

Figure Captions

- Fig. 1.

Energy time decay (eq. 1) 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. 1) 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 figure 2a, but for a normal homopolymer.

- Fig. 3.

The reconstructed correlation functions, for $\epsilon = 6$ and for the pure homopolymer $\epsilon = 0$, for $N = 30$ sites.

References

- [1] M. Mezard, G. Parisi and M. Virasoro, *Spin Glass Theory and Beyond* (World Scientific, Singapore 1987).
- [2] K. H. Fischer and J. A. Hertz, *Spin Glasses* (Cambridge University Press, Cambridge, UK 1991).
- [3] J. D. Bryngelson and P. G. Wolynes, Proc. Natl. Acad. Sci. USA **84** (1987) 7524; T. Garel and H. Orland, Europhys. Lett. **6** (1988) 307; E. I. Shakhnovich and A. M. Gutin, Europhys. Lett. **8** (1989) 327; M. Mezard and G. Parisi, J. Physique **II** (1991) 809.
- [4] H. Frauenfelder, K. Chu and R. Philipp, in *Biologically Inspired Physics*, edited by L. Peliti (Plenum Press, New York, USA 1991), p. 1.
- [5] I. Iben, D. Braunstein, W. Doster, H. Frauenfelder, M. K. Hong, J. B. Johnson, S. Luck, P. Ormos, A. Schulte, P. J. Steinbach, A. H. Xie and R. D. Young, Phys. Rev. Lett. **62** (1989) 1916.
- [6] G. Iori, E. Marinari and G. Parisi, J. Phys. **A** (Math. Gen.) **24** (1992) 5349.
- [7] M. Fukugita, D. Lancaster and M. G. Mitchard, J. Phys. Lett. **A** (Math. Gen.) **25** (1992) L121.
- [8] M. V. Struglia, *Conformational Properties of Random Heteropolymers in the Folded Phase*, Roma *Tor Vergata* preprint ROM2F/92/42 (1992).
- [9] P. Pliszka and E. Marinari *On Heteropolymer Shape Dynamics* Syracuse preprint SCCS 330, hep-lat 9207011 (Syracuse, July 1992).
- [10] F. J. Dyson, Phys. Rev. **91** (1953) 1331.

($\epsilon = 6$). 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 15. In the direct evaluation of the correlation function of section 2 we have found it holds up to ~ 10000 Monte Carlo chain sweeps. This is very smaller than the experimental time scales, which are of order of one second (corresponding to $\sim 10^{10}$ Monte Carlo chain sweeps).

In Fig. 3 we plot the reconstructed correlation functions, for $\epsilon = 6$ and for the pure homopolymer $\epsilon = 0$, for $N = 30$ sites. The stretched exponential fit (with $\gamma = .39$) works very well in the disordered case, while the best fit (with $\gamma = .47$) is very inadequate for the homopolymer. We found a very similar qualitative behavior for $N = 15$: here $\gamma = .33$ for $\epsilon = 6$, and the $\epsilon = 0$ fit, with $\gamma = .56$, is very bad.

For this region of time we have been able to exclude a simple pure exponential behavior in the *folded* phase. We have found a stretched exponential behavior on the time scales where the system is close to a minimum. On longer time scale we could have new relaxation phenomena, but this has not been analyzed in this work. 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} .

Acknowledgments

We thank Luca Biferale, Pawel Pliszka and Felix Ritort for interesting conversations, and especially Maria Vittoria Struglia for continuous discussions and help, and for providing us with the $T = 0$ chain configurations we used to compute normal modes.

$$y^{(n)} \equiv \sum_i \psi_i^{(n)} \delta x_i . \quad (12)$$

It is easy to check that such new variables satisfy the equations

$$\frac{dy^{(n)}}{dt} = -\lambda^{(n)} y^{(n)} + g^{(n)} , \quad (13)$$

where the $g^{(n)}$ are again an uncorrelated white noise with variance

$$g^{(n)}(t)g^{(m)}(t') = 2 T \zeta \delta_{n,m} \delta(t - t') . \quad (14)$$

The correlation functions can be computed by employing the usual techniques. We find

$$\langle y^{(n)}(t) y^{(m)}(t') \rangle = \frac{T \delta_{m,n}}{\lambda^{(n)}} e^{-\lambda^{(n)}|t-t'|} . \quad (15)$$

In the same way we can compute the energy-energy correlation function, finding

$$\langle H(t)H(t') \rangle = N T^2 e^{-2\lambda^{(n)}|t-t'|} . \quad (16)$$

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 15 as a sum of time exponential, with decay factors

$$\tau^{(n)} \equiv \frac{1}{\lambda^{(n)}} . \quad (17)$$

Such an infinite sum can (and will indeed) generate a stretched exponential. 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 [10]), 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 homo-polymeric chain ($\epsilon = 0$) with the strongly disordered heteropolymer

where $\alpha(t)$ is the relaxation function (which coincides with the correlation function apart from some factors T).

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

$$\tilde{h} = T_2 - T_1 , \quad (7)$$

where T_1 is the initial equilibrium temperature ($\beta = 1$ in our case), and T_2 is the final one.

In the following we will discuss how to compute time dependent correlation functions $\langle \mathcal{A}(t)\mathcal{A}(0) \rangle$ (where h has been switched off at $t = 0$). In order to do that we analyze the time evolution of the system. We will describe it by means of the usual Langevin equation

$$\frac{\partial x_i}{\partial t} = -\zeta \frac{\partial H(x)}{\partial x_i} + f_i , \quad (8)$$

where the f_i are random variables with zero expectation value and correlation

$$\langle f_i(t)f_j(t') \rangle = 2 T \zeta \delta(t - t') \delta_{i,j} . \quad (9)$$

Let us start at low T , and look at the system when it is close to a minimum of H . In these conditions we can limit ourselves to consider small fluctuations around the minimum, by introducing the matrix A such that

$$H(x) \simeq \sum_{i,j} \delta x_i A_{i,j} \delta x_j \quad (10)$$

where the δx are the displacements of the system from the position of the minimum. At this stage it is convenient to introduce the eigenvalues and the eigenvectors of A , which we denote respectively by $\lambda^{(n)}$ and $\psi_i^{(n)}$. They satisfy the equation:

$$\sum_k A_{i,k} \psi_k^{(n)} = \lambda^{(n)} \psi_i^{(n)} . \quad (11)$$

Let us now project over the normal modes, so introducing the new variables $y^{(n)}$, by

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 $\beta = 2.0$ in a system made of $N = 15$ sites. We get a very good stretched exponential fit of the form

$$e^{-(\frac{t}{\tau})^\gamma}, \quad (5)$$

with $\gamma \simeq .54$. A fit with a pure exponential behavior would not match the data. We found the same dependence for $\beta = 3.0$: in this case 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.

To stress our point we show in figure 2b the time decay of the energy-energy correlation function for an ordered homopolymer. We have followed the same procedure we used in the case of the heteropolymer, i.e., we have selected all the configurations which go, for $T \rightarrow 0$, in the same configuration. After doing that the exponential behavior is clear. We have used the same time scale we used in figure 2a, to show how dramatic is the difference. In the exponential fit we find a value of the decay time of order 10^2 , compatible with our rough estimate of the dynamical correlation times.

3 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 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

$$\langle \mathcal{A}(t) \rangle_h - \langle \mathcal{A} \rangle_0 = -\alpha(t) \tilde{h} \quad (6)$$

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

$$H \equiv \sum_{i=1}^N \sum_{j>i} E_{i,j} . \quad (4)$$

In our typical runs we have selected values of the parameters close to the ones of ref. [6]. The system is, indeed, in what in ref. [6] we have recognized as the *folded* phase of the heteropolymeric chain. We have studied chains done of $N = 15$, for $R = 2.0$, $A = 3.8$ and $\epsilon = 6.0$. Here using $N = 30$ would have been computationally too demanding. On the contrary in next section we used configurations obtained in [6], at one given value of the temperature.

We have tried to build a numerical experiment close to the experimental conditions of the Frauenfelder group true experiments[4] (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 (1) by choosing as observable A the internal energy, the gyration radius of the chain and the link length (for detailed definitions see ref. [6]). 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. Since the perturbation was small 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. That was checked by freezing the system at $T = 0$ and verifying that it would have not moved to a completely different conformational 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 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.

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.

In Section 2 we recall the definition of our model (IMP in the following, see ref. [6]. For further developments on this model see refs. [7, 8, 9]), we define our Monte Carlo procedure, and we present the results of numerical simulations. In Section 3 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 Monte Carlo Simulations

Let us start by recalling the definition of the IMP model [6]. We consider a chain formed of N sites. They would be identified, in the protein analogy, with *sequences* of amino-acids, i.e., segments of the secondary structure [6]. In our model we consider a single link (with no form factor) as representative of a pre-assembled piece of the secondary structure. At this level we cannot specify details of the short distance dynamics. We are interested in understanding if the disordered nature of the chain is enough to explain, for example, folding in a given shape. The site 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

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

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

$$\langle \eta_{i,j} \eta_{k,l} \rangle = \epsilon^2 \delta_{(i,j),(k,l)}, \quad (3)$$

1 Introduction

The potential relevance of disordered systems [1, 2] for understanding protein folding has received much attention in the last few years (see for examples refs. [3]). 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).

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 parameters 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. [4] 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 correlation functions as

$$\Phi(t) \equiv \frac{\mathcal{A}(t, T) - \mathcal{A}(\infty, T)}{\mathcal{A}(0, T) - \mathcal{A}(\infty, T)}, \quad (1)$$

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 a 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

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 homo-polymeric chain. We discuss the dependence of the relaxation stretching exponent over the system size by studying chains constituted by 15 and 30 points.

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

Giulia IORI^(*), Enzo MARINARI^(*) and Giorgio PARISI

Dipartimento di Fisica,
Università di Roma *Tor Vergata*,
Viale della Ricerca Scientifica, 00173 Roma, Italy
and

Inf, Sezione di Roma *Tor Vergata*

iori@roma2.infn.it marinari@roma2.infn.it parisi@roma2.infn.it

(*): and Dept. of Physics and Npac,
Syracuse University
Syracuse, NY 13244, USA

December 9, 1993

ROM2F-92-35
SCCS 331
hep-lat/9208001