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Slow dynamics of equilibrium density fluctuations in suspensions of colloidal hard spheres near the glass transition

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A mean-field theory for the dynamics of equilibrium suspensions of colloidal hard spheres near the glass transition is presented based on the standpoint recently proposed by the present author. It is shown that although the relative magnitude of the density fluctuations to the mean equilibrium density is small even near the glass transition, they are described by a nonlinear stochastic equation which originates from the long-range hydrodynamic interactions between particles. A nonlinear mean-field equation for the particle mean-square displacement is then derived. This equation is used to analyze the recent experimental data for equilibrium colloidal suspensions. Analyses show that no divergence of the α- and β-relaxation times is found in the experimental data, although the dynamic properties of the colloidal liquid exhibit a drastic slowing down in the so-called supercooled region.

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A number of experiments on colloidal suspensions have shown a transition from a liquid phase to a glass phase, similar to that in glass-forming liquids [1–3]. With the recent development of the mode-coupling theory (MCT) [4–6] for the dynamics of supercooled liquids, much of the recent experimental studies on colloidal suspensions have been designed around the predictions of the MCT. The most striking feature of the MCT is the prediction of two distinct slow relaxation processes, α and β, with the relaxation times t_α and t_β, which diverge as $t_\alpha \sim |\phi/\phi_c - 1|^{-\eta}$ and $t_\beta \sim |\phi/\phi_c - 1|^{-\delta}$, where ϕ is a particle volume fraction and ϕ_c a critical volume fraction. For hard-sphere suspensions, one finds $\phi_c \approx 0.516$, $\eta \approx 2.46$, and $\delta \approx 1.60$ [6]. The transition point ϕ_c does not coincide with the experimental results ranging from 0.571 to 0.580 [2,3]. This discrepancy may result from the fact that the MCT deals with only the direct interactions between particles. In fact, there are two kinds of interactions between particles in the suspension of hard spheres. One is the hydrodynamic interactions between particles through the Oseen tensor. Another is the direct interactions between particles. In the nonequilibrium suspension, it has been shown that the long-range hydrodynamic interactions play an essential role in the slow dynamics near ϕ_g, while the short-range hydrodynamic interactions reduce the effect of the direct interactions drastically [7]. The long-range hydrodynamic interactions lead to a nonlinear deterministic diffusion equation with the dynamic anomaly of the self-diffusion coefficient, where the diffusion coefficient becomes zero at $\phi_g = (4/3)^3/(7\ln 3 - 8\ln 2 + 2) \approx 0.57184\ldots$. This anomaly can enhance even small initial disturbances in space and cause the long-lived, spatial heterogeneities for intermediate times near ϕ_g [8]. As long as the system is away from a critical point, the density fluctuations are small compared to the mean density, even near the glass transition point and obey a linear stochastic diffusion equation. However, the density fluctuations are still important since they are observable through the scattering function by scattering experiments. In fact, those heterogeneities do influence the dynamics of the density fluctuations and lead to the long-known, dynamical properties, such as the von Schweidler law and the Kohlrausch-Williams-Watts formula (or stretched exponential) [8]. The nonequilibrium effects are observable as the waiting time effects in experiments and simulations. On the other hand, in the equilibrium suspensions where most of experiments have been done, the above spatial heterogeneities would be difficult to observe experimentally because their size and magnitude are very small compared to those in the nonequilibrium case. In this Rapid Communication, however, we show that only near ϕ_g the density fluctuations can be described by a nonlinear stochastic diffusion equation with the self-diffusion coefficient, which shows the dynamic anomaly. By employing a mean-field approach, we then derive a nonlinear equation for the particle mean-square displacement from that equation and analyze recent experimental data on equilibrium colloidal suspensions.

We consider a three-dimensional colloidal suspension with the particle volume fraction $\phi = 4\pi a_0^3 n_{\mathrm{eq}}/3$, which consists of N identical spherical particles with radius a_0 and an incompressive liquid in a volume V, where $n_{\mathrm{eq}} = N/V$ is the equilibrium particle number density. In this paper we focus only on a suspension-hydrodynamic stage [7], where the space-time cutoffs (r_c, t_c), which are the minimum wavelength and time of the dynamic process of interest, are set as $r_c \gg l$ and $t_D \gg t_c \gg t_B$. Here l denotes the screening length given by $l = (6\pi a_0 n_{\mathrm{eq}})^{-1/2}$, in which the hydrodynamic interactions between particles become important, t_B the Brownian relaxation time of the particle, and $t_D = a_0^2/D_0$ the structural-relaxation time which is a time required for a particle to diffuse over a distance a_0, where D_0 is a diffusion constant of a single particle. In this stage the relevant variable is the volume fraction fluctuations given by $\delta\phi(\mathbf{r},t) = (4\pi a_0^3/3)\,\delta n(\mathbf{r},t)$, where $\delta n(\mathbf{r},t)$ is the equilibrium density fluctuations around n_{eq}. Hence, we start with the following nonlinear stochastic diffusion equation already described elsewhere [9,10]:

$$\frac{\partial}{\partial t}\delta\phi(\mathbf{r},t) = \boldsymbol{\nabla}\cdot[D_S(\delta\phi)\nabla\delta\phi] + \xi(\mathbf{r},t), \tag{1}$$

with the space-time-dependent self-diffusion coefficient

$$D_S(\delta\phi)=D_S^S(\phi)\,\frac{(1-9\phi/32)(\sigma+\delta\phi/\phi_g)^\gamma}{\phi D_S^S/(\phi_S D_0)+(\sigma+\delta\phi/\phi_g)^\gamma},\qquad(2)$$

where $\gamma=2$ here, and $\sigma=\phi/\phi_g-1$ is the separation parameter and $D_S^S(\phi)$ the short-time self-diffusion coefficient (see Ref. [7] for details). Here $\xi(\mathbf{r},t)$ is the Gaussian, Markov random force and satisfies

$$\langle\xi(\mathbf{r},t)\rangle=\langle\xi(\mathbf{r},t)\,\delta\phi(r',0)\rangle=0,$$

$$\langle\xi(\mathbf{r},t)\xi(\mathbf{r}',t')\rangle$$
$$=-2\,\delta(t-t')(4\pi a_0^3\phi/3)\boldsymbol{\nabla}\cdot[D_S(\delta\phi(\mathbf{r},t))\nabla\,\delta(\mathbf{r}-\mathbf{r}')],\qquad(3)$$

where the brackets denote the average over an equilibrium ensemble.

Equation (1) is a starting equation to study the slow dynamics of the equilibrium density fluctuations near the glass transition. The most important feature of Eq. (1) is that the diffusion coefficient $D_S(\delta\phi)$ becomes dynamically anomalous at $\delta\phi(\mathbf{r},t)=-\sigma\phi_g$ as $D_S(\delta\phi)\propto D_0[\sigma+\delta\phi(\mathbf{r},t)/\phi_g]^2$. We note here that this anomaly originates from the long-range hydrodynamic interactions. Hence, there are two kinds of relaxation regions, slow relaxation regions [glassy regions with $\delta\phi(\mathbf{r},t)\geqslant-\sigma\phi_g$] and fast relaxation regions [liquid regions with $\delta\phi(\mathbf{r},t)<-\sigma\phi_g$]. Similar to the nonequilibrium case [8], the glassy regions are expected to freeze for intermediate times, forming a long-lived, spatially heterogeneous structure. In fact, Eq. (1) can still be nonlinear in $\delta\phi$ as long as the magnitude $|\delta\phi/\phi_g|$ is the same order as $|\sigma|$, although the relative magnitude of the density fluctuations $\delta\phi$ to the mean value ϕ is small. Here we should mention that in the derivation of Eq. (1) the direct correlations were neglected for simplicity, and hence, the present theory is restricted only to the description of the self-diffusion process.

By solving Eq. (1) numerically, one can calculate the self-intermediate scattering function $F_S(k,t)=\langle\delta n_k(t)\delta n_{-k}(0)\rangle$, where $\delta n_k(t)$ is the Fourier transform of $\delta n(\mathbf{r},t)$, and $F_S(k,0)=1$. In the following, however, we simply employ a mean-field approach with the two steps to derive an asymptotic equation for $F_S(k,t)$ [10]. The first step is to split up the variable $\delta\phi_q(t)$ into two parts, a linear part in $\delta\phi_q(0)$ and others; $\delta\phi_q(t)=F(q,t)\delta\phi_q(0)+I_q(t)$, where $F(q,t)$ is the intermediate scattering function given by $F(q,t)=\langle\delta n_q(t)\delta n_{-q}(0)\rangle/S(q)$, with the static structure factor $S(q)=\langle|\delta n_q(0)|^2\rangle$, and $I_q(t)$ describes nonlinear terms in $\delta\phi_q(0)$ and fluctuations. The second step consists of a Gaussian factorization for the many-point correlations of $\delta n_q(0)$, resulting in products of $S(q)$. From Eq. (1), one can thus obtain, to lowest order in $|\delta\phi_q(0)/\phi|$,

$$\frac{\partial}{\partial t}F_S(k,t)=-k^2[D_S^L(\phi)+\{D_S^S(\phi)-D_S^L(\phi)\}\Gamma_S(t)]F_S(k,t),\qquad(4)$$

with the memory term

$$\Gamma_S(t)=\int_0^{a_0/r_c}dqq^2S(q)F(q/a_0,t)^2\Bigg/\int_0^{a_0/r_c}dqq^2S(q),\qquad(5)$$

where the long-time self-diffusion coefficient $D_S^L(\phi)$ is given by [7]

$$D_S^L(\phi)=D_S^S(\phi)\,\frac{(1-9\phi/32)\sigma^\gamma}{\phi D_S^S/(\phi_g D_0)+\sigma^\gamma}.\qquad(6)$$

Here the spatial cutoff r_c was chosen so as to satisfy $\Gamma_S(0)=1$, since the self-diffusion coefficient should be identical with D_S^S for short times.

The memory term $\Gamma_S(t)$ contains $S(q)$ and $F(q,t)$, both of which are unknown. In order to calculate it, therefore, we next employ the following empirical relation for $F(q,t)$ recently proposed by Segrè and Pusey [11,12]:

$$F(q,t)=\exp[-q^2D^c(q)M_2(t)/(6D_S^S)],\qquad(7)$$

where $D^c(q,\phi)$ denotes the q-dependent, short-time collective-diffusion coefficient and $M_2(t)$ represents the particle mean-square displacement given by $M_2(t)=-(6/k^2)\ln F_S(k,t)$. Since the functions $D^c(q)$ and $S(q)$ are still unknown, inserting Eq. (7) into Eq. (5), expanding the nominator of Eq. (5) in powers of $M_2(t)$, and formally performing the integration over q in Eq. (5), one can then rewrite Eq. (5) approximately as $\Gamma_S(t)\approx1-\lambda(\phi)M_2(t)+O(M_2^2)\approx\exp[-\lambda(\phi)M_2(t)]$, where the parameter $\lambda(\phi)$ describes a static collective property of the equilibrium system and is treated as a smooth control parameter. Use of Eq. (4) then leads to

$$\frac{d}{dt}M_2(t)=6D_S^L(\phi)+6[D_S^S(\phi)-D_S^L(\phi)]$$
$$\times\exp[-\lambda(\phi)M_2(t)].\qquad(8)$$

By solving Eq. (8) formally, we thus obtain

$$F_S(k,t)=\exp[-k^2M_2(t)6]$$
$$=[1+(D_S^S/D_S^L)\{\exp(6\lambda D_S^Lt)-1\}]^{-k^2/(6\lambda)}.\qquad(9)$$

Similar to the nonequilibrium case [8], there exist four characteristic time stages near ϕ_g. The first is the early stage $[E]$ for $t\leqslant t_0=1/(6\lambda D_s^s)$. The scattering function $F_S(k,t)$ obeys a short-time exponential decay given by $F_S(k,t)=\exp[-k^2D_s^st]$. After this stage, long-lived, glassy domains are formed. This is the β-relaxation stage $[\beta]$ for $t_0\leqslant t\leqslant t_\alpha$, where t_α is the α-relaxation time. For volume fractions larger than the crossover volume fraction ϕ_β [9], $F_S(k,t)$ obeys two kinds of power-law decays. In the early β-relaxation stage $[\beta_E]$ for $t_0\leqslant t\leqslant t_\beta=1/(6\lambda D_S^L)$, $F_S(k,t)$ obeys a critical decay

$$F_s(k,t)\approx(t/t_0+1)^{-a(k,\phi)},\qquad(10)$$

where $a=k^2/(6\lambda)$. Here t_β represents the crossover time from the short-time self-diffusion process to the long-time self-diffusion process. This power-law decay continues up to

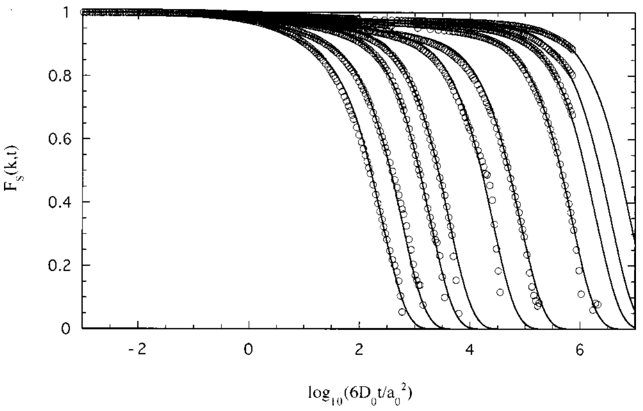

FIG. 1. Self-intermediate scattering function $F_s(k,t)$ vs time at $ka_0=1.3$ for different volume fractions (left to right) $\phi^{\mathrm{exp}}=0.466$, 0.502, 0.529, 0.538, 0.553, 0.558, 0.566, 0.573, 0.578, and 0.583. The open circles indicate the experimental data from Ref. [3] and the solid line from Eq. (9).

the time scale of order t_β. In the late β-relaxation stage $[\beta_L]$ for $t_\beta \leqslant t \leqslant t_\alpha$, $F_S(k,t)$ obeys a power law of the von Schweidler type

$$F_S(k,t)\approx(t/t_0+1)^{-a(k,\phi)}-A(k,\phi)(t/t_\beta)^{b(k,\phi)}, \quad (11)$$

where the exponent $b(k,\phi)$ is to be determined, and $A(k,\phi)$ is a positive constant. This power-law decay continues up to the time scale of order t_α. After this stage, the spatial rearrangement of the glassy domains starts to occur and continues up to the time scale of order $t_L=a^2/D_S^L$. This is the so-called α-relaxation stage $[\alpha]$ for $t_\alpha \leqslant t \leqslant t_L$. $F_S(k,t)$ obeys a stretched exponential decay

$$F_S(k,t)\approx(t/t_0+1)^{-a}\exp[-(t/t_\alpha)^\beta], \quad (12)$$

where $t_\alpha \propto |\sigma|^{-\eta}$, and the exponents β and η satisfy the relation $\beta=\gamma/\eta(<1)$ [8]. After this stage, the glassy domains disappear and the long-time self-diffusion process dominates the system. This is the late stage $[L]$ for $t \geqslant t_L$. $F_S(k,t)$ obeys a long-time exponential decay given by $F_S(k,t)=\exp[-k^2D_S^Lt]$.

Equation (9) is used to analyze the recent experimental data obtained by van Megen *et al.* [3]. The parameter $\lambda(\phi)$ is thus determined from the fitting. The experimental suspension comprises mixtures of polymer particles (98% of total particle volume) and silica particle (2%) suspended in *cis*-decalin, while the present theory deals with identical hard spheres. Hence, the experimental volume fraction ϕ^{exp} must be different from the theoretical volume fraction ϕ for the ideal hard-sphere suspension. For a given value of ϕ^{exp}, therefore, we use the experimental data for D_S^L in Eq. (9), while treating λ as a free parameter and choosing ϕ so that the theoretical, long-time self-diffusion diffusion coefficient $D_S^L(\phi)$ given by Eq. (6) coincides with the experimental one. Figure 1 shows the fitting results for $F_S(k,t)$ for different volume fractions. From the fitting, one can thus find the following interesting relations between ϕ, λ, and ϕ^{exp}:

$$\phi^{\mathrm{exp}}=9.29\times10^{-6}\phi/[\phi_g(\phi_g-\phi)]+0.536\phi+0.781\phi^2, \quad (13a)$$

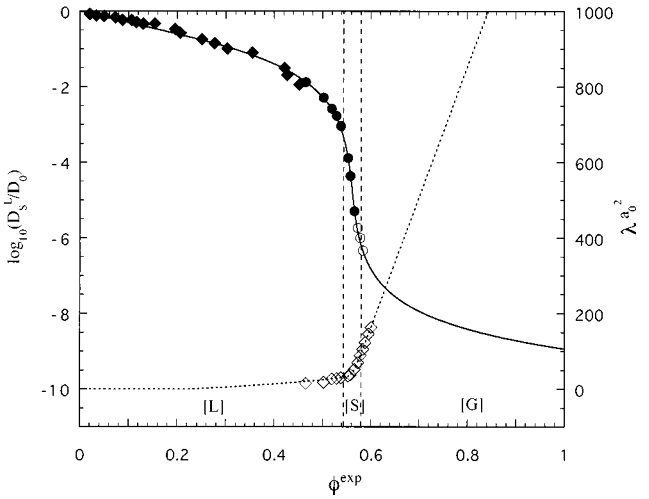

FIG. 2. λ and $\log_{10}(D_S^L)$ vs ϕ^{exp}. The solid line indicates Eq. (6) and the dotted line Eq. (13b). The closed circles show the experimental data from Ref. [3], the closed diamonds from Ref. [12], the open circles the theoretical prediction by the fitting, and the open diamonds the fitting results. The vertical dashed lines are $\phi^{\mathrm{exp}}=0.544$ and 0.580.

$$\lambda=0.032\phi/[\phi_g(\phi_g-\phi)]-57.5\phi+194.6\phi^2. \quad (13b)$$

The volume fraction ϕ^{exp} dependence of λ and D_S^L are shown in Fig. 2 together with the experimental data. As mentioned by van Megen *et al.* [3], the experimental data at $\phi^{\mathrm{exp}}=0.566$ is the most concentrated for which $F_S(k,t)$ decays to zero in the experimental time. For volume fractions higher than 0.566, however, the data fail to decay completely in the

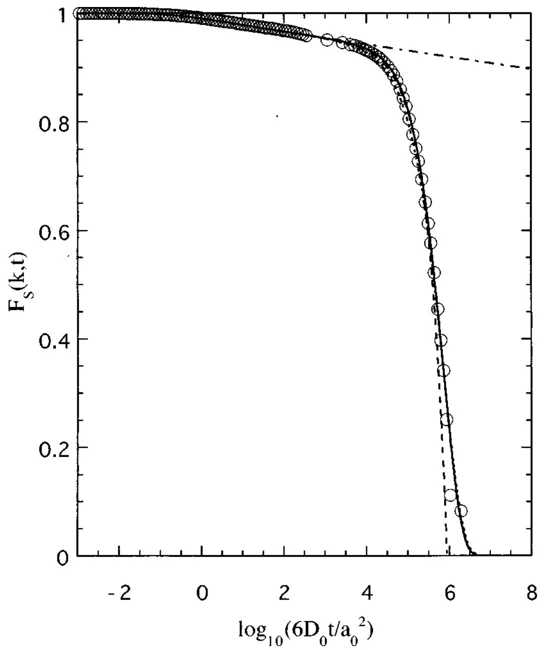

FIG. 3. Power laws at $\phi^{\mathrm{exp}}=0.566$ and $ka_0=1.3$, where $\lambda a_0^2=52$. The solid line indicates Eq. (9), the dotted-dashed line the critical decay given by Eq. (10) with $a=0.0054$, the dashed line the von Schweidler decay given by Eq. (11) with $b=0.972$, and the dotted line the stretched exponential decay given by Eq. (12) with $\beta\approx0.95$. The open circles indicate the experimental data from Ref. [3].

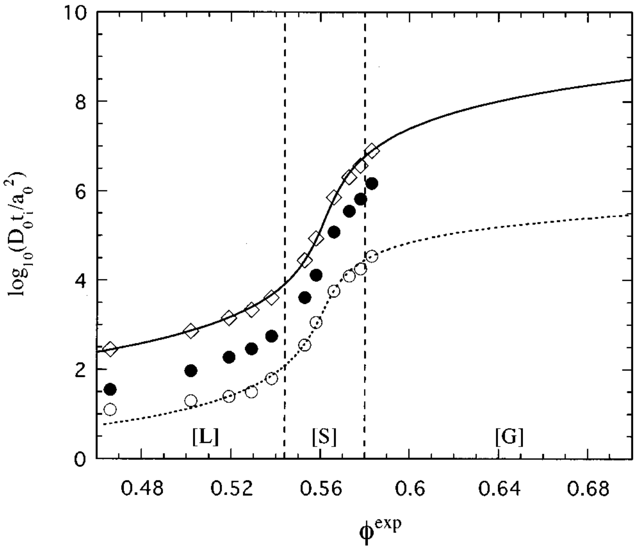

FIG. 4. Characteristic times t_i vs ϕ^{exp} at $ka_0 = 1.3$. The symbols indicate the fitting results for t_β (○), t_α (●), and t_L (◇). The solid line indicates $t_L = 2\pi/(k^2 D_S^L)$ and the dotted line $t_\beta = 1/(6\lambda D_S^L)$. The vertical dashed lines are $\phi_\beta^{\text{exp}} = 0.544$ and $\phi_g^{\text{exp}} = 0.580$.

experimental time window although they show some downward curvature at longer times. Although the long-time self-diffusion coefficient cannot be obtained experimentally for such higher volume fractions, one can predict it theoretically by using Eqs. (13). The predicted values are also shown in Fig. 2. In order to check the validity of the transformation (13a), we also show the experimental data of D_S^L for smaller volume fractions in Fig. 2. A good agreement is indeed seen between the theoretical results and the experimental data.

It is interesting to note from Fig. 2 that both functions λ and D_S^L show a crossover around $\phi^{\text{exp}} = 0.562$ from a small volume fraction behavior to a large volume fraction behavior. In fact, their derivatives, $d\lambda/d\phi^{\text{exp}}$ and $d\log(D_S^L)/d\phi^{\text{exp}}$, change drastically between $\phi^{\text{exp}} = 0.544(\phi_\beta^{\text{exp}})$ and $\phi^{\text{exp}} = 0.580(\phi_g^{\text{exp}})$. With increasing volume fraction ϕ^{exp}, we thus observe a progression from normal colloidal liquid region $[L]$ for $0 < \phi^{\text{exp}} < \phi_\beta^{\text{exp}}$, to supercooled colloidal liquid region $[S]$ for $\phi_\beta^{\text{exp}} \leqslant \phi^{\text{exp}} < \phi_g^{\text{exp}}$, and to glass region $[G]$ for $\phi^{\text{exp}} \geqslant \phi_g^{\text{exp}}$. In Fig. 3 the power laws given by Eqs. (10)–(12) are plotted at $\phi^{\text{exp}} = 0.566$ and $ka_0 = 1.3$ together with the experimental data. From the fitting, we find $\beta \approx 0.95$ and $b = 0.972$. Here we note that the stretched exponent β and the von Schweidler exponent b are close to 1 because the spatial heterogeneities are weak compared to those in the nonequilibrium case. In Fig. 4 the volume fraction ϕ^{exp} dependence of the time scales t_β, t_α, and t_L are also shown. In region $[S]$, therefore, those time scales are shown to obey the power laws

$$t_\beta \sim (D_S^L)^{-\delta/2}, \quad t_\alpha \sim (D_S^L)^{-\eta/2}, \quad t_L \sim (D_S^L)^{-\gamma/2}, \tag{14}$$

where $\delta \approx 1.6$, $\eta \approx 2.1$, and $\gamma = 2(\beta = \gamma/\eta \approx 0.95)$. Thus, we point out that since λ and D_S^L are smooth functions of ϕ^{exp}, the divergence of t_β, t_α, and t_L does not occur at any values of ϕ^{exp}, while in a ϕ space $t_\beta \sim |\sigma|^{-\delta}$, $t_\alpha \sim |\sigma|^{-\eta}$, and $t_L \sim |\sigma|^{-2}$ since $D_S^L(\phi) \sim |\sigma|^2$.

In conclusion, we have shown that as long as the relative magnitude of the density fluctuations $\delta\phi(\mathbf{r},t)$ to the mean value ϕ is the same order as $|\sigma|$, the density fluctuations obey the nonlinear stochastic equation, which results from the long-range hydrodynamic interactions between particles. We have then derived the mean-field nonlinear equation (8) for the particle mean-square displacement. We have thus shown that although the size and the magnitude of the spatial heterogeneities are small, they are still the origin of the α and β relaxations. Equation (8) was used to analyze the recent experimental data. From analyses, we have concluded that the long-time self-diffusion coefficient is a smooth function of ϕ^{exp} and no divergence of the α- and β-relaxation times takes place. Hence, we predict that this would be the case even in fragile (and not so fragile) glass formers, where several laws are proposed to fit the experimental data. In order to check the validity of the present theory, the experimental measurements in a longer time window for higher volume fractions is encouraged.

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