}$$

$$\begin{aligned} X=1&-(2\pi/\Delta)(1+\tfrac{1}{2}\pi\xi_3/\Delta)\rho k^{-3}(k\zeta'-\psi)-(2\pi/\Delta)\rho k^{-2}[(\chi'-\zeta')+(\tfrac{1}{4}\pi\xi_2/\Delta)(\chi''-\zeta'')]\\ &-(\pi/\Delta)^2(\rho/k^2)^2[(\chi-1)(\chi''-\zeta'')-(\chi'-\zeta')^2-(k\zeta'-\psi)(k\zeta'''-\psi'')+(k\zeta''-\psi')^2] \ , \end{aligned} \tag{25}$$

$$\begin{aligned} Y=&(2\pi/\Delta)(1+\tfrac{1}{2}\pi\xi_3/\Delta)\rho k^{-3}(\chi+\tfrac{1}{2}k^2\zeta''-1)-(2\pi/\Delta)\rho k^{-2}[k\zeta''-\psi'+(\tfrac{1}{4}\pi\xi_2/\Delta)(k\zeta'''-\psi'')]\\ &-(\pi/\Delta)^2(\rho/k^2)^2[(k\zeta'-\psi)(\chi''-\zeta'')-2(k\zeta''-\psi')(\chi'-\zeta')+(k\zeta'''-\psi'')(\chi-1)] \ , \end{aligned} \tag{26}$$

and

$$\delta_1=(\pi/\Delta)\{2+(\pi/\Delta)[\xi_3-(\rho/k)(k\zeta'''-\psi'')]\} \ , \tag{27}$$

$$\delta_2=(\pi/\Delta)^2(\rho/k)(k\zeta''-\psi') \ , \tag{28}$$

$$\delta_3=-(\pi/\Delta)^2(\rho/k)(k\zeta'-\psi) \ , \tag{29}$$

$$\delta_4=(\pi/\Delta)[k-(\pi/\Delta)(\rho/k)(\chi'-\zeta')] \ , \tag{30}$$

$$\delta_5=(\pi/\Delta)^2[(\rho/k)(\chi-1)+\tfrac{1}{2}k\xi_2] \ , \tag{31}$$

$$\delta_6=(\pi/\Delta)^2(\rho/k)(\chi''-\zeta'') \ . \tag{32}$$

For details of the derivation of the expressions in Eqs. (20)–(32), the reader is referred to the Appendix.

Values of scattering intensity computed via Eqs. (19) and (20) are presented as a continuous line in Fig. 1 for a particle distribution with a mean diameter of 50 Å, contrast $p=0.234\times10^{-5}$ Å^{-2}, packing fraction $\eta=0.1$, and selected degrees of polydispersity: $z=10^4$, 101, 12.03, 1.618, 0, and -0.5. A width parameter of $z=10^4$ corresponds to an essentially monodisperse system. Similar calculations for samples having a packing fraction of 0.3 are shown in Fig. 2. The intensities given by our equations were compared in these figures with two approximations in current use.[5,6] In model A, the intensity plotted in the figures as a dotted line is given by

$$I(k)=N_p[\langle P^2(k)\rangle+\langle P(k)\rangle^2H(k)] \ , \tag{33}$$

where $\langle P(k)^2\rangle$ is the average of the square of the scattering amplitudes of the particles and $\langle P(k)\rangle^2$ is the square of the average of the scattering amplitude of the particles computed by the method described in Refs. 5 and 6. The $H(k)=S(k)-1$ was computed for the structure function $S(k)$ of a system of monodisperse hard spheres in the PY approximation with size equal to the average size of the Schulz distribution.[9] In model B, the intensity of the other approximation[10] plotted as a dashed line in a given by

$$I(k)=N_p\langle P(k)\rangle^2S(k) \ . \tag{34}$$

Results obtained using Vrij's method are indistinguishable from our results. At small values of k, approximate models A and B both deviate from the correct values, giving a scattering intensity as much as on order of magnitude off at zero angle for high packing fractions and broad size distributions. As k increases, this difference decreases; however, model B still reproduces the scattering pattern poorly, even adding spurious features. Model A overestimates the effect of large particles, since the scattering intensity at zero angle is proportional to the sixth power of the radius. This effect is overshadowed, however, at values of $k\sigma>1.2$, by the effect of second and higher moments of the particle size distribution.

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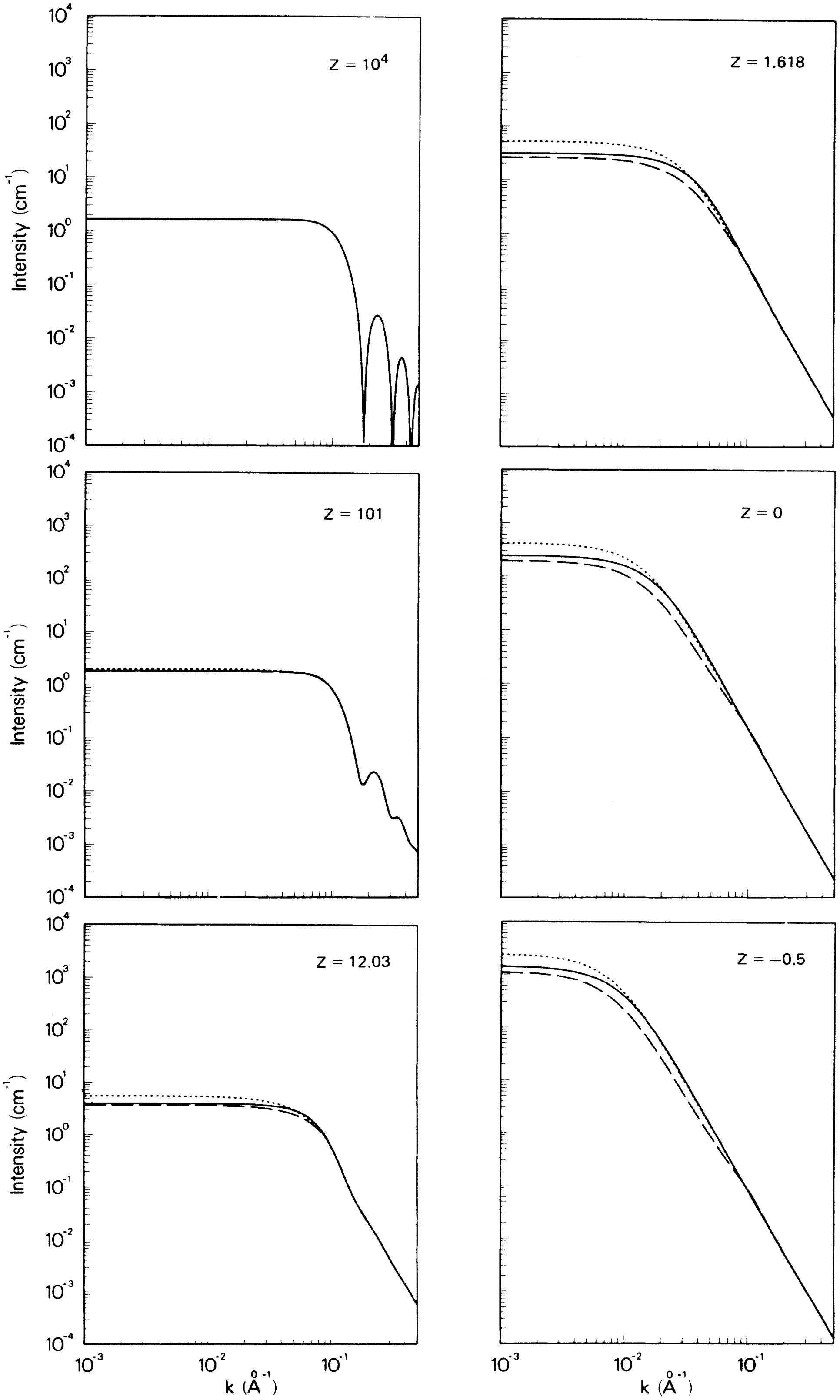

FIG. 1. Scattering intensity calculated for selected Schulz width parameters z and a packing fraction $\eta=0.1$. Legend: analytical solution, solid line; model-A approximation, dotted line; model-B approximation, dashed line.

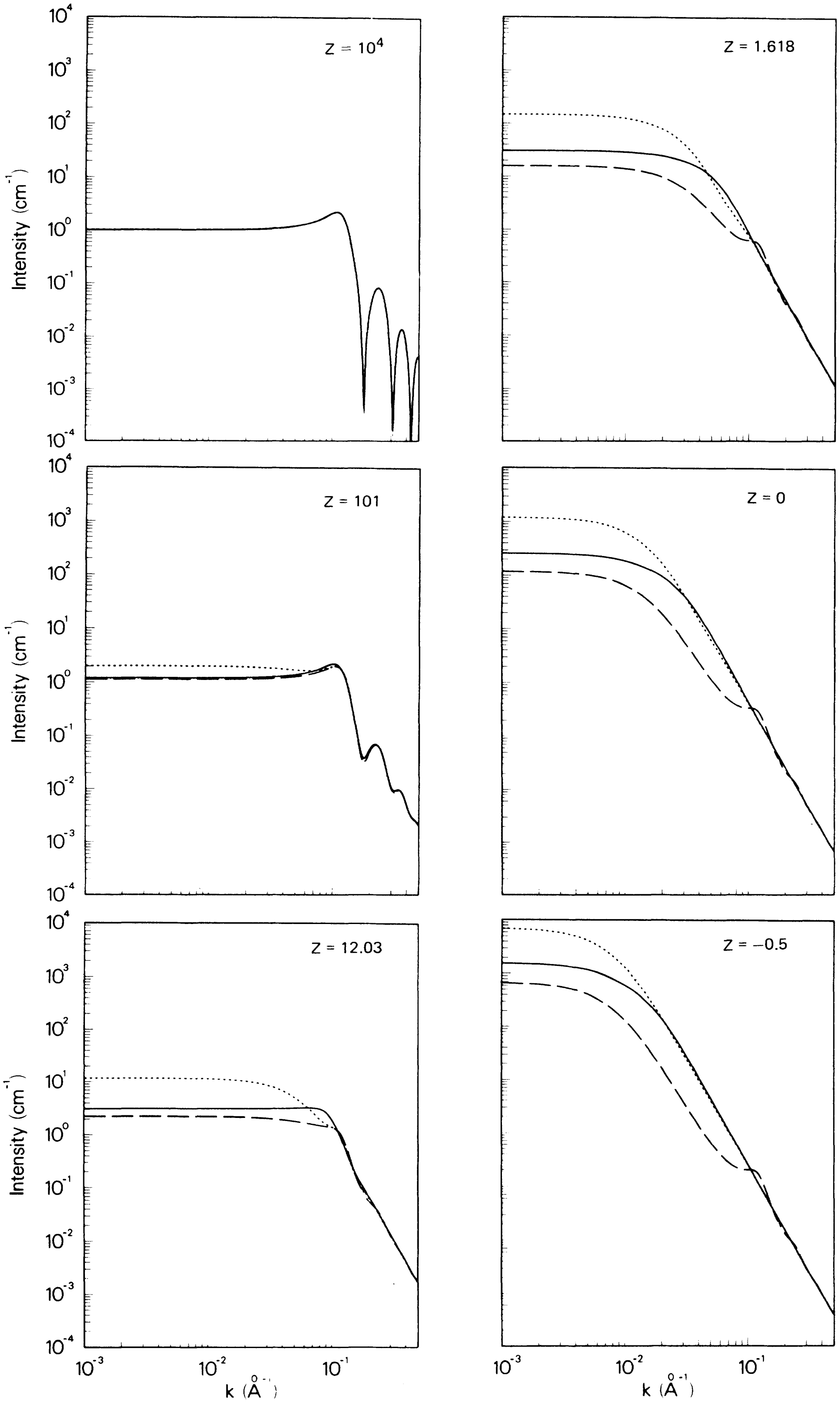

FIG. 2. Scattering intensity calculated for selected Schulz width parameters z and a packing fraction $\eta=0.3$. Legend: analytical solution, solid line; model-A approximation, dotted line; model-B approximation, dashed line.

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APPENDIX: DERIVATION OF EQS. (19)–(26)

For a continuous distribution of particle sizes, it is easier to break up Eq. (16) into parts ($X_n, n=1,3$) to perform the necessary integrations. Let X_1 be the first two terms of Eq. (16). Substituting $x_2(\sigma_k)$ we have

$$X_1 = 1-(2\pi/\Delta)(1+\tfrac{1}{2}\pi\xi_3/\Delta)(\rho k^{-3}) \times \int_0^\infty [k\sigma_k - \sin(k\sigma_k)] f(\sigma_k)\, d\sigma_k \; .$$

Using our notation in Table I we have

$$X_1 = 1-(2\pi/\Delta)(1+\tfrac{1}{2}\pi\xi_3/\Delta)(\rho k^{-3})(k\zeta'-\psi) \; . \tag{A1}$$

Let X_2 be the third term of Eq. (16). Substituting for $x_1(\sigma_k)$ we have

$$X_2 = -(2\pi/\Delta)\rho k^{-2} \int_0^\infty [\cos(k\sigma_k)-1](1+\tfrac{1}{4}\pi\xi_2\sigma_k/\Delta) \times \sigma_k f(\sigma_k)\, d\sigma_k \; .$$

Again using our notation in Table I, we have

$$X_2 = -(2\pi/\Delta)\rho k^{-2}[(\chi'-\zeta')+\tfrac{1}{4}\pi\xi_2/\Delta(\chi''-\zeta'')] \; . \tag{A2}$$

Let X_3 be the last term of Eq. (16). Substituting for $x_1(\sigma_k)$ and $y_1(\sigma_k)$ we have on rearrangement

$$X_3 = -\tfrac{1}{2}(\pi/\Delta)^2\rho \int_0^\infty f(\sigma_l)\, d\sigma_l (\rho k^{-2}) \left[\int_0^\infty (\sigma_k^2 - 2\sigma_l\sigma_k + \sigma_l^2) x_1(\sigma_l)[\cos(k\sigma_k)-1] f(\sigma_k)\, d\sigma_k - \int_0^\infty (\sigma_k^2 - 2\sigma_l\sigma_k + \sigma_l^2) y_1(\sigma_l)[k\sigma_k - \sin(k\sigma_k)] f(\sigma_k)\, d\sigma_k \right] .$$

Carrying out the multiplication and integrating first on σ_k, integrals of the form found in Table I are obtained. Thus,

$$X_3 = -\tfrac{1}{2}(\pi\rho/\Delta)^2 k^{-2} \int_0^\infty f(\sigma_l)[x_1(\sigma_l)(\chi''-\zeta''-2\sigma_l\chi'+2\sigma_l\zeta'+\sigma_l^2\chi-\sigma_l^2) - y_1(\sigma_l k\zeta'''-\psi''-2\sigma_l k\zeta+2\sigma_l\psi'+\sigma_l^2 k\zeta'-\sigma_l^2\psi)]\, d\sigma_l \; .$$

Integrating next on σ_l by substituting for x_1 and y_1, we obtain after collecting like product terms

$$X_3 = -(\pi/\Delta)^2(\rho k^{-2})^2[(\chi-1)(\chi''-\zeta'')-(\chi'-\zeta')^2-(k\zeta'-\psi)(k\zeta'''-\psi'')+(k\zeta''-\psi')^2] \; . \tag{A3}$$

Thus for X,

$$X = X_1 + X_2 + X_3 \; . \tag{A4}$$

In the integrated expression for Eq. (17), Y follows immediately in an analogous manner as for X by breaking Y into parts and integrating as before. The expressions for X and Y do not depend upon σ_i or σ_j; hence, the denominator does not enter into the integration on σ_i or σ_j.

The only terms in Eqs. (7) and (8) which must be integrated with respect to σ_k are R_3 and R_4. These intermediate results will be obtained first. Substituting in Eq. (14) as before and expanding we have

$$R_3 = (\pi\rho/\Delta)^2 k^{-2} \int_0^\infty f(\sigma_k)[\sigma_k^2 - (\sigma_i+\sigma_j)\sigma_k + \sigma_i\sigma_j][k\sigma_k - \sin(k\sigma_k)]\, d\sigma_k \; ,$$

then

$$R_3 = (\pi/\Delta)^2 \rho k^{-2} \int_0^\infty f(\sigma_k)[k\sigma_k^3 - k(\sigma_i+\sigma_j)\sigma_k^2 + k\sigma_i\sigma_j\sigma_k - \sigma_k^2\sin(k\sigma_k) - (\sigma_i+\sigma_j)\sigma_k\sin(k\sigma_k) + \sigma_i\sigma_J\sin(k\sigma_k)]\, d\sigma_k \; .$$

Then substituting as before and simplifying,

$$R_3 = (\pi/\Delta)^2 \rho k^{-2}[(k\zeta'''-\psi'')-(\sigma_i+\sigma_j)(k\zeta''-\psi')+\sigma_i\sigma_j(k\zeta'-\psi)] \; , \tag{A5}$$

and R_4 follows in a similar manner.

Expressing $Z_i, i=1,4$ in terms of half angles to separate σ_i and σ_j, the second term of Eq. (1) becomes upon substitution of Eq. (3) for the scattering amplitudes

$$\begin{aligned} I_2(k) = -32\pi^2\rho^2 p^2 k^{-6} \int_0^\infty & [\sin(k\sigma_i/2)-\tfrac{1}{2}\sigma_i k\cos(k\sigma_i/2)] f(\sigma_i) \\ & \times \int_0^\infty [\sin(k\sigma_j/2)-\tfrac{1}{2}\sigma_j k\cos(k\sigma_j/2)] \\ & \times f(\sigma_j)[\{X[\sin(k\sigma_i/2)\cos(k\sigma_j/2)+\cos(k\sigma_i/2)\sin(k\sigma_j/2)] \\ & \quad + Y[\cos(k\sigma_i/2)\cos(k\sigma_j/2)-\sin(k\sigma_i/2)\sin(k\sigma_j/2)]\} \\ & \times \{(2\pi/\Delta)(1+\tfrac{1}{2}\xi_3\pi/\Delta)-(\pi/\Delta)^2(\rho/k) \\ & \quad \times [(k\zeta'''-\psi'')-(\sigma_i+\sigma_j)(k\zeta''-\psi')+\sigma_i\sigma_j(k\zeta'-\psi)]\} \\ & + Y\{[\sin(k\sigma_i/2)\cos(k\sigma_j/2)+\cos(k\sigma_i/2)\sin(k\sigma_j/2)] \\ & \quad - X[\cos(k\sigma_i/2)\cos(k\sigma_j/2)-\sin(k\sigma_i/2)\sin(k\sigma_j/2)]\} \\ & \times \{k(\pi/\Delta)(\sigma_i+\sigma_j+\tfrac{1}{2}\sigma_i\sigma_j\xi_2\pi/\Delta)+(\pi/\Delta)^2(\rho/k) \\ & \quad \times [(\chi''-\zeta'')-(\sigma_i+\sigma_j)(\chi'-\zeta')+\sigma_i\sigma_j(\chi-1)]\}]\, d\sigma_j\, d\sigma_i/[k^3(X^2+Y^2)] \; . \end{aligned} \tag{A6}$$

Expanding and substituting Eq. (27) into (32) after rearranging by like integral terms in σ_j, we have after substituting for M, M', Λ, and Λ' defined in Eqs. (21)–(24),

$$
\begin{aligned}
I_2(k) = -8\pi^2\rho^2 p^2 k^{-3} \int_0^\infty & [\sin(k\sigma_j/2) - \tfrac{1}{2}\sigma_i k \cos(k\sigma_j/2)] f(\sigma_i) \\
& \times [\Lambda\{[X\sin(k\sigma_i/2)+Y\cos(k\sigma_i/2)](\delta_1+\delta_2\sigma_i)+[Y\sin(k\sigma_i/2)-X\cos(k\sigma_i/2)](\delta_4\sigma_i+\delta_6)\} \\
& \quad +\Lambda'\{[X\sin(k\sigma_i/2)+Y\cos(k\sigma_i/2)][(\pi/\Delta)^2\xi_2+\delta_2+\delta_3\sigma_i] \\
& \quad\quad +[Y\sin(k\sigma_i/2)-X\cos(k\sigma_i/2)](\delta_4+\delta_5\sigma_i)\} \\
& \quad +M([X\cos(k\sigma_i/2)-Y\sin(k\sigma_i/2)]\{2\pi/\Delta-(\pi/\Delta)^2(\rho/k)(k\zeta'''-\psi'') \\
& \quad\quad\quad +[(\pi/\Delta)^2\xi_2+\delta_2]\sigma_i\} \\
& \quad\quad +[Y\cos(k\sigma_i/2)+X\sin(k\sigma_i/2)][(\pi/\Delta)^2(\rho/k)(\chi''-\zeta'')+\delta_4\sigma_i]) \\
& \quad +M'\{[X\cos(k\sigma_i/2)-Y\sin(k\sigma_i/2)][(\pi/\Delta)^2(\xi_2+\delta_2+\delta_3\sigma_i)] \\
& \quad\quad +[Y\cos(k\sigma_i/2)+X\sin(k\sigma_i/2)](\delta_4+\delta_5\sigma_i)\}]d\sigma_i/[k^3(X^2+Y^2)] \; . \qquad \text{(A7)}
\end{aligned}
$$

Now rearranging by integrals in σ_i, and again substituting for Λ, Λ', M, and M', the final result in Eq. (20) is obtained.

The static structure function,

$$
S(k)=\rho\int_0^\infty f(\sigma_i)d\sigma_i + \int_0^\infty f(\sigma_i)\int_0^\infty f(\sigma_j)H_{ij}(k)d\sigma_j d\sigma_i \qquad \text{(A8)}
$$

is a special case of Eq. (1) by letting $P_i(k)=P_j(k)=1$. For this case the final expression we recently published[11] is an almost immediate consequence, since terms in Eqs. (A6) and (A7) that give M, M', Λ, and Λ', as defined in Eqs. (21)–(24), reduce to terms that give μ, μ', λ, and λ', respectively, as defined in Table I. The expressions are also valid for other probability distributions provided the integral transforms exist, and the solutions given in Table I and the moments in Eq. (9) are suitably changed.

Finally, we would like to point out two typographic errors in Eq. (2) of Ref. 11. This equation is correctly printed in Eq. (26) above. The results presented in Ref. 11 are correct since they were computed with the correct equation. We wish to thank R. McRae for pointing out these misprints.

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