Direct Measurements of the Dynamical Correlation Length Indicate its Divergence at an Athermal Glass Transition

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The supercooled $N3$ model exhibits an increasingly slow dynamics as density approaches the random closest packing density. Here, we present a direct measurement of the dynamical correlation function $G_4(r, t)$, showing the emergence of a growing length scale ξ_4 across which the dynamics is correlated. The correlation length measured, up to 120 lattice sites, power law diverges as the density approaches ρ_t, the density at which the fluid phase of the model is predicted to terminate. The four-point susceptibility, often used as an agent to estimate ξ_4, does not depend simply on the latter. Rather, it depends strongly on the short-range behavior of $G_4(r, t)$. Consequently, χ_4 peaks before ξ_4 reaches its maximal value. The two quantities should therefore be studied independently.

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Dynamics of supercooled liquid glass formers is characterized by nonexponential temporal relaxation (see recent review [1]). Two natural, but fundamentally different, explanations can be put forward. Relaxation might be locally exponential, but the typical relaxation timescale varies spatially. Global response functions become nonexponential upon spatial averaging, due to the spatial distribution of relaxation times. Alternatively, relaxation might be complicated and inherently nonexponential, even locally. Experimental and theoretical works [2] suggest that while the latter mechanism is likely to contribute, relaxation (at times of order of the global relaxation time or shorter) is indeed spatially heterogeneous. At an ideal glass transition, the relaxation time diverges and the dynamics remains heterogeneous for arbitrary long times. The study of dynamical heterogeneities has attracted much interest recently [3–9], as part of the attempt to decipher the mystery of glassy dynamics.

A physical characterization of dynamic heterogeneity entails the determination of the typical lifetime of the heterogeneities, as well as their typical length scale. A clear demonstration of the heterogeneous dynamics is obtained by tracking mobile particles at a given time. One observes clusters of highly mobile particles as well as clusters of particles barely moving at all [10–12]. The typical size of these clusters is quantified by the spatial decay of the mobility correlation function. One therefore looks for the correlation between the displacements over a time interval t of particles at mutual distance r. This mobility-mobility correlation function was first introduced in [13], as a tool to discover cooperative regions in numerical simulations of glass-forming liquids. However, the first attempts to analyze these correlation function [13] were very limited, and thus showed no increasing correlation length. It turns out that the essential ingredient to find the dynamical correlations is not really the mobility, but rather the fact that we are calculating a four-point correlation function, in contrast with standard two-point functions. The four-point density correlation

$$G_4(r, t) = \langle \rho(0, 0)\rho(0, t)\rho(r, 0)\rho(r, t)\rangle - \langle \rho(0, 0)\rho(0, t)\rangle\langle \rho(r, 0)\rho(r, t)\rangle, \quad (1)$$

was first suggested in [14] in order to look for a growing correlation length. Yet, direct measurements of G_4 turn out to be technically demanding. Instead, it is common to study its spatial integral, which is nothing but the realization-to-realization fluctuations of the two-point correlation function $\tilde{C}(t) = \langle \rho(0, 0)\rho(0, t)\rangle - \langle \rho(0, 0)\rangle\langle \rho(0, t)\rangle$ (spatially averaged for each realization), or the four susceptibility

$$\chi_4(t) = \int G_4(r, t)dr = N[\langle \tilde{C}(t)^2\rangle - \langle \tilde{C}(t)\rangle^2]. \quad (2)$$

The four susceptibility was indeed shown to exhibit an appreciable increase with the waiting time [15], which was interpreted as a sign for an increase of the dynamical correlation length characterizing the decay of $G_4(r, t)$. The four-point susceptibility was later used extensively to measure dynamical heterogeneities approaching the glass transition and to imply the existence of growing correlation length. The time dependence of $\chi_4(t)$ was suggested to indicate the mechanism underlying the transition [7].

Various theories lead to different relations between the correlation length ξ_4, characterizing the spatial decay of $G_4(r, t)$, and χ_4 [16,17]. Thus, direct measurements of dynamical correlations can play a vital role in distinguishing the various theoretical approaches. In fact, it was pointed out in [7,18] that χ_4 and ξ_4 might depend differently on time. However the calculation of dynamic correlations is hard especially in numerical simulations, because very large systems are needed in order to determine ξ_4 unambiguously. Previous measurement of dynamic correlations were performed indirectly by either scaling the binder cumulant at τ_4 (time at which $\chi_4(t)$ peaks) [9] or

fitting the low q behavior of $G_4(q, t)$ [7,8]. These measurements have shown moderate correlation lengths, up to 10 interparticle distances. Clearly, these do not describe very well the behavior at a regime in which correlation lengths (are expected to) diverge. Here we report measurements of dynamical correlation based on the evaluation of the four-point density correlation $G_4(r, t)$ throughout the relaxation process. Having measured $G_4(r, t)$ directly, the correlation lengths is then extracted by fitting an exponentially decaying function to the long range behavior of $G_4(r, t)$.

The $N3$ model is a simple 2D model on a square lattice. Particles are cross-shaped pentamers, interacting only through hard-core exclusion which blocks up to the 3rd nearest neighbor (see Fig. 1). The model is known to undergo a first order solidification transition [19–21], where density jumps from $\rho_f \simeq 0.161$ to $\rho_s \simeq 0.191$ [21] (the closest packing density is 0.2). The behavior of this model in the supercooled fluid regime was analyzed using the R matrix method [22,23] based on the Mayer cluster coefficients of $N3$. The analysis predicted a critical termination of the supercooled fluid phase at nontrivial density $\rho_t = 0.1717$, close to the random closest packing density of this model [24]. The validity of the R matrix approach in the deeply supercooled regime could be questioned, but extensive MC simulations revealed that the dynamic relaxation of the supercooled fluid becomes increasingly slow as the density increases, diverging at ρ_t [25]. It is therefore plausible to relate the dynamical arrest in the $N3$ model to the predicted termination of the thermodynamic equation of state predicted by the R matrix. The physical origin of the critical termination point is yet to be understood, but one attractive possibility is that it marks the spinodal point, where the supercooled fluid loses its (meta)stability. The $N3$ system is then a simple and convenient model-system for studies of slow dynamics in quenched deeply supercooled fluids.

Here we employ the advantage of the simple two dimensional $N3$ system and study in detail the dynamic correlation length near the predicted termination of the fluid supercooled phase. Simulations of the $N3$ model allowed for an easy and direct measurements of $G_4(r, t)$ throughout the whole relaxation process for a wide range of system sizes. We performed Monte Carlo simulations of the model following the protocol presented in [25]: simulation starts with an infinitely fast cooling, where particles are added whenever possible and diffuse otherwise, this process is stopped when the desired density is reached. The system is then left to relax diffusively at a fixed density, and measurements are performed during this relaxation process. Figure 2 presents the behavior exhibited at the different time regimes. We have studied lattices of sizes up to 1200×1200 sites in the current study (up to 2000×2000 sites in the past). Simulations of such large systems are crucial, as significant finite-size effects are shown to persist to large lattice sizes [25]. In concordance, we measure correlation lengths as large as 120 lattice sites (50 interparticle distances). The correlation length is estimated by fitting an exponential form to the measured $G_4(r, t)$. The only freedom in the fit is the spatial range upon which to fit the exponential form: in all of the ξ_4 measurements below we used the range $30 < r < 90$, even though for cases with large ξ_4 the fit captures the behavior far beyond this chosen range, as seen in Fig. 2.

The picture that emerges from these simulations is the following: at short times $G_4(r, t)$ decays at short range, with no exponential tail observed. However, on intermediate times one clearly sees an exponential decay regime following the short-range decrease. At later times, (later then τ_4),

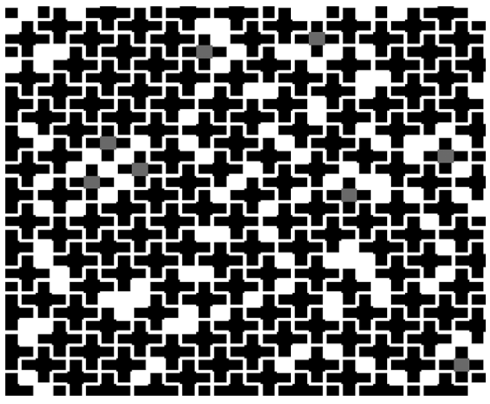

FIG. 1. Random packing of the $N3$ model as produced by the cooling protocol, density set to 0.17. The few particles that are movable at the end of the cooling phase are marked by a gray spot at their center.

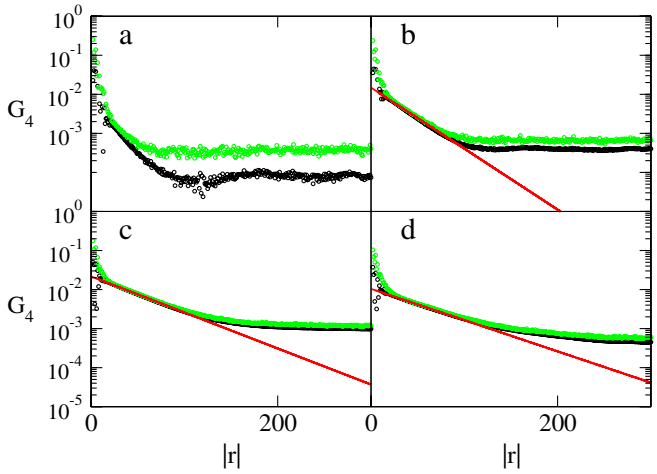

FIG. 2 (color online). Measurements of $G_4(r, t)$ during dynamical relaxation of the $N3$ model, at density $\rho = 0.1713$. Data are binned (bins width 1 lattice constant), the average and maximum values in each bin are presented. (a) $t = 5000$ (b) $t = 10\,000$, a clear exponentially regime emerges. (c) $t = 20\,000$, the correlation length further increases. (d) $t = 30\,000$, further increase of the correlation length. Note that the amplitude of the correlation function $G_4(r, t)$ is smaller in this case, leading to an overall smaller integral χ_4 as compared to the time presented in (c). The exponential fit to the averaged data (straight line) may be used to extrapolate $G_4(r, t)$ to larger distances (see text).

one again sees only the short-range behavior. Figure 3 presents the time dependence of the dynamic correlation length ξ_4, for various densities of the $N3$ model. We find that the correlation length $\xi_4(t)$ grows with time, approaching a plateau. It is not possible to measure ξ_4 at very long times, where $G_4(r, t)$ is very small beyond the short-range regime, and it is not at all clear whether there is an exponential regime in these long times. However, for as long as we are able to measure ξ_4 it does not seem to increase or decrease. Furthermore, the time dependence of $\chi_4(t)$ is determined by the short-range correlation (which dictates the amplitude of the long range behavior) as well as the correlation length itself. Because of the dependence of both ξ_4 and the amplitude of $G_4(r, t)$ on the time t, the time τ_4 at which χ_4 peaks differs from the time at which ξ_4 reaches its maximal value. These findings highlights the nontrivial relation between χ_4 and ξ_4, and the need to study both quantities separately. In addition, our measurements show that the dynamically correlated regions have compact (and not fractal) form in all times measured.

Looking at the microscopic structure of the relaxation dynamics in the $N3$ model, one observes a clear heterogeneous picture similar to that seen, for example, in the kinetically constrained triangular lattice gas models (1)-TLG and (2)-TLG [26]. The dynamics can be described by a growth of mobile regions in the system, as seen in Fig. 4, until all of the particles moved when $C(t) = 0$. In course of time, the mobile regions, or clusters, grow, but there is no creation of new clusters. The measured correlation length fits this observed dynamics. The increase in the correlation length corresponds to the growth of clusters of mobile particles, while in later times further cluster growth is blocked by the neighboring clusters, resulting in a saturation of correlation length.

As seen in Fig. 2, $G_4(r, t)$ does not decay to 0 at very long ranges. The contribution of this tail to χ_4, the spatial integral over G_4, does not decrease with system's size. These spurious infinite-range correlations are introduced during the cooling protocol. In fact, one may study $\rho_m(r, t = 0)$, the density of particles free to move at $t = 0$ (end of cooling). The global density of movable particles at time $t = 0$ is just $m = \langle \rho_m(r, t = 0) \rangle$, and the generalized susceptibility for this density is given by $\chi_m = V[\langle m^2 \rangle - \langle m \rangle^2]$. This quantity is closely related to χ_4 at short times. Indeed, one observes infinite-range contributions to the zero time χ_m. This global effect is amplified in the course of dynamics, as movable particles grow into clusters, and affects strongly χ_4. It is washed out only for relatively long times, often of order τ_4 and more. Obviously, these infinite-range contributions to χ_4 have nothing to do with the dynamics in general, or with the dynamical correlation length, in particular.

Similar effects are expected in other studies, as long as the system is not equilibrated before the measurement starts. Such equilibration is always desired, but usually not possible in systems prone to crystallization (e.g. hard-spheres). Direct measurements of χ_4 in such cases are prone to the effect described above. However, if one measures $G_4(r, t)$, a correction scheme for the initial condition is possible. Instead of calculating χ_4 using $N \cdot \mathrm{Var}(C(t))$, one should extrapolate the exponentially decaying region of $G_4(r, t)$ to infinite r, and find χ_4 by integrating $G_4(r, t)$ exactly over the short-range and adding the contribution of the integral over the exponential regime for larger distances.

The results for the dynamic χ_4 are presented in Fig. 5. Peak values of χ_4 diverges with a power law as ρ_t is

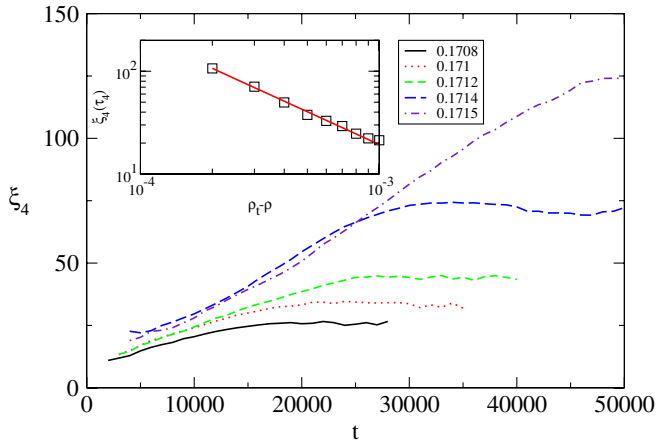

FIG. 3 (color online). Time dependence of the dynamical correlation length for several values of the density. The correlation length increases with time, and then saturates for as long as we are able to measure it. The correlation length as measured at τ_4 power law diverges with critical exponent of 1.0 (inset).

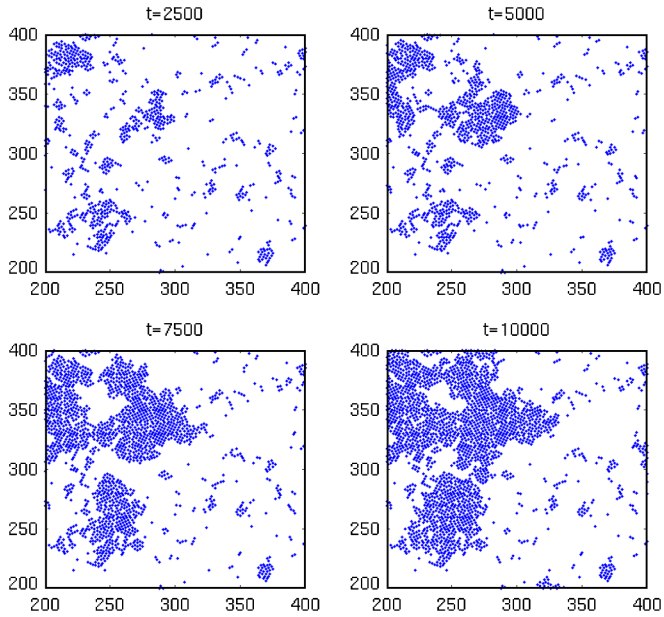

FIG. 4 (color online). Displaying relaxation dynamics of $N3$ model, for $\rho = 0.1713$. Dots represent mobile particles, the growth of mobile regions as well as no creation of new mobile regions with time is observed. An area of 200×200 was chosen out of simulated system of 1000×1000 sites.

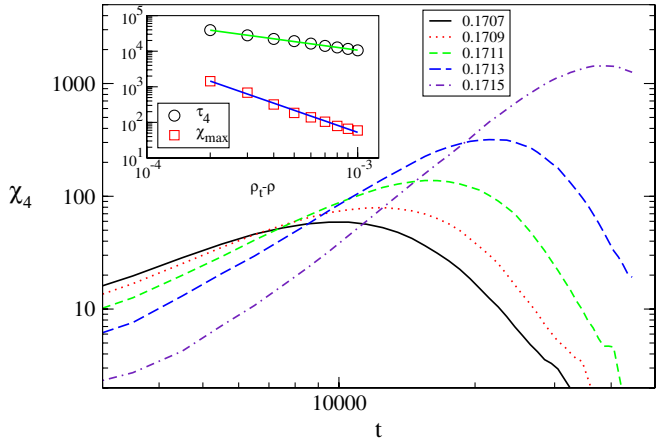

FIG. 5 (color online). Measurements of $\chi_4(t)$ corrected for removal of global effects created while cooling the system. Maximum value as well as the time of maximum power law diverges (inset) as the termination density ρ_t is approached. Maximum value diverges with exponent of 2.0 and the time τ_4 with exponent of 0.8.

approached $\chi_{4,\max} \sim (\rho_t - \rho)^{-2.0}$. The time dependence of $\chi_4(t)$ underscores its dependence on the short-range behavior of $G_4(r, t)$ rather than the long exponential tail. The short-range correlation determines the coefficient multiplying the exponential decay, and has stronger time dependence then $\xi_4(t)$ and so determines $\chi_4(t)$ time dependence.

The divergence of dynamical length and time scales at ρ_t, the termination density of the metastable fluid, suggests a possible relation between a (kinetic) spinodal and a slow dynamics. Such a mechanism was already suggested for a number of models by several authors [27–30]. According to this scenario, as the system is cooled below the kinetic spinodal the fluid becomes unstable towards creating microscopic crystalline domains on time scales shorter than the relaxation time. In this regime, the growth of the microcrystallites is slower than the creation of new ones. Thus, the system gets stuck in a poly-microcrystalline phase, which is indistinguishable from what we call a glassy state [30]. Further research is required to examine the relevance of this picture to the $N3$ and other models.

In summary, we present here a direct measurement of the dynamical correlation function $G_4(r, t)$, showing the emergence of a growing length scale ξ_4 across which the dynamics is correlated. One observes a significant increase in the correlation length, up to 120 lattice sites. As density approaches ρ_t, the density at which the fluid phase of the model is predicted to terminate, the correlation length ξ_4 power law diverges with $(\rho_t - \rho)$. In concordance, peak values of $\chi_4(t)$ diverge, suggesting that the slow down of relaxation processes near the termination of the fluid branch results from a growth in the dynamical correlations. Yet, we show that χ_4 by itself cannot be used as a reliable indirect measure of ξ_4 time dependence.

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