

Theory of slow dynamics in highly charged colloidal suspensions

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A systematic theory for the dynamics of charge-stabilized colloidal suspensions of interacting Brownian particles with both Coulomb and hydrodynamic interactions is presented. A nonlinear deterministic diffusion equation for the average local volume fraction of macroions $\Phi(x,t)$ and a linear stochastic diffusion equation for the nonequilibrium density fluctuations around Φ , both of which contain an anomalous self-diffusion coefficient $D_S \sim [1 - \Phi(x,t)/\phi_g]^\gamma$, are derived, where $\gamma=1$ here. The glass transition volume fraction ϕ_g is found to be small as $\phi_g \sim (Zql_B/a)^{-3}$ for highly charged colloidal suspensions with $Z \gg q$, where Ze is the charge of the macroions, $-qe$ is the charge of counterions, l_B is the Bjerrum length, and a is the radius of the macroions. The dynamic anomaly of $D_S(\Phi)$, which results from the correlations among macroions and counterions, due to long-range Coulomb interactions, is shown to cause slow dynamical behavior near ϕ_g . This situation is exactly the same as that of the hard sphere suspensions previously discussed by the present author, where $\gamma=2$. [S1063-651X(98)51309-8]

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In recent years, there has been considerable experimental and theoretical interest in understanding the mechanism for the liquid-glass transition in colloidal liquids [1–4]. At low electrolyte concentrations, highly charged colloidal suspensions show a glass transition even at extremely low volume fractions, while hard-sphere suspensions show the transition at high volume fractions. In an earlier paper [5], Tokuyama and Oppenheim presented a general theory for the dynamics of concentrated hard-sphere suspensions and showed that the correlations between particles, due to many-body, long-range hydrodynamic interactions, play an important role in the dynamics of the supercooled colloidal fluid near the glass transition volume fraction $\phi_g^{\text{HS}} = (\frac{4}{3})^3 / (7 \ln 3 - 8 \ln 2 + 2) \approx 0.57184 \dots$. On the other hand, our understanding of charge-stabilized colloidal suspensions seems to still be far from complete, although there have been many works on them. In this paper, therefore, we apply the same formalism as that introduced in Ref. [5] to charge-stabilized, monodisperse colloidal suspensions and derive the coupled diffusion equations for the average number density of macroions and the nonequilibrium density fluctuations around it. Thus, we show that the correlations among macroions and counterions, due to many-body, long-range Coulomb interactions, play an important role in the slow dynamics near the glass transition volume fraction $\phi_g(\Gamma)$, which becomes extremely small as $\phi_g \sim \Gamma^{-3}$ for large Γ (see Fig. 1), where $\Gamma = Zql_B/a$ is the dimensionless coupling parameter between macroions and counterions.

We consider a three-dimensional suspension of ionized spherical colloidal particles in a polar fluid. In the following, we restrict ourselves to the simple case in which the concentration of added salt is ignored. Thus, the system consists of two ionized spherical particles in an incompressible fluid with viscosity η and the static dielectric constant ϵ : the macroions of radius a , mass m , charge Ze and position vector $\mathbf{X}_i(t)$ ($i=1,2,\dots,N_m$) with the number density $n_m = N_m/V$, and the counterions of radius a_c , mass m_c , and charge $-qe$ with the number density $n_c = N_c/V$, where V is

the total volume of the system, and $a/a_c \gg 1$, $m/m_c \gg 1$, and $Z/q \gg 1$. Here the global charge neutrality requires that $Zn_m = qn_c$. In the absence of added salt, one can assume the following pair interaction potentials $V_{mm}(r)$, $V_{mc}(r)$, and $V_{cc}(r)$ between macroions and counterions [6]: $\beta V_{mm}(r) = Z^2 l_B / r$ for $r > 2a$ and ∞ for $r \leq 2a$, $\beta V_{mc}(r) = -Zql_B / r$ for $r > a$ and ∞ for $r \leq a$, and $\beta V_{cc}(r) = q^2 l_B / r$, where r is the interparticle distance, $l_B = e^2 / \epsilon k_B T$ is the Bjerrum length, and $\beta = 1/k_B T$. The fluctuating velocity field of the fluid is assumed to be described by the fluctuating, linear Navier-Stokes equation, supplemented by stick boundary conditions at the surfaces of the spheres. Then, the system has three macroscopic characteristic lengths: the radius of macroions a , the hydrodynamic screening length $l_H = (6\pi a n_m)^{-1/2} = a/(9\phi/2)^{1/2}$, within which the hydrodynamic interactions

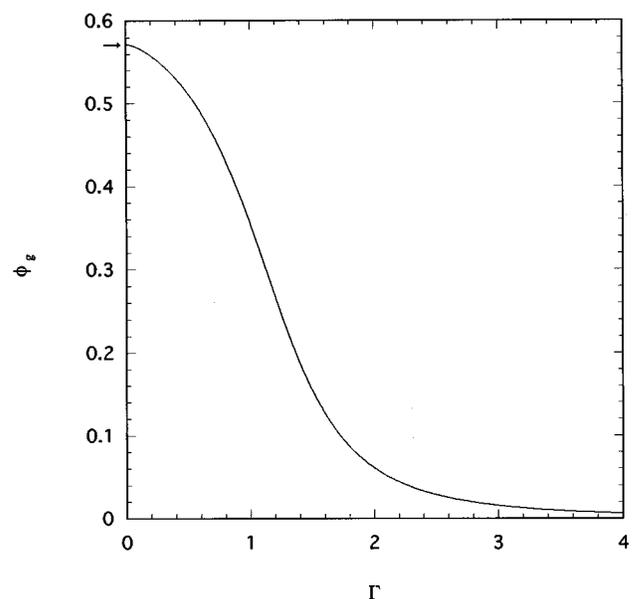


FIG. 1. Glass transition volume fraction ϕ_g versus Γ . The arrow indicates ϕ_g^{HS} at $\Gamma=0$.

between macroions become important [5,6]; and the Debye screening length $\lambda_D = (4\pi n_c q^2 l_B)^{-1/2} = a/(3\phi\Gamma)^{1/2}$, where $\phi = 4\pi a^3 n_m/3$ is the volume fraction of the macroions. For highly charged colloidal suspensions, the lengths l_H and λ_D can be larger than a ; $l_H \sim \lambda_D \gg a \gg a_c$. In fact, for a typical suspension with $\Gamma = 3.684$ where $Z = 280$, $q = 1$, $a = 55.4$ nm, and $l_B = 7.29$ Å [7], we have $\lambda_D \sim 3.64a$, and $l_H \sim 5.7a$ at $\phi = 6.8 \times 10^{-3}$. Hence, there are four important characteristic times: the relaxation time of the momentum contained in the fluid volume of size a , $\tau_f \sim \rho a^2/\eta$; the momentum relaxation time of the macroion $\tau_B \sim m/\zeta$; the screening time $\tau_H \sim \tau_f/\phi$; and the structural relaxation time $\tau_S \sim l_H^2/D_0$, which is a time required for a macroion to diffuse over a distance l_H , where $\zeta = 6\pi\eta a$ is the bare friction coefficient of a macroion, ρ is the fluid mass density, and $D_0 = k_B T/\zeta$ is the single-macroion diffusion coefficient. Here τ_B is the same order as τ_H since $m \langle \dot{\mathbf{X}}_i \rangle^2 \sim m(l_H/\tau_H)^2 \sim k_B T \sim O(1)$, leading to $\tau_S \gg \tau_H \sim \tau_B \gg \tau_f$. Depending on the space-time scales, therefore, there are two characteristic stages. One is a kinetic stage (K), where the space-time cutoff (X_C, τ_C) is set as $l_H \sim \lambda_D \gg X_C \gg a$ and $\tau_H \sim \tau_B \gg \tau_C \gg \tau_f$. The other is a suspension-hydrodynamic stage (SH), where $X_C \gg l_H$ and $\tau_S \gg \tau_C \gg \tau_H$.

The present system obeys the same starting equations as those of the hard-sphere suspension discussed in Ref. [5], except that the forces between particles are now replaced by the Coulomb forces. In the K stage, therefore, one can find a set of Markov Langevin equations for the position $\mathbf{X}_i(t)$ and the velocity $\mathbf{u}_i(t)$ of the macroion i . In order to discuss the kinetic process of the counterions, one can also derive a set of Markov Langevin equations for the position $\mathbf{X}_j^c(t)$ and the velocity $\mathbf{u}_j^c(t)$ of the counterion j , which have the same forms as those of macroions, except that the physical constants, such as m , are replaced by those of the counterions. Starting from those Langevin equations and employing the formalism similar to that in Ref. [5], in the SH stage one can then obtain the diffusion equation for the average number density $n(\mathbf{x}, t)$ of macroions, up to order ∇^2 ,

$$\frac{\partial}{\partial t} n(\mathbf{x}, t) = \nabla \cdot \left\{ \frac{D_S^S(\Phi)}{1 + [\Phi(\mathbf{x}, t) D_S^S(\Phi) / \phi_g^{\text{HS}} D_0]} \times [\nabla n(\mathbf{x}, t) - \mathbf{C}(\mathbf{x}, t)] \right\}, \quad (1)$$

with the correlation term

$$\begin{aligned} \mathbf{C}(\mathbf{x}_1, t) = & \beta \left\{ \int d\mathbf{x}_2 \mathbf{F}_{12}^{\text{mm}} H^{\text{mm}}(\mathbf{x}_1, \mathbf{x}_2, t) \right. \\ & + \int d\mathbf{x}_2^c \mathbf{F}_{12}^{\text{mc}} H^{\text{mc}}(\mathbf{x}_1, \mathbf{x}_2^c, t) \\ & - n(\mathbf{x}_1, t) \int d\mathbf{x}_2 \mathbf{g}_{12} \cdot \mathbf{g}_{21} \\ & \times \left[\int d\mathbf{x}_3 \mathbf{F}_{13}^{\text{mm}} H^{\text{mm}}(\mathbf{x}_2, \mathbf{x}_3, t) \right. \\ & \left. \left. + \int d\mathbf{x}_3^c \mathbf{F}_{13}^{\text{mc}} H^{\text{mc}}(\mathbf{x}_2, \mathbf{x}_3^c, t) \right] \right\}, \quad (2) \end{aligned}$$

where $\Phi(\mathbf{x}, t) = \phi n(\mathbf{x}, t)/n_m$ denotes the time-dependent local volume fraction of the macroions, $\mathbf{F}_{ij}^{\alpha\beta}$ the Coulomb

forces between macroions and counterions, and $D_S^S(\Phi) = D_0(1 - 25\Phi/16)$, the short-time self-diffusion coefficient due to the static hydrodynamic interactions up to order Φ [5]. Here the renormalized Oseen tensor $\mathbf{g}_{12}(t)$ is given by Eq. (4.24) of Ref. [5]. The functions $H^{\text{mm}}(\mathbf{x}_1, \mathbf{x}_2, t)$ and $H^{\text{mc}}(\mathbf{x}_1, \mathbf{x}_2^c, t)$ represent the pair correlation functions between macroions and counterions and obey, to lowest order in ∇_2, ∇_2^c , and ϕ ,

$$\begin{aligned} \frac{\partial}{\partial t} H^{\text{mm}}(\mathbf{x}_1, \mathbf{x}_2) = & D_0(1 + e_{12}) \left\{ \nabla_2^2 H^{\text{mm}}(\mathbf{x}_1, \mathbf{x}_2) - \beta \nabla_2 \right. \\ & \times \left[\mathbf{F}_{21}^{\text{mm}} n(\mathbf{x}_2) n(\mathbf{x}_1) \right. \\ & + \int d\mathbf{x}_3^c \mathbf{F}_{23}^{\text{mc}} n^c(\mathbf{x}_2^c) H^{\text{mc}}(\mathbf{x}_1, \mathbf{x}_3^c) \\ & \left. \left. + \int d\mathbf{x}_3 \mathbf{F}_{23}^{\text{mm}} n(\mathbf{x}_2) H^{\text{mm}}(\mathbf{x}_1, \mathbf{x}_3) \right] \right\}, \quad (3) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial t} H^{\text{mc}}(\mathbf{x}_1, \mathbf{x}_2^c) = & D_0^c(1 + e_{12}) \left\{ \nabla_2^{c2} H^{\text{mc}}(\mathbf{x}_1, \mathbf{x}_2^c) - \beta \nabla_2^c \right. \\ & \times \left[\mathbf{F}_{21}^{\text{cm}} n^c(\mathbf{x}_2^c) n(\mathbf{x}_1) \right. \\ & + \int d\mathbf{x}_3 \mathbf{F}_{23}^{\text{cm}} n^c(\mathbf{x}_2^c) H^{\text{mm}}(\mathbf{x}_1, \mathbf{x}_3) \\ & \left. \left. + \int d\mathbf{x}_3^c \mathbf{F}_{23}^{\text{cc}} n^c(\mathbf{x}_2^c) H^{\text{mc}}(\mathbf{x}_1, \mathbf{x}_3^c) \right] \right\} \\ & + O(D_0/D_0^c), \quad (4) \end{aligned}$$

where D_0^c is the single-counterion diffusion coefficient with $D_0/D_0^c = a_0/a \ll 1$, $n^c(\mathbf{x}_2^c, t)$ is the average number density of the counterions, e_{ij} is the exchange operator between i and j , and $\nabla_2^c = \partial/\partial \mathbf{x}_2^c$. Here the first two terms of Eq. (2) represent the correlation effects of the long-range Coulomb interactions between macroions and counterions separated by a distance of order λ_D and are of order $\phi^{1/2}$. Those terms are similar to the soft-collision term in the one-component plasma [8]. On the other hand, the last two terms of Eq. (2) represent the couplings between the correlation effects of the long-range Coulomb interactions and the long-range hydrodynamic interactions between macroions separated by a distance of order l_H and are of order ϕ . In order to include the effect of the hydrodynamic interactions on Eq. (1), therefore, we have retained the terms up to order ϕ . In order to derive Eq. (2), we have also neglected the terms due to the short-range interactions between particles, since they lead only to corrections at small volume fractions.

In the SH Stage the length scale $|\mathbf{x}_1|$ of interest is longer than λ_D , and the time scale is of order τ_S , while the interparticle distances $|\mathbf{x}_1 - \mathbf{x}_2|$ and $|\mathbf{x}_1 - \mathbf{x}_2^c|$ are of order λ_D . Hence, one can further expand $n(\mathbf{x}_2, t)$ and $n^c(\mathbf{x}_2^c, t)$ about \mathbf{x}_1 . Since $D_0/D_0^c = a_0/a \ll 1$, the dynamics of the counterions surrounding the macroions follows the motion of the macroions in this stage. Then, one can assume that $n^c(\mathbf{x}, t) \approx (Z/q)n(\mathbf{x}, t)$. By solving Eqs. (3) and (4), to lowest

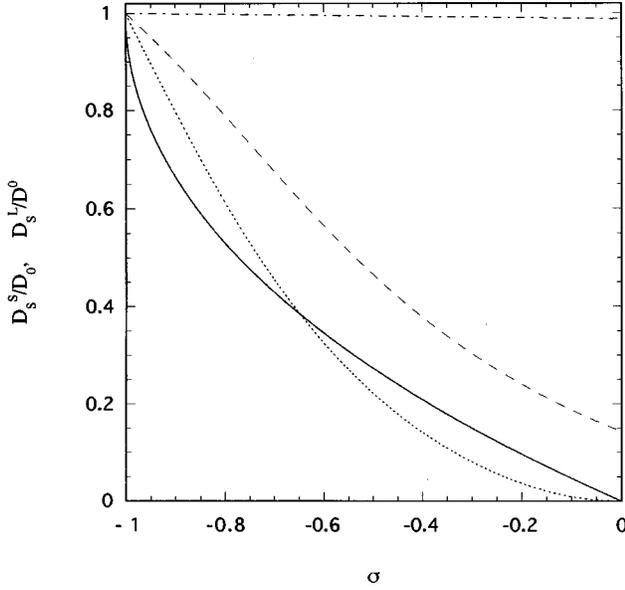


FIG. 2. Short (dotted-dashed line) and long (solid line) time self-diffusion coefficients versus separation parameter σ at $\Gamma = 3.684$. The long-dashed line and the dotted line represent the short- and the long-time, self-diffusion coefficients obtained in Ref. [5], respectively.

order in ∇ and q/Z , we thus obtain the nonlinear deterministic diffusion equation for $n(\mathbf{x}, t)$:

$$(\partial/\partial t)n(\mathbf{x}, t) = \nabla \cdot [D_s(\Phi(\mathbf{x}, t))\nabla n(\mathbf{x}, t)], \quad (5)$$

with the self-diffusion coefficient

$$\begin{aligned} D_s(\Phi) &= D_s^S(\Phi)[1 - \sqrt{3}\{\Phi^{1/2} - (3/\sqrt{8})\Phi\}\Gamma^{3/2} - \Phi/\phi_g^{\text{HS}}] \\ &= D_s^S(\Phi)[1 - (\Phi/\phi_g)^{1/2}][1 - (\Phi/\phi_0)^{1/2}], \end{aligned} \quad (6)$$

where $\phi_0 = (4/3)/[\Gamma^{3/2} - \sqrt{\Gamma^3 - \sqrt{6}\Gamma^{3/2} + 4/(3\phi_g^{\text{HS}})}]^2$ ($\geq \phi_g^{\text{HS}}$). Here the glass transition volume fraction ϕ_g dilute charged colloidal suspension is given by

$$\phi_g = (4/3)/[\Gamma^{3/2} + \sqrt{\Gamma^3 - \sqrt{6}\Gamma^{3/2} + 4/(3\phi_g^{\text{HS}})}]^2, \quad (7)$$

where $\Gamma = Zq l_B/a$. As the value of Γ increases, ϕ_g becomes small, while it reduces to ϕ_g^{HS} in the limit of the hard sphere $\Gamma \rightarrow 0$ (see Fig. 1). As discussed in Ref. [9], the relative magnitude of the density fluctuations $\delta n(\mathbf{x}, t)$ to the causal motion, $|\delta n/n|$, is small. By expanding Eq. (5) in powers of $|\delta n/n|$ and retaining the lowest-order terms, therefore, one can also find the linear stochastic diffusion equation for $\delta n(\mathbf{x}, t)$,

$$(\partial/\partial t)\delta n(\mathbf{x}, t) = \nabla^2[D_s(\Phi(\mathbf{x}, t))\delta n(\mathbf{x}, t)] + \xi(\mathbf{x}, t), \quad (8)$$

where the random force $\xi(\mathbf{x}, t)$ obeys a Gaussian, Markov process with zero mean [9]. Here we note that the last term of Eq. (3) screens the long-range interactions between macroions with the length of order $\lambda_D(q/Z)^{1/2}$, while the last term of Eq. (4) screens the long-range interactions between a macroion and a counterion with the length of order λ_D . In order to find the coefficient $D_s(\Phi)$, therefore, we have used

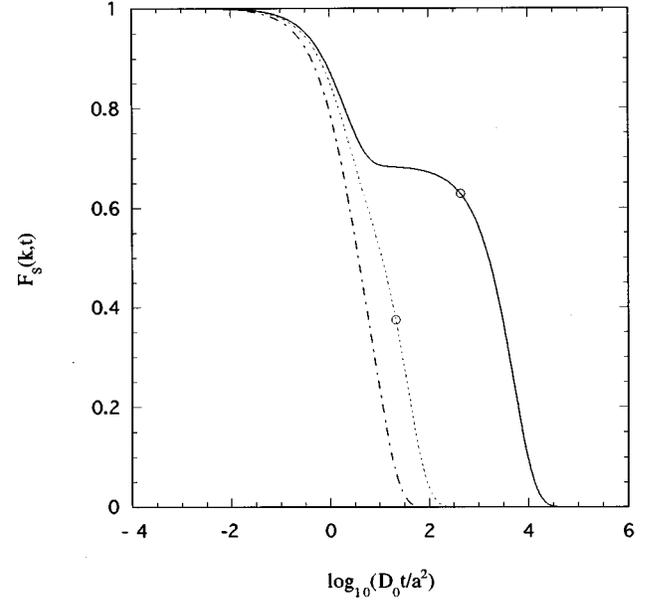


FIG. 3. Self-intermediate scattering function $F_S(k, t)$ as functions of the logarithm of the rescaled time $D_0 t/a^2$ for $\phi = 6.834 \times 10^{-3}$ (dotted-dashed line), 7.609×10^{-3} (ϕ_β) (dotted line), and 7.899×10^{-3} (solid line). The symbol \circ indicates the crossover time t_β .

the fact that the terms screened by the short length of order $\lambda_D(q/Z)^{1/2}$ in $\mathbf{C}(\mathbf{x}, t)$ vanish in the limit $q/Z \rightarrow 0$ at fixed λ_D .

The nonlinear deterministic diffusion equation (5) describes the slow dynamics of spatial heterogeneities near ϕ_g , that is, the time evolution of long-lived, irregularly shaped domains with $\Phi(\mathbf{x}, t) \geq \phi_g$ from completely random, initial configurations with $\Phi(\mathbf{x}, 0)$ to equilibrium uniform state with $\Phi(\mathbf{x}, \infty) = \phi$. On the other hand, the linear stochastic diffusion equation (8) describes the slow relaxation of the density fluctuations around the nonequilibrium state determined by $\Phi(\mathbf{x}, t)$. The most important feature of Eqs. (5) and (8) is that the self-diffusion coefficient $D_s(\Phi)$ becomes zero as $D_s(\Phi) \sim (1 - \Phi/\phi_g)^\gamma$ near ϕ_g , where $\gamma = 1$ here. This dynamic anomaly causes the slow dynamical behavior near ϕ_g . This situation is exactly the same as that of the hard-sphere suspension, discussed in Refs. [9–11], where $\gamma = 2$. In fact, there exists a crossover from the short-time diffusion process with the time scale of order $t_\gamma = 2\pi a^2/D_s^S(\phi)$ to the long-time diffusion process with the time scale of order $t_\alpha \sim 2\pi a^2/D_s^L(\phi)$ around the crossover time $t_\beta \sim 2\pi a^2/(D_s^S D_s^L)^{1/2}$ [9], where $D_s^L(\phi) = D_s(\phi)$ is the long-time self-diffusion coefficient, and $t_\gamma \ll t_\beta \ll t_\alpha$. In Fig. 2 we plot the separation parameter $\sigma = \phi/\phi_g - 1$ dependence of $D_s^L(\phi)$ and $D_s^S(\phi)$ at $\Gamma = 3.684$ ($\phi_g = 0.0079$), where $D_s^L \sim |\sigma|$ near ϕ_g . For comparison, the theoretical results obtained in Ref. [5] are also shown in Fig. 2, where $D_s^L \sim |\sigma|^2$ near ϕ_g .

The dynamics of density fluctuations can be measured by dynamic light scattering through the self-intermediate-scattering function $F_S(k, t)$, which is given by the Fourier transform of the autocorrelation function of the density fluctuations when a scattering vector is much larger than the maximum position of the static structure factor [9]. In Fig. 3,

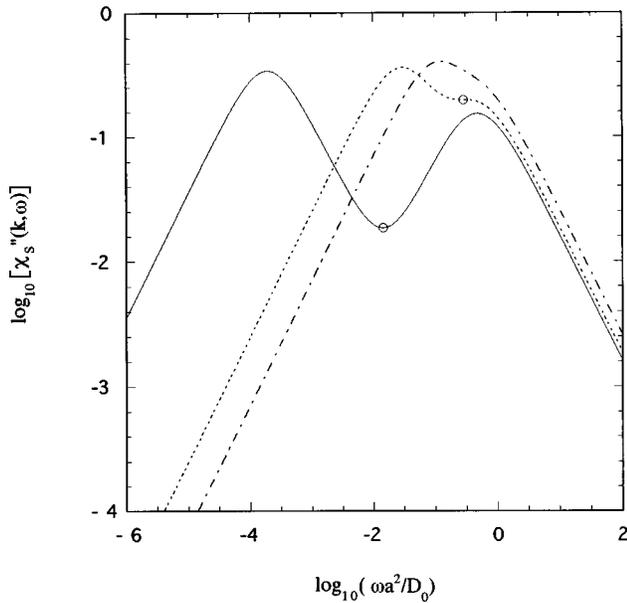


FIG. 4. Log-log plot of the self-part of dynamic susceptibility $\chi_S''(k, \omega)$ as a function of the logarithm of the rescaled frequency $\omega a^2/D_0$. Details are the same as in Fig. 3. The symbol \circ indicates the crossover frequency ω_β .

we show $F_S(k, t)$ at $z_0=0.8$, $ka=1.3$, and $\Gamma=3.684$ for various volume fractions: $\phi=6.834 \times 10^{-3}$, 7.609×10^{-3} (ϕ_β), and 7.899×10^{-3} , where $\phi_\beta(z_0, ka, \Gamma)$, defined below, indicates the crossover volume fraction above which the system becomes a supercooled colloidal fluid. Here the parameter z_0 measures how close the initial state of the system is to the equilibrium state (see Ref. [10] for details). For a small volume fraction less than ϕ_β , $F_S(k, t)$

decays quickly to zero, while above ϕ_β , the shape of $F_S(k, t)$ becomes very sensitive to the value of ϕ , forming a shoulder that becomes a plateau with the height $f^c(z_0, ka, \Gamma)$ at ϕ_g . The plateau height f^c decreases as z_0 decreases or as ka increases, while it is a weak function of Γ .

In Fig. 4 we plot the self-part of the dynamic susceptibility given by $\chi_S''(k, \omega) = \omega \int_0^\infty \cos(\omega t) F_S(k, t) dt$ at the same conditions as those in Fig. 3. Above ϕ_β there are two peaks and one minimum, while below ϕ_β there is one peak at the frequency $\omega_\gamma = 2\pi/t_\gamma$. The first peak is the so-called α peak at $\omega_\alpha = 2\pi/t_\alpha$, and the second peak is the so-called β peak at ω_γ . The minimum at $\omega_\beta = 2\pi/t_\beta$ corresponds to the crossover point in $F_S(k, t)$ at t_β . Thus, the crossover volume fraction ϕ_β is defined by the value of ϕ at which the minimum of χ_S'' appears. With increasing volume fraction at fixed z_0 , ka , and Γ , therefore, we observe a progression from colloidal fluid ($0 \leq \phi < \phi_\beta$) to supercooled colloidal fluid ($\phi_\beta \leq \phi < \phi_g$) to glass ($\phi_g \leq \phi$).

In conclusion, we have derived the coupled diffusion equations (5) and (8) to study the slow dynamics of a dilute, monodisperse suspension of highly charged colloids. The correlations among macroions and counterions, separated by a distance of order λ_D due to the long-range Coulomb interactions, have been shown to cause the dynamic anomaly of the diffusion coefficient. Thus, we have found that the phase behavior and structure of a highly charged colloidal suspension are similar to those of hard-sphere suspensions, discussed in Refs. [9–11], where the correlations between particles separated by a distance of order l_H , due to the long-range hydrodynamic interactions, lead to the dynamic anomaly. The detailed analysis of Eqs. (5) and (8) will be discussed elsewhere.

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