Static structure factor for a colloidal dispersion with size and ''charge'' polydispersities: Mean spherical approximation model in hard-sphere Yukawa fluids

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An analytical model is presented of the static structure factor for a colloidal dispersion with size and ''charge'' polydispersities. The model is based on the mean spherical approximation solution of the Ornstein-Zernike equation in a hard-sphere Yukawa fluid mixture. With the use of the model, the size- and ''charge''-polydispersity effects are investigated on the structure, and characteristics of the effects are discussed. [S1063-651X(99)06702-1]

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I. INTRODUCTION

Due to the mesoscopic or macroscopic nature of colloidal particles, many colloidal fluids are polydisperse in size, shape, or interaction. In order to understand properties of colloids, investigation of the polydispersity effects on measurable quantities would be essential. Since such a colloidal fluid has in general a number of components as a many-particle system, many workers have approached the fluid by analytical methods with the employment of the appropriate models. For example, with the use of analytical expressions for static structures based on the mean spherical aproximation (MSA) solution of the Ornstein-Zernike (OZ) equation, polydispersity effects have been investigated in a polydisperse hard-sphere fluid [1–3], a polydisperse charged hard-sphere fluid [4], and a polydisperse hard-sphere Yukawa (HSY) fluid [5]. In the previous paper [5], the present authors reported the interaction polydispersity effect on the static structure factor in the HSY fluid consisting of same-size particles. As far as the present authors are aware, no report has been published on an extension of the paper [5] to the HSY fluid, polydisperse in both size and interaction.

Let us consider a multicomponent HSY fluid in a volume V with the temperature T. The i component of the fluid consists of $V\rho_i$ particles with diameter σ_i and two particles of i and j components interact via the potential $\phi_{ij}(r)$ outside hard spheres:

$$\phi_{ij}(r)=\varepsilon_0 Z_i Z_j \frac{\sigma_0}{r} e^{-z(r-\sigma_{ij})}, \quad \sigma_{ij}=(\sigma_i+\sigma_j)/2<r, \tag{1.1}$$

where ε_0 is a coupling-energy constant, σ_0 is an average sphere diameter defined below, and z is a damping constant. We shall refer to Z_i as ''charge'' of the i species of the particle. It should be noted, however, that Z_i is a parameter describing the interaction polydispersity, and it does not mean necessarily the real charge.

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The size and ''charge'' polydispersities are represented by distributions of the size parameter σ_i and the ''charge'' parameter Z_i. As measures of the polydispersities, we define polydispersity parameters D_σ and D_Z by

$$D_\sigma=\langle\sigma^2\rangle/\sigma_0^2-1, \quad D_Z=\langle Z^2\rangle/Z_0^2-1, \tag{1.2}$$

where

$$\langle\sigma^n\rangle=\sum_j c_j\sigma_j^n, \quad \langle Z^n\rangle=\sum_j c_jZ_j^n, \quad \sigma_0=\langle\sigma\rangle, \quad Z_0=\langle Z\rangle, \tag{1.3}$$

c_i being the concentration of the i component defined by $c_i=\rho_i/\rho$ with the total number density of spheres, ρ.

The aim of the paper is to present an analytical model of the static structure factor for a colloidal dispersion with the size and ''charge'' polydispersities and report characteristics of D_σ and D_Z effects on the structure. The model is based on the MSA solution of the OZ equation in the HSY fluid above. In Sec. II the analytical model of the structure factor is presented. The polydispersity effects are discussed in Secs. III and IV. Section V gives a discussion.

II. MSA STRUCTURE FACTOR OF HSY FLUID

The partial structure factor related to the i and j components, $S_{ij}(k)$, is calculated from the following general formula [4,5]:

$$S_{ij}(k)=\delta_{ij}-2\,\mathrm{Re}[\{\hat{\gamma}_s(ik)\}_{ij}], \tag{2.1}$$

where the ij element of the symmetric matrix $\hat{\gamma}_s(s)$ is defined by

$$\{\hat{\gamma}_s(s)\}_{ij}\equiv\frac{2\pi}{s}(c_ic_j)^{1/2}\rho\tilde{g}_{ij}(s) \tag{2.2}$$

with the Laplace transform defined by

$$\tilde{g}_{ij}(s)\equiv\int_0^\infty dr\, rg_{ij}(r)e^{-sr},$$

$g_{ij}(r)$ being the partial radial distribution function. The total structure factor $S(k)$ is defined by

$$S(k)=\sum_{ij}(c_ic_j)^{1/2}S_{ij}(k). \tag{2.3}$$

Therefore, the calculation of the structures is reduced to that of $\hat{\gamma}_s(s)$. Below, we shall present MSA expressions of $S_{ij}(k)$ and $S(k)$.

Now, in the HSY system corresponding to Eq. (1.1), the MSA for the OZ equation is defined by the closure relation

$$g_{ij}(r)=0,\quad \sigma_{ij}>r,$$
$$c_{ij}(r)=\frac{KZ_iZ_j}{r}e^{-z(r-\sigma_{ij})},\quad \sigma_{ij}<r,$$

where $c_{ij}(r)$ is the partial direct correlation function and $K=-\varepsilon_0\sigma_0/k_BT$.

In the Baxter formalism of the OZ equation, the MSA solution is given by the Baxter function $Q_{ij}(r)$ or its transform $\tilde{Q}_{ij}(is)$ as [6,7]

$$\tilde{Q}_{ij}(is)=\int_{\lambda_{ji}}^{\infty}dr\,Q_{ij}(r)e^{-sr}$$
$$=e^{s\lambda_{ij}}\Bigg[\sigma_i^3\psi_1(s\sigma_i)A_j+\sigma_i^2\varphi_1(s\sigma_i)\beta_j+C_{ij}e^{-z\sigma_{ij}}\left(\frac{e^{z\sigma_i}-e^{-s\sigma_i}}{s+z}-\frac{1-e^{-s\sigma_i}}{s}\right)+\frac{D_{ij}e^{-z\lambda_{ji}}}{s+z}\Bigg], \tag{2.4}$$

where $\lambda_{ji}=(\sigma_j-\sigma_i)/2$ and the simplest expressions of coefficients A_j, β_j, C_{ij}, and D_{ij} are [8,9]

$$A_j=\frac{2\pi}{\Delta}\left(1+\frac{\pi\zeta_2}{2\Delta}\sigma_j\right)+\frac{\pi}{\Delta}P_Na_j, \tag{2.5a}$$

$$\beta_j=\frac{\pi}{\Delta}\sigma_j+\Delta_Na_j, \tag{2.5b}$$

$$C_{ij}=\left(Z_i-\frac{B_ie^{-z\sigma_i/2}}{z}\right)e^{z\sigma_{ij}}a_j, \tag{2.5c}$$

$$D_{ij}=-Z_ie^{z\sigma_{ij}}a_j. \tag{2.5d}$$

In these equations, $\zeta_m=\Sigma_l\rho_l\sigma_l^m$, $\Delta=1-\eta$ with $\eta=\pi\zeta_3/6$,

$$P_N=\sum_l\rho_l\sigma_lX_l-\frac{\Delta z}{\pi}\Delta_N, \tag{2.6a}$$

$$a_j=\frac{2\Gamma}{D_2}X_j, \tag{2.6b}$$

$$\sigma_jB_je^{z\sigma_j/2}\varphi_0(z\sigma_j)=X_j-Z_j-\sigma_j\Delta_N, \tag{2.6c}$$

where

$$\Delta_N=\frac{(2\pi/\Delta z^2)\{\lambda^{(1)}[\xi^{(0)}-z/2-\Gamma-(\pi\zeta_2/2\Delta)]-\lambda^{(0)}(1+\xi^{(1)})\}}{1+\xi^{(1)}+(2\pi/\Delta z^2)\{\eta^{(1)}[\xi^{(0)}-z/2-\Gamma-(\pi\zeta_2/2\Delta)]-\eta^{(0)}(1+\xi^{(1)})\}}, \tag{2.7a}$$

$$X_j=\lambda_j-\frac{\xi_j\lambda^{(1)}}{1+\xi^{(1)}}-\Delta_N\left(\eta_j-\frac{\xi_j\eta^{(1)}}{1+\xi^{(1)}}\right), \tag{2.7b}$$

$$D_m=\sum_l\rho_lX_l^m \tag{2.7c}$$

with

$$\xi^{(n)}=\sum_l\rho_l\sigma_l^n\xi_l,\quad \eta^{(n)}=\sum_l\rho_l\sigma_l^n\eta_l,\quad \lambda^{(n)}=\sum_l\rho_l\sigma_l^n\lambda_l, \tag{2.8a}$$

ξ_i, η_i, and λ_i being defined as

$$\xi_i=\frac{(\pi/2\Delta)\sigma_i^2\varphi_0(z\sigma_i)}{1+\varphi_0(z\sigma_i)\sigma_i\Gamma},\quad \eta_i=\frac{(z\sigma_i)^2\psi_1(z\sigma_i)\sigma_i}{1+\varphi_0(z\sigma_i)\sigma_i\Gamma},$$

$$\lambda_i=\frac{Z_i}{1+\varphi_0(z\sigma_i)\sigma_i\Gamma}. \tag{2.8b}$$

Above, we used the functions as $\varphi_0(x)=(1-e^{-x})/x$, $\psi_1(x)=[1-x/2-(1+x/2)e^{-x}]/x^3$, and $\varphi_1(x)=(1-x-e^{-x})/x^2$ and the parameter Γ is defined as the physical solution of the following nonlinear equation:

$$\Gamma^2+z\Gamma=-\pi KD_2. \tag{2.9}$$

Now, with the use of the MSA solution, the Laplace transform of the OZ equation yields the following [6,7]:

$$\sum_l 2\pi\tilde{g}_{il}(s)[\delta_{lj}-c_l\rho\tilde{Q}_{lj}(is)]=\left\{\left(1+\frac{s\sigma_i}{2}\right)A_j+s\beta_j\right\}\frac{e^{-s\sigma_{ij}}}{s^2}-\frac{z}{s+z}e^{-(s+z)\sigma_{ij}}C_{ij}. \tag{2.10}$$

Using Eq. (2.2), Eq. (2.10) can be written in a matrix form as

$$\hat{\gamma}_s(s)\hat{Q}(is)=\hat{\Lambda}(s), \tag{2.11}$$

where the ij elements of the matrices $\hat{Q}(is)$ and $\hat{\Lambda}(s)$ are defined by

$$\{\hat{Q}(is)\}_{ij}\equiv\delta_{ij}-(c_ic_j)^{1/2}\rho\tilde{Q}_{ij}(is), \tag{2.12}$$

$$\Lambda_{ij}(s) \equiv \frac{(c_i c_j)^{1/2}\rho}{s} e^{-s\sigma_{ij}} \left[\left\{ \left(1+\frac{s\sigma_i}{2}\right) A_j + s\beta_j \right\} \frac{1}{s^2} - \frac{z}{s+z} e^{-z\sigma_{ij}} C_{ij} \right]. \quad (2.13)$$

From Eq. (2.11), we get

$$\hat{\gamma}_s(s) = \hat{\Lambda}(s)\hat{R}(s), \quad (2.14)$$

where $\hat{R}(s)$ is defined by

$$\hat{Q}(is)\hat{R}(s) = 1. \quad (2.15)$$

Now, with the use of Eqs. (2.5a)–(2.5d), Eq. (2.13) gives

$$\Lambda_{ij}(s) \equiv (c_i c_j)^{1/2} e^{-s\sigma_{ij}} \sum_n w_i^{(n)}(s)\alpha_j^{(n)}, \quad (2.16)$$

where

$$\alpha_j^{(1)} = 1, \quad (2.17a)$$

$$\alpha_j^{(2)} = \sigma_j, \quad (2.17b)$$

$$\alpha_j^{(3)} = a_j, \quad (2.17c)$$

$$w_i^{(1)}(s) = \frac{2\pi\rho}{\Delta s^3}\left(1+\frac{s\sigma_i}{2}\right), \quad (2.18a)$$

$$w_i^{(2)}(s) = \frac{\pi\rho}{\Delta s^3}\left\{ s + \frac{\pi\zeta_2}{\Delta}\left(1+\frac{s\sigma_i}{2}\right)\right\}, \quad (2.18b)$$

$$w_i^{(3)}(s) = \rho\left\{ \frac{\pi P_N}{\Delta s^3}\left(1+\frac{s\sigma_i}{2}\right) + \frac{\Delta_N}{s^2} - \frac{z}{s(s+z)}\left(Z_i - \frac{e^{-z\sigma_i}}{z} B_i e^{z\sigma_i/2}\right)\right\}, \quad (2.18c)$$

while the substitution of Eq. (2.4) into Eq. (2.12) and the use of Eqs. (2.5a)–(2.5d) yield

$$\{\hat{Q}(is)\}_{ij} = \delta_{ij} - (c_i c_j)^{1/2} e^{s\lambda_{ij}} \sum_n Y_i^{(n)}(s)\alpha_j^{(n)}, \quad (2.19)$$

where

$$Y_i^{(1)}(s) = \frac{2\pi\rho}{\Delta}\sigma_i^3\psi_1(s\sigma_i), \quad (2.20a)$$

$$Y_i^{(2)}(s) = \frac{\pi\rho}{\Delta}\left\{\frac{\pi\zeta_2}{\Delta}\sigma_i^3\psi_1(s\sigma_i) + \sigma_i^2\varphi_1(s\sigma_i)\right\}, \quad (2.20b)$$

$$Y_i^{(3)}(s) = \rho\left\{ \frac{\pi P_N}{\Delta}\sigma_i^3\psi_1(s\sigma_i) + \Delta_N\sigma_i^2\varphi_1(s\sigma_i) + \left(Z_i - \frac{e^{-z\sigma_i}}{z}B_i e^{z\sigma_i/2}\right)\left(\frac{e^{z\sigma_i}-e^{-s\sigma_i}}{s+z} - \frac{1-e^{-s\sigma_i}}{s}\right) - \frac{Z_i e^{z\sigma_i}}{s+z}\right\}. \quad (2.20c)$$

Equations (2.15) and (2.19) give

$$R_{ij}(s) = \delta_{ij} + (c_i c_j)^{1/2} e^{s\lambda_{ij}} \sum_n Y_i^{(n)}(s) L_j^{(n)}(s), \quad (2.21)$$

where $R_{ij}(s)$ is the *ij* element of $\hat{R}(s)$ and

$$L_j^{(n)}(s) \equiv c_j^{-1/2} \sum_l c_l^{1/2} e^{s\lambda_{jl}} \alpha_l^{(n)} R_{lj}(s). \quad (2.22)$$

From Eqs. (2.21) and (2.22), we get

$$L_j^{(n)}(s) = \alpha_j^{(n)} + \sum_m F^{(n,m)}(s) L_j^{(m)}(s), \quad (2.23)$$

where

$$F^{(n,m)}(s) = \sum_i c_i \alpha_i^{(n)} Y_i^{(m)}(s). \quad (2.24)$$

Therefore,

$$L_j^{(n)}(s) = \sum_m G^{(n,m)}(s)\alpha_j^{(m)}, \quad (2.25)$$

where $G^{(n,m)}(s)$ is the *nm* element of matrix $\hat{G}(s)$ defined by

$$\hat{G}(s)[1-\hat{F}(s)] = 1, \quad (2.26)$$

the *nm* element of matrix $\hat{F}(s)$ being $F^{(n,m)}(s)$.

Therefore, with the substitution of Eqs. (2.16) and (2.21) into Eq. (2.14) and with the use of Eqs. (2.23), (2.24), and (2.25), we get

$$\{\hat{\gamma}_s(s)\}_{ij} = (c_i c_j)^{1/2} e^{-s\sigma_{ij}} \sum_n \sum_m w_i^{(n)}(s) G^{(n,m)}(s)\alpha_j^{(m)}. \quad (2.27)$$

Substitution of Eq. (2.27) into Eq. (2.1) gives

$$S_{ij}(k) = \delta_{ij} - (c_i c_j)^{1/2} 2\,\mathrm{Re}\left[e^{-s\sigma_{ij}} \sum_n \sum_m w_i^{(n)}(s) G^{(n,m)} \times (s)\alpha_j^{(m)} \right]_{s=ik}. \quad (2.28)$$

From Eqs. (2.3) and (2.28), we get

$$S(k) = 1 - 2\,\mathrm{Re}\left[\sum_n \sum_m F_w^{(n)}(s) G^{(n,m)}(s) F_\alpha^{(m)} \right]_{s=ik}, \quad (2.29)$$

where

$$F_w^{(n)}(s) \equiv \sum_i c_i e^{-s\sigma_i/2} w_i^{(n)}(s), \tag{2.30a}$$

$$F_\alpha^{(n)}(s) \equiv \sum_i c_i e^{-s\sigma_i/2} \alpha_i^{(n)}. \tag{2.30b}$$

The substitutions of Eqs. (2.17a)–(2.17c) into Eq. (2.30b) and Eqs. (2.18a)–(2.18c) into Eq. (2.30a) give explicit expressions of $F_\alpha^{(n)}$ and $F_w^{(n)}$, respectively. On the other hand, from Eq. (2.26) the expression of $G^{(n,m)}$ is obtained in terms of $F^{(n,m)}$, which are calculated with the substitution of Eqs. (2.17a)–(2.17c) and (2.20a)–(2.20c) into Eq. (2.24). Thus, from Eqs. (2.28) and (2.29) we now obtain explicit and analytical expressions of the static structure factors.

III. $S(k)$ OF A HARD-SPHERE FLUID WITH SCHULZ DISTRIBUTED DIAMETERS

As a special and simplest application of the model above, we consider a polydisperse fluid consisting of hard spheres with no interaction outside spheres. We assume that the polydispersity is intrinsic and is modeled by the Schulz distributed diameters: when we write the number of particles with diameters in a domain of $(\sigma, \sigma+d\sigma)$ as $V\rho f(\sigma)d\sigma$, the Schulz distribution is defined by

$$f(\sigma) = \left[\frac{t+1}{\sigma_0}\right]^{t+1} \frac{\sigma^t}{t!} \exp\left(-\left[\frac{t+1}{\sigma_0}\right]\sigma\right), \tag{3.1}$$

where we assume t to be a non-negative integer and σ_0 is defined by Eq. (1.3).

Since all charge parameters are zero here,

$$F_\alpha^{(3)} = 0, \quad F_w^{(3)} = 0, \quad F^{(3,n)} = 0, \quad F^{(n,3)} = 0, \tag{3.2}$$

where $n = 1,2,3$.

The component sums in the remaining elements needed in Eq. (2.29) are easily calculated with the use of the following:

$$t_m \equiv \frac{1}{\sigma_0^m} \sum_j c_j \sigma_j^m = \frac{1}{\sigma_0^m} \int_0^\infty d\sigma\, f(\sigma) \sigma^m = \frac{(t+m)!}{t!(t+1)^m}, \tag{3.3}$$

$$f_m(a) \equiv \frac{1}{\sigma_0^m} \sum_j c_j \sigma_j^m e^{-a\sigma_j/\sigma_0} = \frac{1}{\sigma_0^m} \int_0^\infty d\sigma\, f(\sigma) \sigma^m e^{-a\sigma/\sigma_0} = t_m \left(1 + \frac{a}{t+1}\right)^{-(t+m+1)}. \tag{3.4}$$

In the last steps of calculations in Eqs. (3.3) and (3.4), we used Eq. (3.1).

From Eq. (2.30b) with Eqs. (2.17a) and (2.17b),

$$F_\alpha^{(1)} = f_0\left(\frac{s\sigma_0}{2}\right), \quad F_\alpha^{(2)} = \sigma_0 f_1\left(\frac{s\sigma_0}{2}\right), \tag{3.5}$$

while from Eq. (2.30a) with Eqs. (2.18a) and (2.18b),

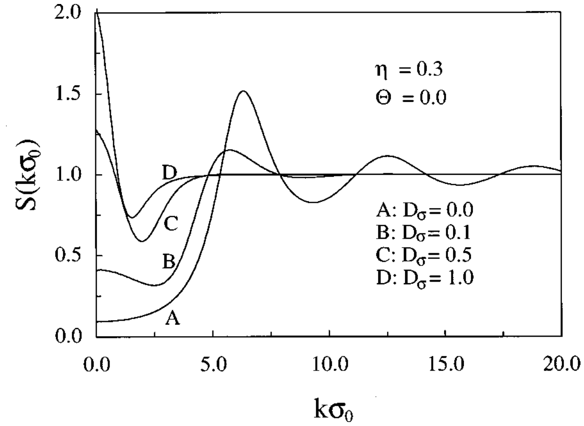

FIG. 1. D_σ dependence of $S(k\sigma_0)$ in the case of $\eta = 0.3$ and $\Theta = 0.0$ (no Yukawa-type interaction): $D_\sigma = 0.0$ (curve *A*), 0.1 (curve *B*), 0.5 (curve *C*), and 1.0 (curve *D*).

$$F_w^{(1)} = \frac{2\pi\rho\sigma_0^3}{\Delta} \frac{1}{(s\sigma_0)^3} \left[f_0\left(\frac{s\sigma_0}{2}\right) + \frac{s\sigma_0}{2} f_1\left(\frac{s\sigma_0}{2}\right)\right], \tag{3.6a}$$

$$F_w^{(2)} = \frac{1}{\sigma_0} \frac{\pi\rho\sigma_0^3}{\Delta} \frac{1}{(s\sigma_0)^3} \left[\left(s\sigma_0 + \frac{\pi\zeta_2\sigma_0}{\Delta}\right) f_0\left(\frac{s\sigma_0}{2}\right) + \frac{\pi\zeta_2\sigma_0}{\Delta} \frac{s\sigma_0}{2} f_1\left(\frac{s\sigma_0}{2}\right)\right]. \tag{3.6b}$$

On the other hand, from Eq. (2.24) with Eqs. (2.17a), (2.17b), (2.20a), and (2.20b),

$$F^{(1,1)} = \frac{2\pi\rho\sigma_0^3}{\Delta} f_a(s\sigma_0), \tag{3.7a}$$

$$F^{(2,1)} = \sigma_0 \frac{2\pi\rho\sigma_0^3}{\Delta} f_b(s\sigma_0), \tag{3.7b}$$

$$F^{(1,2)} = \frac{1}{\sigma_0} \left[\left(\frac{\pi}{\Delta}\right)^2 \rho\zeta_2\sigma_0^4 f_a(s\sigma_0) + \frac{\pi\rho\sigma_0^3}{\Delta} f_c(s\sigma_0)\right], \tag{3.7c}$$

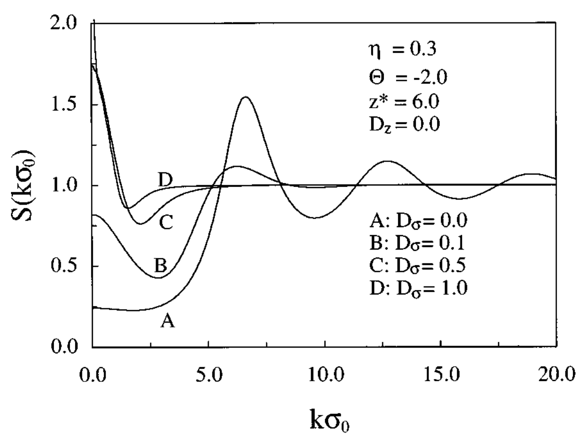

FIG. 2. D_σ dependence of $S(k\sigma_0)$ in the case of $\eta = 0.3$, $z^* = 6.0$, $\Theta = -2.0$, and $D_z = 0.0$: $D_\sigma = 0.0$ (curve *A*), 0.1 (curve *B*), 0.5 (curve *C*), and 1.0 (curve *D*).

$$F^{(2,2)}=\left(\frac{\pi}{\Delta}\right)^2\rho\zeta_2\sigma_0^4 f_b(s\sigma_0)+\frac{\pi\rho\sigma_0^3}{\Delta}f_d(s\sigma_0),\quad (3.7d)$$

where

$$f_a(s\sigma_0)=\frac{1}{\sigma_0^3}\sum_j c_j\sigma_j^3\psi_1(s\sigma_j)$$
$$=\frac{1}{(s\sigma_0)^3}\left[1-\frac{s\sigma_0}{2}-f_0(s\sigma_0)-\frac{s\sigma_0}{2}f_1(s\sigma_0)\right],\quad (3.8a)$$

$$f_b(s\sigma_0)=\frac{1}{\sigma_0^4}\sum_j c_j\sigma_j^4\psi_1(s\sigma_j)$$
$$=\frac{1}{(s\sigma_0)^3}\left[1-\frac{s\sigma_0}{2}t_2-f_1(s\sigma_0)-\frac{s\sigma_0}{2}f_2(s\sigma_0)\right],\quad (3.8b)$$

$$f_c(s\sigma_0)=\frac{1}{\sigma_0^2}\sum_j c_j\sigma_j^2\varphi_1(s\sigma_j)$$
$$=\frac{1}{(s\sigma_0)^2}[1-s\sigma_0-f_0(s\sigma_0)],\quad (3.8c)$$

$$f_d(s\sigma_0)=\frac{1}{\sigma_0^3}\sum_j c_j\sigma_j^3\varphi_1(s\sigma_j)$$
$$=\frac{1}{(s\sigma_0)^2}[1-s\sigma_0 t_2-f_1(s\sigma_0)].\quad (3.8d)$$

Note that from Eqs. (1.2) and (3.3),

$$t=1/D_\sigma-1,\quad t_2=D_\sigma+1,\quad t_3=t_2(2D_\sigma+1).\quad (3.9)$$

As is seen from Eq. (2.29) and all equations in this section, $S(k)$ is determined by D_σ and the packing fraction η:

$$\eta=\rho v_0 t_3\quad \text{with}\quad v_0=\frac{\pi\sigma_0^3}{6}.\quad (3.10)$$

Now, by choosing a set of parameters (η,D_σ), we can investigate the size-polydispersity effect on $S(k)$.

Figure 1 shows the dependence of $S(k)$ on D_σ in the case of $\eta=0.3$ (and $\Theta=0.0$): $D_\sigma=0.0$ (curve *A*), 0.1 (curve *B*), 0.5 (curve *C*), and 1.0 (curve *D*). We investigated the D_σ dependences for various values of η, and obtained basically the same behaviors as in Ref. [3]. See also Fig. 2.

IV. POLYDISPERSITY EFFECTS IN HSY FLUID

In this section, we consider the HSY fluid with the intrinsic size and ‘‘charge’’ polydispersities. We assume the fluid to be described by a model in which the distribution of the diameters and the charges is given by a distribution function $f(\sigma,Z)$, where we write the number of particles having diameters and charges in domains of $(\sigma,\sigma+d\sigma)$ and $(Z,Z+dZ)$, respectively, as $V\rho f(\sigma,Z)d\sigma\, dZ$. The function is thus non-negative and satisfies the following normalization condition:

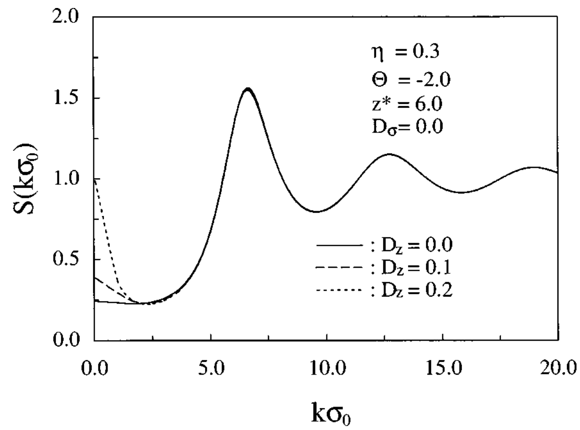

FIG. 3. D_z dependence of $S(k\sigma_0)$ in the case of $\eta=0.3$, $z^*=6.0$, $\Theta=-2.0$, and $D_\sigma=0.0$: $D_z=0.0$ (solid line), 0.1 (dashed line), 0.2 (dotted line).

$$\int_0^\infty d\sigma\int_{-\infty}^\infty dZ\, f(\sigma,Z)=1.$$

When the number of particles having diameters in a domain of $(\sigma,\sigma+d\sigma)$ regardless of ‘‘charges’’ is written as $V\rho f(\sigma)d\sigma$, $f(\sigma)$ is given as follows:

$$f(\sigma)=\int_{-\infty}^\infty dZ\, f(\sigma,Z).$$

Here, for $f(\sigma)$ we employ the Schulz distribution function [Eq. (3.1)]. Thus, all the equations except Eq. (3.2) in the preceding section are satisfied in this section as well. As for the counterparts of the elements of Eq. (3.2), the component sums may be somewhat difficult, as is seen from Eqs. (2.17c), (2.18c), and (2.20c) with Eqs. (2.6a)–(2.6c), (2.7a)–(2.7c), (2.8a), (2.8b), and (2.9). Since we need detailed knowledge of $f(\sigma,Z)$ in order to go forward, we assume here the following uncorrelated case:

$$f(\sigma,Z)=f(\sigma)f_1(Z),\quad (4.1)$$

where $f_1(Z)$ is a distribution function of ‘‘charges.’’ As a result, in this case $S(k)$ does not depend on any more detail

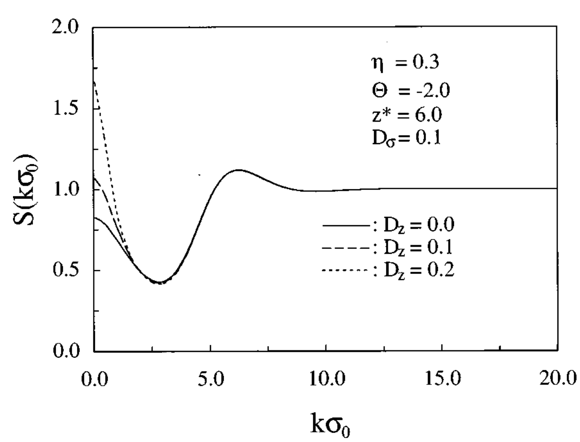

FIG. 4. D_z dependence of $S(k\sigma_0)$ in the case of $\eta=0.3$, $z^*=6.0$, $\Theta=-2.0$ and $D_\sigma=0.1$: $D_z=0.0$ (solid line), 0.1 (dashed line), 0.2 (dotted line).

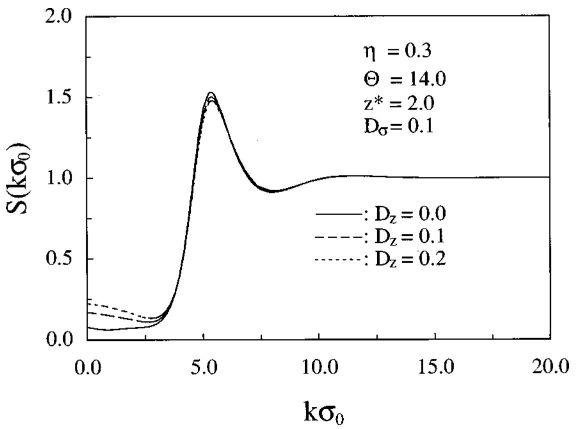

FIG. 5. D_z dependence of $S(k\sigma_0)$ in the case of $\eta=0.3$, $z^*=2.0$, $\Theta=14.0$, and $D_\sigma=0.1$: $D_z=0.0$ (solid line), 0.1 (dashed line), 0.2 (dotted line).

of the functional form of $f_1(Z)$ [5,10,11]. The most difficult thing is the determination of Γ by solving Eq. (2.9) self-consistently, which is concerned with the following type of component sums [11]:

$$I_{lm}(n)=\int_0^\infty dx\, f(\sigma_0 x)x^n \frac{[x\varphi_0(z^*x)]^l}{[1+x\varphi_0(z^*x)\Gamma^*]^m},$$

where n, l, and m are appropriate integers and $x=\sigma/\sigma_0$. In a previous paper [11], we treated this integral with the use of the approximation for $z\sigma_0 \gg 1$. Since we consider the cases of $z\sigma_0=2.0$ and $z\sigma_0=6.0$ below, however, we calculate the integrals above numerically by computer.

As is seen from the expressions above, $S(k)$ is specified by a parameter set of $(\eta,D_\sigma,\Theta,z^*,D_Z)$, where Θ and z^* are defined as

$$\Theta=\varepsilon_0 Z_0^2/k_BT, \quad z^*=z\sigma_0. \tag{4.2}$$

Now, we can investigate the polydispersity effects by choosing various sets, and below we shall investigate the effects in the case of $\eta=0.3$: a typical value for a concentrated colloid.

Let us investigate $S(k)$ of the HSY fluid interacting attractively with $\Theta=-2.0$ and $z^*=6.0$. Figure 2 shows D_σ dependences of $S(k)$ in the case of $D_z=0.0$: $D_\sigma=0.0$ (curve A), 0.1 (curve B), 0.5 (curve C), and 1.0 (curve D). Comparing the behavior in Fig. 2 with that in Fig. 1, we see that (i) D_σ dependences of $S(k)$ in both cases are qualitatively the same, and (ii) the Yukawa interaction (Θ effect) makes $S(k)$ go up in the low k part and makes the positions of maxima and minima of $S(k)$ shift slightly toward higher values of k. The D_z dependences of $S(k)$ are shown in Fig. 3 for $D_\sigma=0.0$ and in Fig. 4 for $D_\sigma=0.1$: $D_Z=0.0$ (solid line), 0.1 (dashed line), 0.2 (dotted line). The figures show that the behaviors of $S(k)$ due to the increase of D_z are qualitatively the same in both figures and the low k part of $S(k)$ goes up as D_z increases.

As for the D_z dependences of $S(k)$ of the HSY fluid with repulsive interaction ($\Theta=14.0$ and $z^*=2.0$), the D_z dependences are shown in Fig. 5 for $D_\sigma=0.1$: $D_z=0.0$ (solid line), 0.1 (dashed line), 0.2 (dotted line). For $D_\sigma=0.0$, we refer to figure 1 in Ref. [5]. From the figures, we see that the behaviors of $S(k)$ due to the increase of D_z are qualitatively the same, and as D_z increases, (i) the low k part of $S(k)$ goes up, (ii) the height of the first peak of $S(k)$ goes down, and (iii) the positions of the maxima and minima of $S(k)$ are shifted slightly toward higher values of k.

As is seen from the comparison of the D_z effects in Figs. 3, 4, and 5 with the D_σ effects in Figs. 1 and 2, the interaction polydispersity has weaker effects on $S(k)$ than the size polydispersity. This conclusion is consistent with the conjecture by Senatore and Blum [4].

V. DISCUSSION

As in previous papers [5,10,11], we introduced the multicomponent HSY fluid consisting of particles interacting through Eq. (1.1) as a model system of the colloidal dispersion with the size and "charge" polydispersities. In the model system, we presented the explicit and analytical expressions of the static structure factors, $S_{ij}(k)$ and $S(k)$, which are given by Eqs. (2.28) and (2.29). It should be noted that the expressions are applicable to the HSY fluid with an arbitrary number of components and tractable even in such intrinsic polydisperse fluid as in Sec. IV. The expression [Eq. (2.29)] thus can be given a role as an analytical model for the colloidal dispersion. In this paper, the size and "charge" polydispersities are described by the distribution function $f(\sigma,Z)$, and Eqs. (4.1) and (3.1) are assumed for $f(\sigma,Z)$ and $f(\sigma)$, respectively, in order to investigate the polydispersity effects on $S(k)$.

The polydisperse Percus-Yevick hard-sphere fluid was considered by many workers [1–3]. Blum and Stell [2] gave the analytical structure factor, and by calculating the structure factor in the case of the Schulz distributed diameters, Griffith *et al.* [3] discussed the polydispersity effect. This polydisperse Percus-Yevich fluid corresponds to the special case of our model with no Yukawa interaction which was discussed in Sec. III. It should be emphasized that the explicit and analytical expression of $S(k)$ obtained is extremely simple: as is seen from Eqs. (3.4), (3.6a), (3.6b), (3.7a)–(3.7d), and (3.8a)–(3.8d), the expression is written in terms of the first three simple basic functions, $f_m(a)$ $(m=0,1,2)$. In order to mention the dependence of $S(k)$ on moments of the Schulz distribution function, let us consider the moment expansion of $f_m(a)$; it is easily obtained from Eq. (3.4) as

$$f_m(a)=\sum_{n=0}^\infty \frac{(-1)^n a^n}{n!} t_{n+m},$$

where t_{n+m} is the nondimensional $(n+m)$th moment defined by Eq. (3.3). The expansion shows that $S(k)$ depends on all the moments in the case of $k\neq 0$. As for the moment dependence in the case of $k\to 0$, $S(k)$ depends only on t_m for $m=0,1,2,3$ since $f_m(0)=t_m$ and $\eta=\rho v_0 t_3$. This conclusion is consistent with that of the MSA or PY treatment of thermodynamical properties of the polydisperse hard-sphere fluid [12].

In this paper, we investigated the polydispersity effects in the special case that size and "charge" distributions are uncorrelated and described by Eq. (4.1). In a charge-stabilized colloid as an example, however, the amount of "charge" on a colloidal particle would depend in general on its size: the assumption has been employed that the distributions of sizes and ''charges'' are strongly correlated in such a way that the ''charge'' on a colloidal particle is proportional to the square of its diameter. In the context of the model in Sec. IV, this assumption means the following choice for $f(\sigma,Z)$:

$$f(\sigma,Z)=f(\sigma)\,\delta(Z-Z_0\sigma^2/\langle\sigma^2\rangle).$$

D'Aguanno and Klein [13] considered the HSY fluids consisting of colloidal particles with continuous size and charge distributions. They described the size distribution in terms of the Schulz function and discussed the description of the polydispersity by means of the reduction of the continuous distributions to three components. In the present model, however, we can directly consider the continuous distributions described by the function above. This is one of our forthcoming works.

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