

Slow Dynamics of Magnetic Colloidal Chains Confined in Thin Films under a Magnetic Field¹

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Summary

The Brownian dynamics simulations are performed for the monodisperse magnetic colloidal chains, the binary colloidal chains, and the polydisperse colloidal chains confined in the thin films. As the magnetic field is increased, it is shown that the long-time self-diffusion coefficient decreases for any chain lengths on those suspensions of chains. It is also shown that the decrease of the long-time self-diffusion coefficient in those suspensions with increasing the external magnetic field and the chains lengths resembles closely each other in a liquid state and a supercooled liquid state.

1. Introduction

The external magnetic field is applied to the suspensions of the magnetic colloidal particles. Above a certain critical value of it, it is known that the colloidal chains of the particles are formed parallel to the field. Those dense suspensions of the magnetic colloidal suspensions are put into practice [1, 2]. The research for the dilute suspensions of the magnetic colloidal chains confined in the thin films which is several times as thick as the diameter of the colloidal particles has recently become an interesting subject of discussion among researchers. If the enough strong magnetic field is applied perpendicular to the film, the colloidal chains are also formed perpendicular to it and those chains diffuse in a plane parallel to the film. The slowing down of the chain motions has been observed on those suspensions, as the magnetic field is increased. The crossover phenomena from a liquid state to a supercooled liquid state have been observed in the dilute suspension of the polydisperse magnetic colloidal chains [3, 4]. The thin limit of the film thickness is the monolayer. The slowing down of the particle motions in a plane parallel to the film has been also observed on the monolayer suspensions [5, 6, 7]. In the dilute

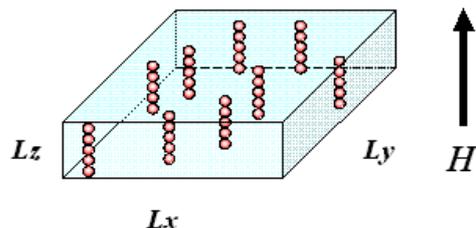


Fig.1 Schematic illustration of the dilute suspensions of colloidal chains confined in the thin film.

suspension of the monolayer binary colloidal particles, there also exist the crossover phenomena from a liquid state to a supercooled liquid state [5]. On the other hand, the phase transition from a liquid phase to a crystal phase has been observed in the dilute suspensions of the monolayer colloidal particles [6, 7]. The purpose of this paper is to study the slow dynamics of those systems by performing the Brownian dynamics simulations.

2. Model

We consider the model system confined in the thin film with thickness L_z which contains N_{xy} magnetic colloidal chains dispersed in an equilibrium solvent with a viscosity η at temperature T (see Fig. 1). The external magnetic field $\mathbf{H}(= H\mathbf{e}_z)$ is applied perpendicular to the film where \mathbf{e}_z is the unit vector of z direction. The colloidal chains are in a direction par-

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allel to the external field. We set the lengths of all colloidal chains to be nearly equal to the thickness of the film. The fluctuations within the chains can be neglected, because we assume that the applied external field is enough strong to stabilize the colloidal chains. The center mass of the chains lies on the center plane of the film. Here the α th colloidal chain consists of N_z^α magnetic colloidal particles and the colloidal particle i in the α th colloidal chain has the susceptibility χ_i^α , the mass $M_i^\alpha (= 4\pi a_i^3 \rho/3)$, and the radius a_i^α , where ρ is the mass density of the colloidal particle. We set the value of ρ as the same as the mass density of the solvent. N_z denotes the average number of the colloidal particles which form one colloidal chain. The area fraction of the colloidal chains σ is given by $\sigma = \pi \sum_{\alpha=1}^{N_{xy}} a_1^{\alpha 2}/S$ where the total area of the film is S . The time evolution of the position of the α th chain projected on the film (xy plane) \mathbf{X}_α is described by the stochastic diffusion equation on the time scale $t_c (= a^2/D_c)$

$$\begin{aligned} & \frac{d}{dt} \mathbf{X}_\alpha(t) \\ &= \frac{1}{\sum_{i=1}^{N_z^\alpha} M_i^\alpha} \sum_{\beta \neq \alpha} \sum_{i=1}^{N_z^\alpha} \sum_{j=1}^{N_z^\beta} \frac{\mathbf{F}(\mathbf{r}_{ij}^{\alpha\beta}) M_i^\alpha}{\gamma_i^\alpha} + \mathbf{V}_\alpha(t), \quad (1) \end{aligned}$$

where t_c is the relaxation time for the colloidal chain to diffuse a distance of the average radius a and D_c an average diffusion coefficient of a single chain. A dipole force between particle i in the α th chain and particle j in the β th chain $\mathbf{F}(\mathbf{r}_{ij}^{\alpha\beta}) (= -\nabla U)$ is given by the dipole potential U defined by

$$\begin{aligned} & U(\mathbf{r}_{ij}^{\alpha\beta}) \\ &= \frac{1}{4\pi\mu_0} \left(-\frac{\mathbf{m}_i^\alpha \cdot \mathbf{m}_j^\beta}{r_{ij}^{\alpha\beta 3}} + 3 \frac{(\mathbf{m}_i^\alpha \cdot \mathbf{r}_{ij}^{\alpha\beta})(\mathbf{m}_j^\beta \cdot \mathbf{r}_{ij}^{\alpha\beta})}{r_{ij}^{\alpha\beta 5}} \right) \quad (2) \end{aligned}$$

where \mathbf{m}_i^α denotes the magnetic dipole moment of 1 particle i in the α th chain, $\mathbf{r}_{ij}^{\alpha\beta} = \mathbf{r}_i^\alpha - \mathbf{r}_j^\beta$ and $r_{ij}^{\alpha\beta} = |\mathbf{r}_{ij}^{\alpha\beta}|$. We assume that the dipole moment of the particle is only proportional to an external field, that is, $\mathbf{m}_i^\alpha \simeq \frac{4}{3}\pi a_i^{\alpha 3} \mu_0 \chi_i^\alpha \mathbf{H}$, because we only consider the dilute suspensions and the applied external field is enough strong. μ_0 is the absolute permeability of vacuum here. $\mathbf{V}_\alpha(t)$ denotes a Gaussian, Markov

random velocity with zero mean and satisfies

$$\langle \mathbf{V}_\alpha(t) \mathbf{V}_\beta(t') \rangle = 2 \frac{\sum_{i=1}^{N_z^\alpha} M_i^\alpha {}^2 D_i^\alpha \delta_{\alpha,\beta} \delta(t-t') \mathbf{E}}{\left(\sum_{i=1}^{N_z^\alpha} M_i^\alpha \right)^2}, \quad (3)$$

where the brackets denote the ensemble average, D_i^α the diffusion constant of the particle i in the α th chain, and \mathbf{E} d dimensional unit matrix.

3. Simulation Results and Discussions

We discuss three cases, the suspensions of (a) the binary colloidal chains ($N_{xy} = 6400$), (b) the colloidal chains with 15% polydispersity ($N_{xy} = 6400$), and (c) the monodisperse colloidal chains ($N_{xy} = 10000$). In the suspensions of the binary chains, we set the parameters of the particles as those in Table 1 from the experiment [5] except for the mass density. The small (or big) colloidal chain consists of all identical small (or big) particles. The size polydispersity of the colloidal particles in the polydisperse system obeys the Gaussian distribution with standard deviation $s = 0.15$. The particles with the different sizes are homogeneously distributed in all chains on the polydisperse systems. Each chain is identical to other chain in the suspensions of the monodisperse chain.

Figure 1 shows the mean-square displacement of the chains on xy plane given by $M_2(t) (= \langle |\mathbf{X}_\alpha(t) - \mathbf{X}_\alpha(t=0)|^2 \rangle)$. $M_2(t)$ is proposed by Tokuyama based on the mean-field theory [8]

$$M_2(t) = \ell^2 \ln \left[1 + \left(\frac{D_c}{D_S^\ell} \right) \{ e^{4D_S^\ell t/\ell^2} - 1 \} \right], \quad (4)$$

where ℓ indicates the mean-free path and D_S^ℓ the long-time self-diffusion coefficient. $M_2(t)$ is asymptotically described by

$$M_2(t) = \begin{cases} 4D_c t, & t < t_c \\ 4D_S^\ell t, & t \gg t_c \end{cases}. \quad (5)$$

Table 1 The properties of the binary colloidal particles in [5].

	radius [μm]	χ^p * [Am^2/T]	$\frac{\chi^p}{\chi^b}$
(b) Big particle	2.35	6.2×10^{-11}	1
(s) Small particle	1.4	6.6×10^{-12}	0.5035

* χ^p : Susceptibility of each particle p

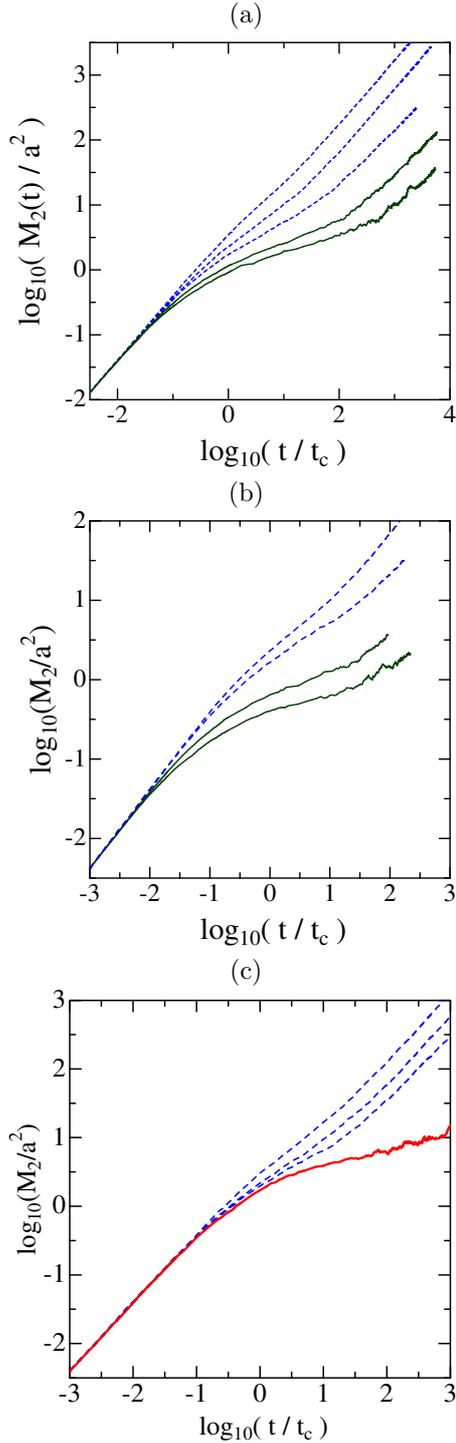


Fig.2 A log-log plot of the mean-square displacement vs. time at $\sigma = 0.03$. (a) monolayer binary colloidal particles with $\omega = 0.1$ at $\Gamma = 10.00, 55.25, 110.5, 221.0,$ and 331.6 , for (b) the polydisperse colloidal chains with $N_z = 5$ at $\Gamma = 5.195, 10.39, 51.96,$ and 103.9 , and for (c) monodisperse colloidal chains with $N_z = 2$ at $\Gamma = 5.195, 15.59, 20.78,$ and 25.98 from top to bottom. The dashed lines indicate the simulation results on the liquid state, the thin solid lines the supercooled liquid state, and the thick solid line the crystal state.

At the short-time region, $M_2(t)$ of the chains for any cases depends on the average chain lengths only, because the many-body interactions among chains have little influence on the diffusive motions of chains yet. Hence, $M_2(t)$ can be described by D_c only. Then, the diffusion of them comes under the influence of those interactions among chains with time. The value of D_S^L is therefore smaller than that of D_c . As Γ is increased, the mean-square displacement at the long-time region decreases. The reason comes from the fact that the number of the pair of the particles in the chains which contribute to the many-body interactions among the chains is increased as the lengths of the chains is increased. Here the dimensionless parameter $\Gamma(= \frac{U(\ell_0)}{k_B T} \propto H^2)$ is the indicator of the intensity of the dipole potential energy in the system [7, 5, 8], where $\ell_0(= a/\sqrt{\sigma})$ is the average distance between the chains on xy plane. The simulation results on the monolayer binary colloidal particles with $\omega = 0.1$ are shown in Fig. 2(a), where ω denotes the number ratio of the small colloidal chains to all chains. Figure 2(b) shows those of the polydisperse chains with $N_z = 5$. We could not distinguish between them qualitatively, although the chain lengths are different and there exist the different distributions for the radius of the particles in those suspensions. On those suspensions, the system approaches to the supercooled liquid state without the crystallization, as the magnetic field is increased. Even though Γ is very high, $M_2(t)$ is proportional to t at the long-time region in both suspensions. On the other hand, the crystallization occurs at high Γ region on the suspensions of the monodisperse colloidal chains. $M_2(t)$ at the long-time region at $\Gamma = 25.98$ approaches to a constant value in Fig.2(c). It is related with the amplitude of the lattice vibration on a crystal phase. Despite the crystal phase, $M_2(t)$ at the long-time region on the monodisperse case is also proportional to t . We can obtain the long-time self-diffusion coefficient on the liquid state and the supercooled state.

The colour scale maps of the relative long-time self-diffusion coefficient to the diffusion constant of the single chain on $N_z - \Gamma$ plane for those suspensions are shown in Fig. 3. The relative long-time self-diffusion coefficient D_S^L/D_c at any N_z decreases, as Γ is increased. The only difference in those systems with different chain lengths is that the relative long-time self-diffusion coefficient of all chains confined in the

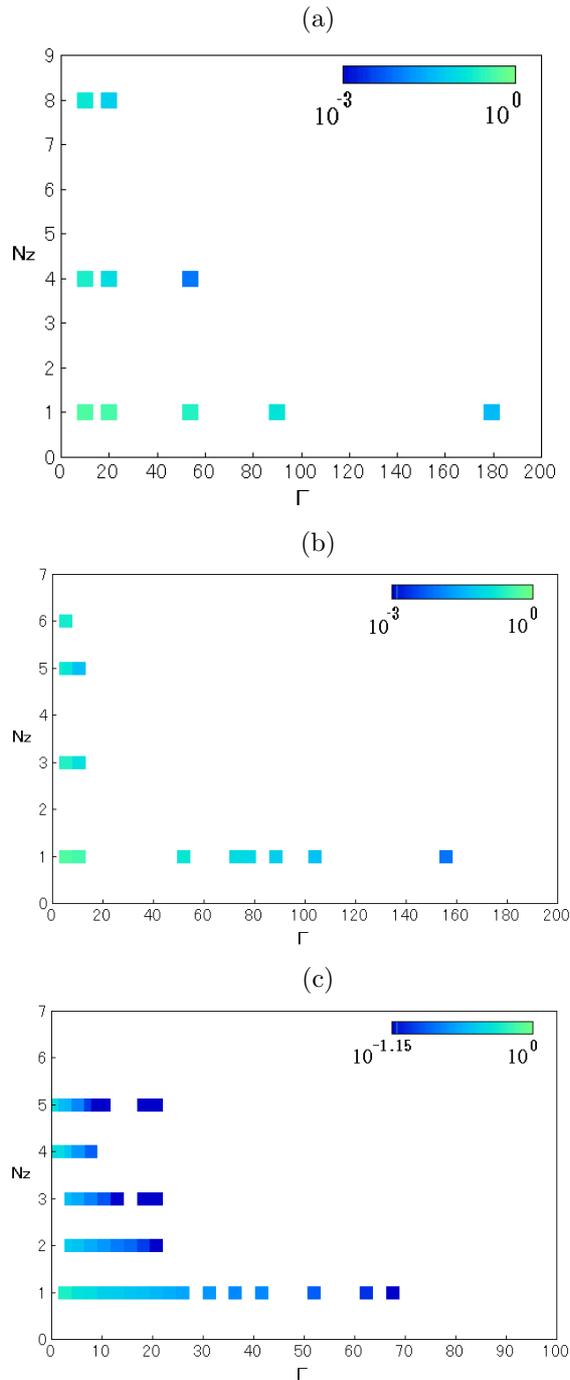


Fig.3 The colour scale map of the relative long-time self-diffusion coefficient to the diffusion constant of the single chain on $N_z - \Gamma$ plane for (a) the binary colloidal chains with $\omega = 0.5$, for (b) the polydisperse colloidal chains, and for (c) the monodisperse colloidal chains. The colour indicates the value of the relative long-time self-diffusion coefficient.

thin film is bigger than that in the thick film at a constant Γ . The reason is that the many-body interactions between the long chains confined in the thick film is much stronger than those in the thin film. For

$D_S^L/D_c < 0.07 \simeq 10^{-1.15}$ on monodisperse colloidal suspensions, the crystallization occurs in Fig. 3(c). On the polydisperse systems and the binary systems, the long-time self-diffusion coefficient is obtained for $D_S^L/D_c < 0.07$. Here the region of the supercooled state is proposed for $D_S^L/D_c < 0.00295 \simeq 10^{-2.53}$ by Tokuyama with analyzing the experiments and the simulations in several systems based on the mean-field theory [9].

4. Conclusion

In this paper, we performed the extensive Brownian dynamics simulations on the suspensions of the binary magnetic colloidal chains, the polydisperse chains, and the monodisperse chains confined in the thin films. It was found that the crystallization is avoided on the suspensions of the polydisperse chains and the binary chains. On both suspensions, the small relative long-time self-diffusion coefficient is obtained below the supercooled point $D_S^L/D_c = 0.00295$ proposed by Tokuyama [9] and there exist the supercooled liquid state. It was also found that the decrease of the relative long-time self-diffusion coefficient in those three suspensions is similar to each other in a liquid state and a supercooled state as Γ and N_z are increased. We will discuss the details of the crossover phenomena from a liquid state to a supercooled liquid state on the suspensions of the binary chains and the polydisperse chains elsewhere.

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