Anomalous relaxation and self-organization in nonequilibrium processes

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We study thermal relaxation in ordered arrays of coupled nonlinear elements with external driving. We find that our model exhibits dynamic self-organization manifested in a universal stretched-exponential form of relaxation. We identify two types of self-organization, cooperative and anticooperative, which lead to fast and slow relaxation, respectively. We give a qualitative explanation for the behavior of the stretched exponent in different parameter ranges. We emphasize that this is a system exhibiting stretched-exponential relaxation without explicit disorder or frustration.

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The world around us is full of nonequilibrium and nonstationary processes, many of which are robust and easy to measure. However, there is no *a priori* reason to believe that these nonequilibrium processes should fulfill universal laws in the way that equilibrium systems fulfill laws of thermodynamics and statistical mechanics. It is, therefore, important to recognize examples of complex nonequilibrium processes organizing themselves in a simple and universal way, a phenomenon termed ''self-organization'' or ''emergent behavior'' [1,2]. Kolmogorov turbulence [3] is an example of such a nonequilibrium process: Liquid, forced at macroscopic length scales produces a flow of energy from large to small length scales and this flow organizes itself into a stationary universal distribution. Turbulence is a steady, though nonequilibrium, process; the flow of energy is constant and the resulting self-organized probability distribution does not change in time. It is important to establish, whether boundaries of self-organization can be expanded to include nonequilibrium and nonstationary processes. In this paper we show that *dynamic self-organization* can indeed be found in relaxational dynamics of extended systems and is manifested in stretched-exponential dependence on time of physical quantities.

Stretched-exponential ($\propto \exp[-(t/t_{rel})^{\alpha}]$) relaxation laws have been observed in a large variety of physical and biological processes, such as recombination of carriers in semiconductors and polymers [4,5], protein relaxation [6], and folding [7,8], ligand binding to myoglobin [9,10], relaxation in magnetic clusters [11], superconducting vortices [12] and charge density waves [13,14], dynamics of alloys [15], and glasses [16]. In the case of glasses, the stretching exponent α defines a glass transition temperature T_g, i.e., $\alpha=1$ for $T>T_g$, and $\alpha<1$ for $T<T_g$. The nonexponential dynamics of glasses has long been related to the high degree of disorder, which leads to the existence of a large number of metastable states [17].

Observations of nonexponential behavior in simpler systems, such as magnetic clusters [11] and proteins [6,7], suggests that a high degree of disorder is *not* a necessary requirement for a system to display anomalous relaxation. Especially notable are recent observations of folding dynamics in proteins, yeast phosphoglycerate kinase (PGK), and ubiquitin mutant [7]. These proteins fold according to a ''downhill folding'' scenario [18], meaning that the folding path between the unfolded and folded states is free of deep metastable minima, so the process of folding is ''downhill'' relaxation along this path. Nevertheless, the number of folded proteins, as a function of time, displays stretched-exponential behavior over a large time interval [7].

In this paper we present a simple minimal model that is translationally invariant and *without* disorder or explicit frustration [19], which displays perfect stretched-exponential relaxation over wide time intervals. The stretched exponent α changes continuously from slow relaxation $\alpha<1$ to fast relaxation $1\leqslant\alpha\leqslant 2$ as parameters of the system vary. We identify *dynamic self-organization* as the origin of the stretched-exponential relaxation and show that slow and fast relaxation are caused by *anticooperative* and *cooperative* behavior, respectively. We provide a theoretical explanation of the discrete and continuous limiting cases. We also present a qualitative theory, which accounts for behavior of the stretched exponent in the intermediate range of parameters.

Real life systems [4–9] are much more complex than our simple model. However, we conjecture that at least one underlying reason for stretched-exponential relaxation is universal. Namely, *self-organization*, with fast and slow relaxation corresponds to cooperative and anticooperative behavior. We suggest that proteins belong to the anticooperative universality class. Our argument is, that initially the protein is loose and deforms easily. When folding into a particular local pattern occurs, this part becomes stiff, making folding of neighboring parts more difficult, and therefore behaving in an anticooperative way. Similar anticooperative behavior occurs in our model system for negative values of the coupling as we discuss below.

Let us now specify the model. We consider a chain of nonlinear bistable elements. Each element is described by the order parameter u_n. The local energy $E(u)$ has two minima, one of which is a metastable state (local minimum of energy), the other one is the absolutely stable state (absolute minimum of energy). We assume overdamped dynamics of

u_n in the presence of delta-correlated thermal noise. Equations of motion of the system are

$$\frac{\partial u_n}{\partial t} = \beta(u_{n+1} + u_{n-1} - 2u_n) + F(u_n) + f_n^{\mathrm{stc}}. \qquad (1)$$

Here β represents linear coupling of neighboring sites, $F(u) = -dE/du = -u(u-u_0)(u-1)$ is a forcing term, corresponding to the bistable polynomial potential $E(u) = (1/4)u^4 - (1/3)(u_0+1)u^3 + (1/2)u_0u^2$. The potential has two minima, $u=0$ and $u=1$, separated by a barrier $u=u_0$. At $u_0 = 1/2$ the minima have equal energy. For $u_0 < 1/2$ the minimum $u=1$ becomes absolutely stable and $u=0$ becomes metastable, with energy difference given by $\Delta E = 1/12 - 1/6u_0$. The stochastic term f^{stc} is given by a delta-correlated Langevin force

$$\langle f_n^{\mathrm{stc}}(t_1) f_m^{\mathrm{stc}}(t_2) \rangle = T\delta_{mn}\delta(t_1 - t_2), \qquad (2)$$

where T defines the temperature in our system [20]. Equation (1) can be viewed as a discrete one-dimensional Ginzburg-Landau equation with noise.

Let us first review equilibrium properties of our system. At $T=0$ the system is in the absolutely stable phase. When temperature is introduced, some (small) number of particles overcome the barrier because of equilibrium thermal fluctuations. The relative number of particles in the metastable phase is determined by Boltzmann statistics and is exponentially small for temperatures much less than the energy difference between potential wells.

Our goal is to study the nonequilibrium and nonstationary process of relaxation from the metastable phase to the absolutely stable phase. We assume that all sites are initially in the metastable phase and then introduce the thermal noise. Due to fluctuations, particles start to overcome the barrier and the number of particles in the absolutely stable phase increases. We monitor relaxation by introducing the function $n(t) = N(t)/N_0(T)$, which describes the ratio between the concentration of particles in the absolutely stable phase at time t and their equilibrium number $N_0(T)$. In the thermodynamic limit of infinite chain length, $n(t)$ is a well-defined smooth function, which satisfies the conditions $n(0)=0$ and $n(\infty)=1$.

We study relaxation numerically by integrating the Langevin equations (1) defined on long chain segments ($N = 200$) and averaging the resulting functions $n(t)$ over many noise realizations. To improve numerical convergence, we use an implicit integration scheme. Details of the numerical method will be reported elsewhere [21].

A typical function $n(t)$ is given in Fig. 1. Important global features of the relaxation, valid in all ranges of parameters, areas follows.

(i) After a short transient time t_0 (Fig. 1), the system self-organizes and $n(t)$ starts to obey the stretched-exponential form $n(t) = 1 - \exp[-(t/t_{rel})^{\alpha}]$. Note, that there are only two parameters in our fit, which are the stretched exponent α and the relaxation time t_{rel}. The precision of the stretched-exponential fit is extremely high and is about 0.1% for $t > t_0$.

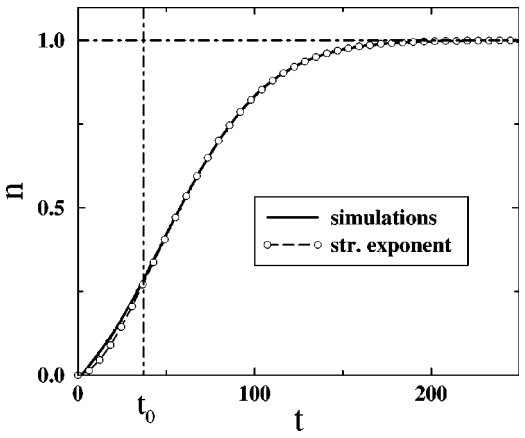

FIG. 1. Plot of a typical function $n(t)$. Solid line represents the result of numerical simulations. Dashed line is a stretched-exponential fit. Parameters are $T=0.01$, $u_0=0.35$, $\beta=0.04$.

(ii) The stretched exponent α changes continuously as temperature T and coupling β vary, see Figs. 2 and 3. The observed relaxation is fast ($\alpha > 1$) for positive values of β and slow ($\alpha < 1$) for negative values of β. As temperature T is increased, the stretched exponent α approaches the Arrhenius law ($\alpha = 1$), corresponding to the intrinsic frustration being overcome thermally.

(iii) The stretched exponent α approaches the value $\alpha = 2$ in the continuous limit of large β, representing a binary relaxation channel.

The dependence of α on β is given in Fig. 2. At zero β the system represents a set of uncoupled nonlinear sites. Each site is described by a one-dimensional Fokker-Planck equation. In this case relaxation is known to be described by an exponential (Arrhenius) law, with decay time determined by the lowest excited state of the Fokker-Planck operator [20]. Therefore, for $\beta=0$ one has $\alpha=1$.

Let us now explain, why introducing positive (negative) β corresponds to cooperative (anticooperative) behavior. If β is positive, one may think of the intersite coupling β as an

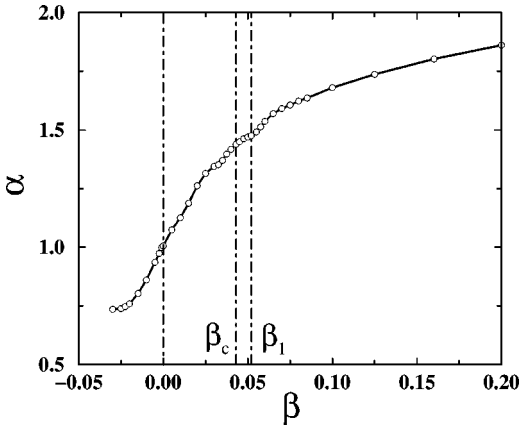

FIG. 2. Stretched exponent α as a function of intersite coupling β for u_0 and T same as in Fig. 1. Propagation failure bifurcation and one-site nucleus bifurcation are marked as β_c and β_1, respectively.

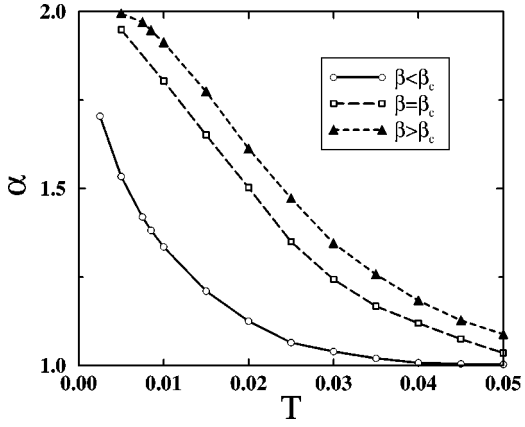

FIG. 3. Stretched exponent α as a function of temperature T for three different values of β, above, below, and at the propagation failure bifurcation point. Parameters are $u_0=0.35$, $\beta=0.03,0.043,0.06$. Other parameters are the same as in Fig. 1.

elastic chain connecting neighboring sites n and $n+1$. If a particle overcomes the barrier, it attracts its neighbors and makes it, therefore, easier for them to jump over the barrier. Contrary to this, negative coupling corresponds to a repulsive force, which makes relaxation of nearest neighbors more difficult. (Indeed in the limit of large negative β, our model produces a strong staggered dimerization of the lattice.) We conclude from Fig. 2 that the cooperative behavior leads to fast relaxation, $\alpha>1$, and anticooperative behavior leads to slow relaxation, $\alpha<1$.

We will now discuss the behavior of the stretched exponent α at large positive β. In this limit the system becomes continuous and is described by the continuous Ginzburg-Landau equation,

$$\frac{\partial u}{\partial t}=\beta\frac{\partial^2 u}{\partial x^2}+F(u)+f(x,t)^{\mathrm{stc}}. \tag{3}$$

In the absence of thermal noise, topological excitations of this equation are fronts (kinks), which separate the absolutely stable and metastable phases. Due to the energy difference between the phases, the fronts propagate at finite velocity v, increasing the size of the absolutely stable phase. When temperature is introduced, local fluctuations of the order parameter give birth to kink-antikink pairs (Fig. 4). These pairs counter propagate, replacing the metastable phase by the absolutely stable one. Let us now estimate the probability for the order parameter $u(0,t)$ at $x=0$ to stay in the metastable phase after time t. This probability is approximately equal to the probability $P(t,l)$ that no kink-antikink pair will be created by fluctuations during time t at a distance $l\lesssim vt$ from the origin. If such a pair is created, then the newly born kink has enough time to reach $x=0$ before the time interval t elapses and annihilate the metastable phase, see Fig. 4. Since fluctuations are local, one can estimate $P(l,t)$ as $\exp(-lt/\eta)$, where η is a constant. Therefore, the probability to stay in the metastable phase after time t is approximately $\exp(-vt^2/\eta)$. Since the number of particles in the metastable phase after time t is proportional to this probability, we conclude that in the continuous limit the stretched exponent $\alpha=2$. Our numerical data (see Fig. 2) are in a good agreement with this prediction.

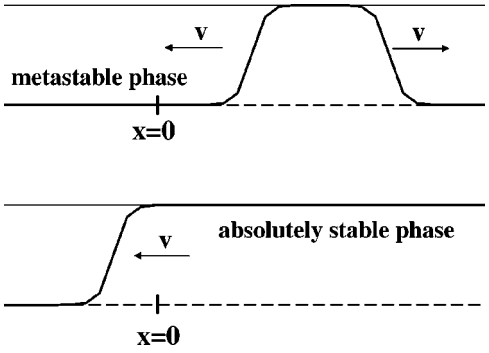

FIG. 4. New phase nucleation through birth and propagation of kink-antikink pairs (schematic).

The fact that the stretched exponent $\alpha=2$ in the continuous case is striking and has important consequences. Namely, *space discreteness is necessary to observe continuous dependence of α on parameters*. We can rephrase this statement as follows. It is known, that critical properties of equilibrium systems are described by continuous models and these models can be organized into universality classes, such that each universality class has a set of universal critical exponents [23,24]. We conjecture, that effective models for nonequilibrium, nonstationary self-organization, in particular relaxation, must include discreteness in order to incorporate the continuous dependence of stretched exponents on parameters.

Let us now consider the nontrivial dependence of the stretched exponent α on the coupling β and temperature T, for the intermediate values of β, given in Figs. 2 and 3 (a more detailed discussion of these effects will be given in [21]). In the absence of noise, the topological excitations of system (1) undergo a sequence of bifurcations as described in [22,25,26]. The most important of these bifurcations is the propagation failure bifurcation at which fronts cease to propagate, being pinned by the lattice. We denote the corresponding value of the coupling β as β_c. An analytical expression for β_c was derived by us in [26]. The second important bifurcation point is β_1. At this point, a one-site nucleus of the globally stable phase, representing a bound state of a kink and antikink pair, becomes unstable and ''bursts'' into counter-propagating kink and antikink. In [25] we have shown, that there exist an infinite number of bifurcation points β_n, such that $\beta_c\leqslant\cdots\leqslant\beta_n\leqslant\beta_{n-1}\leqslant\cdots\leqslant\beta_1$, corresponding to the instabilities of a one-site, two-site, three-site, etc. nuclei. In Fig. 2 we see the corresponding change of shape in the coupling-dependence of the stretched exponent α in the interval $\beta_c<\beta<\beta_1$. Accordingly, Fig. 3 demonstrates a transition in the temperature dependence of α, with β crossing β_c. We conclude from Figs. 2 and 3 that this region of bifurcations is manifested as a characteristic feature of the nonequilibrium relaxation of the system.

In conclusion, we have introduced a model of dynamic self-organization and conjectured that it should be applicable to stretched-exponential relaxation in many biological and

physical systems. We studied properties of self-organization in a simple model and showed that fast (slow) relaxation is related to cooperative (anticooperative) behavior. We showed, that neither explicit disorder nor frustration are necessary requirements for anomalous relaxation laws. In view of this, an experimental evidence of anomalous relaxation in a physical system should not be considered as automatic proof of disorder or frustration in the system. Appropriate nonlinearity (arising, for example, from coupled degrees of freedom with feedback) can alone produce both the ingredients of local structures (''intrinsic disorder'') and competition (of length scales), leading to a distribution of metastable states and anomalous dynamics [19]. The detailed analytical description of dynamic self-organization is a promising direction for future study. This will include extensions to higher dimensions as well as specific physical models. We also note that stretched exponents were also observed in *equilibrium* correlation functions [27] and it is important to understand whether they can be related to their nonequilibrium counterparts.

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