Nature of slow dynamics in a minimal model of frustration-limited domains

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We present simulation results for the dynamics of a schematic model based on the frustration-limited domain picture of glass-forming liquids. These results are compared with approximate theoretical predictions analogous to those commonly used for supercooled liquid dynamics. Although model relaxation times increase by several orders of magnitude in a non-Arrhenius manner as a microphase separation transition is approached, the slow relaxation is in many ways dissimilar to that of a liquid. In particular, structural relaxation is nearly exponential in time at each wave vector, indicating that the mode-coupling effects dominating liquid relaxation are comparatively weak within this model. Relaxation properties of the model are instead well reproduced by the simplest dynamical extension of a static Hartree approximation. This approach is qualitatively accurate even for temperatures at which the mode-coupling approximation predicts loss of ergodicity. These results suggest that the *thermodynamically disordered* phase of such a minimal model poorly caricatures the slow dynamics of a liquid near its glass transition.

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I. INTRODUCTION

Several microscopic scenarios have been proposed as underlying mechanisms for dynamical arrest in supercooled liquids [1–5]. Because this dramatic slowing down is accompanied by the onset of dynamical heterogeneity [6–8], a promising candidate model should account for the spontaneous segregation of rapidly relaxing and slowly relaxing domains. The theory of frustration-limited domains has been developed with this condition in mind [9,10]. The basic units of this theory are microscopic regions of low internal energy whose spatial extent is limited by long-ranged interactions or constraints. Nelson and co-workers suggested that such domains form in simple ''atomic'' liquids (such as metallic glass formers) [11]. For small clusters of particles, icosahedral arrangements are energetically preferred over close-packed configurations representative of the crystalline state [12]. It is thus argued that a supercooled atomic liquid is rich in low-energy icosahedral clusters which, for geometric reasons, cannot extend indefinitely. In this case, frustration is a consequence of the vanishing curvature of Euclidean space. One can imagine that the nature of local order and source of frustration are somewhat different for other more complicated materials.

The frustration-limited domain theory has several attractive features. By associating relaxation kinetics with the interfacial area of domain walls, it predicts a crossover in the temperature dependence of structural rearrangement times from Arrhenius to a super-Arrhenius form. Such a crossover is prominent in experiments with fragile glass formers [13]. Further, the theoretical scaling exponent for the asymptotic super-Arrhenius temperature dependence appears to be consistent with experimental data. Finally, the notion of frustration-limited domains resonates with the picture of heterogeneous dynamics that has emerged from experiments [6–8] and simulations [14–16]. While local structure within low-energy clusters may be effectively frozen on a molecular time scale, relaxation can be facile at the strained interfaces between domains. This argument is the essence of Stillinger's ''tear and repair'' picture of shear flow in fragile liquids [17].

Although these dynamical predictions of frustration-limited domain theory are suggestive, they are fundamentally thermodynamic in nature and thus indirect. In order to make such arguments precise, Grousson *et al.* have recently focused on the explicit dynamics of minimal models exhibiting frustration-limited domains [18]. Specifically, they have simulated stochastic dynamics of several classical spin models that pit short-ranged ferromagnetic interactions against long-ranged antiferromagnetic interactions. In addition to confirming super-Arrhenius relaxation for these models at low temperatures, they have demonstrated that the ''fragility'' of the dynamics (i.e., the degree of deviation from Arrhenius form) varies continuously with the relative strength of the long-ranged frustration. Quite recently, Grousson *et al.* have performed dynamical mode-coupling calculations for the same models, but no direct comparisons to their earlier simulations were made [19]. In this paper, we perform similar calculations that are compared directly to numerical simulations.

Schmalian and co-workers have also argued that such a Coulomb-frustrated ferromagnet should display essential features of glassy dynamics [20–22]. In their analysis, it is a proliferation of metastable states that drives vitrification. With the aid of replica mean field theory, this perspective predicts a scaling of fragility with frustration strength that agrees well with the simulation results of Ref. [18]. But like the theory of frustration-limited domains, this analysis is *thermodynamic* in nature, relying on an assumed correspondence between particular subensembles of high free energy

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and genuine dynamical bottlenecks.

This paper addresses the extent to which the slow relaxation in such simplified models truly resembles that of molecular glass-forming liquids. For this purpose we investigate in detail the *dynamics* of a model closely related to those studied in Refs. [18,20]. The model and dynamical propagation rules we consider, which are free of artificially quenched disorder and kinetic constraints, are described in Sec. II. For several values of the frustration strength, we compare the time dependence of spin correlations computed in simulations with those predicted by approximate theoretical approaches.

Two self-consistent dynamical equations obtained from theory are discussed in Sec. III. They correspond to resummations of an exact, infinite diagrammatic series for time correlations. The first resummation, yielding exponential relaxation at each wave vector, is a direct dynamical generalization of Brazovskii's static result for this class of models [23]. Calculations based on this straightforward approach agree remarkably well with simulation results, described in Sec. IV, even for temperatures approaching a thermodynamic transition to a fully ordered state. The second resummation is formally analogous to the idealized mode-coupling theory of liquids. As such, it predicts loss of ergodicity at finite temperature. By contrast, we find no evidence of nonergodic behavior or two-step relaxation for simulated disordered states of this model.

Surprisingly, then, the Hartree approach is the more accurate approximation for slowly relaxing disordered states of the model system. Detailed comparison of simulation and theory confirms that sluggishness indeed arises from de Gennes narrowing (i.e., from dramatic changes in static correlations), in contrast to complex dynamical mechanisms such as mode coupling. In this respect, the minimal model we have studied does not capture important aspects of supercooled liquid dynamics, specifically the intermediate time plateau and long time stretching of dynamical correlators. Implications of this result are discussed in Sec. V, along with issues related to fragility and local conservation of magnetization. In Sec. VI we conclude.

II. MODEL

We consider fluctuations of a field $\phi(\mathbf{r})$ at position $\mathbf{r}$ in three dimensions, with energy [23–25]

$$\beta\mathcal{H}[\phi(\mathbf{r})]=\int d\mathbf{r}\left[\frac{1}{2}\phi(\mathbf{r})[\tau+k_0^{-2}(\nabla^2+k_0^2)^2]\phi(\mathbf{r})+\frac{\lambda}{4!}\phi^4(\mathbf{r})\right]. \tag{1}$$

Here, the energy scale β^{-1} characterizes typical fluctuations of a surrounding heat bath. The physical meaning of the field ϕ may be somewhat abstract in the context of supercooled liquids, for example, representing the degree of a particular local packing symmetry. The application of Eq. (1) to diblock copolymer melts is more intuitive [26–28]. In this case, ϕ represents the local excess number density of one monomer type, and τ describes the preferential affinity of monomers for others of the same type. Because our interest in this model is motivated by the work in Ref. [18], we will imagine that ϕ simply represents a coarse-grained, scalar spin density. Here, τ is a dimensionless temperature measuring the distance from an underlying critical temperature when $k_0=0$. For any physical interpretation, the wave vector $k_0\neq 0$ characterizes long-ranged order of a low-temperature, microphase separated state. The coefficient λ multiplying the ϕ^4 term in Eq. (1) will later be used to order terms in perturbation series, although in calculations its numerical value will be of order unity.

For wave vectors near k_0, the action in Eq. (1) corresponds to that studied by Schmalian and Wolynes [20–22] and (in a hard-spin lattice version) by Grousson *et al.* [18]. In their work, frustration is explicit in competing interactions of square gradient $[J|\nabla\phi(\mathbf{r})|^2]$ and Coulomb $[Q\phi(\mathbf{r})\phi(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|]$ forms. The relative strengths of these interactions determine the periodicity of the ground state, $k_0\propto(Q/J)^{1/4}$, in which spin-up and spin-down domains alternate in stripes or lamellae [29]. In the model defined by Eq. (1), this frustration is instead implicit in nonzero k_0, but has the same physical effect. Namely, homogeneous domains are energetically favored at small length scales, while net magnetization is effectively constrained to vanish at larger length scales. In the context of diblock copolymers, this effective constraint reflects the stoichiometry imposed by polymer connectivity [26–28].

In two dimensions and higher, the presence of nonzero k_0 in Eq. (1) has a subtle but profound effect on the thermodynamics of the paramagnetic state. Specifically, the large entropy of fluctuations near $|\mathbf{k}|=k_0$ significantly reduces the free energy of the disordered phase. Within a Hartree approximation, this contribution is sufficient to make the paramagnetic state stable or metastable for all finite τ. As a consequence, the transition to a phase with long-ranged order is first (rather than second) order and occurs at a temperature $\tau_{\mathrm{tr}}<0$. This effect was first recognized by Brazovskii [23] and has been summarized lucidly by Binder and Fredrickson [28]. Its qualitative features have been subsequently confirmed in experiments with diblock copolymers [30]. Because, in this picture, statistics of the disordered state are dominated by fluctuations near k_0, we expect the model of Eq. (1) to belong to the same universality class as those of Refs. [18,20–22]. Later, we will demonstrate that slow dynamics of this state are dominated by the very same fluctuations.

The action in Eq. (1) is not a true Hamiltonian, and thus has no intrinsic dynamics. We consider two commonly used stochastic propagation rules which generate a canonical ensemble of fluctuations consistent with Eq. (1). Attention will be primarily focused on a simple Langevin equation,

$$\frac{\partial\phi(\mathbf{r})}{\partial t}=-\frac{\delta\mathcal{H}[\phi]}{\delta\phi(\mathbf{r})}+\eta(\mathbf{r},t), \tag{2}$$

where $\eta(\mathbf{r},t)$ is a random force whose statistics are Gaussian, and

$$\langle \eta(\mathbf{r},t)\,\eta(\mathbf{r}',t')\rangle = 2\beta^{-1}\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t'). \tag{3}$$

In Eq. (3), angular brackets denote an average over all possible realizations of the random force. The above equation of motion, along with the energetics of Eq. (1) and the statistics of Eq. (3), has been studied previously, most notably in the context of nucleation and nonequilibrium pattern formation following a rapid quench to $\tau < \tau_{\rm tr}$ [24,25,31,32]. To the best of our knowledge, the detailed equilibrium dynamics of the paramagnetic phase very close to the transition (i.e., $\tau \gtrsim \tau_{\rm tr}$) have not until now been fully explored.

The dynamics generated by Eq. (2) do not conserve the field $\phi(\mathbf{r},t)$ [32]. Because the slow relaxation of supercooled liquids results in part from the conservation of hydrodynamic densities, this feature of Eq. (2) may be somewhat troubling (particularly in the context of diblock copolymers, in which the number density is clearly conserved). For this reason, we consider a second form of dynamics that conserves $\phi(\mathbf{r},t)$ by construction. Trajectories of this dynamics are chains of microstates generated by a Metropolis Monte Carlo algorithm. In detail, a random displacement of the field $\phi(\mathbf{r})$ is attempted at discrete time steps, and is accepted with probability

$$P_{\rm acc} = \min[1, \exp(-\beta\Delta\mathcal{H})], \tag{4}$$

where $\Delta\mathcal{H}$ is the change in energy produced by the displacement. Local conservation of the field is achieved by restricting the choice of random displacements to those which do not alter the local net magnetization. Further details of this procedure will be described in Sec. IV. Simulation results presented in that section demonstrate that the decay of spin correlations produced by Eqs. (2) and (4) are nearly identical, within an arbitrary rescaling of time in the Monte Carlo chain of states. The physical meaning of this fact will be discussed in Sec. V.

III. THEORY

In this section we discuss two approximations for relaxation of the field $\phi(\mathbf{r},t)$. Specifically, we derive closed equations of motion for the correlation function

$$C_{\mathbf{k}}(t-t') = \langle \phi_{\mathbf{k}}(t)\,\phi_{-\mathbf{k}}(t')\rangle, \tag{5}$$

where Fourier components of the field are defined in the standard way:

$$\phi_{\mathbf{k}}(t) = \int d\mathbf{r}\,\phi(\mathbf{r},t)e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{6}$$

The first equation of motion is linear in $\phi_{\mathbf{k}}(t)$ and resembles phenomenological theories of high-temperature liquid state dynamics, such as the wave vector dependent viscoelastic theory [33]. The second is nonlinear and has the form of the idealized mode-coupling approximation to the dynamics of density fluctuations in supercooled liquids [1]. This equation contains the feedback mechanism responsible for the interruption of particle diffusion at intermediate time scales due to constraints imposed by slowly reorganizing local environments (the ''cage'' effect).

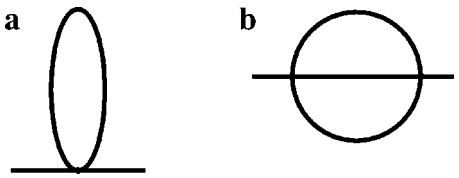

FIG. 1. Diagrams representing low-order terms in a perturbation series for the dynamics generated by Eq. (2). Lines represent instantaneous correlations of the field at two points in space, while vertices represent interactions.

Treating λ as a perturbation parameter, the solution to Eq. (2) may be written as an infinite series of terms, each representing a collection of field interactions and periods of free propagation. As a result, $C_{\mathbf{k}}(t)$ and its associated response function $G_{\mathbf{k}}(t) = -\beta dC_{\mathbf{k}}(t)/dt$ can be expanded in powers of λ. [We focus exclusively on the portion of the phase diagram in which dynamics are ergodic, so that $C_{\mathbf{k}}(t)$ and $G_{\mathbf{k}}(t)$ are related by the fluctuation-dissipation theorem.] Figure 1 shows diagrammatic representations of the first two terms in the series for $C_{\mathbf{k}}(t)$. The development of this expansion, as well as the partial series resummations underlying our approximations, have been discussed thoroughly in the context of other models. We will describe physically significant highlights of the procedure and refer the reader to Refs. [19,34] for details.

A linear equation of motion for $C_{\mathbf{k}}(t)$ results from summing only terms in the series whose diagrams have the basic topology shown in Fig. 1(a). In the irreducible segments of these ''tadpole'' diagrams, all interactions coincide in time. Consequently, such a summation renormalizes only the static portion of the basic tadpole diagram of Fig. 1(a). The dynamics predicted by this Hartree resummation scheme are identically those of a variationally optimized harmonic reference system [35]. They are thus obtained more directly by assuming Gaussian statistics for $\phi_{\mathbf{k}}(t)$. Specifically, we multiply the Fourier transform of Eq. (2) by $\phi_{-\mathbf{k}}(0)$ and average over the noise history, yielding

$$\frac{\partial C_{\mathbf{k}}(t)}{\partial t} = -[\tau + k_0^{-2}(k^2-k_0^2)^2]C_{\mathbf{k}}(t) + \frac{\lambda}{3!}\sum_{\mathbf{k}',\mathbf{k}''}\langle \phi_{\mathbf{k}'}(t)\phi_{\mathbf{k}'}(t)\phi_{\mathbf{k}-\mathbf{k}'-\mathbf{k}''}(t)\phi_{-\mathbf{k}}(0)\rangle. \tag{7}$$

Equation (7) is the first member of a complicated hierarchy of equations relating multipoint fluctuations to correlations of higher order. But if we assume that $\phi_{\mathbf{k}}(t)$ is a Gaussian random variable, the hierarchy closes immediately:

$$\frac{\partial C_{\mathbf{k}}^{\mathrm{H}}(t)}{\partial t} = -\mu_{\mathbf{k}}^{\mathrm{H}} C_{\mathbf{k}}^{\mathrm{H}}(t). \tag{8}$$

Here, the renormalized mass τ_{H} that appears in the expression for the structure factor $\mu_{\mathbf{k}}^{\mathrm{H}} = 1/C_{\mathbf{k}}^{\mathrm{H}}(0) = \tau_{\mathrm{H}} + k_0^{-2}(k^2 - k_0^2)^2$ is determined self-consistently by

$$\tau_{\mathrm{H}} = \tau + \frac{\lambda}{2} \sum_{\mathbf{k}'} C_{\mathbf{k}'}^{\mathrm{H}}(0). \tag{9}$$

Equation (9) is precisely Brazovskii's static approximation [23]. The relaxation described by Eq. (8), while simply exponential, occurs with rates that are significantly renormalized by the entropy of fluctuations near $|\mathbf{k}| = k_0$.

More elaborate, nonlinear approximations for $C_{\mathbf{k}}(t)$ result from incorporating diagrams with more complicated topologies [19,34]. The mode-coupling approximation (MCA) is an example, including diagrams with the ''sunset'' shape of Fig. 1(b). Summing all terms that renormalize the propagators (but not the vertices) of the basic sunset diagram yields the MCA. Because these contributions involve more than one unique time variable, they are capable in principle of capturing nontrivial memory effects. As shown in Ref. [34], the self-consistent result of this resummation is

$$\frac{\partial C^{\mathrm{MCA}}(t)_{\mathbf{k}}}{\partial t} = -\mu_{\mathbf{k}}^{\mathrm{MCA}} C_{\mathbf{k}}^{\mathrm{MCA}}(t) - \frac{\lambda^2 \beta}{6} \int_0^t dt' \times \sum_{\mathbf{k}',\mathbf{k}''} [C_{\mathbf{k}'}^{\mathrm{MCA}}(t-t') C_{\mathbf{k}''}^{\mathrm{MCA}}(t-t') \times C_{\mathbf{k}-\mathbf{k}'-\mathbf{k}''}^{\mathrm{MCA}}(t-t')] \frac{\partial C_{\mathbf{k}}^{\mathrm{MCA}}(t')}{\partial t'}. \tag{10}$$

The final, nonlinear term of Eq. (10) explicitly couples the dynamics of fluctuations at different wave vectors, so that the decay of $C_{\mathbf{k}}^{\mathrm{MCA}}(t)$ is not simply exponential. The mode-coupling estimate of the static structure factor, $C_{\mathbf{k}}^{\mathrm{MCA}}(0) = 1/\mu_{\mathbf{k}}^{\mathrm{MCA}}$, is determined by a self-consistent equation involving both the tadpole and sunset diagrams. We avoid this static calculation by instead replacing $\mu_{\mathbf{k}}^{\mathrm{MCA}}$ in Eq. (10) with the exact form of $C_{\mathbf{k}}^{-1}(0)$ from numerical simulations. This procedure is commonly employed in mode-coupling studies of supercooled liquids.

As the microphase transition point is approached from high temperature, we expect that only modes near the ordering wave vector k_0 will remain important. In this regime, a reduced model without reference to the coupling of specific length scales should capture the qualitative behavior of Eq. (10). Such a schematic model is similar to that studied by Leutheusser for structural glass-forming liquids [36]. [Indeed, Eq. (10) is only slightly different from that encountered in the idealized mode-coupling theory of supercooled liquids [1]. In particular, the memory kernel involves a two-point correlation function raised to the third, rather than second, power.] Restricting attention to $|\mathbf{k}| = k_0$, and neglecting coupling to other wave vectors, Eq. (10) reduces to the dynamical equation exactly describing the p-spin model of a mean field spin glass (with $p=4$). Since for $p>2$ the critical properties of such models are essentially p independent, we expect that near a critical point, Eq. (10) will exhibit a plateau and an eventual transition to nonergodic behavior [37].

The character of the slow dynamics resulting from the theories underlying Eqs. (8) and (10) are fundamentally different. The dynamical Hartree theory [Eq. (8)] may exhibit a rapid slowing of dynamics as a function of inverse temperature *only* if the statics, as expressed through the renormalized mass τ_{H}, are strongly temperature dependent. On the other hand, due to the nonlinearity of Eq. (10), a slight change in the structure factor may result in a dramatic change in relaxation times. It is well known that glass-forming liquids show little change in static structure as the glass transition is approached [13]. Thus, theories of the type given in Eq. (8) are not relevant near the glass transition. In the following sections, the predictions of Eqs. (8) and (10) will be compared with simulations for the Coulomb-frustrated system.

The renormalized perturbation theories developed in this section are strictly valid only in the limit of weak coupling, i.e., for small λ or large, positive τ. In our simulation work, we fix $\lambda = 1$. It is thus instructive to ask at what value of τ these theories are expected to break down. To answer this question, we follow the arguments of Hohenberg and Swift [24]. Specifically, we compare the Hartree approximation to the renormalized mass τ_{H} with corrections introduced by mode coupling (i.e., the renormalized sunset diagram). These corrections are comparatively small when

$$|\tau| \lesssim 0.2 k_0^{7/5}. \tag{11}$$

In this regime the Hartree and mode-coupling approximations are controlled, and differ only quantitatively from one another. For larger $|\tau|$, however, the two approximations can differ substantially, as we will see in numerical results presented in the following section. It has been noted previously that the static Hartree approximation can be accurate beyond its strict range of validity. There is thus no guarantee that a range of τ exists in which the mode-coupling approximation significantly improves upon an appropriately chosen harmonic reference system.

IV. SIMULATIONS

In order to follow the dynamics of Eq. (2) or Eq. (4) numerically, it is necessary first to coarse grain the field $\phi(\mathbf{r},t)$ in space. This procedure yields a (periodically replicated) finite set of dynamical variables, whose time evolution may be integrated approximately over short intervals. We select a coarse-graining length $a = 2\pi/nk_0$, and define new fields at lattice points $\mathbf{r}_i$:

$$\Phi_i(t) = a^{-3} \int_{v_i} d\mathbf{r}\phi(\mathbf{r},t), \tag{12}$$

where v_i is bounded by a cube of side length a centered at $\mathbf{r}_i$. In the calculations described below, $n=8$, so that a domain of wavelength π/k_0 comprises several "soft spins" Φ_i. To lowest order in a and a small time increment Δt, these renormalized fields evolve according to

$$\Phi_i(t+\Delta t) = \Phi_i(t) - \Delta t\Big[[\tau + k_0^{-2}(\mathcal{L}+k_0)^2]\Phi_i(t) + \frac{\lambda}{3!}\Phi_i^3(t)\Big] + \overline{\eta}_i(t). \tag{13}$$

Here, the lattice approximation to the Laplacian operator acting on a function of space, $\mathcal{L}f(x_i) = a^{-2}\Sigma_{j\in \mathrm{nn}}[f(x_j) - f(x_i)]$, is taken to include a sum over nearest neighbors only (denoted by nn). After coarse graining, statistics of the random force remain Gaussian, with $\langle \overline{\eta}(\mathbf{r}_i,t_m)\overline{\eta}(\mathbf{r}_j,t_n)\rangle = 2\beta^{-1}(\Delta t/a^3)\delta_{ij}\delta_{mn}$.

The simulation algorithm described above (which is very similar to those of Refs. [25,31]) has several advantages over the numerical approach of Ref. [18], which employs "hard spins" ($\Phi_i = \pm 1$) and explicit frustration. First, spins interact only with nearest and next-nearest neighbors, providing linear scaling of computational effort with system size. Because cumbersome techniques associated with long-ranged forces are not required, a larger set of dynamical variables may be considered. In our calculations, the periodically replicated unit cell includes 64^3 spins arranged on a cubic lattice. More importantly, the coarse-graining procedure allows the dimensions of the unit cell to scale with the physically relevant length k_0^{-1}. As a result, the unit cell spans several correlation lengths, even for very small values of k_0. By contrast, in the work of Ref. [18], the unit cell is comparable to a single natural lamellar spacing for several of the simulated states (particularly those corresponding to fragile systems). In those cases, significant finite size effects are possible. In effect, Grousson *et al.* cutoff slowly relaxing fluctuations at small $\mathbf{k}$ rather than the rapidly relaxing fluctuations at large $\mathbf{k}$ that are integrated out in our approach. In Sec. V we discuss the dynamical implications of such a cutoff.

Using Eq. (13), we have computed the dynamics of several states of the model system at temperatures above the microphase separation transition ($\tau \gtrsim \tau_{\mathrm{tr}}$). We focus on three values of k_0 (0.1, 0.5, and 1.0) corresponding to a somewhat broader range of model parameters than was considered in Ref. [18]. In each case, $\lambda = 1$, so that the microscopic dynamics is in principle strongly nonlinear. Representative configurations of the system are depicted in Fig. 2, typifying the high-temperature paramagnetic phase (a), the disordered phase near the microphase separation transition (b), a nonequilibrium state produced by rapid quenching of a disordered system to low temperature (c), and the ordered lamellar phase (d).

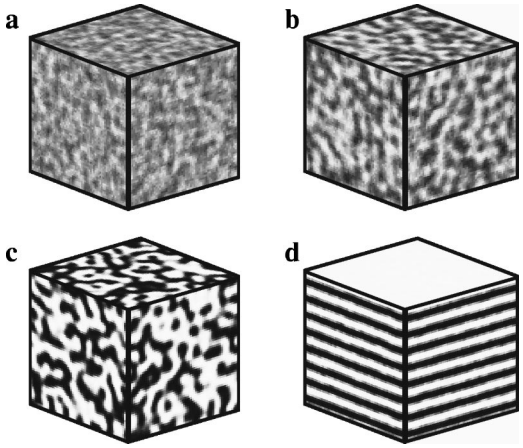

FIG. 2. Representative equilibrium configurations of the model system for $k_0 = 0.5$ and $\tau = 0$ (a), $\tau = -0.12$ (b), and $\tau < \tau_{\mathrm{tr}}$ (d). The configuration depicted in (c) was obtained from the nonequilibrium evolution of a nearly random state quenched instantaneously to $\tau < \tau_{\mathrm{tr}}$.

For each value of k_0 we consider, the relaxation of spin correlations slows dramatically near the transition to microphase separation. The time required for single-spin correlation,

$$C(t) \equiv \langle \Phi_i(0)\Phi_i(t)\rangle = N^{-1}\int \frac{d\mathbf{k}}{8\pi^3} C_{\mathbf{k}}(t), \tag{14}$$

to decay to 10% of its initial value, $\overline{t}$, is plotted as a function of τ in Fig. 3. The growth of relaxation times as τ ap-

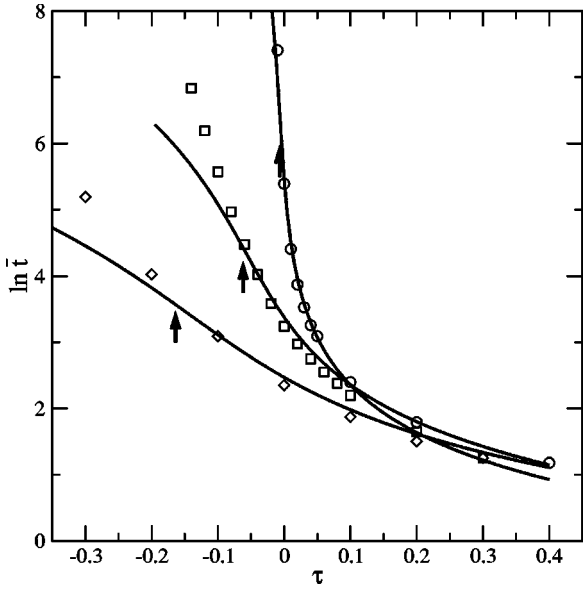

FIG. 3. Time $\overline{t}$ required for spin correlations to decay to 10% of their initial values, as a function of scaled temperature τ. Circles, squares, and diamonds show numerical results for $k_0 = 0.1$, $k_0 = 0.5$, and $k_0 = 1.0$, respectively. Solid lines are predictions of the Hartree approximation described in the text. Arrows indicate temperatures at which this approximation is expected to break down for each value of k_0, as estimated using Eq. (11).

proaches τ_{tr} is sharpest for the smallest value of k_0. Indeed, critical fluctuations are suppressed least strongly in this case, as evidenced by the onset of sluggishness very near $\tau=0$.

Grousson *et al.* have likened systems corresponding to large and small values of k_0 to ''strong'' and ''fragile'' glass formers, respectively [18]. For fragile cases, they have even shown that the temperature dependence of $\bar{t}$ is well fit by the Vogel-Fulcher form found for supercooled liquids. Although this functional form suggests an emerging importance of activated processes, the dramatic growth of relaxation times is in fact well captured by the harmonic reference system described in Sec. III. Numerical solutions of Eq. (9) (plotted as solid lines in Fig. 3), corresponding to this Hartree approximation, are especially accurate in the most fragile case ($k_0=0.1$). Even for the least fragile case ($k_0=1$), computed rates differ from predicted values by at most a factor of 2. Activated barrier crossing is manifestly absent on a harmonic landscape, strongly implying that slow dynamics are driven by static renormalization, rather than by fundamental changes in the structure of trajectory space [5]. The static structure factor $C_{\mathbf{k}}(0)$ in fact becomes more sharply peaked in a way that mirrors the sudden growth in $\bar{t}$. In other words, the slowing of relaxation appears to be an example of de Gennes narrowing [33].

The time dependence of spin correlations provides further evidence for this interpretation. Specifically, even when relaxation is very slow, correlations decay nearly exponentially at each wave vector. In Fig. 4, $C_{\mathbf{k}}(t)$ is plotted for many k values for a system very near microphase separation ($k_0=0.5$, $\tau=-0.1$). Included wave vectors span a range from the lowest accessible spatial frequency ($k=2\pi/L$) to several multiples of k_0. In no case is relaxation detectably caged or stretched at long times. The single-spin correlation function $C(t)$ in Eq. (14) is a superposition of all $C_{\mathbf{k}}(t)$, and thus does not decay as a single exponential. At long times, however, relaxation is dominated by the slowest modes, those with wave vectors lying in a spherical shell with $|\mathbf{k}|\approx k_0$, and is very nearly exponential. Since static correlations are strongest for these modes, especially near the microphase separation transition, $C(t)$ is nonexponential only over a small range of the total decay.

Remarkably, spin relaxation is essentially identical for a very different choice of microscopic propagation rules which conserve the field Φ. In this Monte Carlo dynamics, described in Sec. II, each trial move simultaneously displaces Φ at randomly chosen site i and at a site j randomly chosen from the nearest neighbors of i. The displacement at i, $\Delta\Phi_i$, is exactly compensated by that at j, i.e., $\Delta\Phi_j=-\Delta\Phi_i$. In this way, Φ is conserved at all length scales greater than or equal to the lattice spacing a. In general, such a constraint can influence dynamical behavior dramatically. For instance, scaling exponents for unstable domain growth in similar models depend intimately on the conservation of order parameters [32]. The relaxation described above, however, is modified by the constraint only at very short times.

The insensitivity of slow dynamics to field conservation in this model was anticipated by Sachdev, who noted that the corresponding constraint couples strongly only to fluctuations with very small wave vector ($|\mathbf{k}|\approx 0$) 10. The long-lived correlations in Fig. 4, however, are governed not by these modes, but instead by fluctuations of finite wave vector ($|\mathbf{k}|\approx k_0$), which couple relatively weakly to the constraint. Conservation is thus of only modest importance at long times in the *disordered* phase. These facts can lead in principle to dramatic finite size effects in numerical simulations. Specifically, the smallest periodically replicated unit must accommodate fluctuations with wavelengths several times k_0. Otherwise, the absence of truly long wavelength fluctuations will generate spuriously strong coupling of conservation constraints to the slowest accessible modes. As a result, artificial

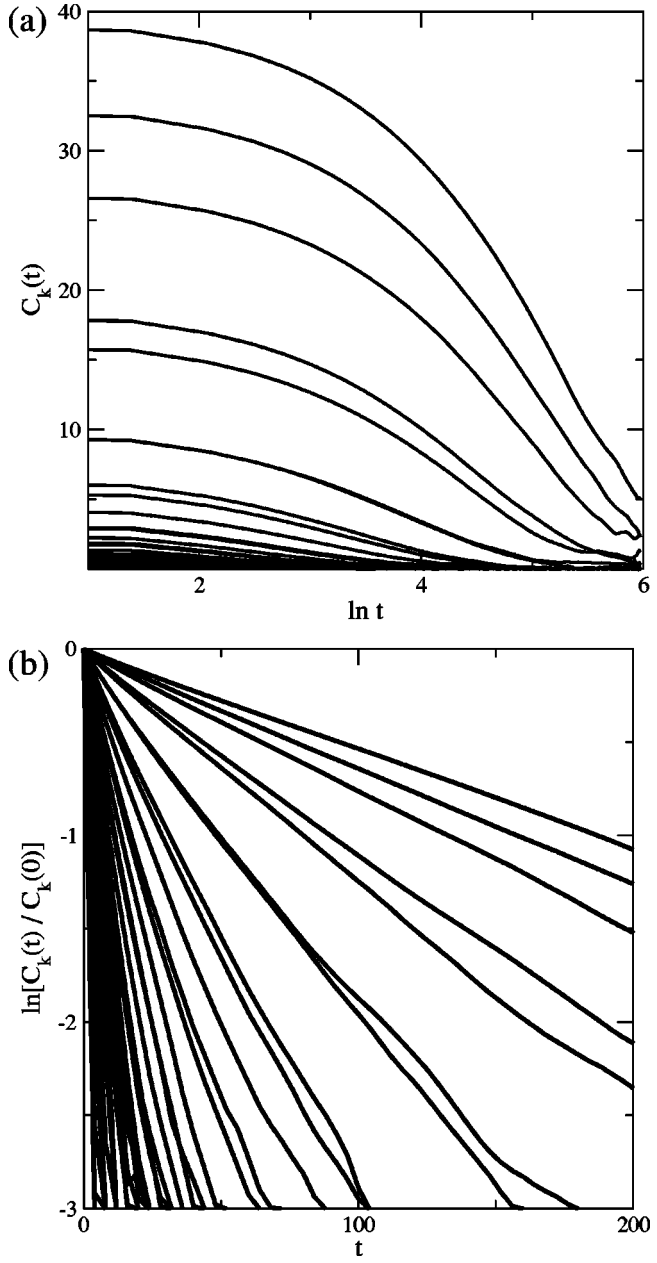

FIG. 4. $C_{\mathbf{k}}(t)$ and $\ln[C_{\mathbf{k}}(t)/C_{\mathbf{k}}(0)]$ for several $|\mathbf{k}|$ as a function of $\ln t$ and t, respectively, for the state $k_0=0.5$, $\tau=-0.1$. The uppermost curve in each panel corresponds to $|\mathbf{k}|=k_0$ and exhibits the slowest decay.

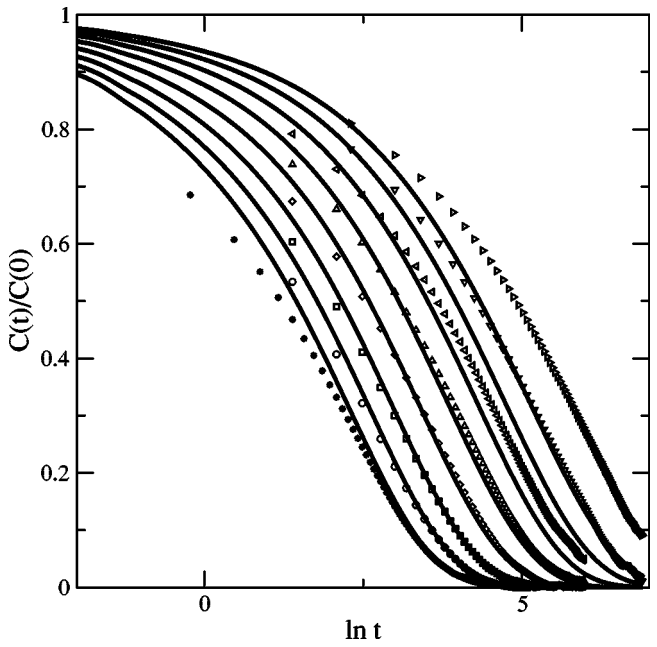

FIG. 5. Decay of spin correlation $C(t)$ predicted by Hartree approximation (lines), compared with results of numerical simulations (symbols) for several thermodynamic states: $\tau=-0.14$, $\tau=-0.12$, $\tau=-0.1$, $\tau=-0.08$, $\tau=-0.06$, $\tau=-0.04$, $\tau=-0.02$, $\tau=0$ (in order from top to bottom in the plot). In each case, $k_0=0.5$.

dynamical features may appear at long times. For model energetics that are similar to but different from Eq. (1), stretched exponential relaxation has been computed from simulations in which system dimensions are comparable to k_0^{-1} [18]. To the extent that fluctuations near $|\mathbf{k}|=k_0$ are independent of model details, such anomalous dynamics should not survive in the thermodynamic limit.

The persistence of exponential relaxation into the neighborhood of microphase separation, obtained numerically both for Langevin and Monte Carlo dynamics, is consistent with the dynamical Hartree approximation described in Sec. III. In fact, this simple theory also predicts with remarkable accuracy the time scales of relaxation, even as they grow by several orders of magnitude. Results for the case $k_0=0.5$ are compared in Fig. 5 by plotting $C(t)/C(0)$ obtained from theory and simulation for several values of τ.

The success of the harmonic reference system provides further evidence that ''vitrification'' in this model is driven by dramatic changes in structural order rather than novel relaxation mechanisms. Indeed, several dynamical features that would seem to be related to activated barrier crossing may be well rationalized in the Hartree picture. For example, the fragility parameter defined empirically by

$$\bar{t} \propto \exp\left(\frac{T_K D}{T-T_K}\right) \tag{15}$$

appears to scale as $D\sim Q^{1/2}$ in the simulations of Ref. [18]. Here, T_K is a fitted Kauzmann temperature at which relaxation times appear to diverge. Schmalian and Wolynes have suggested that this scaling arises from the entropy of activation for structural rearrangement of mesoscopic domains [20–22]. The Hartree approximation offers a simpler explanation. Fitted relaxation times follow $\bar{t}\sim\tau_H^{-1}\sim\exp(D/\tau)$ rather well. It is easy to show by dimensional scaling that the renormalized mass is a function only of $\tau/Q^{1/3}$, yielding immediately $D\sim Q^{1/3}$ [29]. This slightly different scaling form fits the results of Grousson *et al.* equally well [18]. For the simulations of larger systems we have presented, the Hartree prediction appears to be superior.

The dynamical scenario predicted by the simplified mode-coupling theory of Sec. III, on the other hand, is not borne out in our simulations. Most significantly, we observe neither loss of ergodicity nor two-step relaxation over the relevant range of $\tau>\tau_{tr}$. These failures of the dynamically nonlinear approximation are evident in Fig. 6, comparing the MCA and simulation results for the same system and thermodynamic states considered in Fig. 5. Interestingly, the MCA predicts trapping at values of τ for which the Hartree approximation remains reasonable. The infinite series of terms incorporated in the mode-coupling approximation thus adds little realism to the lower order description, and eventually leads to incorrectly anomalous behavior. This series of terms must be compensated to a large degree by omitted terms at each order. There have been suggestions that similar cancellation occurs in mode-coupling expansions of supercooled liquid dynamics [38]. In that case, however, signatures of idealized mode coupling (i.e., two-step relaxation) survive despite the existence of omitted relaxation channels. In our model, no such signatures are evident in the range of τ we have simulated.

The thermodynamic states we have so far considered lie exclusively in the disordered phase of our model system, $\tau>\tau_{tr}$. We have confirmed this fact by computing the work to reversibly impose long-range order (i.e., nonzero $\langle|\Phi_{\mathbf{k}}|\rangle$ at $|\mathbf{k}|=k_0$). Although the static Hartree approximation suggests that the states of lowest temperature considered for each k_0 have global free energy minima in ordered configurations, the computed free energy of the paramagnetic state is in fact lower for each case. This quantitative failure of Brazovskii's approximation is not surprising, as the relevant states lie outside the strict range of validity of the approximation for $\lambda=1$ [23,24].

We have therefore not addressed dynamics in a narrow region of the disordered state just above τ_{tr}, or when the thermodynamically stable state of the system possesses long-range order. As τ approaches τ_{tr} from above, relaxation becomes prohibitively slow, and relevant time scales exceed those accessible by our simulation techniques. So while glassy behavior is not manifest for $\tau\gtrsim\tau_{tr}$, we cannot rule out the existence of caging or trapping extremely close to the microphase separation temperature. It is possible that qualitatively new dynamical behavior arises in this region, but it cannot account for the dramatic slowing down we have demonstrated at higher temperature, which is driven by extreme structural changes rather than activated processes. Furthermore, the sudden onset of nontrivial behavior would be in stark contrast to the more gradual onset of caging and stretched exponential behavior in real liquids.

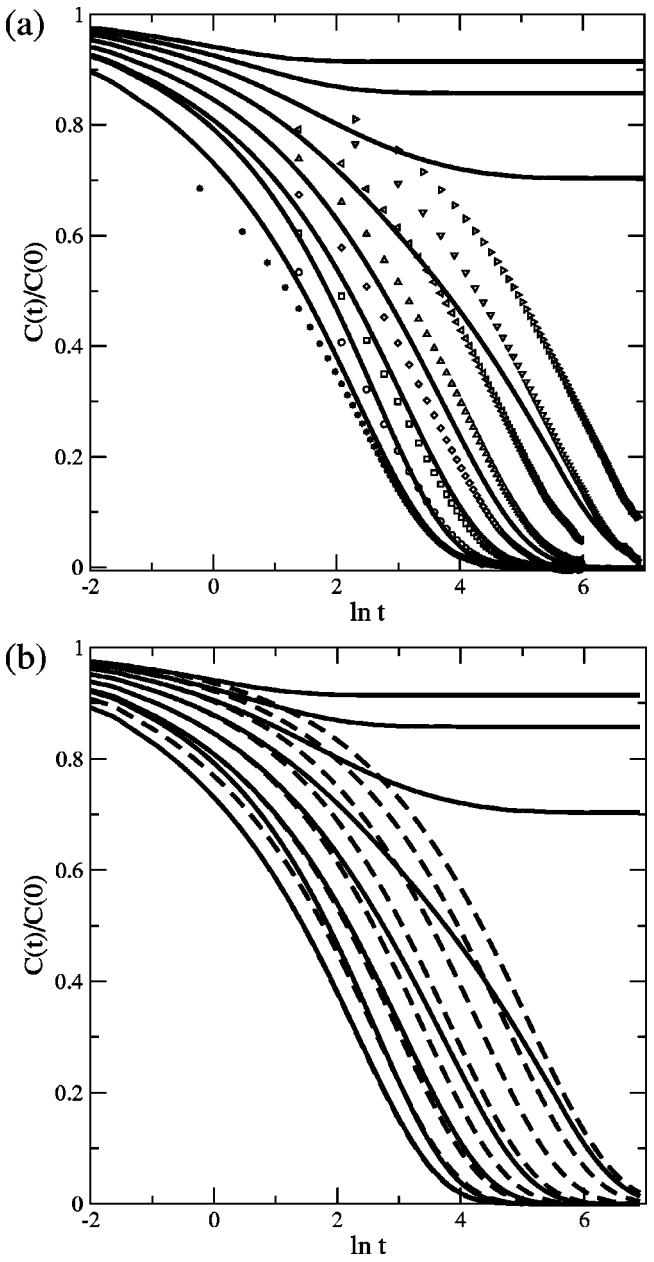

FIG. 6. Comparison of MCA (solid lines) with numerically simulated dynamics (symbols) (a) and MCA (solid lines) with Hartree approximation (dashed lines) (b). Results are shown for thermodynamic states identical to those plotted in Fig. 5. According to Eq. (11), contributions of mode coupling become significant around $\tau \simeq -0.06$ (fifth line from the top). Note that this temperature is very near the critical temperature at which MCA predicts loss of ergodicity.

Analogies that have been drawn between this model system and supercooled liquids suggest that relaxation should become still more sluggish when disordered configurations are cooled below $\tau_{\rm tr}$. There may indeed be a small range of $\tau \lesssim \tau_{\rm tr}$ in which our system follows this trend. But outside the neighborhood of the transition, dynamics are qualitatively different from the fluctuations observed in disordered states. We have investigated several examples of dynamically evolving disordered states below $\tau_{\rm tr}$ for $k_0 = 0.5$. Initial configurations were either taken from equilibrium simulations at $\tau = -0.12 > \tau_{\rm tr}$, or were generated by selecting values of $\phi_{\rm k}$ from Gaussian distributions consistent with the correlation function $C_{\rm k}(0)$. For this region of the phase diagram we used the form of $C_{\rm k}(0)$ predicted by the theory of Ref. [39] for the disordered state at low temperature. At $\tau = -0.2 < \tau_{\rm tr}$, each configuration rapidly began to develop order, with lamellar domains growing in and then aligning. The mechanism of this coarsening, widely believed to proceed in a self-similar manner, is distinct both from typical aging of supercooled liquids and from nucleation and growth of crystalline order in a liquid following a shallow quench below the freezing transition [31,40,41]. While according to the Hartree approximation the disordered state is thermodynamically metastable for all finite τ, the disordered configurations we have studied are dynamically *unstable*.

V. CONCLUSIONS

We have examined in detail a simple model that is closely related to the frustration-limited domain theory of Kivelson and co-workers [9], and to the uniformly frustrated ''stripe-glass'' model studied by Schmalian and Wolynes [20–22]. The disordered phase of this model system indeed displays some hallmarks of molecular glass-forming liquids. But its slow dynamics, driven by the same Gaussian fluctuations that give rise to first-order microphase separation, differ qualitatively from generic glassy behavior in several respects.

While relaxation times increase dramatically in these models in a non-Arrhenius fashion as temperature is lowered, we find that an optimized harmonic reference system captures the time dependence of fluctuations semiquantitatively. In contrast to the vitrification of molecular liquids, the onset of this sluggishness is *not* accompanied by significant power law or stretched exponential decay of correlations in time. Perhaps most importantly, we find that the slow decay of dynamical correlations mirrors significant changes in static structure. An idealized mode-coupling theory captures these changes less accurately than the simpler harmonic approach, predicting caging and eventual trapping at temperatures where the simulated dynamics remain exponential and ergodic. Since the mode-coupling theory of liquid state dynamics may overestimate the location of apparent power law viscosity divergences by as much as a factor of 2, the relevance of the breakdown of the MCA in the system studied in this work deserves further comment [42]. While for liquids mode-coupling theory predicts a transition to a vitreous state at temperatures where relaxation remains ergodic, there is a robust correlation between the locations of the predicted glass transition temperature and the onset of strong caging, as demonstrated in molecular dynamics simulations [43]. In our simulations of Eq. (1) we have probed effective temperatures below that at which the MCA predicts a divergence of relaxation times, observing no multistep nonexponential relaxation in $C_{\mathbf{k}}(t)$. This point highlights important differences between the dynamics generated by the simple Hamiltonian (1) and that of real glass-forming liquids.

We emphasize that our study does not address certain as-

pects of model (1) and others closely related to it. Eastwood and Wolynes have constructed a Ginzburg criterion to estimate the rounding of an underlying ideal glass transition due to surface tension effects in systems with short-ranged interactions [44]. It is indeed possible that behavior typical of an entropy crisis may exist for model parameters outside the range of our study. Furthermore, terms that might be added to Eq. (1) may stabilize a glassy state below the microphase separation temperature. Possibilities include cubic nonlinearities or quenched disorder. Our results also do not conclusively rule out the existence of glassy behavior in other models inspired by the frustration-limited domain concept of Kivelson and co-workers, such as the spherical Coulomb-frustrated Ising model. Indeed, a thorough investigation of a range of models will be needed to understand whether frustration is a generic and fundamental cause of slow dynamics in supercooled liquids.

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