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Analytical structure function of a polydisperse Percus-Yevick fluid with Schulz (gamma) distributed diameters

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Analytical expressions for the static structure function for a polydisperse Percus-Yevick fluid with Schulz (gamma) distributed particle diameters have been obtained. Results obtained with the expression for selected width factors and particle densities are presented.

The structure of a fluid is a function of the size distribution, density, and temperature of its constituent particles. In such isotropic fluids, the correlation function $g(r)$ provides a sufficient description of the microscopic structure to permit calculation of the variation of particle density with distance r from a reference particle, whereas the static structure function $S(k)$ reflects the experimentally determined average distribution of molecular separations in the fluid. To date, theoretical structure functions for multicomponent systems have largely been determined by numerical methods. We are presenting an analytical solution for the structure function of a polydisperse Percus-Yevick (PY) fluid with particle sizes continuously distributed according to a Schulz, or gamma, distribution.

The static structure and the total correlation function, $h(r)=g(r)-1$, and 2θ, the scattering angle, are related by means of a Fourier integral,

$$S(k)=1+4\pi\rho k^{-1}\int_0^\infty rh(r)\sin(kr)dr \quad ,$$

where $k=4\pi\sin\theta/\lambda$ and ρ is the particle density. Through the Ornstein-Zernike equation, $h(r)$ is related to another function, the direct correlation function, $c(r)$, which also plays a fundamental role in a number of modern theories of fluids:

$$h(r)=c(r)+\rho\int_0^\infty h(|r-r'|)c(|r'|)dr' \quad .$$

To obtain $h(r)$ or $S(k)$ for a given system, one can solve the Ornstein-Zernike equation with proper closures. Impenetrability of particles provides one closure. This is generally reflected by setting $h(r)=-1$ inside the particle. The form chosen for $c(r)$ provides another closure. The two common closures for $c(r)$ are the mean spherical approximation, $c(r)=\beta U(r)$ for r greater than the particle diameter, where $\beta=(kT)^{-1}$, $U(r)$ is the potential function, and the hypernetted-chain approximation,

$$c(r)=-\beta U(r)+h(r)-\ln[1+h(r)] \quad .$$

The potential function $U(r)$ is a function of the system considered. The simplest, and perhaps the most studied, fluid is the so-called "hard sphere" fluid whose potential is infinite when r is less than the hard-core diameter and zero otherwise. Blum and Stell[1] have derived an analytical expression of the Fourier transform $h(k)$ of the correlation function for a discrete size distribution of hard sphere particles. We performed the analytic integration of $h(k)$ over a Schulz (gamma) distribution. Our choice of the Schulz distribution function arises from its widespread acceptance and a mathematical tractability.[2]

The multicomponent system structure function for the continuous case may be written in terms of partial structure functions $h_{ij}(k)$ as given by Blum and Stell using PY closure as

$$S(k)=\rho\int_0^\infty f_i d\sigma_i+\rho\int_0^\infty d\sigma_i d\sigma_j f(\sigma_i)f(\sigma_j)h_{ij}(k) \quad , \tag{1}$$

where $f(\sigma)$ is the probability density function of the particle diameters, σ.

For a gamma (Schulz) distribution, the probability density function is given by

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

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."

The partial structure functions, $h_{ij}(k)$ are given by Blum and Stell:

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

where

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

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

and

$$Z_3=Q_{ij}''-kR_3 \quad ,$$

where Q_{ij}'' is redefined[3] with respect to the definition given for it in Ref. 1 by

$$Q_{ij}''(\sigma_{ij})=(2\pi/\Delta)(1+\tfrac{1}{2}\xi_3\pi/\Delta) \quad ,$$

where $\sigma_{ij}=(\sigma_i+\sigma_j)/2$ and $\Delta=1-\pi\xi_3/6$, and

$$Z_4=kQ_{ij}'+kR_4 \quad .$$

Here Q_{ij}' is defined as

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

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

$$\xi_1=\rho bc \quad ,$$

$$\xi_2=\rho b^2c(c+1) \quad ,$$

$$\xi_3=\rho b^3c(c+1)(c+2) \quad .$$

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. 1 (see also Ref. 3) by

$$x_1(\sigma)=k^{-2}[\cos(k\sigma)-1],\quad y_1(\sigma)=k^{-2}[k\sigma-\sin(k\sigma)],$$

$$x_2(\sigma)=k^{-3}[k\sigma-\sin(k\sigma)],\quad y_2(\sigma)=-k^{-3}[\cos(k\sigma)+\tfrac{1}{2}k^2\sigma^2-1]\ .$$

Then,

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

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

It turns out that the analytical solution for Eq. (1) is a function of 14 integrals. In all cases it is desirable to define functions to express these integrals as the product of $G=b^c\Gamma(c)$ and a function of $b,c,$ and k to avoid calculating $\Gamma(c)$ for large arguments as follows:

$$\int_0^\infty e^{-\sigma/b}\sigma^{c-1}d\sigma=\Gamma(c)/b^{-c}=G1\ ,$$
$$\int_0^\infty e^{-\sigma/b}\sigma^{c}d\sigma=\Gamma(c+1)b^{c+1}=\Gamma(c)b^c(bc)=G\zeta'\ ,$$

where $\zeta'=bc$; similarly for $r=c+1,\ c+2$, and

$$\int_0^\infty e^{-\sigma/b}\sigma^{c+1}d\sigma=\Gamma(c+2)b^{c+2}=\Gamma(c)b^c[c(c+1)b^2]=G\zeta''\ ,$$
$$\int_0^\infty e^{-\sigma/b}\sigma^{c+2}d\sigma=\Gamma(c+3)b^{c+3}=\Gamma(c)b^c[c(c+1)(c+2)b^3]=G\zeta'''\ .$$

The remaining ten integrals involve sine and cosine.

$$\int_0^\infty e^{-\sigma/b}\sigma^{c-1}\sin(k\sigma)=\Gamma(c)b^c v_1^{c/2}\sin[c\tan^{-1}(bk)]=G\psi\ ,$$

where $v_n=[n^2+(bk)^2]^{-1}$, and ψ is defined by $\psi=v_1^{c/2}\sin[c\tan^{-1}(bk)]$. Similarly for $r=c+1$ and $c+2$,

$$\int_0^\infty e^{-\sigma/b}\sigma^{c}\sin(k\sigma)d\sigma=\Gamma(c)b^c(bc\,v_1^{(c+1)/2})\sin[(c+1)\tan^{-1}(bk)]=G\psi'\ ,$$
$$\int_0^\infty e^{-\sigma/b}\sigma^{c+1}\sin(k\sigma)d\sigma=\Gamma(c)b^c c(c+1)b^2v_1^{(c+2)/2}\sin[(c+2)\tan^{-1}(bk)]=G\psi''\ .$$

Solutions involving half-angles also needed are as follows:

$$\int_0^\infty e^{-\sigma/b}\sigma^{c-1}\sin(k\sigma/2)d\sigma=\Gamma(c)2^cb^cv_2^{c/2}\sin[c\tan^{-1}(bk/2)]=G\mu\ ,$$
$$\int_0^\infty e^{-\sigma/b}\sigma^{c}\sin(k\sigma/2)d\sigma=\Gamma(c)2^{c+1}b^cbc\,v_2^{(c+1)/2}\sin[(c+1)\tan^{-1}(kb/2)]=G\mu'\ .$$

Analogous integrals are needed which are the same as for the above with cosine substituted for sine. Analogous functions for cosine are χ, χ', and χ''; and λ and λ' for the corresponding half-angle integrals, respectively. The integrated form of the second integral in Eq. (1) using these functions is

$$\begin{aligned}h(k)=-2\rho\{&\lambda[\lambda(\Upsilon\delta_1-\Xi\delta_6)+\lambda'(\Upsilon\delta_2-\Xi\delta_4)+\mu(\Xi\delta_1+\Upsilon\delta_6)+\mu'(\Xi\delta_2+\Upsilon\delta_4)]\\&+\lambda'[\lambda(\Upsilon\delta_2-\Xi\delta_4)+\lambda'(\Upsilon\delta_3-\Xi\delta_5)+\mu(\Xi\delta_2+\Upsilon\delta_4)+\mu'(\Xi\delta_3+\Upsilon\delta_5)]\\&+\mu[\lambda(\Xi\delta_1+\Upsilon\delta_6)+\lambda'(\Xi\delta_2+\Upsilon\delta_4)+\mu(\Xi\delta_6-\Upsilon\delta_1)+\mu'(\Xi\delta_4-\Upsilon\delta_2)]\\&+\mu'[\lambda(\Xi\delta_2+\Upsilon\delta_4)+\lambda'(\Xi\delta_3+\Upsilon\delta_5)+\mu(\Xi\delta_4-\Upsilon\delta_2)+\mu'(\Xi\delta_5-\Upsilon\delta_3)]\}/[k^3(\Xi^2+\Upsilon^2)]\ ,\end{aligned}\tag{2}$$

where

$$\Xi=1-(2\pi/\Delta)(1+\tfrac{1}{2}\pi\xi_3/\Delta)(\rho k^{-3})(k\zeta'-\psi)-(\pi/\Delta)\rho k^{-2}[(\chi'-\zeta')+(\tfrac{1}{4}\pi\xi_2/\Delta)(\chi-\zeta'')]$$
$$-(\pi/\Delta)^2(\rho/k^2)^2[(\chi-1)(\chi''-\zeta'')-(\chi'-\zeta')^2-(k\zeta'-\psi)(k\zeta'''-\psi'')+(k\zeta''-\psi')^2]\ ,$$

$$\Upsilon=(2\pi/\Delta)(1+\tfrac{1}{2}\pi\xi_3/\Delta)(\rho k^{-3})(\chi+\tfrac{1}{2}k^2\zeta''-1)-(2\pi\rho/\Delta k^2)[k\zeta''-\psi'+(\tfrac{1}{4}\pi\xi_2/\Delta)(k\zeta'''-\psi'')]$$
$$-(\pi/\Delta)^2(\rho/k^2)^2[(k\zeta'-\psi)(\chi''-\zeta'')-2(k\zeta''-\psi')(\chi'-\zeta')+(k\zeta'''-\psi'')(\chi-1)]\ ,$$

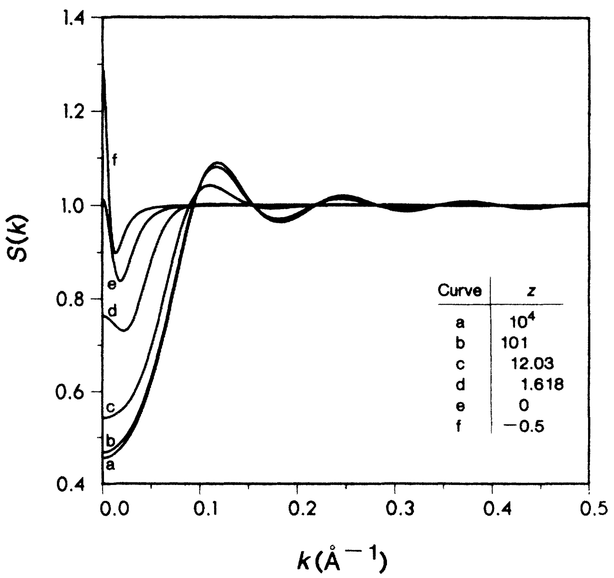

FIG. 1. Polydisperse structure functions calculated for selected Schulz width parameters z and a packing fraction, $\eta = 0.1$.

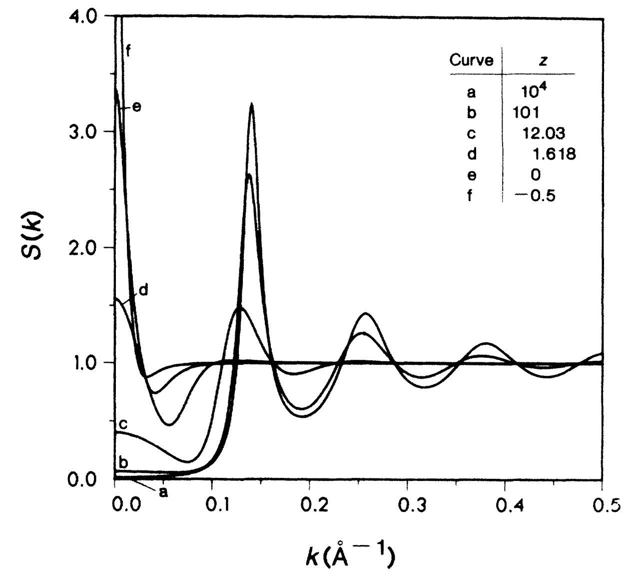

FIG. 3. Polydisperse structure functions calculated for selected Schulz width parameters z and a packing fraction $\eta = 0.5$.

and

$$\delta_1 = (\pi/\Delta)\{2 + (\pi/\Delta)[\xi_3 - (\rho/k)(k\zeta''' - \psi'')]\} \ ,$$
$$\delta_2 = (\pi/\Delta)^2(\rho/k)(k\zeta'' - \psi') \ ,$$
$$\delta_3 = -(\pi/\Delta)^2(\rho/k)(k\zeta' - \psi) \ ,$$
$$\delta_4 = (\pi/\Delta)[k - (\pi/\Delta)(\rho/k)(\chi' - \zeta')] \ ,$$
$$\delta_5 = (\pi/\Delta)^2[(\rho/k)(\chi - 1) + \tfrac{1}{2}k\xi_2] \ ,$$
$$\delta_6 = (\pi/\Delta)^2(\rho/k)(\chi'' - \zeta'') \ .$$

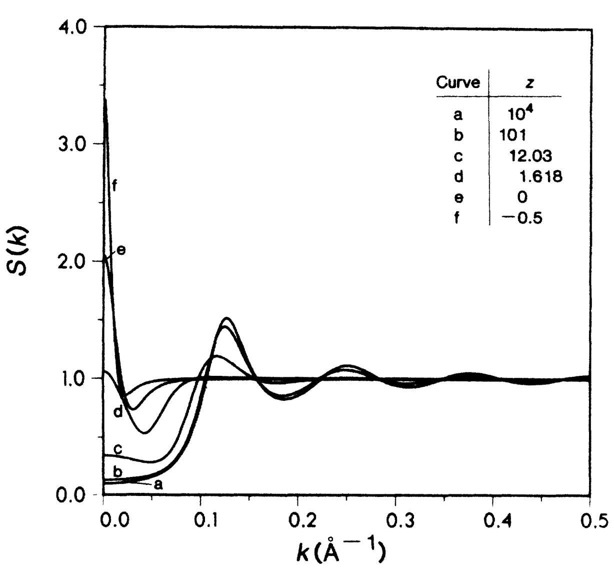

FIG. 2. Polydisperse structure functions calculated for selected Schulz width parameters z and a packing fraction $\eta = 0.3$.

Computed values of $S(k) = 1 + h(k)$ via Eqs. (1) and (2) are presented in Fig. 1 for a particle distribution with a mean diameter of 50 Å, 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. The values for $z = 101$ are basically coincident with those obtained for $z = 10^4$. Similar calculations for samples having packing fractions of 0.3 and 0.5 are shown in Figs. 2 and 3. The effect of polydispersity is to smooth the oscillations in $S(k)$, as previously noted by Vrij,[4] while dramatically increasing its low-k region due to an increase in the thermodynamic limit of the structure function. The wide range of particle sizes available increases density fluctuations which, in turn, increase $S(k)$ in the low-k domain.

For PY fluids, the calculation method presented here can be extended to compute the compressibility and the scattering intensity of a polydisperse fluid. This appears particularly useful in permitting a rigorous evaluation of the intensities obtained in small angle scattering experiments on nonionic micellar fluids, as will be described in a forthcoming paper. In that paper, we will provide a detailed comparison between structure functions derived by Vrij as a factorization of scattering intensities with our analytical solution. Vrij, of course, was the first to assess the effect of polydispersity on the structure function, deriving an effective $S(k)$ by factoring the scattering intensity with the particle form factor.

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[1](a) L. Blum and G. Stell, J. Chem. Phys. **71**, 42 (1979); (b) **72**, 2212 (1980).

[2]G. V. Schulz, Z. Phys. Chem. Abt. B **43**, 25 (1939); B. H. Zimm, J. Chem. Phys. **16**, 1099 (1948); M. Kotlarchyk and S. H. Chen, *ibid.* **79**, 2461 (1983).

[3]Two errors were corrected in Eq. (2.58) of Ref. 1(b). The sign of $y_2 \mathrm{Im}[\phi_2(\sigma)]$ in Eq. (2.52) of Ref. 1 (a), was changed, and Q_{ij}'' in Eq. (2.58) of Ref. 1(b) is not the same as given in Eq. (2.20) of Ref. 1(a).

[4]A. Vrij, J. Chem. Phys. **71**, 3207 (1979); P. van Beurten and A. Vrij, *ibid.* **74**, 2744 (1981).