Kinetic glass behavior in a diffusive model

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Three properties of the Edwards-Anderson model with mobile bonds are investigated which are characteristic of kinetic glasses. First is two-time relaxation in aged systems, where a significant difference is observed between spin and bond autocorrelation functions. The spin subsystem does not show two-time behavior, and the relaxation is stretched exponential. The bond subsystem shows two-time behavior, with the first relaxation nearly exponential and the second similar to the spin one. Second is the two-temperature behavior, which can be tuned by bond dilution through the full range reported in the literature. Third is the rigid-to-floppy transition, identified as a function of bond dilution. Simple Glauber Monte Carlo evolution without extraneous constraints reproduces the behavior of classical kinetic simulations, with the bond (spin) degree of freedom corresponding to configurational (orientational) disorder.

Kinetic glasses are long-lived nonequilibrium systems of considerable technological importance. The basic insight into their microscopic origin was provided by Kauzmann:[1] there is a slowdown in configurational rearrangement, caused by obstruction of kinetic motion. Despite a consensus in this view and advances in theoretically enlightened phenomenology of known glass formers,[2,3] there is at present no unifying view of vitrification. This is in remarkable contrast with its practical simplicity: put honey into the freezer or let egg whites dry, and a kinetic glass appears without effort.

Out of equilibrium, subdominant microscopic correlations multiply, and finding the one responsible for macroscopic structural arrest is even more difficult than doing so for equilibrium transitions. Simulations of abstract model systems have developed into an important tool to extract generic behavior in such a situation, although of course they do not substitute for direct physical insight into real cases.[4–8] While many models have been found which exhibit some kind of slowed-down response, their relationship with one another, and with physical reality, is still the subject of continuous investigation.

Molecular dynamics (MD) simulations of two-component Lennard-Jones fluids are intuitively closest to real systems.[9] They have been compared with the predictions of mode-coupling theory,[10–12] a high-temperature microscopic approach, which depends on the explicit introduction of a three-particle scattering term.

More abstract, and schematic, are constrained kinetics simulations.[13] These are lattice gas models in which updates are not dictated by pure coupling to the thermostat, but are supplemented with special rules, standing in for higher-order correlations, which otherwise cannot be included in a random walk.

A separate class of models, sometimes used to understand vitrification, are models of spin glasses.[14] It requires some abstraction, or leap of faith, to identify the former microscopic physical spin with a hypothetical "mesoscopic" order parameter, representative of the slowed-down configuratonal rearrangement. Nevertheless, particular quenched systems have remarkable parallels with other models of kinetic vitrification, the reasons for which have lately become better understood.[15–18]

Monte Carlo (MC) simulations play an important role in many of these investigations. In the time domain, they simplify joint probabilities as $p(x_1,t_1;x_2,t_2;x_3,t_3) = p(x_1,t_1;x_2,t_2)$ for times $t_1 > t_2 > t_3$, since the underlying random walk has no memory. Here x_i is the system configuration and the times are measured with a resolution $\Delta\tau$ shorter than the thermalization time, but long enough for all correlations, retaining information of the initial conditions, to die out, except the two-time ones. Such a random walker is a minimal model of fluctuations in a concrete thermostat. Since physical three-particle correlations are generally three-time correlations, in ensemble language one may say MC simulations take two-particle physical correlations as input and build higher correlations statistically as output, on scales coarser than $\Delta\tau$.

In this work we address the issue as to how much needs to be said physically to obtain vitrification statistically. From this point of view, all of the approaches above suffer from some surfeit. Full Newtonian evolution does all the work physically, with no lower limit on $\Delta\tau$ in principle. Mode coupling has a three-particle kernel as input. Constrained kinetics has memory, since an update can overrule the thermostat. Conversely, to enforce the rules by the energy balance requires multibody forces, stronger than two-body. Random quenched disorder cannot be the input, since the comparatively well-organized vitreous disorder[19,20] is a consequence of evolution and by a Hamiltonian which has an ordered ground state.

Our main result is that less needs to be said than suspected so far. We apply a natural annealment dynamics to the Edwards-Anderson model for spin glasses.[21] While the equilibrium state of the model was described[22,23] long ago, it turns out the approach to equilibrium is meaningful for kinetic glasses. When nearest-neighbor bond diffusion is added to spin flips, vitreous delay appears in the ordinary random walk. The difference with most other theoretical approaches is that there are two different degrees of freedom in interaction, so the physical correlation responsible for vitrification appears to be a second-order off-diagonal term (mixed in conjugate fields). In contrast to other spin-glass models, it turns out that the bond, not spin, degree of freedom corre-

sponds to the configurational one. Bond movement gives the model an unexpected "off-lattice" character.

We study the two-dimensional short-range Edwards-Anderson model,[21] as before,[24,25] at $B=0$:

$$H = - \sum_{\langle i,j \rangle} J_{ij}S_iS_j - M \cdot B, \qquad (1)$$

where $S_i = \pm 1$ and we shall use both a Gaussian distribution of J_{ij} with half-width J and a bimodal $\pm J$ distribution. We investigate a two-dimensional lattice of size 500×500 with Glauber dynamics. Between each two spin trials (flips) is a bond trial: a positive and negative bond impinging on the same site, and chosen at random, are allowed to exchange places, subject to the same criterion as the spin trials. The concentration p_{AF} of antiferromagnetic (AF) bonds is taken to be 50%.

Bond updates quickly anneal the sample, and after a transient of ~ 100 updates per site it enters a long-lived state with glasslike dynamics[24] and a second, much longer relaxation time.[36] The "glassiness" of the metastable spin state is not topological: the underlying bond distribution has low frustration at any instant in time, so much so that it can be mapped onto a disordered ferromagnet,[26] with a finite transition temperature.[27] Bond diffusion nevertheless prevents the spins from settling into any given ordered state, leading to a decay of correlations even below the hidden phase transition.

When bonds move, the model theoretically evolves towards an annealed equilibrium.[22,23] However, as long as bond updates are kept local, their diffusion is not very efficient in finding the optimal configurations, despite efficient annealment in energy. We do not establish directly that the configurations are suboptimal, but when bond hops of arbitrary range are allowed, the configurations obtained are quite different than those found here, having a strong tendency to dropletlike phase separation.[28] Although equilibration is delayed from the point of view of correlations, evolution passes only through a small subclass of energetically favorable states, though bond updates imply that not only the equilibrium spin manifold is being sampled. This is similar to the situation in real kinetic glasses, while in spin glasses the average configuration energy is much higher.[24] We find that isotropic spatial correlation functions fall off rapidly within a few lattice spacings, in accordance with recent thinking.[29]

In Fig. 1, we show the autocorrelation functions of two copies of an aged sample, for spins given by

$$C(t) = \frac{1}{V} \sum_{i=1}^{V} \langle S_i(t_0)S_i(t_0+t) \rangle, \qquad (2)$$

and similarly for bonds, for the Gaussian distribution. "Aged" means t_0 long enough for no transients to survive after quenching, so the system is in the long-lived metastable state. The spin and bond autocorrelation functions are different. The spin autocorrelation decays as a stretched exponential $\exp[-(t/\tau)^\beta]$, which is the usual behavior in disordered spin models. The bond autocorrelation shows obvious two-time behavior, with a plateau separating the fast, closer to exponential decay ($\beta \approx 0.9$), from a slow, stretched exponen-
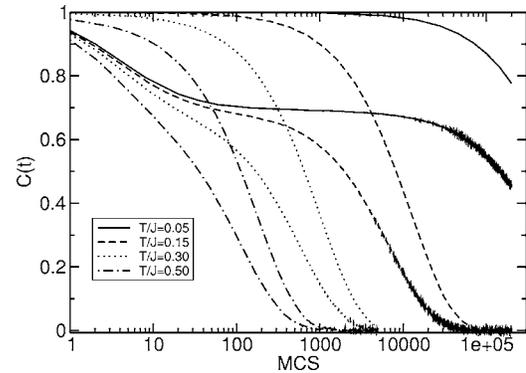

FIG. 1. Spin and bond autocorrelation functions in an aged sample. In each pair of curves, the bond autocorrelation is the one with the plateau at intermediate times. The solid, dashed, dotted, and dot-dashed curves correspond to temperatures $T/J=0.05$, 0.15, 0.30, and 0.50, respectively. Each Monte Carlo step (MCS) consists of a spin and a bond update per site.

tial component ($\beta \approx 0.8$). The plateau is characteristic of configurational relaxation in kinetic glasses and observed in classical simulations of binary systems.[9] The fast component "shakes out" those configurations which may be relaxed locally, while the slow component refers to "locked-in" ones, whose relaxation is impeded by intermediate-range correlations. We recall[1] that the orientational degree of freedom is generally not affected by the glass transition, being slowed down already above T_g. As the temperature is lowered, the spin and bond responses decouple ever more, which is visible in the figure as an extended plateau in the bond response. This is also analogous to real systems, where there are more translations relative to rotations the deeper one goes into the glassy regime.[3] If spin updates are discontinued, the bond response loses the second relaxation component, and the plateau then extends to the longest times investigated. The reason is that fixed annealed spins create barriers of satisfied bonds, which mobile bonds find difficult to cross, so the system is broken into uncommunicating regions. When spin updates are allowed, these regions themselves evolve slowly, accounting for the second relaxation time. Rare spin updates at low temperature correspond to activated hops in constrained kinetics, absent from mode coupling, which similarly retains the plateau *ad infinitum*.

Next, we investigate how the interplay of the two degrees of freedom affects departures from the fluctuation-dissipation theorem (FDT), expected in the same context.[14] Here we plot $C(t)$ for spins [Eq. (2)] against the spin susceptibility normalized by temperature:

$$T\chi(t) = \frac{T}{V} \lim_{\Delta B \to 0} \left. \frac{\Delta M}{\Delta B} \right|_{t_0+t}, \qquad (3)$$

for $\Delta B(t_0+t)$ a step function at $t=0$. Although such violations are well established for models with quenched disorder, it is not clear that annealing caused by bond diffusion will not quickly lead to equilibration. In fact, it does not, and for the same Gaussian bond distribution as above, we obtain in Fig. 2 the "many-temperature" violation curve, known from pre-
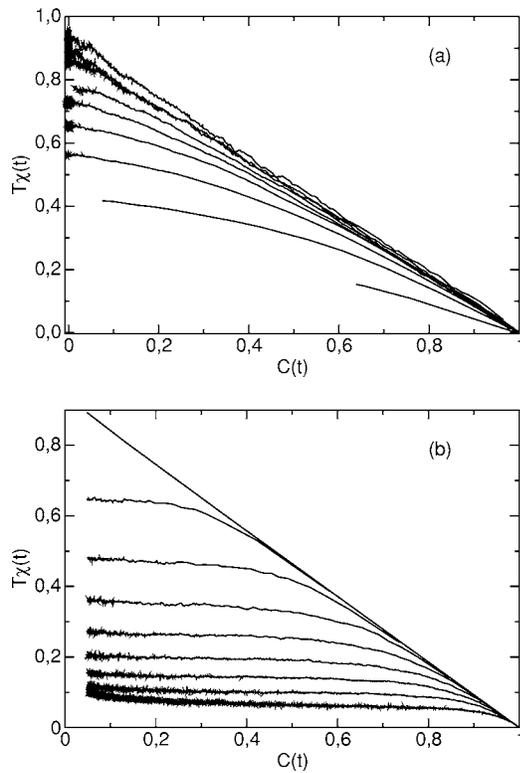
FIG. 2. Violations of the fluctuation-dissipation theorem for an (a) Gaussian and (b) bimodal distribution. (a) Bottom to top: T/J $=0.05, 0.01, 0.015, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6$, respectively. (b) Top to bottom: $p_0 = 100\%, 90\%, 80\%, 70\%, 60\%, 40\%, 30\%, 20\%$, 10%, respectively, at $T/J = 0.2$.

vious investigations of spin models and observed in some experiments.[30] Since the model is only coupled to a simple thermostat, the violation is evidently generated internally.

Even more interesting is the case of the $\pm J$ bond distribution. We introduce bond dilution through a fixed proportion p_0 of bonds with $J=0$. For $p_0=1$, an ordinary paramagnet, the FDT is evidently observed. As the dilution is reduced there are again violations, but instead of many temperatures, the "two-temperature" shape appears, familiar from MD simulations of two-sphere models.[31] However, in the $\pm J$ case there is no plateau in the bond response, indicating that a fine energy scale is needed for the creation of inherent structures.

The rigid-to-floppy transition has emerged as an important paradigm in a wide range of glass formers.[4,7] The basic idea[19,20] is that a glassy system can be either overdetermined (rigid) or underdetermined (floppy), with some ideal "unstrained-but-stiff" configuration in the middle. Figure 3 shows this model's version of the rigid-to-floppy transition. It gives the fraction p of spins in a zero local field ("indifferent") as a function of bond dilution p_0. As $p_0 \to 1$ (paramagnet), all spins become indifferent: $p(1)=1$ is the extreme floppy limit. However, the curves $p(p_0)$ also show a sharp minimum at a finite p_0. This is not difficult to understand: an indifferent spin in an undiluted system occurs wherever two positive and two negative bonds impinge on the same site. It can be oriented by putting a single zero bond in place of one of them. Hence the number of indifferent spins initially decreases with dilution. The minimum corresponds to the least-
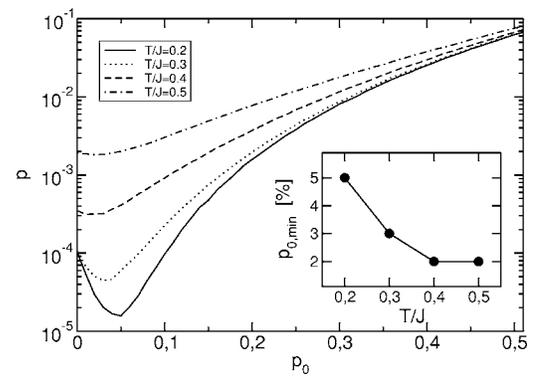

FIG. 3. Rigid-to-floppy transition. The fraction of indifferent spins is shown as a function of bond dilution. The minimum corresponds to the least-strained system. The inset shows the minimum as a function of temperature.

strained state in the sense above: to the left, p increases because there are too many constraints and, to the right, because there are too few. The trend of the minimum with temperature is also reasonable; one expects that the lower the temperature of the quench, the more zero bonds are needed to effectively unstrain the system.

Experimental evidence suggests that vitrification is a two-stage process. The first stage is dominated by quantum mechanics—i.e., chemical bonding—which determines what is "locally favorable." Once the first stage has given rise to entities at the scale of $\sim 1-10$ nm, their further evolution may be imagined in classical or geometrical terms. Most investigations study this second stage of vitrification, including the present work. The paradigm of a macroscopic internally generated potential, borrowed from phase transitions, is evidently sensible, since something is certainly precluding window glass from free flow. However, the universally observed liquid structure factor[32] means this potential varies in a way irreconcilable with a divergent length scale. Thus the notion of an internally generated field is more general than that of a phase transition. In addition, macroscopic approaches,[33,34] based on dynamic scaling ideas, indicate that the time scales of the internal that field are finite as well.

Given that classical simulations do not at present correspond to any well-defined physical objects—indeed the "configurational degree of freedom" is as intuitive a concept today as when its importance was first noted[1]—it is reasonable to ask whether their success in reproducing particular observed aspects of glassy dynamics comes from the side of the thermostat, rather than being a higher-order effect of precise mechanical evolution. From this point of view, ordinary Monte Carlo simulations are a fundamental tool. They build up high-order correlations without microscopic trajectories, enabling one to study how close to equilibrium glasses really are.

The present work obtains a vitreous response with a minimal disturbance of the annealed spin equilibrium and the minimal physical input to date. All that seems required is dynamical evolution of two different degrees of freedom with a local interaction. Hence vitrification in the model is due to a second-order off-diagonal correlation, rather than a

higher-order diagonal one, typical of models with one kind of degree of freedom. It raises the possibility that the same could be true in real systems, such as large molecules, the interdependence of translation and rotation (both kinetic) in a log-jam coming readily to mind. The idea of configurational rearrangement agrees with the interpretation of off-diagonal correlations as conditional probabilities: a particle cannot move *unless* another one does. However, the definite identification of the correlation involved depends on finding a natural conjugate field, a nontrivial task, even in a simple model such as ours. Reproducing MD by pure MC[35] simulations is very similar to the present result; we have removed from it one more physical prop, the realistic potential, so it only seems important that there be two kinds of little balls. This fits well with binary (and ternary) mixtures being easier to vitrify than pure substances.[7,8]

Another issue is that the model has a hidden ferromag-

netic transition.[26,27] It is analogous to the avoided crystallization in vitreous liquids. The bond autocorrelation implies that discontinuing spin updates triggers a true transition, as is known to happen in mode coupling.

To conclude, we have given a concrete example of vitrification in a simple model, where it is by default due to a second-order off-diagonal correlation. The appearance of vitreous slowdown in the bond response of the Edwards-Anderson model when bond diffusion is introduced points to its kinetic origin. We believe this type of correlation may be responsible for vitrification in at least some real glasses, where it would provide the minimal physical content of the configurational degree of freedom.

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[36] Figure 6 of Ref. 24 refers to spins only and begins at the quench, unlike Fig. 1 here, taken long after the quench.