Anomalous relaxation and self-organization in non-equilibrium 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 anti-cooperative, 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.

The world around us is full of non-equilibrium and non-stationary processes, many of which are robust and easy to measure. However, there is no a priori reason to believe, that these non-equilibrium processes should fulfill universal laws, in a way equilibrium systems fulfill laws of thermodynamics and statistical mechanics. It is, therefore, important to recognize examples of complex non-equilibrium 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 non-equilibrium processes: 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 non-equilibrium, 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 non-equilibrium and non-stationary 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], ligand binding to myoglobin [8], relaxation in magnetic clusters [9], superconducting vortices [10], and charge density waves [11,12], dynamics of alloys [13] and glasses [14]. In the case of glasses, the stretching exponent $\alpha$ defines a glass transition temperature, $T_g$, i.e. $\alpha = 1$ for $T > T_g$ and $\alpha < 1$ for $T < T_g$. The non-exponential 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 [15].

Observations of non-exponential behavior in simpler systems, such as magnetic clusters [9] and proteins [16], 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 [17]. 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 [19].

In this Letter we present a simple minimal model which is translationally invariant and without disorder or explicit frustration [16], which displays perfect stretched-exponential relaxation over wide time intervals. The stretched exponent $\alpha$ changes continuously from slow relaxation $\alpha < 1$ to fast relaxation $1 \leq \alpha \leq 2$, 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 anti-cooperative 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 corresponding to cooperative and anti-cooperative behavior. We suggest that proteins belong to the anti-cooperative 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 anti-cooperative way. Similar anti-cooperative 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 $u_n$ at the presence of delta-correlated thermal noise. Equations of motion of the system are:

$$\frac{\partial u_n}{\partial t} = \beta(u_{n+1} + u_{n-1} - 2u_n) + F(u_n) + f_{n}^{\text{stc}}. \quad (1)$$

Here $\beta$ 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 $u = u_0$. At $u_0 = 1/2$ the minima have equal energy. For $u_0 < 1/2$ the minimum $u = 1$ becomes absolutely stable and $u = 0$ metastable, with energy difference given by $\Delta E = 1/12 - 1/6u_0$. The stochastic term $f_{n}^{\text{stc}}$ is given by a delta-correlated Langevin force

$$\langle f_{n}^{\text{stc}}(t_1)f_{m}^{\text{stc}}(t_2) \rangle = T \delta_{mn}(t_1 - t_2), \quad (2)$$

where $T$ defines the temperature in our system [28]. Eq. (1) can be viewed as discrete one-dimensional Ginzburg-Landau equation with noise.

Our goal is to study non-equilibrium and non-stationary process of relaxation from the metastable phase to the absolutely stable phase. We assumes that all sites are initially in the metastable phase, and then introduces 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 [27].

![Plot of a typical function $n(t)$](image1)

**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 $T = 0.01$, $u_0 = 0.35$, $\beta = 0.04$.

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.

![Stretched exponent $\alpha$ as a function of inter-site coupling $\beta$](image2)

**FIG. 2.** Stretched exponent $\alpha$ as a function of inter-site coupling $\beta$, for $u_0$ and $T$ the same as in Fig. 1. Propagation failure bifurcation and one-site nucleus bifurcation are marked as $\beta_c$ and $\beta_1$, respectively.

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

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 $\alpha$ and the relaxation time $t_{rel}$. The precision of the stretched-exponential fit is extremely high, and is about 0.1% for $t > t_0$.

ii) The stretched exponent $\alpha$ changes continuously, as temperature $T$ and coupling $\beta$ vary, see (Figs. 3 and 4).
The observed relaxation is fast ($\alpha > 1$) for positive values of $\beta$ and slow ($\alpha < 1$) for negative values of $\beta$. As temperature $T$ is increased, the stretched exponent $\alpha$ approaches the Arrhenius law ($\alpha = 1$), corresponding to the intrinsic frustration being overcome thermally;

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

The dependence of $\alpha$ on $\beta$ is given in Fig. 3. At zero $\beta$ 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 $\alpha = 1$.

FIG. 3. Stretched exponent $\alpha$ as a function of temperature $T$, for three different values of $\beta$, 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. 4.

Let us now explain, why introducing positive/negative $\beta$ corresponds to cooperative/anti-cooperative behavior, respectively. If $\beta$ is positive, one may think of the intersite coupling $\beta$ as an 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 $\beta$, 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 anti-cooperative behavior leads to slow relaxation, $\alpha < 1$.

We will now discuss the behavior of the stretched exponent $\alpha$ at large positive $\beta$. In this limit the system becomes continuous and is described by the continuous Ginzburg-Landau equation.

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

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 $l \leq vt$ 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 $P(l,t) = \exp[-lt/\eta]$, where $\eta$ 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. 3) 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 $\alpha$ 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 univer-
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