Supporting Information

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SI Text

Comparison of Slow Glassy Dynamics of Supercooled Colloidal Suspensions Between Brownian Dynamics (BD) Simulations and Confocal Microscopy Experiments. To show how powerful BD simulations are, we compare results of slow glassy dynamics of supercooled colloidal suspensions between BD simulations with the canonical, constant temperature–constant volume (NVT) ensemble and confocal microscopy experiments. In confocal experiments, we can track the coordinates of individual particles as a function of time in 3D. In both BD simulations and confocal microscopy experiments, thus, we can calculate the structural relaxation time τ_α from the decay of the self part of the intermediate scattering function $F_s(q_p,t)$, where q_p is the wavenumber corresponding to the first peak of the structure factor $S(q)$. Fig. S1 shows a comparison of τ_α obtained in this way between BD simulations and confocal experiments. The results of our BD simulations almost perfectly coincide with those of our confocal microscopy experiments of colloidal suspensions (by Mathieu Leocmach in our group) without any adjustable parameters, indicating the potential of brute-force BD simulations for crystal nucleation phenomena.

Finite Size Effects on the Crystal Nucleation Frequency. Here we study the finite size effects on crystal nucleation. In our NVT simulations, crystal nucleation necessarily leads to the formation of depleted regions around nuclei, reflecting the conservation of the particle density (see Fig. 5). This nonlocal coupling might lead to significant finite size effects. We have checked this result by changing the system size. As shown in Fig. S2, there are almost no finite size effects for a system containing more than 4,000 particles. Although there appears finite size effects for $N = 1,024$, even for this case the effects on the crystal nucleation frequency I_r are rather weak (less than a factor of 10) (see Fig. S2*D*). So the finite size effects cannot explain the large discrepancy in I_r between us and Auer and Frenkel (1). We recently confirmed (2) that there are few finite size effects on MRCO also for $N \geq 4,096$ in an accessible ϕ range. This result is consistent with the above results, on noting that a crystal nucleus always appears inside a region of high MRCO and thus the critical nucleus size should be smaller than the characteristic size of MRCO.

Crystal Nucleation Process in a System of *N*=4,096. Here we show a crystal nucleation process in a system of a smaller size ($N = 4,096$) in Fig. S3, because it may be easier to see the details of crystal nucleation for a smaller system (see also Movie S2).
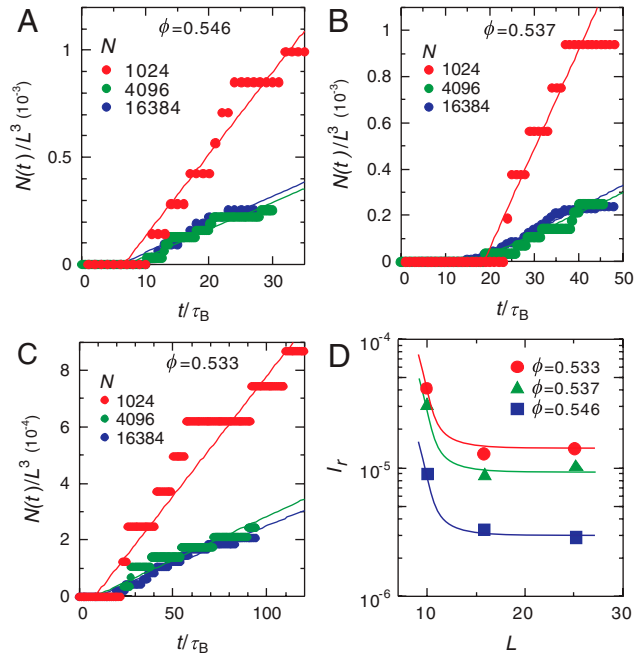
Comparison Between the Coarse-Grained Sixfold Bond Orientational Order Parameter Q_6 and S_{ij}. First we review the discussion by Lechner and Dellago (3) on how the choice of an order parameter affects the detection of crystalline order. First we mention that S_{ij}, which measures the correlation between the structures surrounding particles i and j, distinguishes between solid- and liquid-like particles but does not discriminate between different crystal structures. This insensitivity of S_{ij} to the difference in crystal structures is actually the very reason why this parameter is used by Auer and Frenkel in their study of the kinetics of crystal nucleation (1) (see blow). Lechner and Dellago (3) showed that the crystal structure determination can be improved by using the spatially averaged form of the local bond order parameters Q_6^i (see *Materials and Methods*), which we used in our study. To calculate Q_6^i, one uses the local orientational order vectors $\bar{q}_{6m}^i$ averaged over particle i and its surroundings. Although q_6^i (see

Materials and Methods for the definition) holds the information of the structure of the first shell around particle i, its spatially averaged version Q_6^i also takes into account the second shell. They concluded that using the parameter Q_6^i instead of q_6^i increases the accuracy of the distinction of different crystal structures at the price of a coarsening of the spatial resolution. We find that medium-range crystalline order (MRCO) in a supercooled liquid can be detected by both Q_6^i and S_{ij} (see below) but not so well by q_6^i. This difference arises from the fact that the second particle shell is effectively taken into account in both Q_6^i and S_{ij}, but not in q_6^i (3). Thus, q_6^i is not a good measure to detect the bond orientational order (MRCO) in a supercooled liquid. Note that q_6^i is not so resistive to fluctuations, which are large in a liquid state. Some coarse-graining of the order parameter seems to be essential to detect hidden structural order in a supercooled liquid.

In Fig. S4*A*, we show the distribution of $S_{ij} = q_6(i)^* \cdot q_6(j)$ (here * means the complex conjugate) for an equilibrium and a supercooled liquid and body-centered cubic (bcc), hcp, random hexagonal close packing (rhcp), and face-centered cubic (fcc) crystals. This parameter was used by Auer and Frenkel (1) as the order parameter to characterize crystal nuclei and its kinetic pathway of crystallization. If we set the threshold at $S_{ij} = 1.5$, we can distinguish a supercooled liquid and crystals. However, this criterion cannot allow us to detect MRCO in a supercooled liquid, as can be seen in Fig. S4*B*: There are very few yellow particles there. On the other hand, we can distinguish high MRCO regions by using Q_6 as shown in Fig. S4*C*. A similar pattern can be detected even by S_{ij} if we set the threshold at $S_{ij} \geq 0.75$ (see blue particles in Fig. S4*B* and compare it with *C*). Then, however, we cannot distinguish crystal nuclei from high MRCO regions with this single threshold. On the other hand, we can see crystals clearly if we set $S_{ij} = 1.5$ or $Q_6 = 0.4$, as shown in Fig. S4 *D* and *E*. This result means that we need at least two thresholds for the order parameter, S_{ij} or Q_6, to detect both MRCO and crystals separately. Furthermore, to detect the continuous development of MRCO in a supercooled liquid with an increase in ϕ, we need to see the change of the distribution (or at least the average value) of Q_6 or S_{ij}. As discussed in the main text, structural ordering in a supercooled liquid should decrease its free energy, which affects the free-energy gain upon crystal formation as well as the interfacial energy cost for creating crystal nuclei. So it may be crucial to characterize the structural order in a supercooled liquid before and after nucleation.

Possible origins of the discrepancy between our results and those of Auer and Frenkel (1) on crystal nucleation frequency. Here we discuss possible causes of the difference between our results and those of Auer and Frenkel (1). To do so, we first explain their approach. They used the fact that the crystallization rate is the product of a static term, i.e., the probability for the formation of a critical nucleus P_c, and a kinetic factor Γ that describes the rate at which such nuclei grow. Then they used umbrella sampling (with a biased potential) to compute the former (P_c) and kinetic Monte Carlo simulations to compute the latter (Γ). The combined nucleation rate was compared to experimental data. This method is elegant, but requires a few assumptions. For example, to estimate P_c, we need to define a reaction coordinate that measures the degree of crystallinity of the system. So we need a structural order parameter sensitive to the crystallinity itself, but insensitive to the difference between possible crystal structures. This latter requirement is so to use the biased sampling, which enhances the probability having crystal clusters around a certain size but

without selecting a specific type of crystal structure. As an order parameter satisfying these requirements they employed the correlation function of the vector $q_6(i) \equiv (q_{6m}^i)$ of neighboring particles i and j, $S_{ij} = q_6(i)^* \cdot q_6(j)$ (here * means the complex conjugate). Two particles i and j are defined to be connected if S_{ij} is larger than a given value. A particle is then regarded as solids if the number of connections with its neighbors is above a certain threshold. Using this criterion, they estimated the free energy barrier to have a crystal nucleus having cluster size n. The maximum barrier height as a function of n provides the free-energy barrier for nucleation ΔG_c. The first question we raise is how crystal nucleation is affected by MRCO. We note that even a supercooled liquid without any crystal nuclei already has bond orientational order, which is characterized by high Q_6 (or S_{ij}), as described above. An increase in ϕ leads to higher MRCO in a supercooled liquid, which leads to the decrease in the free energy of the system. This ϕ dependence of the free energy of a supercooled liquid before crystallization (a state of $n = 0$) was overlooked in the above method, because the criterion for crystal formation based on a single threshold of S_{ij} is insensitive to the development of MRCO. Furthermore, in the NVT ensemble and in a real colloidal system, the nonconserved structural order parameter is also coupled with density (4): As shown in Fig. 5 E–G, crystal nuclei dress depleted regions around them, reflecting the conservation of the particle density. Neglecting these additional degrees of freedom may affect the estimation of the Gibbs free energy $\Delta G(n)$ for the formation of a nucleus of size n. For example, the bias potential used for probing large clusters acts selectively on the above-defined crystals, decoupled from these other degrees of freedom. However, in a real system, there may be strong couplings between them. In other words, crystallization may not be described by a simple picture assuming only two states, which are characterized by a threshold of the single order parameter S_{ij}. For example, we can see a spatial coupling between crystallinity (green particles) and MRCO (red particles) in Fig. 2, whereas we see a coupling between crystallinity and density in

Fig. 5 E–G. We believe that such coupling is a possible cause of the discrepancy.

On the kinetic factor Γ, the difference in the ensemble used in simulations may also play an important role. We employed NVT ensemble, whereas Auer and Frenkel employed the isothermal–isobaric (NPT) ensemble. In real experiments, the number of colloidal particles are conserved. So the natural choice of the ensemble is NVT. This conclusion is supported by experimental observation of a peak in $S(q)$ in the process of crystallization of colloidal suspensions (4). Thus we believe that Brownian dynamics simulations in NVT ensemble are the most natural way to simulate the dynamics of colloids, although it still ignores hydrodynamic interactions. The difference between NVT and NPT ensembles also becomes crucial when we consider the kinetic factor Γ. The growth of nuclei is controlled by the mobility of colloid particles surrounding the nuclei, i.e., the rate at which the barrier to nucleation is crossed. In a real colloidal system, crystal nucleation should lead to the depletion of colloidal particles around nuclei because of the mass conservation (4), which enhances particle mobility. Note that in a supercooled liquid state the mobility is strongly dependent on ϕ. However, if we impose a constraint of constant pressure, nucleation does not induce such clear depleted regions around crystal nuclei and the above mentioned enhanced mobility around nuclei should be much less significant. This constraint may lead to the smaller value of Γ for NPT than for NVT, which can also be another cause of the discrepancy. In sum, we speculate that the difference in the ensemble used for simulations may be one of the major causes of the discrepancy.

Finally, we note that the significant increase of the speed of computers compared to 10 years ago when Auer and Frenkel (1) tackled this problem, now allows us to perform brute-force Brownian dynamics simulations of crystal nucleation, which is free from any assumptions. The almost perfect agreement of slow dynamics between our BD simulations with the NVT ensemble and results of 3D confocal microscopy experiments of a polydisperse colloidal suspension in a supercooled liquid region (see Fig. S1) supports the validity of this approach.

1. Auer S, Frenkel D (2001) Prediction of absolute crystal-nucleation rate in hard-sphere colloids. Nature 409:1020–1023.
2. Tanaka H, Kawasaki T, Shintani H, Watanabe K (2010) Critical-like behavior of glass-forming liquids. Nat Mater 9:324–331.
3. Lechner W, Dellago C (2008) Accurate determination of crystal structures based on averaged local bond order parameters. J Chem Phys 129:114707.
4. Schätzel K, Ackerson BJ (1993) Density fluctuations during crystallization of colloids. Phys Rev E 48:3766–3777.

Fig. S1. Dynamics of a supercooled state of a polydisperse colloidal suspension with the polydispersity $\Delta = 6\%$. The ϕ dependence of τ_α for both BD simulations and confocal microscopy experiments. The solid line indicates the fitting by the Vogel–Fulcher–Tammann relation (see Fig. 1B).
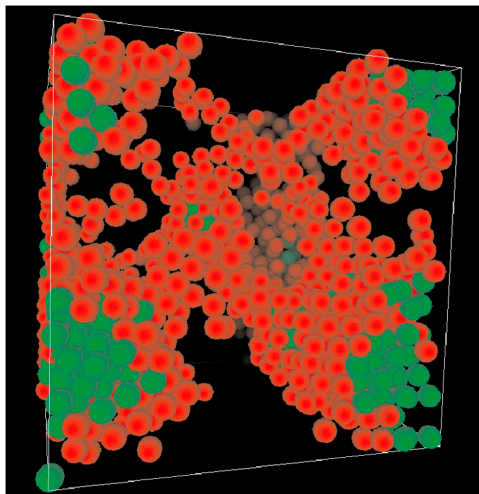
Fig. S2. System size dependence of the crystal nucleation. Temporal change of the number of crystal nuclei for three systems (N = 1,024; 4,096; and 16,834) for ϕ = 0.546 (*A*), ϕ = 0.537 (*B*), and ϕ = 0.533 (*C*). (*D*) System size dependence of the reduced crystal nucleation frequency I_r, which is estimated from the rate of the increase in the number of crystal nuclei (*A*–*C*). We can see that there is almost no system size dependence for $N \geq 4,096$.

Fig. S3. Birth of a crystal nucleus from medium-range structural order. The process of nucleation of a crystal at ϕ = 0.537 (N = 4,096) (see also Movie S2). Particles with intermediate Q_6 ($0.27 \leq Q_6 \leq 0.40$) are colored red, whereas those with high Q_6 ($Q_6 \geq 0.4$) are colored green. The time unit is the Brownian time of a particle, τ_B. We can see the birth of a crystal and its growth. Time $t = t'$ is when a supercooled liquid reaches a sort of quasi-equilibrium steady state after the initiation of simulations from a random disordered state.

Fig. S4. The order parameter distributions and their spatial distribution for a supercooled liquid state and a liquid-crystal coexistence state. (*A*) The probability distribution function of S_{ij}, $P(S_{ij})$, for an equilibrium liquid ($\phi = 0.421$), a supercooled liquid ($\phi = 0.533$) before crystal nucleation, bcc ($\phi = 0.577$), hcp ($\phi = 0.577$), rhcp ($\phi = 0.577$) and fcc ($\phi = 0.577$) crystals. The threshold suitable for distinguishing crystals and a supercooled liquid is $S_{ij} = 1.5$, which is indicated by the vertical dashed line. (*B*) Particles colored by the value of S_{ij} for a supercooled liquid before nucleation ($\phi = 0.533$ and $N = 16384$) [the same as the system in Fig. 2 ($t = t'$)]. Particles with $S_{ij} < 0.75$, with $0.75 \leq S_{ij} < 1.5$, and with $S_{ij} \geq 1.5$ appear transparent, blue and yellow, respectively. (*C*) Particles colored by the value of Q_6 for the same system as (*B*). Particles with $Q_6 < 0.28$, with $0.28 \leq Q_6 < 0.40$, and with $Q_6 \geq 0.40$ appear transparent, red, and green, respectively. (*D*) Particles colored by the value of S_{ij} for a liquid-crystal coexistence state in a system ($\phi = 0.533$ and $N = 16384$) [the same as the system in Fig. 2 ($t = t' + 110$)]. Particles with $S_{ij} < 0.75$, with $0.75 \leq S_{ij} < 1.5$, and with $S_{ij} \geq 1.5$ appear transparent, blue, and yellow, respectively. (*E*) Particles colored by the value of Q_6 for the same system as *D*. Particles with $Q_6 < 0.28$, with $0.28 \leq Q_6 < 0.40$, and with $Q_6 \geq 0.40$ appear transparent, red, and green, respectively.

Movie S1. A birth process of a crystal nucleus from medium-range structural order in a supercooled liquid ($N = 16,384$) at $\phi = 0.533$ (the same process as in Fig. 2). Particles with higher Q_6 ($Q_6 \geq 0.27$) are colored red, whereas those with even higher Q_6 ($Q_6 \geq 0.4$) are colored green. The entire process corresponds to about 100 τ_B (τ_B, the Brownian time of a particle).

Movie S1 (AVI)

Movie S2. A birth process of a crystal nucleus from medium-range structural order in a supercooled liquid ($N = 4,096$) at $\phi = 0.537$ (the same process as in Fig. S3). Because of the small size of the system, we can see more details of a nucleation process of crystals. Particles with higher Q_6 ($Q_6 \geq 0.27$) are colored red, whereas those with even higher Q_6 ($Q_6 \geq 0.4$) are colored green. The entire process corresponds to about 60 τ_B (τ_B, the Brownian time of a particle).
Movie S2 (AVI)