

## Correlation between dynamic heterogeneity and medium-range order in two-dimensional glass-forming liquid

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ガラス転移にともなうスローダイナミクスの物理的機構は、いまだ未解明な問題である。我々は、ガラス化は、結晶化に対するフラストレーションの帰結であるという考え方に立ち、ガラス転移現象のモデル系である二次元多分散コロイド系の計算機実験を進めてきた。本研究では、幾何学的フラストレーションの度合いを粒径の分散性により制御することで、結晶状態からガラス状態までを系統的に研究可能なモデルを構築した。フラストレーションの強さを系統的に制御し、構造、ダイナミクスの両面から、本系で実現されるガラス状態を調べた結果、液体中に過渡的に結晶性の高い領域（結晶的中距離秩序）が形成されることを見出し、この系においては、これがスローダイナミクスの起源となっていることを明確な形で示した。

Despite a long history of research, the origin of glass transition remains elusive. One of the key features of the glass transition is that viscosity, or the structural relaxation time, changes over 10 orders of magnitude upon cooling toward  $T_g$  without accompanying a noticeable change in the static structure. Recently it was reported that dynamic heterogeneity emerges in a supercooled liquid state and it may cause slow dynamics (see, e.g., [1]). Furthermore, Shintani and Tanaka recently demonstrated that the cluster of the medium-range crystalline order (MRCO) appear in a supercooled liquid state of a model 2D liquid [3], which is consistent with a previous experimental report suggesting the growth of MRCO in a molecular liquid [2]. Here we study the relationship between the dynamic heterogeneity and MRCO by means of 2D Brownian dynamics simulation of a polydisperse colloidal dispersion, where particles are interacting with each other via the Weeks-Chandler-Andersen (WCA) repulsive potential [4]. We introduce the Gaussian distribution of particle size. Its standard deviation  $\Delta$  characterizes the degree of polydispersity. In this model, the glass-forming ability can be controlled by changing the degree of polydispersity  $\Delta$ . The higher the polydispersity, the higher the nucleation barrier. In this model polydispersity plays a role as the geometrical frustration on crystallization. We note that polydisperse colloidal dispersions have often been used in experiments as a model-glass forming liquid. Without polydispersity a system simply crystallizes for both experiments and simulations.

Here we focus on the glass-forming  $\Delta(\geq 9\%)$  region. We found medium-range crystalline order (MRCO) grows in size and lifetime with an increase in the colloid volume (area) fraction  $\phi$  or with a decrease in polydispersity (or, frustration)  $\Delta$ . MRCO is characterized by using sixfold bond-orientational order parameter time averaged over the relaxation time  $\tau_\alpha$ ;  $\bar{\Psi}_6^i = \frac{1}{\tau_\alpha} \int_{t'}^{t'+\tau_\alpha} dt \left| \frac{1}{n_i} \sum_{m=1}^{n_i} e^{j6\theta_m^i} \right|$ , where  $n_i$  is the number of nearest neighbors of particle  $i$ ,  $j = \sqrt{-1}$ , and  $\theta_m^i$  is the angle between  $(\vec{r}_m - \vec{r}_i)$  and the  $x$ -axis, where particle  $m$  is a neighbor of particle  $i$ . Note that  $\bar{\Psi}_6^i = 1$  means the perfect hexagonal arrangement of six nearest-neighbor particles around particle  $i$  and  $\bar{\Psi}_6^i = 0$  means a random arrangement. The characteristic size of MRCO,  $\xi$ , is estimated by  $\xi = \sqrt{N_c}$ , where  $N_c$  is the average number of particles belonging to a cluster with  $\bar{\Psi}_6^i \geq 0.75$ . We found that  $\xi$  is increasing with an increase in  $\phi$ . We also estimate the  $\xi_4$  from the four-point density correlation function [5]. It has been well established that  $\xi_4$  characterizes the size of dynamic heterogeneity of translational particle motion. With an increase in  $\phi$ , both  $\xi$  and  $\xi_4$  increase for all  $\Delta$ 's. The  $\phi$ -dependence of  $\xi$  ( $\xi_4$ ) is well fitted by the following power

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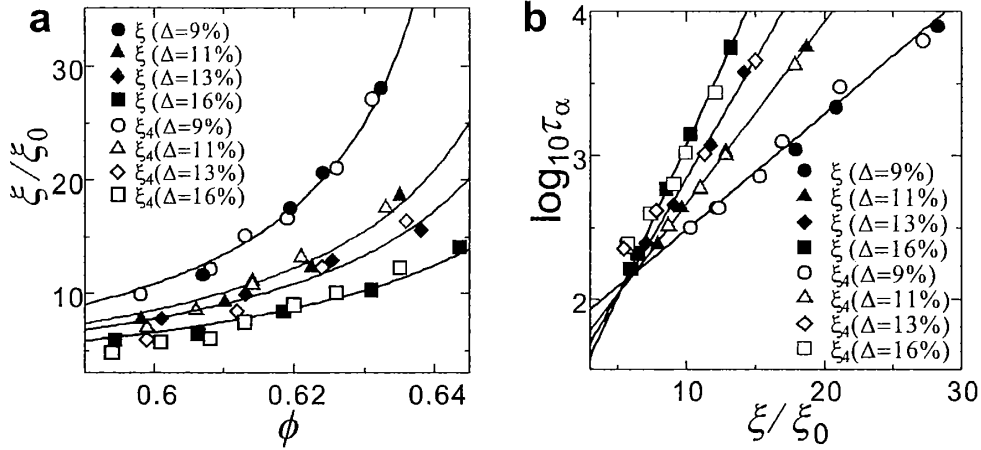


Figure 1: (a)  $\phi$ -dependence of  $\xi$  and  $\xi_4$  for  $\Delta = 9, 11, 13$  and  $16\%$ . The solid lines represent  $\xi_{(4)} = \xi_{(4)0}[(\phi^{-1} - \phi_0^{-1})/(\phi_0^{-1})]^{-1}$ . The cluster size is smaller for higher  $\Delta$  at the same  $\phi$ . (b) Relationship of  $\tau_\alpha$  to  $\xi/\xi_0$  and  $\xi_4/\xi_{40}$ . The solid lines represent  $\tau_\alpha = \tau_0 \exp(D\xi/\xi_0)$ .

law [see Fig.1 (a)]

$$\xi_{(4)} = \xi_{(4)0} \left[ \left( \phi^{-1} - \phi_0^{-1} \right) / \left( \phi_0^{-1} \right) \right]^{-1}, \quad (1)$$

where  $\phi_0$  is the ideal glass transition volume fraction obtained from the Vogel-Fulcher fittings. Furthermore, we found that  $\xi/\xi_0 \cong \xi_4/\xi_{40}$ , indicating that the dynamic heterogeneity of translational motion, which is usually characterized by  $\xi_4$ , is indeed caused by medium-range ordering. We also found its size  $\xi$  and the relaxation time of the system  $\tau_\alpha$  has the following relation:

$$\tau_\alpha = \tau_0 \exp \left[ D \left( \frac{\xi}{\xi_0} \right) \right], \quad (2)$$

where  $D$  is the fragility index obtained from the Vogel-Fulcher fittings [see Fig.1 (b)]. This suggests an intriguing scenario that vitrification may be a process of hidden crystalline ordering under frustration. This not only provides a physical basis for better glass-forming ability, but also may provide an answer to a longstanding question on the structure of amorphous materials: “order in disorder” is an intrinsic feature of a glassy state of material. Thus our scenario makes a natural connection between structure and dynamics in glass-forming materials.

## References

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