Geometrical Explanation and Scaling of Dynamical Heterogeneities in Glass Forming Systems

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We show how dynamical heterogeneities in glass forming systems emerge as a consequence of the existence of dynamical constraints, and we offer an interpretation of the glass transition as an entropy crisis in trajectory space (space-time) rather than in configuration space. To illustrate our general ideas, we analyze the one-dimensional ($d = 1$) Fredrickson-Andersen and East models. Dynamics of such dynamically constrained systems are shown to be isomorphic to the statics of ($d + 1$)-dimensional dense mixtures of polydisperse noninterpenetrating domains. The domains coincide with arrested regions in trajectory space.

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A glass forming system, such as a supercooled liquid, exhibits a precipitous onset of slowness. As temperature is decreased in these systems, typically in a range of a few decades, relaxation times and viscosities increase by several orders of magnitude, eventually surpassing experimentally accessible times. For practical purposes, these systems effectively freeze at the glass transition temperature T_g. For reviews, see [1]. Interestingly, this dynamical arrest carries no evident static structural signature of growing length scales. Rather, experiments and simulations show that supercooled liquids are *dynamically* heterogeneous [2,3]. Molecules in one region of the liquid translate or rotate several orders of magnitude faster or slower than those in a neighboring region. The spatial extent of these dynamical heterogeneities is mesoscopic, and the time scale of the slowest domains increases with decreasing temperature at least as fast as the relaxation time of the system. Such structural behavior seems beyond description with homogeneous methods such as mode coupling [4] and mean field theories [5], and it is widely neglected in analytical treatments (see, however, [6–8]). Nevertheless, we show here that, for a broadly applicable mechanism of dynamical arrest, these heterogeneities are intrinsic to the nature of glass forming systems.

Our central result is that dynamical heterogeneities are a manifestation of the existence of nontrivial structure in the trajectories of glassy systems. This structure associated with dynamics is independent of any specific static properties. Instead, the nontrivial dynamical structure is a consequence of local dynamical rules that significantly restrict the size of accessible trajectory space. For example, consider a highly compressed (or supercooled) glass former. Atoms in most regions of space are jammed, making mobility possible in only a relatively low fraction of spatial regions. These rare regions are those that are already unjammed, or those that may be close in space to an unjammed region. In the evolution of such a system, one therefore expects a clustering of mobile regions and thus a mesoscopic demixing of mobile and static regions. Macroscopic demixing is not expected because dynamics should conserve a canonical distribution. This picture of the origin of dynamic heterogeneity is in accord with the idea that glassiness is not necessarily a consequence of either disorder or frustration in the static interactions but of the existence of effective constraints on the dynamics of the system [9].

The simplest microscopic models that illustrate this view are the Fredrickson-Andersen (FA) model [10] and the East model [11]. They consist of a chain of Ising spins $\sigma_i = \pm 1$ ($i = 1, \ldots, N$), with trivial Hamiltonian $H = \sum_i \sigma_i$, and single spin flip dynamics subject to local kinetic constraints. In the FA model, a spin can flip if either of its nearest neighbors is in the up state [10]. In the East model, a spin can flip only if its nearest neighbor to the right is up [11]. The equilibrium behavior of both models is that of an uncorrelated spin system, with $c = 1/(1 + e^{1/T})$ being the average concentration of up spins at temperature T. The competition between decreasing the energy and the need for facilitating spins leads to a glassy slow down at low temperatures. The relaxation times go as $\tau \propto e^{3/T}$ in the FA model, and as $\tau \propto e^{1/(T^2 \ln 2)}$ in the East model. These models therefore correspond to a strong and a fragile glass former, respectively. See [12] for a short review.

Let us first establish that both the FA and East models display dynamical heterogeneities. Consider the coarse grained spins $s_i(t; \Delta t) \equiv (\Delta t)^{-1} \int_0^{\Delta t} dt' \, \sigma_i(t + t')$. Fast and slow spins in the time window of width Δt at time t will correspond to low and high values of $s_i^2(t; \Delta t)$, respectively. The spatial distribution of $s_i^2(t; \Delta t)$ will determine the extent to which the system is dynamically heterogeneous. The heterogeneity made evident with this field depends on the coarse graining time. For Δt very short, only the trivial uncorrelated static structure is probed. The same is true for Δt much larger than the relaxation time where ergodicity is restored. For intermediate values of Δt, however, we may expect to see spatial structure in the $s_i^2(t; \Delta t)$. In Fig. 1 we show that this is indeed the case

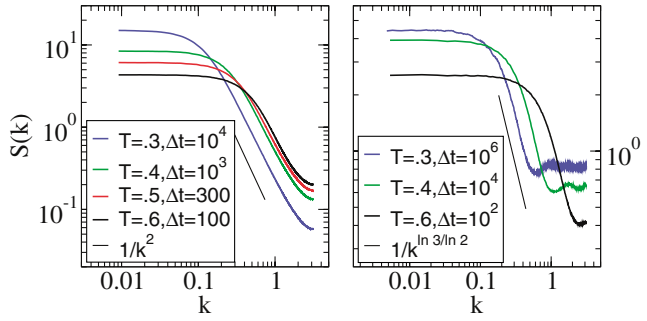

FIG. 1. Structure factor $S(k)$ of $s_i^2(t;\Delta t)$ for the FA (left) and East model (right). The $S(k)$ are the spatial Fourier transforms of the normalized correlation functions $\langle s_i^2(t;\Delta t)s_j^2(t;\Delta t)\rangle/\langle s_i^4(t;\Delta t)\rangle$ ($j = i, i \pm 1, \ldots$). $\langle\cdot\rangle$ indicates equilibrium ensemble average, so $S(k)$ is independent of t.

by plotting the structure factor, $S(k)$, for the field $s_i^2(t;\Delta t)$ calculated from simulations of the FA model (left panel) and the East model (right panel). We have used coarse graining times of about a fifth of the relaxation time, and simulations were performed using continuous time Monte Carlo [13] for systems of 10^5 spins averaged over 10^3 samples. For both models, the existence of a correlation length $\xi_{\Delta t}$ is clear. Moreover, $\xi_{\Delta t}$ grows, albeit slowly, with decreasing temperature and, thus, increasing relaxation time. For the FA model, the structure factor decays approximately as $S(k) \sim k^{-2}$ for large k. In the East model, at intermediate k, the structure factor goes as $S(k) \sim k^{-\ln 3/\ln 2}$. For larger momenta, the structure factor is oscillatory, a feature which becomes more pronounced with decreasing temperature.

In order to understand these behaviors, we study the generating functional for the trajectories of these systems. Consider a trajectory $\{\vec{\sigma}_t\} \equiv (\vec{\sigma}_0, \vec{\sigma}_1, \vec{\sigma}_2, \ldots, \vec{\sigma}_{\mathcal{T}})$, where $\vec{\sigma}_t \equiv (\sigma_{1t}, \sigma_{2t}, \ldots, \sigma_{Nt})$ denotes the configuration of the N spin system at time t. Each trajectory has a probability $P(\{\vec{\sigma}_t\})$, so that the total probability of going from $\vec{\sigma}_0$ to $\vec{\sigma}_{\mathcal{T}}$ is the weighted sum of such trajectories, $Z_{\vec{\sigma}_0,\vec{\sigma}_{\mathcal{T}}} \equiv \sum_{\{\vec{\sigma}_t\}} P(\{\vec{\sigma}_t\})$. This partition sum, $Z_{\vec{\sigma}_0,\vec{\sigma}_{\mathcal{T}}}$, can be written as [14]

$$Z_{\vec{\sigma}_0,\vec{\sigma}_T} = \sum_{\{\vec{\sigma}_t\}} e^{S_0[\{\vec{\sigma}_t\}]}\left[\prod_{it}\delta(h_{it})\right]e^{\Delta S[\{\vec{\sigma}_t\}]}. \qquad (1)$$

The first factor in the summand of (1) corresponds to the probability of a trajectory in the absence of dynamical constraints. Its action is just that of N noninteracting ferromagnetic Ising chains in uniform fields, $S_0(\{\vec{\sigma}_t\}) = \sum_{i=1}^{N}\sum_{t=0}^{\mathcal{T}-1}(J_{+--}\sigma_{it}\sigma_{it+1} + J_{-+-}\sigma_{it} + J_{--+}\sigma_{it+1} + J_{+++})$, where $J_{\mu\nu\varepsilon} \equiv \{\ln[1-\gamma\delta t(1-c)] + \mu\ln(1-\gamma\delta tc) + \nu\ln[\gamma\delta t(1-c)] + \varepsilon\ln(\gamma\delta tc)\}/4$, γ is a microscopic rate, and δt is the time step. The second factor in the summand of (1) embodies the kinetic constraint. Only trajectories which satisfy the condition $h_{it} = 0$ at all space-time points are allowed. If h_{it} is chosen to be a positive number when the constraint is not satisfied, then $\prod_{it}\delta(h_{it}) = \delta(\mathcal{H}) = e^{-\lambda\mathcal{H}}$, where $\mathcal{H} \equiv \sum_{it} h_{it}$ and $\lambda \to \infty$. The infinite coupling constant means that the space of allowed trajectories is that of the ground states of $\mathcal{H}$. The respective forms of $\mathcal{H}$ for the FA and East models are

$$\mathcal{H}_{\mathrm{FA}} = \sum_{it}(1-\sigma_{it}\sigma_{it+1})(1-\sigma_{i+1t})(1-\sigma_{i-1t})/8,$$

$$\mathcal{H}_{\mathrm{East}} = \sum_{it}(1-\sigma_{it}\sigma_{it+1})(1-\sigma_{i+1t})/4,$$

so that the ith term is zero unless the spin i flips and the facilitating spins are in the down state. The third factor in the summand of Eq. (1) accounts for preservation of norm and detailed balance. Trajectories which are allowed by the constraints have different probabilities than they would in the unconstrained case. In particular,

$$\Delta S_{\mathrm{FA}} = \sum_{it}(1-\sigma_{i+1t})(1-\sigma_{i-1t})(\tilde{J}_-\sigma_{it} + \tilde{J}_+)/4,$$

$$\Delta S_{\mathrm{East}} = \sum_{it}(1-\sigma_{i+1t})(\tilde{J}_-\sigma_{it} + \tilde{J}_+)/2,$$

where $\tilde{J}_\pm \equiv J_{\pm 00} + \ln[1-\gamma\delta t(1-c)e^{-\lambda}]/4 \pm \ln(1-\gamma\delta tce^{-\lambda})/4$. These expressions describe a proper dynamics for any λ. When $\lambda = 0$, the expressions reduce to the trivial model of independent spins with unconstrained dynamics. When $\lambda \to \infty$, they correspond to the FA and East models.

$\mathcal{H}$ and ΔS introduce competing spatial interactions in the space of trajectories. Those of $\mathcal{H}$ are strong, and they are ferromagnetic in the sense that they favor the clustering of like spins. In contrast, those of ΔS are weak and antiferromagnetic. Moreover, the scaling with distance of interactions in $\mathcal{H}$ is different than that for those in ΔS, so that nontrivial structure in the space of trajectories can be expected. In Fig. 2, we show samples of equilibrium trajectories for the unconstrained case (left), the FA (middle), and the East models (right), at $T = 1.0$. The difference between the constrained and unconstrained dynamics is striking. The trajectories in both the FA and East models display an extensive number of domains of down spins. These domains are the origin of the dynamical heterogeneities. Spins within these domains do not change, so,

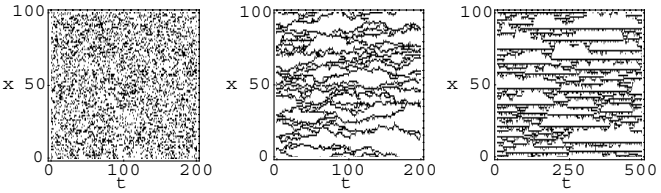

FIG. 2. Equilibrium trajectories at $T = 1.0$ for the unconstrained case (left), the FA (middle), and the East model (right). The vertical direction is space, corresponding to a spatial window of systems of size $L = 10^5$. The horizontal direction is time. Black/white corresponds to the up/down spins.

when coarse grained in time, they correspond to slow regions. To the extent that lowering temperature and thus energy in an atomic system coincides with decreasing facilitating spin concentration c, the structures observed in Fig. 2 coincide with the correlation observed in the simulation of supercooled liquids [3]. In particular, slow and fast dynamical heterogeneities correlate with regions of low and high energy, respectively. Since each column of the pictures in Fig. 2 is an equilibrium configuration of the noninteracting H, the structure seen in the trajectories is purely dynamical.

Down spins must form closed domains in a trajectory as a consequence of the local and causal nature of the dynamical constraints. This fact is apparent from the illustration in Fig. 3. A spin is able to flip only if an appropriate neighboring spin is in the up state at the same time. It therefore will have flipped up previously and/or it will flip down later. As such, a well-defined closed boundary must exist between regions of up and down spins. These boundaries are formed out of segments with shapes similar to those depicted on the top of Fig. 3, with the possibility of different slopes. In the FA model, the dynamical constraint is spatially symmetric, and four possible kinds of boundary segments are allowed, with the restriction that all the segments of the first (second) kind must be below those of the third (fourth) kind. It follows that spin down domains must form semiconvex polygons such as that pictured at the bottom left of Fig. 3. Namely, any spatial line cuts the boundary only twice. In the case of the East model, only the third and fourth boundary segments are allowed, which restricts the domains to shapes such as that pictured at the bottom right of Fig. 3. Since slow dynamical heterogeneities correspond to spatial projections of the compact space-time down spin domains, they are necessarily compact, while the converse is true for fast regions. This observation is in agreement with what is found with computer simulations of atomistic models [3].

The geometrical construction described above implies that spin down domains cannot penetrate each other.

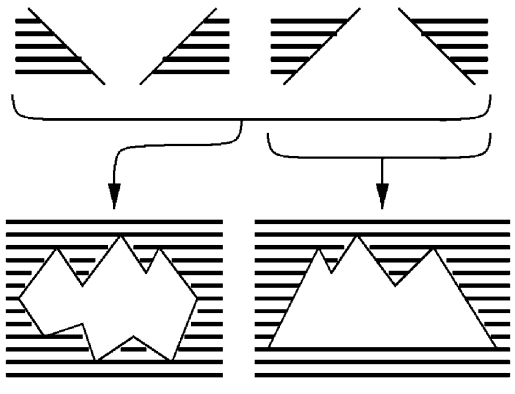

FIG. 3. Geometry of slow domains imposed by the dynamical constraints. Top: Allowed boundaries between regions of up (black) and down spins (white). Bottom: Shape of domains in the FA model (left) and in the East model (right).

Therefore, the set of trajectories maps to the configuration space of a two-dimensional mixture of polydisperse noninterpenetrating objects of all the possible shapes allowed by the dynamical constraints. This observation motivates a description of the dynamics in terms of $\rho(l,t)$, the density of domains of typical spatial size (height) l, and extension in time (length) t. The partition function for trajectories is then $Z \sim \int D\rho(l,t) \exp\{-\Omega[\rho(l,t)]\}$, where $\Omega[\rho(l,t)]$ is the free energy functional of this density. Whatever estimate is used for $\Omega[\rho(l,t)]$, it is crucial that it enforces the constraint,

$$\int dt\, \rho(l,t) = \rho_{\mathrm{eq}}(l) = ce^{-cl}. \tag{2}$$

This condition ensures that any spatial cut of the equilibrium trajectories is an equilibrium configuration. For a density functional theory, it provides an approximation to the effects of the antiferromagnetic interactions of ΔS.

In general, $\rho(l,t) = \rho(l|t)p(t)$, where $\rho(l|t)$ is the probability density of l conditioned on t, and $p(t)$ is the probability density of domains of length t. In the case of the FA model, a domain is bounded by the random walks of two up spins between successive encounters, and $\rho(l|t)$ can be obtained by standard arguments [15],

$$\rho(l|t) \sim l^2(Dt)^{-3/2} \exp(-l^2/Dt), \tag{3}$$

with $D \sim c$. If the domains were isolated, $p(t)$ would be given by the probability of first return of a random walker, which goes as $p(t) \sim t^{-3/2}$ for large t, leading to $\langle t \rangle \to \infty$, and to the formation of unbounded domains. This result, however, corresponds to only the ferromagnetic part of the interactions in trajectory space. It is frustrated by the condition (2). By combining (3) with (2), we have instead $p(t) \sim (\tau t)^{-1/2} e^{-\sqrt{t/\tau}}$, with $\tau \sim D^{-1}c^{-2} \sim e^{3/T}$. This result for τ is precisely the relaxation time in the FA model. The forms of $\rho(l|t)$ and $p(t)$ are verified in simulations of the FA model [14]. We also see that, in terms of the scaling variables $l^* = cl$ and $t^* = t/\tau$, the density $\rho(l^*, t^*)$ is independent of temperature. An illustration of these scaling relations is given in Fig. 4. The typical height of domains grows with the cubic root of the relaxation time, thus explaining the slow increase of the correlation length $\xi_{\Delta t}$ with decreasing temperature in the structure factors of Fig. 1. Slow growth and domains being mesoscopic

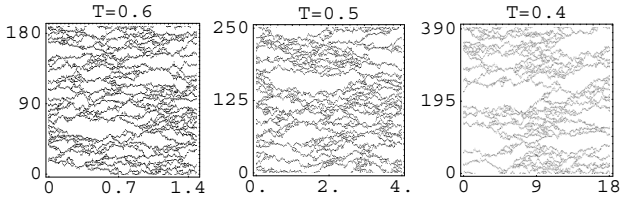

FIG. 4. Equilibrium trajectories in the FA model for $T = 0.6$, 0.5, 0.4. Vertical direction is space, which scales with $1/c$, and horizontal is time ($t/10^3$), which scales with τ.

rather than macroscopic are consistent with experimental observations [2]. Moreover, since the trajectories are extensive in interfaces, the form of the structure factor for large k corresponds to a spatial projection of Porod's law $S(k) \sim k^{-(d+1)}$ [16].

In the case of the East model, typical distances and times are related at low temperatures by a T dependent dynamic exponent $z(T) \sim 1/(T \ln 2)$ [12,17]. We therefore expect the conditional probabilities to be $\rho(l|t) \propto \exp[-l^{z(T)}/t]$. The condition (2) then leads to a stretched exponential form for the persistence function, $\int_t^\infty dt'\, p(t') \sim \exp[-(t/\tau)^{\beta(T)}]$, where $\beta(T) \sim 1/z(T)$ and $\tau \sim c^{-z(T)}$, in accordance with previous results [18]. In this case, $\xi_{\Delta t}$ increases even more slowly with decreasing T than in the FA model. The geometry of the domains also explains the differences in the FA and East structure factors shown in Fig. 1. In contrast to the FA case, where neighboring domains can be compressed to the point of contact, the boundary between domains in the East model cannot be formed just by a single line of up spins in space-time. Instead, to decrease energy and thus increase probability, the boundary is wet by smaller domains, ideally as in Fig. 5. This structure has fractal dimension $d_f = \ln 3/\ln 2$, and gives rise to the behavior $S(k) \sim k^{-d_f}$ at intermediate momenta. At larger k, $S(k)$ probes the granular structure of the boundary, and thus exhibits the oscillatory behavior shown in Fig. 1 [19].

The ideas presented here in detail for the FA and the East models generalize to higher dimensions provided the dynamical constraints are causal and local, so that excitations favor the creation of neighboring excitations. In general, dynamical constraints will appear only below a crossover temperature T_x or above a corresponding packing fraction. This can be incorporated into our description by allowing the coupling λ to be a function of temperature or packing fraction, increasing with decreasing T or increasing packing. The temperature T_x will then coincide with the so-called "landscape" temperature [1].

The domains that thus appear for $T < T_x$ and grow with further decrease in T can lead to a broken symmetry. Consider, for example, the partition function $Z_T(q, \mathcal{T})$ for trajectories between configurational fluctuations with overlap q at time difference $\mathcal{T}$, $Z_T(q, \mathcal{T}) \equiv \sum_{\{\vec{\sigma}_0, \vec{\sigma}_\mathcal{T}\}} \hat{\rho}(\vec{\sigma}_0) Z_{\vec{\sigma}_0, \vec{\sigma}_\mathcal{T}} \delta(q - N^{-1} \sum_i \delta\sigma_{i0} \delta\sigma_{i\mathcal{T}})$, where $\delta\sigma_{it} \equiv \sigma_{it} - \langle\sigma\rangle$, and $\hat{\rho}$ is the Boltzmann distribution. Since $Z_T(q, \mathcal{T})$ is proportional to the number of such trajectories, it is natural to write it as $Z_T(q, \mathcal{T}) \propto \exp[N \omega_T(q, \mathcal{T})]$, where $\omega_T(q, \mathcal{T})$ is the entropy density in trajectory space. It is approximately the entropy of mixing of the slow domains in trajectory space. At values of T for which the temporal extension of these domains is much smaller than $\mathcal{T}$, $\omega_T(q, \mathcal{T})$ is extensive in time, and $Z_T(q, \mathcal{T})$ is peaked at $q = 0$. In this case, correlation functions are exponential.

Nonzero overlap is probable, i.e., $Z_T(q, \mathcal{T})$ is peaked at finite q, only when $\mathcal{T}$ is comparable to or smaller than the length of typical slow domains. As temperature is decreased, the size of these domains increases, constricting the available trajectory space. At a low enough temperature, we may therefore expect $\omega_T(q, \mathcal{T})$ to become subextensive, leading to a probable finite q throughout a relatively large range of $\mathcal{T}$. This change in behavior of $\omega_T(q, \mathcal{T})$ signals a dramatic change in the number of available trajectories and a corresponding onset of dynamical arrest. In this picture, therefore, the glass transition coincides with an entropy crisis in trajectory space, rather than in configuration space.

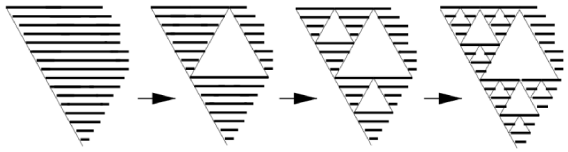

FIG. 5. Energetically favored wetting of the boundary of a spin down domain in the East model.

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[1] C. A. Angell, Science **267**, 1924 (1995); P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).
[2] See, e.g., H. Sillescu, J. Non-Cryst. Solids **243**, 81 (1999); M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).
[3] See, e.g., D. Perera and P. Harrowell, Phys. Rev. E **54**, 1652 (1996); C. Donati *et al.,* Phys. Rev. E **60**, 3107 (1999).
[4] W. Götze and L. Sjogren, Rep. Prog. Phys. **55**, 241 (1992).
[5] T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. Lett. **58**, 2091 (1987); T. R. Kirkpatrick and P. Wolynes, Phys. Rev. B **36**, 8552 (1987).
[6] S. Franz *et al.,* Philos. Mag. B **79**, 1827 (1999).
[7] X. Xia and P. G. Wolynes, Proc. Natl. Acad. Sci. U.S.A. **97**, 2990 (2000); Phys. Rev. Lett. **86**, 5526 (2001).
[8] H. E. Castillo *et al.,* Phys. Rev. Lett. **88**, 237201 (2002).
[9] R. G. Palmer *et al.,* Phys. Rev. Lett. **53**, 958 (1984).
[10] G. H. Fredrickson and H. C. Andersen, Phys. Rev. Lett. **53**, 1244 (1984).
[11] J. Jäckle and S. Eisinger, Z. Phys. B **84**, 115 (1991).
[12] M. R. Evans, J. Phys. Condens. Matter **14**, 1397 (2002).
[13] M. E. J. Newman and G. T. Barkema, *Monte Carlo Methods in Statistical Physics* (Oxford University Press, Oxford, 1999).
[14] D. Chandler and J. P. Garrahan (to be published).
[15] M. E. Fisher, J. Stat. Phys. **34**, 667 (1984).
[16] A. J. Bray, Adv. Phys. **43**, 357 (1994).
[17] P. Sollich and M. R. Evans, Phys. Rev. Lett. **83**, 3238 (1999).
[18] A. Buhot and J. P. Garrahan, Phys. Rev. E **64**, 021505 (2001).
[19] The idea of wet interfaces in configuration space appears in a recent equilibrium theory of glass formers [7], but it is difficult to see a connection between that idea pertaining to statics and the wet interfaces of trajectory space discussed here.