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Non-Exponential Relaxation Time Scales in Disordered Systems: an Application to Protein Dynamics

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Abstract

We study the dynamics of an heteropolymeric chain relaxing toward a new equilibrium configuration after the action of an external perturbation. We compare the results from Monte Carlo simulations with the results of a Langevin normal mode decomposition. We discuss, for sake of comparison, the case of an ordered homopolymeric chain.

1 Disordered System Dynamics

Disordered system[1, 2] potential relevance for understanding protein folding has received much attention in the last few years (see for example refs. [3, 4, 5, 6, 7]. They differ from their ordered counterpart in being characterized from a dynamical behavior which is different on different (and many) time scales. A large number of experiments (for a discussion see for example ref. [2]) has been done in order to probe such complex dynamical features (where up to 15 different orders of magnitude can be relevant).

Typically a single experiment can only probe one scale at time, since the relaxation processes which occur on faster time scales can be already equilibrated when the ones with larger characteristic times are yet completely frozen. It is fortunate that in the *aging* experiments [8] the relevant degrees of freedom act on at least two time scales simultaneously.

These dynamic phenomena are called *dispersive* as they are characterized by long tailed waiting time distribution where the first moment diverges. Many toy models (see for example ref. [9]) have been proposed to shed light on such multi-timescale systems.

These models are generally explicitly hierarchical. It would be more satisfying to have model in which a hierarchical structure would emerge naturally, as for example happens in the Sherrington Kirkpatrick model (SK).

The description of a very simple model[2] can be useful. It describes a particle at temperature T which can hop among hierarchically grouped states. One can study the solution of the Fokker-Planck equation for the probability $P(x,t)$ of finding the particle in a given one of the allowed states. One introduces a matrix of transition rates between states that has the same kind of ultrametrix structure as the q replica order parameter matrix in the mean field theory. A possible interesting choice for the dependence of the transition rates on the ultrametric distance is assuming that the barriers δ between states increase linearly (with a proportionality constant Δ) with the ultrametric distance k

$$\delta(k) = \Delta\ k\ . \tag{1}$$

In this case one can find that the probability P_0 (which in a spin system can be identified with the spin autocorrelation function) of remaining in the initial state evolves according to a power law

$$P_0 \simeq t^{\frac{-T \log 2}{\Delta}} \ . \tag{2}$$

If the barriers grow too slowly with the ultrametric distance the system delocalizes. The case which is most interesting for us is the *marginal* one, where we select for the barrier height $\delta(k)$ a logarithmic dependence over the ultrametric distance k:

$$\delta(k) = \Delta \ \log k \ . \tag{3}$$

In that case the time evolution of P_0 is found to have a *stretched exponential* dependence (as first introduced by Kohlrausch[10]):

$$P_0 \simeq \exp(-t^{\frac{T}{\Delta}}) \ . \tag{4}$$

In the following we will focus our attention to such stretched exponential behaviors, as found in the dynamics of the heteropolymeric chains.

In Section 2 we discuss what happens in disordered spin systems. In Section 3 we define the quantities needed to discuss relaxation dynamics. In Section 4 we recall the definition of our model (IMP in the following, see ref. [11]. For further developments on this model see refs. [12, 13, 14]), we define our Monte Carlo procedure, and we present the results of numerical simulations. In Section 5 we introduce the Langevin Equation approach and its connection to a stretched exponential dynamics, and we discuss our results from a normal mode decomposition.

2 Spin Glass Dynamics on Large Time Scales

We will be interested in studying time-dependent effects in the broken phase of a disordered system. The typical example is the replica broken phase of a mean-field SK model[1]. In this case broken ergodicity makes the analysis very difficult: one has to be careful in examining phenomena typical of the different time scales relevant for the dynamical evolution.

Let us assume that we are dealing with a system which has many pure states. In this case for a sample in the thermodynamic limit (infinite volume) the time evolution is confined to one of the available pure states: the system will not be able to escape to another valley in a finite time. This relaxational dynamics inside one state has been studied in mean field theory by Sompolinsky and Zippelius[15] and shows a power law time decay (for the case of an IMP heteropolymer a power behavior for the dynamics inside one state has been found in the numerical simulations of ref. [14]).

Many efforts have also been done to understand the dynamics on time scales which diverge with the volume of the system. In such a way one can focus on time scales which, for increasing volume, allow transitions between the different states (indeed the precursors of what will be the states in the thermodynamical limit). The basic hypothesis, put forward by Sompolinsky[16], is here that the large time limit of the dynamic evolution is governed by a strong hierarchy of time scales.

The precise understanding of the asymptotic regime require a detailed knowledge of the properties of the system for large finite size: for example informations about the height of the free energy barriers between states can give lot of helpful information. One reasonable assumption, that one needs in absence of more detailed informations about the barriers between the states, consists in assuming that the time needed for the system to jump from one state to another is correlated with the distance between the two states. Under this assumption one can associate to each value of the distance k a typical hopping time scale τ. At any given time τ the system is described by a given equilibrium measure.

Mackenzie and Young[17] have studied numerically the maximum relaxation time τ_M as a function of the system size N, for the mean field SK system. They have found that

$$\log(\tau_M) \simeq N^{\frac{1}{4}} \ . \tag{5}$$

Similar studies on equilibrium relaxation dynamic have also been done on system like the Random Energy Model[18] where no hierarchical organization between states is present (since replica symmetry is broken only at first order). Work by De Dominicis, Orland and Lainée[19] shows that also this model exhibit a non-exponential relaxation, suggesting that ultrametricity is not necessarily needed to obtain this kind of behavior. A stretched exponential dynamical behavior has also been find in the case of the Spherical Spin model in ref. [20].

3 Non Equilibrium Dynamics

In the following we will look at the problem of the relaxation dynamics of a disordered system not far from equilibrium. The system, at equilibrium for some given values of the external parameters, undergoes an external perturbation (some of the parameter values are abruptly modified). We will study the subsequent search of a new equilibrium configuration.

Let us assume that the system just goes out of its local (free energy) minimum, without moving too far away from its initial conformation. Eventually we expect the system to relax in the free energy valley of the chosen minimum. Here the system will only undergo very small conformational modifications. We will show this relaxation to have a stretched exponential form.

This matter has been studied experimentally in the pioneering work on proteins by Frauenfelder and collaborators (see ref. [21] and references therein). They measure different quantities $\mathcal{A}(t,T)$, which depend on the time t and on the temperature T, and define the relaxation functions as

$$\Phi(t) \equiv \frac{\mathcal{A}(t,T) - \mathcal{A}(\infty,T)}{\mathcal{A}(0,T) - \mathcal{A}(\infty,T)} \ , \tag{6}$$

where the time $t = 0$ is the one just after the perturbation was applied. After a stress in temperature or pressure $\Phi(t)$ was shown to have a non-exponential behavior.

In the next sections of this note we will study the dynamical behavior of an heteropolymeric system. We will look at what we believe to be the relaxation in a given free energy minimum (see the former discussion), but we will be working at times which are very shorter than the experimental ones (which can be of the order of seconds). We will show that in this case we cannot explain our results with a simple exponential relaxation law, and that the introduction of a stretching parameter will lead us to a very good fit of the numerical results.

An analytical study of the Langevin equation normal modes decomposition will show how such temporal evolution can be associated to the existence of a long tail (in the small frequency region) in the eigenvalue spectrum of the relevant dynamical operator.

4 Montecarlo Simulations

Let us start by recalling the definition of the IMP model[11]. We consider a chain formed of N sites (they would be identified, in the protein analogy,with *sequences* of amino-acids, i.e. preassembled segments of the secondary structure): their position in *continuum* 3 dimensional space is characterized by the 3 values of the coordinates x_i^μ. We define the energy between two sites of the chain as

$$E_{i,j} \equiv \delta_{i,j+1}\ r_{i,j}^2 + \frac{R}{r_{i,j}^{12}} - \frac{A}{r_{i,j}^6} + \frac{\eta_{i,j}}{r_{i,j}^6}\ , \tag{7}$$

where $r_{i,j}$ is the usual Euclidean distance between the sites i and j.

The harmonic term couples the first neighbors on the chain. The deterministic part of the potential has the usual Lennard-Jones form. The quenched disordered part of the potential is built on the η variables, which are distributed with a zero expectation value and with a second moment

$$\langle \eta_{i,j}\ \eta_{k,l} \rangle = \epsilon\ \delta_{(i,j),(k,l)}\ , \tag{8}$$

where $\langle\rangle$ indicates the expectation value over the quenched distribution, which we have chosen to be uniform, ϵ characterizes the disorder strength, and $\eta_{i,j} = \eta_{j,i}$.

The Hamiltonian of the model is defined as

$$H \equiv \sum_{i=1}^{N} \sum_{j>i} E_{i,j}\ . \tag{9}$$

In our typical run we have selected values of the parameters close to the ones of ref. [11]. The system is, indeed, in what in ref. [11] we have recognized as the *folded* phase of the heteropolymeric chain. We have studied chains done of $N = 15$ and 30 sites, for $R = 2.0$, $A = 3.8$ and $\epsilon = 6$.

We have tried to build a numerical experiment close to the experimental conditions of the Frauenfelder group true experiments[21] (also if, as we said, our time scales are very shorter). We have been starting from a chain thermalized at $\beta = 1$, and we have abruptly decreased its temperature T ($T \equiv \frac{1}{\beta}$) to values ranging from $\beta = 2$ to $\beta = 10$. We have computed the relaxation function (6) by choosing as observables $\mathcal{A}$ the internal energy, the gyration radius of the chain and the link length (for detailed definitions see ref. [11]). For each β value we have averaged the relaxation functions over 500 Monte Carlo stories.

We have been careful to check that the perturbation was small enough not to produce big changes in the conformation of heteropolymer. The system was only allowed to change in similar *quasi-states* (in Frauenfelder terminology) and not to have a transition to a completely different state. This is for us good evidence (consistently with Frauenfelder experiments) that the non-exponential behavior we are discussing is not generated from the visiting of comformationally different minima with different underlying time scales, but from the fact that the dynamics in a single minimum is itself non-exponential.

All our runs are consistent with a stretched exponential relaxation for the correlation function with a stretching parameter γ in the range of order .5.

In fig. 1 we show the energy decay, as a function of the Monte Carlo time (in logarithmic scale), for four different values of the final β, i.e. for stronger and weaker perturbations.

In Fig. 2a we show, as an example, the decay of the energy for $\beta = 2.0$ (after perturbing a configuration thermalized at $\beta = 1.0$) in a system done of $N = 15$ sites. We get a very good stretched exponential fit of the form

$$e^{-(\frac{t}{\tau})^{\gamma}} \ , \tag{10}$$

with $\gamma \simeq .54$. A fit with a pure exponential behavior would not match the data. In Fig. 2b we show the same dependence for $\beta = 3.0$. Here γ is smaller, $\sim .38$. For higher values of β (i.e. for stronger perturbations) we did not succeed to get good fits. In this region the validity of the linear approximation is far from being clear.

5 The Normal Mode Analysis

The fluctuation-dissipation theorem shows that a simple relation between the equilibrium fluctuations of a system and its linear response to an external perturbation exists.

Let us consider the case where a constant field $h = \tilde{h}$ is applied to the system for a long time. Eventually the system reaches equilibrium. At a time, that we define as $t = 0$, h is switched off. The change in h, $\delta h = -\tilde{h}$, changes the average value of the physical quantities from their original values at equilibrium with $h = \tilde{h}$. If the field is weak we can assume that the change is a linear functional of the field

$$\langle \mathcal{A}(t) \rangle_h - \langle \mathcal{A} \rangle_0 = -\alpha(t)\ \tilde{h}\ , \tag{11}$$

where $\alpha(t)$ is the relaxation function.

In the case the have discussed in the previous section the perturbation field can be identified with the temperature variation

$$\tilde{h} = T_2 - T_1\ , \tag{12}$$

where T_1 is the initial equilibrium temperature ($\beta = 1$ in our case), and T_2 is the final one. Under these conditions the fluctuation-dissipation theorem gives

$$\alpha(t) = \frac{1}{k_B T} \langle \mathcal{A}(t) \mathcal{A}(0) \rangle_c\ , \tag{13}$$

where the correlation function on the right hand side is the connected part.

In the following we will discuss how to compute time dependent correlation functions $\langle \mathcal{A}(t) \mathcal{A}(0) \rangle_c$ (where h has been switched off at $t = 0$). In order to do that we define the time dependent non-equilibrium probability distribution function $P(x, t)$, and discuss it in the framework of the Langevin equation.

The Langevin equation for the dynamics of a generic site of the chain can be written as

$$\frac{\partial x_i}{\partial t} = -\zeta\ \frac{\partial H(x)}{\partial x_i} + f_i\ . \tag{14}$$

The probability distribution of the solutions of eq. (14) satisfies the Fokker-Planck equation

$$\frac{\partial P(t)}{\partial t} = \sum_i \{ -\frac{\partial}{\partial x_i} (\frac{F_i}{\zeta} P(t)) + \Omega \frac{\partial^2 P(t)}{\partial x_i^2} \}\ , \tag{15}$$

where F_i is the force acting on the i-particle, and Ω is the variance of the f_i. In the following we will focus on oscillations close to a minimum of the energy, so we will ignore the effect of the thermal noise f_i, by setting $\Omega = 0$, and we will use the fact that the gradient of H is zero. This means that, in the subsequent analysis of numerical data, we will look at configurations at

$T = 0$ (cooled by steepest descent procedure). The probability distribution function can be written as

$$P(x,t) = \psi_0(x)\rho(x,t) \ , \tag{16}$$

where

$$\psi_0(x) \simeq e^{-\frac{\beta H}{2}} \ , \tag{17}$$

is the eigenvector of $\mathcal{H}_{FP}$ with zero eigenvalue, and in the linearized approximation ρ satisfies

$$\frac{\partial \rho(x,t)}{\partial t} = -\mathcal{H}_{FP} \ \rho \ , \tag{18}$$

where

$$\mathcal{H}_{FP} \equiv -\frac{1}{2}\frac{\partial^2 H}{\partial x_i^2} \ . \tag{19}$$

We define the orthonormal basis of eigenvectors $\{\psi_n\}$ of $\mathcal{H}_{FP}$

$$\mathcal{H}_{FP} \ \psi_n = \lambda_n \psi_n \ . \tag{20}$$

We can decompose the time dependent probability distribution as

$$P(x,t) = \psi_0(x)\sum_n c_n \psi_n(x) e^{-\lambda_n t} \ , \tag{21}$$

where the c_n are constant coefficients (which depend only on the initial condition) and $c_0 = 1$.

The evaluation of the time dependent correlation function gives as result

$$\langle \mathcal{A}(t)\mathcal{A}(0)\rangle_c = \sum_{i=1}^{3N} e^{-\lambda_i t} | < \psi_0 | \mathcal{A} | \psi_i > |^2 \ . \tag{22}$$

We will use this relation to reconstruct the energy time dependent correlation functions from the knowledge of the eigenvalues of the Fokker-Planck Hamiltonian $\mathcal{H}_{FP}$. The correlation function has been expressed in (22) as a sum of time exponential functions, with decay factors

$$\tau_i \equiv \frac{1}{\lambda_i} \ . \tag{23}$$

Such an sum can (and will indeed) generate a stretched exponential behavior. This can happen if the smallest λ_i is not very different from the larger ones, i.e. if there is no large *gap*. We expect that to happen indeed it is well known, for simple disordered systems (for example a disordered chain in $d = 1$, see ref. [22]), that the frequency spectrum of the normal modes has a sizeable tail (in the small frequency region), which is absent in the corresponding ordered system. Such a difference from the ordered case tends to become more important with increasing space dimensionality.

We have looked at chains of $N = 15$ and $N = 30$ sites, by comparing the homopolymeric chain ($\epsilon = 0$) with the strongly disordered heteropolymer ($\epsilon = 6$). We have computed the $\mathcal{H}_{FP}$ eigenvalues for the minimum energy states (at $T = 0$) by using an imsl routine.

We have obtained a stretched exponential behavior for times up to ~ 100 in equation (22). In the direct evaluation of the correlation function of section (4) we have found it holds up to ~ 10000 Monte Carlo chain sweeps. This is very smaller than the macroscopic experimental time scales (corresponding to $\sim 10^{10}$ Monte Carlo chain sweeps).

In Fig. 3a we plot the reconstructed correlation functions, for $\epsilon = 6$ and for the pure homopolymer $\epsilon = 0$, for $N = 15$ sites. The stretched exponential fit (with $\gamma = .33$) works very well in the disordered case, while the best fit (with $\gamma = .56$) is very inadequate for the homopolymer. In Fig. 3b the same fits for $N = 30$, where we find a very similar qualitative behavior: here $\gamma = .39$ for $\epsilon = 6$, and the $\epsilon = 0$ fit, with $\gamma = .58$, is very bad. For this region of time we have been able to exclude a simple pure exponential behavior in the *folded* phase. For long times, as expected, the behavior becomes exponential. We have checked that an exponential fit gives, in this region, a very good result, with a decay which is characterized from the lowest eigenvalue of $\mathcal{H}_{FP}$.

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Figure Captions

- Fig. 1.

  Energy time decay (eq. (6)) versus Monte Carlo time for a chain done of $N = 15$ points, relaxing from $\beta = 1.0$ to $\beta = 2.0, 3.0, 8.0, 10.0$. The point labelled with $\beta = 1$ is the starting value of the energy for the four different relaxation runs.

- Fig. 2a.

  Energy time decay (eq. (6)) versus Monte Carlo time for a chain done of $N = 15$ points, relaxing from $\beta = 1.0$ to $\beta = 2.0$. The open dots are from the Monte Carlo data (average over 500 time periods), the smooth curve is the best, stretched exponential fit, with a stretching exponent $\gamma = .54$

- Fig. 2b.

  As in fig. 2a, but final $\beta = 3.0$. Here $\gamma = .38$.

- Fig. 3a.

  The reconstructed energy connected correlation functions, for $\epsilon = 6$ and for the pure homopolymer $\epsilon = 0$, for $N = 15$ sites.

- Fig. 3b.

  As in Fig. 3a, but $N = 30$.