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Landau-like theory of glassy dynamics

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An exact solution of a Landau model of an order-disorder transition with *activated* critical dynamics is presented. The model describes a funnel-shaped topology of the order parameter space in which the number of energy lowering trajectories rapidly diminishes as the ordered ground state is approached. This leads to an asymmetry in the effective transition rates which results in a nonexponential relaxation of the order-parameter fluctuations and a Vogel-Fulcher-Tammann divergence of the relaxation times, typical of a glass transition. We argue that the Landau model provides a general framework for studying glassy dynamics in a variety of systems.

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Introduction. Glassy dynamics occur in a large variety of systems, such as supercooled liquids, foams, and granular matter. They are characterized by an extremely rapid increase of relaxation times and by a nonexponential decay of time-dependent correlation functions [1]. The rapid increase in time scales is typically fit by an exponential, Vogel-Fulcher-Tammann (VFT) dependence on a control parameter such as temperature or density. In this Rapid Communication, we propose a Landau model of order-parameter dynamics in the vicinity of a critical point that exhibits these features.

The canonical theoretical framework for dynamics near a critical point is the time-dependent Ginzburg-Landau equation [2]. It successfully describes the phenomenon of critical slowing down, whereby the relaxation time for order-parameter fluctuations scales as a power of the correlation length, which in turn diverges as the critical point is approached. A natural question to ask is whether this framework can be adapted to describe glassy dynamics. Here we show analytically that a master equation, based on a Landau free energy, where the energy and entropy play asymmetric roles in determining the transition rates, naturally leads to a VFT divergence and a broad distribution of relaxation time scales near a critical point.

The microscopic basis for the asymmetry in the transition rates can be found in the topology of the space of trajectories. Namely, we consider the situation where the number of energy lowering trajectories diminishes as the ordered ground state is approached. A similar funnel-like topology of the trajectory space for a simple kinetic model of protein folding has been identified recently as a possible explanation of fast folding [3]. Here we show that such a topology of the trajectory space, when a system is driven to a critical point, can result in glassy critical dynamics. Furthermore, we hypothesize that diverse systems such as foams, granular matter and supercooled liquids owe their glassy features to such a mechanism, and propose computational tests of this idea.

Model. We start with a mean-field model of a continuous phase transition for a scalar order parameter ρ that takes values on the integers. We describe dynamics of ρ as a random walk on a one-dimensional lattice.

The Landau free energy in the disordered phase ($\mu < \mu^*$) is assumed to be quadratic,

$$\beta F(\rho) = \beta F^0 + \frac{\mu^* - \mu}{2}\rho^2; \tag{1}$$

μ is the dimensionless control parameter and μ^* is its critical value. The energy and the entropy are also assumed to be quadratic functions of the order parameter: $\beta E(\rho) = \beta E^0 - \mu\rho^2/2$, and $S(\rho) = S^0 - \mu^*\rho^2/2$ [4]. The free energy $\beta F = \beta E - S$ leads to a mean-field phase transition as $\mu^* - \mu \to 0$. Below we shall be interested in the order parameter dynamics as the phase transition point is approached from the disordered phase.

In the Landau approach to critical dynamics, $P(\rho, t)$, the probability for the order parameter to take the value ρ at time t, is the solution to the master equation

$$\Delta_t P(\rho) = -(W_{\rho\to\rho-1} + W_{\rho\to\rho+1})P(\rho) + W_{\rho-1,\rho}P(\rho-1) + W_{\rho+1\to\rho}P(\rho+1), \tag{2}$$

where $\Delta_t P \equiv P(t+\Delta t) - P(t)$ is the discrete time derivative. The transition rates (see Fig. 1), $W_{\rho\to\rho'}$, depend on the free

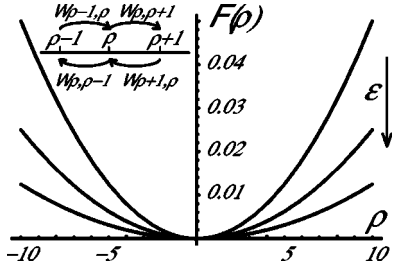

FIG. 1. The Landau free energy, $\beta F(\rho)$, is a parabola whose width increases as the transition is approached ($\epsilon \to 0$). The order parameter ρ performs a random walk with rates dictated by the energy and the entropy, which are functions of ρ.

energy, the canonical choice being, $W_{\rho\to\rho'}=\exp\{-[\beta F(\rho')-\beta F(\rho)]/2\}$. These rates satisfy detailed balance and yield the equilibrium Gibbs distribution, $P_{\rm eq}(\rho)\propto\exp[-\beta F(\rho)]$, as the steady state solution to Eq. (2). Relaxation processes described by these rates implicitly assume that neither energy nor entropy barriers impede the fluctuations of the order parameter around its equilibrium value, $\rho_{\rm eq}=0$.

The canonical scenario described above can be altered dramatically if the microscopic dynamics are constrained in some way. An example is provided by a system of hard spheres at densities approaching random close packing. At these large densities only correlated motions of many spheres are available to the system in order to relax a density perturbation [5]. We consider the case where such constraints in the microscopic dynamics can be encoded as an asymmetry in the way energy and entropy enter the transition rates $W_{\rho\to\rho'}$. In particular, we assume that energy lowering transitions can proceed only from a small subset of microstates at given ρ. If the system finds itself in one of these microstates the transition occurs at a fixed rate independent of the value of ρ. The number of states available for the energy lowering transitions is taken to be proportional to the number of microstates in the target state, ρ'. Thus, the rate of energy lowering transitions is proportional to the ratio of the number of microstates in ρ' and ρ, and is therefore a function of the *entropy* change only. Taking the requirement of detailed balance also into account leads to

$$W_{\rho\to\rho'}=\begin{cases} e^{-[S(\rho)-S(\rho')]} & \text{if } E(\rho')<E(\rho) \\ e^{-[\beta E(\rho')-\beta E(\rho)]} & \text{if } E(\rho')>E(\rho). \end{cases} \tag{3}$$

These rates imply a funnel-like topology of the trajectory space since the number of paths leading downhill in energy decreases continually as the system approaches its ground state.

Using the quadratic expressions for the energy and entropy in the transition rates leads to the master equation (for $\rho>0$ [6])

$$\Delta_t P(\rho)=-(e^{-\mu\rho}+e^{-\mu^*(\rho+\Delta\rho)})P(\rho)+e^{-\mu^*\rho}P(\rho-\Delta\rho)+e^{-\mu(\rho+\Delta\rho)}P(\rho+\Delta\rho); \tag{4}$$

$\Delta\rho=1$ is the microscopic step size in the order parameter space. Since the rates are invariant under $\rho\to-\rho$, the equation for $\rho<0$ has a similar form. Close to the critical point ($\mu^*-\mu\ll 1$) typical values of ρ are much greater than one, and we expect significant variations of $P(\rho)$ to occur on scales much larger than $\Delta\rho$. A well defined continuum-ρ limit of the master equation,

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial\rho}\left[\epsilon\rho e^{-\mu^*|\rho|}P+2De^{-\mu^*|\rho|}\frac{\partial P}{\partial\rho}\right], \tag{5}$$

is obtained by taking $\Delta\rho\to 0$, $\Delta t\to 0$, and $\mu^*-\mu\to 0$, while keeping $D=(\Delta\rho)^2/2\Delta t$ and $\epsilon=(\mu^*-\mu)\Delta\rho/\Delta t$ finite. We note that a direct consequence of the asymmetric transition rates is the exponentially decaying factor multiplying both the drift and the diffusion terms in Eq. (5). The time-invariant probability distribution obtained from this equation is the normalized, equilibrium distribution $P_{eq}(\rho)=\sqrt{\epsilon/4\pi}e^{-(\epsilon/4D)\rho^2}$.

Scaling solution at the critical point. For $\epsilon=0$, the Laplace transform $\tilde{P}(\rho,s)=\int_0^\infty P(\rho,t)e^{-st}dt$ is

$$\tilde{P}(\rho,s)=\frac{1}{\sqrt{8sD}}e^{\mu^*|\rho|/2}\frac{K_1\left(\sqrt{\frac{2s}{D\mu^{*2}}}e^{\mu^*|\rho|/2}\right)}{K_0\left(\sqrt{\frac{2s}{D\mu^{*2}}}\right)}. \tag{6}$$

The long-time limit ($t\to\infty$) corresponds to the $s\to 0$ limit in Laplace space and Eq. (6) suggests the scaling limit $s\to 0$ and $|\rho|\to\infty$ while keeping $\sqrt{s}e^{\mu^*|\rho|/2}$ fixed. Using the scaling variable $z=e^{\mu^*|\rho|/2}/\sqrt{t}$, the scaling form of the solution to Eq. (5) can be written as

$$P(\rho,t)=\frac{\mu^*}{2\ln Dt}F(z). \tag{7}$$

The scaling function $F(z)=(\mu^*/2)e^{-z^2/2\mu^{*2}}$ is determined by substituting the scaling form, Eq. (7), in Eq. (5) with $\epsilon=0$, and matching the leading order terms for large t. This solution immediately gives us the mean square fluctuation of ρ for large t,

$$\langle\rho^2(t)\rangle=\frac{\int_0^\infty\rho^2\exp\left[-\frac{e^{\mu^*\rho}}{2\mu^{*2}Dt}\right]d\rho}{\int_0^\infty\exp\left[-\frac{e^{\mu^*\rho}}{2\mu^{*2}Dt}\right]d\rho}\sim\ln^2(2\mu^{*2}Dt). \tag{8}$$

The fluctuations grow logarithmically with time, in contrast to the standard $\sqrt{t}$ scaling expected at a normal critical point.

Scaling solution for $\epsilon\neq 0$. Away from the critical point, the Fokker-Planck equation, Eq. (5), has a normalizable stationary solution. The equation obtained by substituting $P(\rho,t)=e^{-\epsilon\rho^2/4D}\psi(\rho,t)$ in Eq. (5) allows a scaling solution for $\psi(\rho,t)$ in the limit $t\to\infty$, $\rho\to\infty$ but keeping the combination $e^{\mu^*\rho}/t$ fixed. Repeating the same steps as described above for the $\epsilon=0$ case we compute

$$P(\rho,t)=\frac{\exp\left(-\epsilon\rho^2/4D-\frac{e^{\mu^*|\rho|}}{2\mu^{*2}Dt}\right)}{2\int_0^\infty d\rho\exp\left(-\epsilon\rho^2/4D-\frac{e^{\mu^*\rho}}{2\mu^{*2}Dt}\right)}. \tag{9}$$

In the limit $t\to\infty$, this solution recovers the equilibrium distribution. From Eq. (9), it is clear that at a given large t, there are two length scales in ρ space: the equilibrium length scale, $\sqrt{\langle\rho^2\rangle_{eq}}=\sqrt{2D/\epsilon}$, and a time-dependent length scale, $\rho_c=(1/\mu^*)\ln(\mu^{*2}Dt)$. For $\rho\ll\rho_c$, $P(\rho,t)$ reduces to the equilibrium Gaussian distribution while for $\rho\gg\rho_c$ the distribution of ρ is superexponential (see Fig. 2). At long times ρ_c becomes much larger than the equilibrium ρ and the system "knows" that it is in equilibrium. This defines a crossover time $t_c\sim e^{\mu^*\sqrt{2D/\epsilon}}$ obtained by equating ρ_c with $\sqrt{\langle\rho^2\rangle_{eq}}$. Below we also compute the relaxation time from the the mean-square fluctuation of the order parameter, $\langle\rho^2(t)\rangle$ and show that it diverges as $\exp[1/\epsilon]$, which is precisely the VFT law.

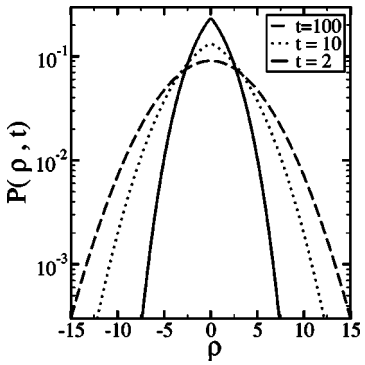

FIG. 2. The probability distribution, $P(\rho,t)$, for three different times, with $\epsilon=0.1$, $D=1$, and $\mu^*=1$. For these parameters, $\rho_c=0.69$, 2.3, 4.6 for $t=2$, 10, 100, respectively, and $t_c=88$. Note that at $t=2$ the distribution is essentially superexponential and for $t=100$ it is a Gaussian.

An interesting conclusion that can be drawn about the Landau model is that its critical dynamics cannot be characterized by a single diverging time scale.

We have seen earlier that in the $\epsilon=0$ case, $\langle\rho^2(t)\rangle \sim \ln^2(t)$ for large t. For $\epsilon\neq 0$ this quantity will relax to its equilibrium value $\langle\rho^2\rangle_{eq}=2D/\epsilon$. From Eq. (9), we find in the scaling limit,

$$\langle\rho^2(t)\rangle = \frac{\int_0^\infty \rho^2 \exp\left(-\epsilon\rho^2/4D - \frac{e^{\mu^*\rho}}{2\mu^{*2}Dt}\right)d\rho}{\int_0^\infty \exp\left(-\epsilon\rho^2/4D - \frac{e^{\mu^*\rho}}{2\mu^{*2}Dt}\right)d\rho}. \quad (10)$$

Thus one can write

$$\langle\rho^2(t)\rangle = -\frac{\partial \ln[Z(A)]}{\partial A}, \quad (11)$$

where $A=\epsilon/4D$, and the generating function $Z(A)$ is given by

$$Z(A) = \int_0^\infty d\rho \exp\left(-A\rho^2 - \frac{e^{\mu^*\rho}}{2\mu^{*2}Dt}\right). \quad (12)$$

From Eq. (11) we find that for large t and small A,

$$\langle\rho^2(t)\rangle \approx \langle\rho^2\rangle_{eq} - \frac{4D}{\epsilon^2}e^{D\mu^{*2}/\epsilon}\frac{1}{t}. \quad (13)$$

Thus, at late times, the mean square fluctuation relaxes to its equilibrium value in a power law $(\sim 1/t)$ fashion. A standard way to estimate the relaxation time τ is to define it as the time needed for the difference $\langle\rho^2\rangle_{eq}-\langle\rho^2(t)\rangle$ to decay to a given value of order one. From Eq. (13) we immediately obtain

$$\tau \propto \frac{D}{\epsilon^2}e^{D\mu^{*2}/\epsilon}, \quad (14)$$

which diverges in the VFT manner as $\epsilon\to 0$.

Activated dynamics at a critical point were previously shown to occur in systems with quenched disorder [7] and it had been suggested that a similar situation might exist in nondisordered systems with frustration [8]. The emergence of a glass state in the latter case could then be associated with a critical point at which relaxation times would acquire astronomical values long before any discernible spatial correlations indicative of an ordered state could be established. The dynamical Landau model presented here provides an explicit realization of this scenario.

The scaling solution to our model demonstrates that a seemingly innocuous change in the transition rates leads to an exponential divergence of time scales at a critical point, while all its static properties are described by mean-field Landau theory. The dynamics of the Landau model are characterized by a multitude of time scales and by nonexponential relaxations even away from the critical point. Namely, the mean-square fluctuation of ρ can be written in terms of the density of states $\Omega(E)$ as $\langle\rho^2(t)\rangle=\int dE\Omega(E)e^{-Et}$. The power law decay for $\epsilon\geqslant 0$, Eq. (13), implies that $\Omega(E)$ is proportional to $\delta(E)$-const with the δ function guaranteeing the equilibrium value. At the critical point, the logarithmic decay of the fluctuations implies $\Omega(E)\propto \ln^2(E)/E$. The glass transition in our model is, therefore, not characterized by a vanishing gap in the energy spectrum [of Eq. (5)] but instead by an accumulation of states near $E=0$. This then translates to a distribution of time scales with increasing weight in the tails of the distribution corresponding to long times.

In the Landau model with a quadratic entropy function the entropy goes to zero at $\rho^2_{max}=2S_0/\mu^*$ and our analysis is, therefore, strictly valid for $\langle\rho^2\rangle_{eq}\leqslant\rho^2_{max}$ or $\epsilon\geqslant\mu^*/2S_0$. For smaller values of ϵ the relaxation time-scale divergence is cut off by the system size.

Microscopic models. The transition rates given by Eq. (3), which formed the basis of our dynamical equation and led to the VFT divergence of time scales, are explicitly realized in the interacting three-color model [9]. The configurations of the three-color model on the honeycomb lattice can be mapped on to loop packings and the loops can be identified with equal height contours of a discrete height field which lives on the dual triangular lattice [10]. Coloring configurations can be organized into topologically distinct sectors characterized by the number of nonzero winding number loops, which correspond to different global tilts in the height representation. The introduction of a long-range interaction between one of the colors leads to a phase transition from a flat to a completely tilted state [9] with the tilt playing the role of the order parameter ρ.

Microscopic dynamics for the three-color model can be defined in terms of loop updates [9] with transitions between different loop configurations satisfying detailed balance. Simulations were performed to extract the transition rates between different tilt states and it was shown that they take the form described by Eq. (3). The asymmetry in the rates owes its origin to the loop dynamics. A ρ-reducing (energy-increasing) transition involves deleting an existing nonzero winding number loop. The rate of this transition is determined *only* by the change in *energy* since all loop configurations at a given ρ can lead to a configuration with $\rho'<\rho$. On the other hand, a transition that increases ρ and consequently decreases the energy, involves introducing a new nonzero winding number loop. Since only a small subset of

loop configurations at a given ρ can accommodate a new nonzero winding number loop, this transition rate depends only on the change of entropy. We believe similar mechanisms are operative in other systems where transitions between macrostates involve large scale rearrangements that, due to the presence of constraints, can occur only through coordination of many microscopically rearranging regions.

In this paper, we identify a concrete physical mechanism by which dynamical barriers are established in the free energy landscape. The dynamics in the order parameter space in our model is thus reminiscent of diffusion on hierarchical lattices [11,12] and trap models [13]. Recently, attempts have been made to identify inherent structures in supercooled liquids as providing a microscopic basis for traps [14,15]. If we identify inherent structures with the order parameter ρ in our model then the predicted distribution of trapping times, $\tau_\rho = 1/(W_{\rho\to\rho-1}+W_{\rho\to\rho+1})$, is log-normal with a width that increases as $1/\epsilon$. This is consistent with the behavior observed in supercooled liquid simulations [14].

Studies of kinetically constrained models [16] have identified dynamical heterogeneities [17,18] resulting from the kinetic constraints and an entropy crisis in trajectory space which leads to rapidly increasing time scales [18,19]. In our model, the asymmetry of the rates results in an entropy crisis and, combined with the existence of an equilibrium critical point, leads to an exponential divergence of relaxation time scales for a finite value of the control parameter.

The coarse-grained dynamical model presented here suggests a new way of analyzing atomistic simulations of glassy materials. From molecular dynamics simulations one can measure the transition rates between macrostates characterized by different values of a slow variable that plays the role of an order parameter, e.g., the metabasin energies in supercooled liquids [14,15]. This approach avoids making specific assumptions about the origin of the transition rates. Dynamics in order parameter space can be constructed explicitly and analyzed for the types of asymmetries and related dynamical barriers discussed here within a simple Landau model. Work along these lines is currently in progress.

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[1] M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).
[2] N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Addison-Wesley, New York, 1992).
[3] J. Schonbrun and K. A. Dill, Proc. Natl. Acad. Sci. U.S.A. **100**, 12678 (2003).
[4] We will show below that by taking limits appropriately, the entropy does not become negative.
[5] A. R. Kansal, S. Torquato, and F. H. Stillinger, Phys. Rev. E **66**, 041109 (2002).
[6] The $\rho=0$ point is included in the continuum equation; Satya N. Majumdar (unpublished).
[7] D. S. Fisher, Phys. Rev. Lett. **56**, 416 (1986).
[8] J. P. Sethna, J. D. Shore, and M. Huang, Phys. Rev. B **47**, 14661 (1993).
[9] D. Das, J. Kondev, and B. Chakraborty, Europhys. Lett. **61**, 506 (2003).
[10] J. Kondev, J. deGier, and B. Nienhuis, J. Phys. A **29**, 6489 (1996).
[11] S. Teitel, Phys. Rev. Lett. **60**, 1154 (1988).
[12] R. G. Palmer *et al.*, Phys. Rev. Lett. **53**, 958 (1984).
[13] C. Monthus and J.-P. Bouchaud, J. Phys. A **29**, 3847 (1996).
[14] R. A. Denny, D. R. Reichman, and J. P. Bouchaud, Phys. Rev. Lett. **90**, 025503 (2003).
[15] B. Doliwa and A. Heuer, Phys. Rev. E **67**, 030501 (2003).
[16] F. Ritort and P. Sollich, Adv. Phys. **52**, 219 (2003).
[17] J. P. Garrahan and D. Chandler, Proc. Natl. Acad. Sci. U.S.A. **100**, 9710 (2003).
[18] J. P. Garrahan and D. Chandler, Phys. Rev. Lett. **89**, 035704 (2002).
[19] C. Toninelli, G. Biroli, and D. S. Fisher, Phys. Rev. Lett. **92**, 185504 (2004).