Crossover from fragile to strong glassy behavior in kinetically constrained systems

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We show the existence of fragile-to-strong transitions in kinetically constrained systems by studying the equilibrium and out-of-equilibrium dynamics of a generic constrained Ising spin chain that interpolates between the symmetric and fully asymmetric cases. We find that for large but finite asymmetry the model displays a crossover from fragile to strong glassy behavior at finite temperature, which is controlled by the asymmetry parameter. The relaxation in the fragile region presents stretched exponential behavior, with a temperature dependent stretching exponent that is predicted. Our results are confirmed by numerical simulations.

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Glasses are everywhere in nature. It is difficult to find a liquid that when supercooled does not form the amorphous, microscopically disordered solid we call a glass. The salient feature of supercooled liquids is their dramatical slowing down with decreasing temperature, signaled by the increase of their relaxation times and viscosities by several orders of magnitudes in a temperature range of a few decades. For reviews see Refs. [1–3].

Given the generic nature of the glassy state, universal principles for the classification of glass-forming materials are of paramount importance. Central to this is the concept of fragility [4,1], which measures the speed with which viscosity and relaxation times grow as a system approaches the glass transition temperature. Liquids that display Arrhenius behavior, that is, the logarithm of their viscosity or relaxation time grows linearly with inverse temperature, are classified as ''strong'' [4,1], as, for example, network liquids like SiO_2 and GeO_2, and define one of the extremes of the classification by fragility. Most liquids, however, behave in a non-Arrhenius manner, and the larger the departure from Arrhenius behavior, the more ''fragile'' [4,1], the most fragile liquids, which define the second extreme in fragility, being polymeric in nature. An exception to this classification is supercooled water [5]: at temperatures close to its melting point it behaves as extremely fragile, while near the glass transition it is very strong. Supercooled water has a fragile-to-strong transition.

Some of the simplest systems that display the slow cooperative relaxation characteristic of glasses are the facilitated kinetic Ising models, first introduced by Fredrickson and Andersen [6], in which glassiness is not a consequence of either disorder or frustration in the interactions, but of the presence of kinetic constraints in the dynamics of the system. Depending on whether the constraints are isotropic [6], or fully directed [7], these models may behave as strong or fragile glasses, and the low temperature dynamics can be understood in terms of activation over energy barriers [8–11]. They are particularly useful in the study of activated processes, which become highly relevant for supercooled liquids near the glass transition, but are not taken into account by approximations like mode-coupling theory [12] or mean-field models [13,14].

The purpose of this paper is to show that fragile-to-strong transitions also occur in kinetically constrained systems. We prove this for the simplest case of the one spin facilitated Ising chain. We study a generalization of the kinetically constrained Ising chain that interpolates between the cases of symmetric [6] and fully asymmetric constraints [7]. We show that for large but finite asymmetry the model displays a fragile-to-strong crossover at finite temperature. The crossover temperature is controlled by the asymmetry parameter, which also determines the largest time scale and energy barrier of the problem. The relaxation in the fragile region presents stretched exponential behavior, with a temperature dependent stretching exponent that is obtained analytically. We performed extensive numerical simulations to confirm our results.

We consider a chain of Ising spins $\sigma_i \in \{0,1\}$ ($i=1,\ldots,N$), with periodic boundary conditions, and Hamiltonian $H=\Sigma_i \sigma_i$. The dynamics is restricted to single flips of spins that have at least one nearest neighbor in the up state. The rates for the possible transitions are in general different depending on whether the up neighbor is on the right or left, and are given by

$$11 \overset{b}{\rightarrow} 01, \quad 01 \overset{b\epsilon}{\rightarrow} 11, \quad 11 \overset{1-b}{\rightarrow} 10, \quad 10 \overset{(1-b)\epsilon}{\rightarrow} 11, \qquad (1)$$

where $b \in [0,1]$ and $\epsilon \equiv \exp(-1/T)$. Detailed balance is obeyed, and the stationary distribution is the Boltzmann distribution at temperature T for the Hamiltonian H. The parameter b sets the degree of asymmetry of the kinetic constraints. The limiting values $b=1/2$ and $b=0$ (or 1) correspond to the Fredrickson-Andersen (FA) model [6] and the asymmetrically constrained Ising chain (ACIC) [7], respectively.

Due to the noninteracting nature of the Hamiltonian the thermodynamical properties of the model are trivial, and are the same for any b. The energy density is given by the concentration c of up spins (or ''defects''), which in equilibrium becomes $c_{\rm eq}=\epsilon/(1+\epsilon)$. At low temperatures c is very small, and since defects facilitate the dynamics, the system slows down: isolated up spins are locally stable and the system has to overcome energy barriers to evolve.

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In contrast with the statics, the low temperature dynamics depends strongly on the value of b (except at T strictly zero [11]). In the symmetric limit $b=1/2$, which corresponds to the FA model, isolated defects can diffuse to the left (resp. right) by means of processes (ii) and (iii) [resp. (iv) and (i)] of Eq. (1). Each move requires the temporary creation of one defect, so there is a single activation barrier to diffusion $\Delta E=1$. This constancy of the energy barriers implies that relaxation times follow the Arrhenius law $\tau_{\rm FA}\sim\exp(\Delta E/T)$, characteristic of strong glass behavior [8,11]. The decay of the concentration of up spins, in the out of equilibrium regime, is well approximated by the coagulation process $A+A\to A$, which means that the typical lengthscale grows as $l\sim(t/\tau)^{1/2}$ [8]. The situation in the asymmetric limit $b=0$ or 1, which corresponds to the ACIC model [7], is very different. Here the activated diffusion mechanism of the symmetric case is absent: a defect at a distance $2^{n-1}<d\leqslant 2^n$ from the nearest defect (in the direction of the constraint) has to cross a barrier $\Delta E=n$ to move [10], i.e., barriers grow with the logarithm of the size of relaxing regions. This means that typical length scales grow as $l\sim t^{T\ln 2}$, which leads to a relaxation time at low temperatures of the form $\tau_{\rm ACIC}\sim\exp(1/T^2\ln 2)$ [10]. This is the Bässler law [15,2] used as an alternative to the Vogel-Fulcher equation [1,2] to represent fragile behavior. The absence of a finite temperature singularity is consistent with the trivial statics of the ACIC model.

We now consider the behavior at intermediate values of the asymmetry b. We first focus on the relaxation towards equilibrium after a quench from infinite temperature. When b is not far from the symmetric limit $b=1/2$, the rates of Eq. (1) for reactions to the left and right are comparable and the symmetric diffusive mechanism is still effective: the behavior is essentially that of the FA model. The region of large but finite asymmetry, that is, when b (or $1-b$) is small, is more interesting. In this case rates (i) and (ii) of Eq. (1) are very much suppressed respect to rates (iii) and (iv) (or vice versa), the system can only make use of the asymmetric mechanism to relax, and behaves like the ACIC. The time scales associated with the asymmetric process, however, grow as the relaxing regions become larger: the time scale for relaxation of a region of length $2^{n-1}<d\leqslant 2^n$ is $\tau_A^{(n)}\sim\epsilon^{-n}$, and the dynamics takes place in stages labeled by n [10]. The time scale for the symmetric process, $\tau_S\sim[b(1-b)\epsilon]^{-1}$, is large, but not infinite, except in the ACIC limit, and in contrast to the asymmetric one does not grow with increasing length. This means that eventually τ_S becomes comparable to $\tau_A^{(n)}$ for some value of n. This defines the last stage of asymmetric relaxation n^* before the system switches to symmetric behavior:

$$n^*\sim 1-T\ln[b(1-b)]. \tag{2}$$

In Fig. 1 we show the decay of defect concentration c (the energy density of the system) as a function of time t after a quench from an initial state at $T_0=\infty$ to a low temperature $T=1/6$, for several values of the asymmetry b. For the $b=0$ ACIC limit, at least four plateaus in the concentration are visible, which correspond to the different stages in the dynamics. The number of plateaus decreases with increasing b in accordance with Eq. (2): there are three plateaus for $b=10^{-5}$($n^*=2.9$), two for $b=10^{-4}$ and 10^{-3} ($n^*=2.5$ and 2.2), and only one for $b=10^{-2}$ and 1/2 ($n^*=1.7$ and 1.1), the latter being the FA limit. The inset shows how the typical length scale $l\equiv 1/c$ grows with time. While in the ACIC case it follows $t^{T\ln 2}$ (lower dashed line), for all the nonzero values of b the system eventually switches to the diffusive $t^{1/2}$ behavior of the FA case (upper dashed line).

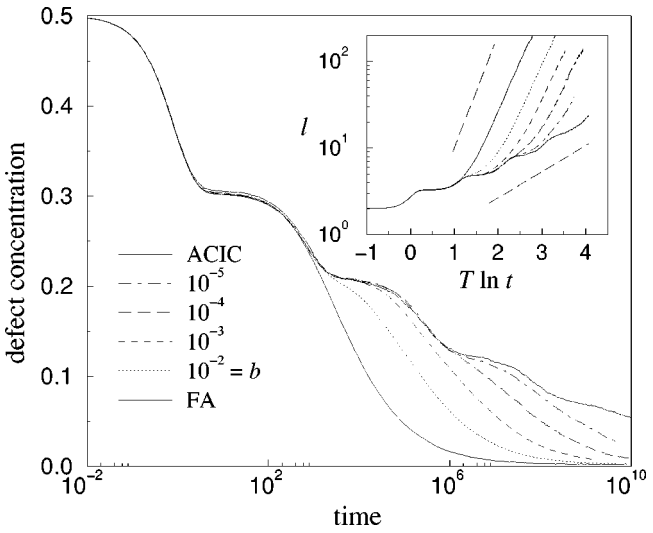

FIG. 1. Defect concentration c as a function of time t after a quench from infinite temperature to $T=1/6$, for values of the asymmetry $b=1/2$ (FA model), 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, and 0 (ACIC model). Inset: typical length scale $l\equiv 1/c$ against scaled time variable $T\ln t$. The upper dashed line corresponds to $t^{1/2}$ and the lower one to $t^{T\ln 2}$. Simulations were performed using a continuous time Monte Carlo/Metropolis algorithm [16,17] for a system of 10^5 spins.

Let us turn to the implications that a finite asymmetry has on the relaxation time of the system. For arbitrary b, the symmetric and asymmetric processes compete. The relaxation time scale is given by $\tau\sim(\tau_S^{-1}+\tau_{\rm ACIC}^{-1})^{-1}$, assuming that the corresponding rates add up. The factor $b(1-b)$ in the symmetric relaxation time scale τ_S can be interpreted as an entropic barrier: $\tau_S\sim\exp\{[\Delta E-T\ln b(1-b)]/T\}$, where $\Delta E=1$. Notice that this ''free energy'' barrier is precisely n^* of Eq. (2). Thus, the suppression of the symmetric mechanism due to b decreases with decreasing temperature. The consequence of this on the relaxation time for a fixed value of b is the following. At higher temperatures the asymmetric process dominates, $\tau\sim\tau_{\rm ACIC}$, and the system displays fragile relaxation. At lower temperatures, the symmetric process becomes dominant, $\tau\sim\tau_S$, and the behavior is strong. The crossover temperature for this fragile-to-strong transition is determined by b,

$$T_c\sim\frac{1-\sqrt{1-4\ln[b(1-b)]/\ln 2}}{2\ln[b(1-b)]} \tag{3}$$

corresponding to $\tau_S\sim\tau_{\rm ACIC}$.

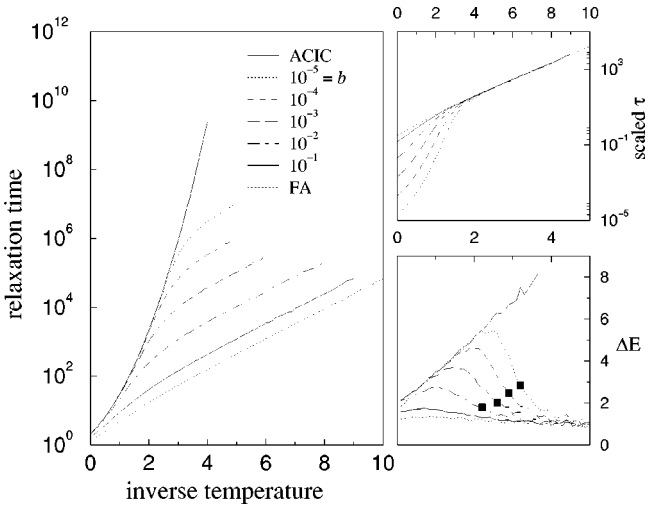

FIG. 2. Equilibrium relaxation time τ as a function of inverse temperature $1/T$, for values of the asymmetry $b=1/2$ (FA model), 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, and 0 (ACIC model). Top right: rescaled time $b(1-b)\tau$ against $1/T$. Bottom right: effective activation barrier ΔE as a function of $1/T$. Black squares on the curves indicate the values of $1/T_c(b)$ expected from Eq. (3). Simulations were performed for system sizes that varied from 10^5 for high temperatures to 5×10^6 for low ones, and data points were averaged over 20 runs.

In Fig. 2 we show the equilibrium relaxation time τ as a function of inverse temperature $1/T$. Given that the static properties of the system are known exactly it is simple to construct low temperature equilibrium configurations by randomly drawing each spin independently with the equilibrium probabilities $p(\sigma)=(1-\sigma)(1-c_{\rm eq})+\sigma c_{\rm eq}$. This allows to study the equilibrium dynamics down to really low temperatures in contrast with most glassy systems where only out of equilibrium quantities are accessible. We obtain the relaxation time through the connected equilibrium autocorrelation function, $C(t)\equiv N^{-1}\Sigma_i\langle\sigma_i(t)\sigma_i(0)\rangle-c_{\rm eq}^2$, where τ is defined by $C(\tau)=e^{-1}C(0)$. Alternative definitions of the equilibrium relaxation time scale give similar results. The figure shows the following features: (i) in the $b=0$ ACIC limit, the relaxation time has the fragile behavior $\tau_{\rm ACIC}$ for all temperatures, as expected; (ii) for small b, τ crosses over from fragile $\tau_{\rm ACIC}$ at higher temperatures to strong τ_S behavior at lower ones, the crossover taking place around T_c given by Eq. (3) (see bottom-right panel of Fig. 2); (iii) for larger b the fragile region shrinks, and disappears completely at the FA limit $b=1/2$. The displacement of the curves in the strong regime is due to the entropic barrier. Rescaling the relaxation time by $\tau\to b(1-b)\tau$ makes them collapse, as shown in the top-right panel of Fig. 2. The bottom-right panel gives the effective activation barrier $\Delta E\equiv d\ln\tau/d(1/T)$. The crossover here appears as a change from the linear growth in the ACIC to the constant barrier of the FA model. The crossover is sharper the smaller b. The high temperature behavior of τ is exponential in $1/T$, which gives the offset in the straight line for $b=0$, and becomes irrelevant at low temperatures. The slope of ΔE is about 1.7 rather than 2/ln2. This difference is due to the nonexponential nature of the autocorrelation, which does not affect the $1/T^2$ behavior of the log of τ.

The fragile-to-strong crossover can also be observed in the behavior of equilibrium dynamical quantities. The simplest one to study is the equilibrium persistence, $P(t)\equiv N^{-1}c^{-1}\Sigma_i\langle\Pi_{t'=0}^{t}\sigma_i(t')\rangle$, which measures the fraction of defects of the initial configuration that have never flipped between times 0 and t. It is closely related to the equilibrium autocorrelation $C(t)$, but is free from the problem of the recurrence of defects that makes the analysis of the latter more tricky, particularly in one dimension.

As mentioned before, in the asymmetric limit, the probability to flip a defect depends on the distance to the nearest defect in the direction of the constraint. In equilibrium, the probability distribution of these distances is independent of time. The persistence may be then approximated by the sum of the independent exponential relaxation of defects at different distances from their neighbors, $P(t)\sim c_{\rm eq}e^{-t/\tau_0}+\Sigma_{n=1}^{\infty}p_n e^{-t/\tau_A^{(n)}}$, where $\tau_0\sim1$ is the time scale associated with the initial T independent transient, and $p_n=(1-c_{\rm eq})^{2^{n-1}}-(1-c_{\rm eq})^{2^n}$ is the probability for a defect to have a chain of spins zero of length $2^{n-1}\leqslant d<2^n$ next to it, which takes into account the fact that the relaxation time for the corresponding distances is $\tau_A^{(n)}$. The equilibrium condition is crucial to assume an independent relaxation of the different length scales. If the initial configuration is an out of equilibrium one, the probability distribution of distances evolves in time and the approximation considered is no longer valid. For short times the persistence is dominated by the fastest exponential decay, leading to $-\ln P\sim t/\tilde{\tau}$ for low temperatures, where $\tilde{\tau}\equiv\tau_0/c_{\rm eq}$ defines the timescale for short times. The long time behavior may be estimated replacing the sum by an integral that is evaluated in the saddle point approximation, in a manner similar to that of Ref. [18]. As a result we obtain a stretched exponential $P(t)\sim\exp[-(t/\tau_{\rm ACIC})^{\beta}]$, with a stretching exponent

$$\beta=(1+1/T\ln 2)^{-1}. \tag{4}$$

Notice that this is an alternative method to obtain $\tau_{\rm ACIC}$ to the one of Ref. [10]. In the symmetric limit the persistence is simply the sum of the relaxation of defects with and without an up neighbor. At low temperatures it reads $P(t)\sim 2c_{\rm eq}e^{-t/\tau_0}+(1-2c_{\rm eq})e^{-t/\tau_S}$. The small time behavior is similar to the asymmetric case, while the long time one is given by $P(t)\sim\exp(-t/\tau_S)$.

The behavior of the persistence for $b=10^{-5}$ and $b=10^{-3}$ at different temperatures is shown in Fig. 3. We present the data in a double log scale for P and a log scale for t to display the different stretching exponents. As in the case of the out of equilibrium relaxation, the decay is first dominated by the asymmetric process corresponding to the fragile regime. For short times it is exponential with a characteristic time scale $\tilde{\tau}\sim\epsilon^{-1}$, as described above. At longer times we see a change of slope in the plot, which corresponds to stretched exponential behavior, with an exponent given by Eq. (4). The stretching region is larger for smaller b, as expected. The fragile-to-strong crossover then takes place, and the persistence becomes exponential again, now with a time

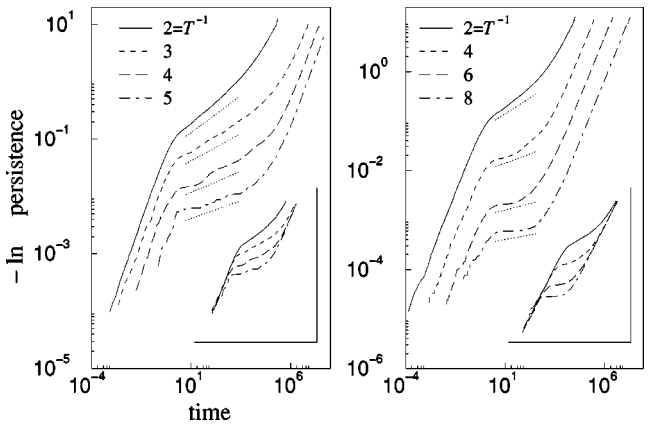

FIG. 3. Persistence P as a function of time t, for $b=10^{-5}$ (left panel) and $b=10^{-3}$ (right panel). Notice that we plot $-\ln P(t)$ in a log-log scale. The dotted lines are the expected stretching exponents β. Insets: same as main panels with time rescaled as $t\to t\epsilon$. Details of simulations are the same as in Fig. 2.

scale τ_S. In the insets we rescale time by a factor of ϵ to superimpose the curves in the exponential regimes of short and long times. The two limiting lines correspond to $\exp(-t/\tilde{\tau})$ and $\exp(-t/\tau_S)$.

We conclude with a comment on the explicit spatial asymmetry in the definition of the model studied here. It seems that to obtain other than strong behavior in systems with kinetic constraints it is necessary to consider cases in which spatial isotropy is explicitly broken, like in the ACIC [7] or its generalizations, which is a rather unphysical feature. This is also the case of systems with interactions, but which display a dynamical behavior similar to the spin facilitated models [19]. The system considered in this work, however, can be defined in an alternative but explicitly spatially symmetric formulation, which also clarifies the relation between the asymmetry b and the time scale and length scale at which the fragile-to-strong crossover takes place [20]. Consider b as a collective field $b(t)$ that takes values 0 and 1 with a characteristic time scale for flipping τ_b. The simplest physical choice for this dynamics would be a Poisson process. $b(t)$ may also have a spatial dependence, but on length scales larger than the typical ones for the spin system. Since $\langle b(t)\rangle = 1/2$ spatial symmetry is unbroken. The instantaneous value of $b(t)$ is either 0 or 1, so for times smaller than τ_b the behavior is that of the asymmetric case. For times much larger than τ_b the system effectively sees the average of $b(t)$ and the behavior is the symmetric one. τ_b sets the time scale for the fragile-to-strong crossover. This argument is easily generalized to higher dimensions by considering a collective vector field instead.

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