Tracking Heterogeneous Dynamics During the α Relaxation of a Simple Glass Former

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We study the relaxation process in a simple glass former—the Kob-Andersen lattice gas model. We show that, for this model, structural relaxation is due to slow percolation of regions of cooperatively moving particles, which leads to heterogeneous dynamics of the system. We find that the size distribution of these regions is given by a power law and that their formation is encoded in the initial structure of the particles, with the memory of initial configuration increasingly retained with increasing density.

Glass-forming systems are disordered materials whose relaxation dynamics become extremely slow on decreasing the temperature or increasing the density. Despite intensive research in this domain, a proper understanding of these materials is still missing [1,2]. The observation, in experiments and simulations, of spatio-temporal dynamical heterogeneity in glass formers has been an important step forward in elucidating the mechanism for relaxation processes, and currently, considerable research is being focused on understanding the lifetime and spatial extent of these dynamical heterogeneities.

A key question in this domain is the conundrum regarding whether or not there is a causal link between structural properties of glass-forming systems and their dynamical behavior. It has recently been shown [3] that the spatial heterogeneity in the propensity of particles to move is correlated with the local environment of the particles, characterized by the local Debye-Waller factor. However, this influence seems to exist only over time scales which are much less than the structural relaxation time [4]. It was also observed that structural properties are indeed correlated with collective dynamical fluctuations, but no quantitative analysis was made [5]. More recently, it has also been reported [6] that for a supercooled liquid configuration, its localized low-frequency normal modes correlate with the irreversible structural reorganization of its constituent particles.

In recent times, extensive studies of kinetically constrained models (KCMs) [7], which are one of the simplest models showing glassy dynamics, have been carried out in order to understand their relaxation process. These models, which are motivated by the hypothesis that the slow dynamics in glass formers is only due to geometrical constraints, show heterogeneous dynamics similar to real glass formers [8]. In this Letter, we study one such KCM—the Kob-Andersen (KA) lattice gas [9] in which particles are allowed to move on a lattice following certain dynamical rules and which at high densities shows signatures of apparently diverging relaxation times [9–11]. Recently it has been proven analytically [12] and numerically [13] that

for this model there exists no dynamical transition at finite density, ρ, and it was argued [12] that eventually, due to the presence of migrating macro-vacancies, the system relaxes, albeit extremely slowly. However, from a practical point of view this model still is a good model for a glass-forming systems. Using Monte Carlo simulations we show that its structural relaxation is related to the growth of mobile regions and that this process quickly slows down with increasing ρ, resulting in the observed slow dynamics. We also demonstrate that the formation of the mobile regions is directly related to structural properties of the system.

We have studied the 3D version of the KA model: N particles populate a cubic lattice of size L^3 with the constraint that a lattice site can be occupied by only one particle. All possible configurations have the same energy and thus the same Boltzmann weight. The imposed stochastic dynamics consists of the following process: A randomly selected particle can move to any one of the neighboring empty lattice site provided it has m or fewer occupied nearest neighbor sites and that the target empty site has $m + 1$ or fewer occupied nearest neighbor sites. A choice of $m = 3$ results in glassy dynamics for this model [9]. For efficient sampling of the configuration space at high $\rho = N/L^3$, we have carried out event-driven Monte Carlo [9] simulations of the model. Using periodic boundary conditions, we have investigated system sizes $L = 20$, 30, and 50, which avoid finite-size effects, with densities spanning from $\rho = 0.65$ to $\rho = 0.89$.

Experiments and simulations in which the motion of single particles were tracked have helped to demonstrate the existence of heterogeneous dynamics in glassy systems [2]. For example, by measuring the self part of the van Hove function $G_s(r, t)$, i.e., the distribution of particle displacements $[G_s(r, t) = \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_i(0)|) \rangle$, where $\mathbf{r}_i(t)$ denotes the position of particle i at time t], it has been possible to demonstrate that the particles have varying mobilities. In Fig. 1, we show $G_s(r, t)$ for different times t, measured in units of Monte Carlo steps, at $\rho = 0.87$. For diffusive motion, $G_s(r, t)$ is a Gaussian and we
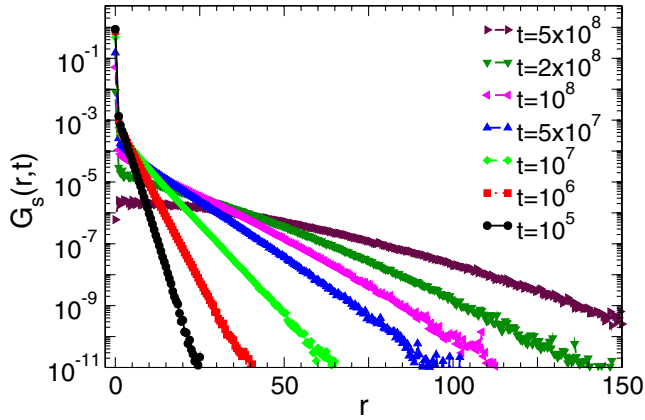
FIG. 1 (color online). $G_s(r, t)$ for different times at $\rho = 0.87$.
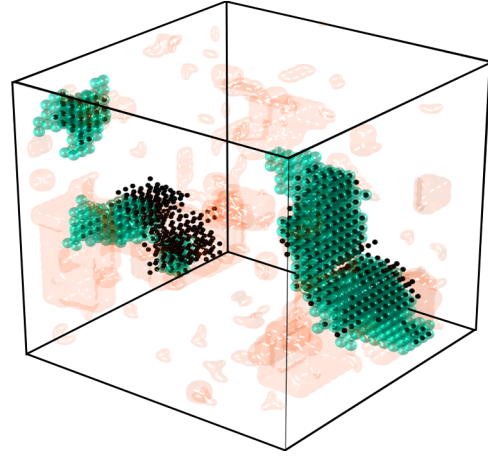The α-relaxation time at this density is $\tau_\alpha \approx 1.8 \times 10^7$.

FIG. 2 (color online).   Light and dark points: Sites that have
been visited by the trajectory of two mobile particles. Pale blobs:
The mobility regions. $t = 10^7$ and $\rho = 0.88$.

observe that for the KA model, like other glass formers
[14], this Gaussian behavior is only observed at times ($t \approx
5 \times 10^8$) that are much larger than the structural relaxation
time τ_α (defined as the time at which the self-intermediate
scattering function has decayed to $1/e$, which at $\rho = 0.87$
is $\tau_\alpha \approx 1.8 \times 10^7$). At intermediate times, we see that
$G_s(r, t)$ has an exponential tail, a signature of the presence
of rare events in the dynamics of the particles, similar to
other glassy systems [15]. Thus we can conclude that while
most of the particles remain frozen at their initial positions
[resulting in large values for $G(0, t)$], there is a small
population which is extremely mobile; i.e., the system
has a very heterogeneous dynamics.

By tracking the mobile particles, i.e., particles which
contribute to the tail of $G_s(r, t)$, we see that at short times
they explore a compact region (a "blob") around their
initial locations. With increasing t these blobs slowly ex-
pand and coalesce with other blobs to form a labyrinthine
structure. This structure allows particles, which were hith-
erto confined to one blob, to travel longer distances. In
Fig. 2 we have plotted the lattice sites (marked by light and
dark spheres) visited by two such mobile particles at $\rho =
0.88$ and $t = 10^7$ (at this density, $\tau_\alpha \approx 4.4 \times 10^8$). It can
be clearly seen that the dynamics is spatially heteroge-
neous since the trajectories consist of connected blobs.
Note that initially each blob is a region of cooperative
motion since all the particles which occupy these lattice
points are found to be mobile. As the backbone is formed,
particles from one blob begin to explore other blobs. The
relaxation of the system thus happens with the slow growth
of this backbone, within which the particles can move
relatively quickly. This is demonstrated in Fig. 2: indeed,
the two trajectories overlap even though they originate
from two different lattice sites which initially did not
belong to the same blob.

Further insight into the spatial nature of the relaxation
process can be obtained by observing the so-called "mo-
bility regions" [16–18]: A lattice site is defined to be an
"active site" if either a particle or a vacancy has moved out
of it during the time of observation and the collection of

these sites constitute the mobility regions. Earlier studies
of KCMs have shown that the active sites tend to cluster
and act as seeds for subsequent mobility [16–18] and that it
is possible to extract from the mobility regions a length
scale which increases with density [16]. In Fig. 2 we have
also included the location of the active sites, and we can see
that these lattice sites are indeed clustered in space
(marked by the pale blobby shapes) and have a labyrinthine
structure. It gives us an idea of the structure of pathways, at
high densities, available to the mobile particles for explo-
ration. We can clearly see that, on this time scale, the two
mobile particles have only explored a part of the available
volume and that the geometry of the mobility regions and
the blob structure of the trajectories are intimately con-
nected to each other.

The number density of active sites, $n_{act}(t)$, allows us to
estimate the volume accessible to the mobile particles, and
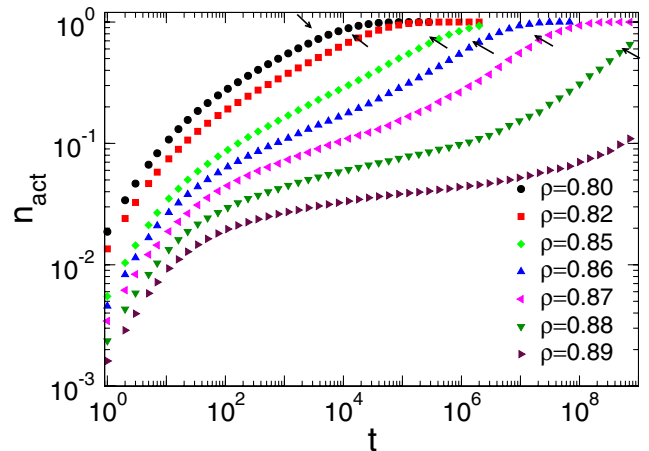in Fig. 3 we plot $n_{act}(t)$ for different ρ. We see that, at short

FIG. 3 (color online).   Growth of number of active sites, n_{act}, as
a function of time, for different ρ. The arrows mark τ_α.

times, $n_{act}(t)$ increases quickly, and we find $n_{act}(t) \sim 1 - \exp(-t/\theta)$ with $\theta \approx 5$, independent of ρ. This regime corresponds to the initial growth of the blobs. Subsequently the shape of $n_{act}(t)$ depends strongly on ρ. For $\rho = 0.80$ the number of inactive sites, $1 - n_{act}$, decays with a stretched exponential tail, with a stretching exponent of around 0.6, a functional form that is found for all ρ. At even larger ρ, $n_{act}(t)$ shows three regimes, with the second regime being a period of extremely slow growth, almost logarithmic and thus similar to the coarsening process in disordered media [19]. Note that at short t the typical distance between the blobs increases with ρ and the growth of the blobs slows down with increasing ρ, since it needs the presence of active sites (which are rare at high density). This is the reason why the increase of $n_{act}(t)$ at intermediate times becomes very slow with increasing ρ. We also observe that at $\rho = 0.89$, which is higher than the density of $\rho_c = 0.881$ at which an apparent divergence of relaxation time scales was observed [9], $n_{act}(t)$ is still an increasing function, suggesting that the system will eventually relax [12]. Note that although these three regimes are in qualitative agreement with the predictions of Ref. [12], there are important differences since, e.g., the diffusion of macro-vacancies discussed in Ref. [12] would lead to a linear growth of $n_{act}(t)$ at long times, a behavior which is not seen in Fig. 3. This might be due to the fact that the calculations presented in Ref. [12] apply only at densities that are extremely close to 1.0.

In order to characterize the geometry of the growing clusters of active sites we have calculated $P(s)$, the distribution of clusters that have exactly size s. In Fig. 4, we have plotted $P(s)$ for $\rho = 0.88$ and different times. At short times, $t = 10$, $P(s)$ has an exponential shape. This corresponds to the initial geometry of active sites at few random locations when particles explore their neighborhood. With increasing time $P(s)$ quickly transforms into a power law,
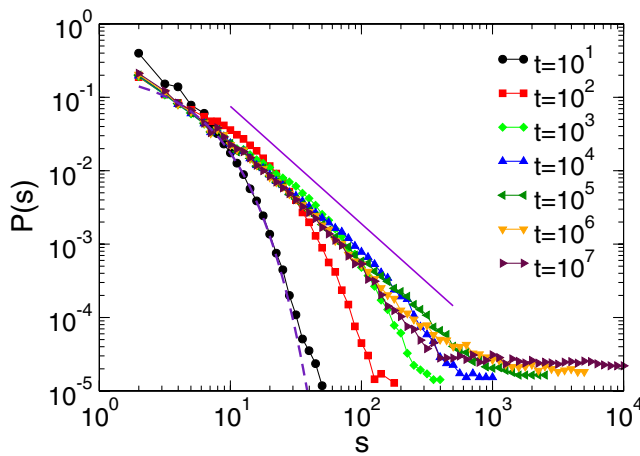
$P(s) \sim s^{-\nu}$, with an exponent $\nu \approx 1.6$. This indicates that the growth process is different from random percolation for which $\nu = 2.2$. This difference is likely related to the fact that there is a wide variation in the size of the cooperatively rearranging regions seen at short times. At even later times, the largest cluster starts growing and the tail in $P(s)$ shifts to larger and larger sizes, until the entire space is filled up. Note that the observed largest cluster depends on system size and thus the tail of $P(s)$ is affected by finite size effects.

Finally we investigate to what extent the dynamics is encoded in the structure. We have seen that structural relaxation is correlated with the development of the mobile regions. Therefore it is interesting to check how the properties of these regions depend on the trajectories that start from the same initial configuration. For this, we check along several such trajectories how different are the configurations of active sites formed at the same observation time. To quantify that, we define the overlap function $Q_{act}(t) = [\langle q^{\alpha\beta}(t)\rangle_{ic} - n_{act}^2(t)]/[n_{act}(t) - n_{act}^2(t)]$, where $q^{\alpha\beta}(t) = L^{-3}\sum_i n_i^\alpha(t)n_i^\beta(t)$, with $n_i(t) = 1$ if site i is active at time t and $n_i(t) = 0$ otherwise. $\langle .\rangle_{ic}$ is the average over the isoconfigurational ensemble [3], i.e., the ensemble of all possible trajectories starting from the same configuration of which α and β are two different members. Defined in this way, $Q_{act}(t) = 1$ if at time t the configuration of active sites for two different trajectories are exactly the same and $Q_{act}(t) = 0$ if the two configurations are totally different, apart from the trivial statistical overlap. Thus Q_{act} is a direct measure for the influence of the initial structure on the mobility regions.

In Fig. 5, we show the time dependence of $Q_{act}(t)$ for different ρ. At short times $Q_{act}(t)$ is independent of ρ, and its value is small since the mobile particles can find random directions to explore, which result in different configurations of active sites and hence a small Q_{act}. Subsequently $Q_{act}(t)$ has a peak at a time which approximately corresponds to the time at which $n_{act}(t)$ enters the final regime of
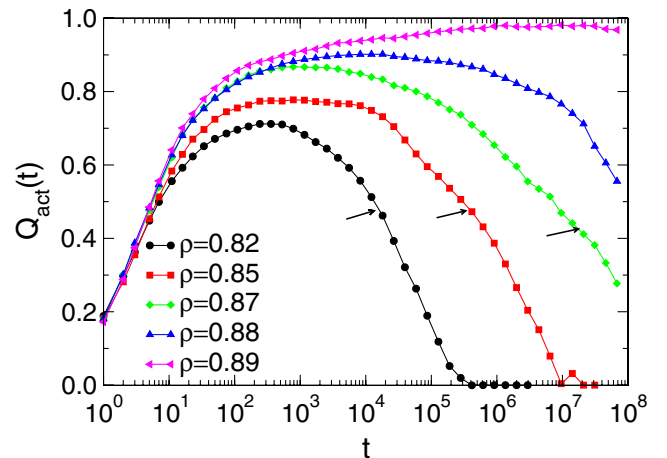

FIG. 4 (color online). Distribution of cluster size, $P(s)$, where s is the size of cluster, for different times at $\rho = 0.88$. Also shown (dashed line) is an exponential fit to $P(s)$ at $t = 10$ and (solid line) the function $s^{-1.6}$ to highlight the emergence of power law behavior of $P(s)$ at intermediate times.

FIG. 5 (color online). Variation of $Q_{act}(t)$ with time, for different ρ. The arrows mark τ_α.
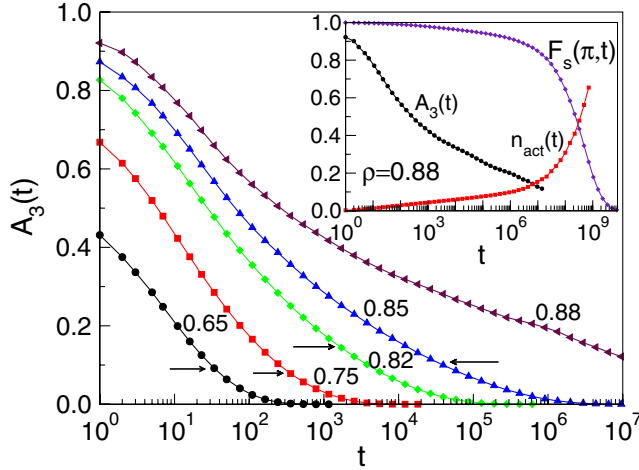
FIG. 6 (color online).   The time evolution of overlap, $A_3(t)$, for different ρ. The arrows mark τ_α. Inset: Comparison of different temporal functions at $\rho = 0.88$.

growth, see Fig. 3, and which is much smaller than τ_α (marked by arrows). For large value of ρ the height of this peak is close to unity and it becomes extremely broad so that $Q_{act}(t)$ is quite large even at τ_α. This shows that the configuration of active sites is, in a broad time window, basically independent of the trajectory and thus encoded in the initial structure, even for times of the order of τ_α (but depends of course on the initial configuration). Note that these results seem to be in contradiction to the claims made in Ref. [4] since there it was argued that the structure influences the dynamics only on time scales much shorter than τ_α. However, in that work the authors considered this influence on the level of individual particles whereas the overlap $Q_{act}(t)$ considered here is a collective quantity. Therefore there is not necessarily a contradiction.

What structural property determines mobility? It is obvious that for a site to be active, it needs empty space in its neighborhood. Earlier work on lattice models has shown that the high propensity sites are located near clusters of empty sites [17]. In order to investigate the relation between structure and mobility we define another overlap function. A lattice site is considered to be a generalized vacancy of type k if the site and its six nearest neighbors contains a total of at least k holes. Then we calculate, as a function of time, the overlap of the active sites with these generalized vacancies. The quantity we measure is $A_k(t) = \sum_i a_i^k n_i(t)/\sum_i n_i(t) - \tilde{a}^k$. Here, $a_i^k = 1$ if at $t = 0$ the site i is a generalized vacancy of type k and 0 otherwise. Thus, $A_k(t)$ is the probability that a generalized vacancy of type k in the configuration at $t = 0$ is an active site at time t, with the trivial overlap $\tilde{a}^k$ (the density of generalized vacancies of type k in the configuration at $t = 0$) subtracted. Such a quantity enables us to have a good measure of the correlation between structure and dynamics. For low density, i.e., $\rho = 0.65$, $A_3(t)$ has a fast decay, see Fig. 6. (Other values of k have a qualitatively similar behavior.) With

increasing ρ, the characteristic time scale for the decay increases with the tail becoming stretched in shape, the underlying slowing down of the relaxation process resulting in the retention of the memory for longer time. In the inset of Fig. 6, we have plotted different correlation functions at $\rho = 0.88$: the overlap function $A_3(t)$, the self-intermediate scattering function $F_s(\pi, t)$, and the fraction of active sites $n_{act}(t)$. At this density, the α-relaxation time $\tau_\alpha \approx 4.4 \times 10^8$. For this time scale, the fraction of active sites is $n_{act}(\tau_\alpha) \sim 0.50$. However, if one extrapolates $A_3(t)$ to these time scales, the overlap is small. Therefore, although measurement of $Q_{act}(t)$ showed that the configuration of active sites, at $t \approx \tau_\alpha$, is significantly determined by initial structure, the use of generalized vacancies does not fully demonstrate this strong dependence. Hence, a better characterization of initial structure is necessary for improving prediction for formation of mobile regions.

In conclusion, we have shown that, for the KA lattice gas, the α-relaxation occurs via the percolation of mobile regions in which particles move cooperatively. These regions are encoded in the initial structure of the system with a memory time that is on the order of τ_α. We emphasize, however, that the initial structure does not necessarily determine the trajectory of an individual particle but only the location and the shape of the regions in which cooperative dynamics is observed.

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