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Glassy Relaxation Dynamics and Ruggedness beyond the Ultrametric Limit

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We study the relaxation behavior of hierarchical systems whose conformation space topology deviates from ultrametricity under selective controllable conditions. While the Debye law is obtained in the ultrametric case, Kohlrausch relaxation is shown to be directly related to the level of ruggedness beyond the ultrametric limit, making the β exponent computationally accessible.

KEY WORDS: Ultrametricity; Monte Carlo simulations; glassy relaxation; rugged energy landscapes; Kohlrausch exponent; statistical mechanics.

Glassy relaxation is the subject of considerable theoretical and experimental current research. This phenomenon has been found to underlie the dynamics of a vast range of complex systems belonging to a broad spectrum of interdisciplinary areas, ranging from disordered condensed matter to molecular biophysics.(1–26) Thus, the understanding of its generic basis emerges as a universal issue.

Within this context, the empirical fit known as Kohlrausch law(1) is ubiquitous in the relaxation phenomenology of a wide range of strongly interacting systems including spin glasses,(2–6) glasses,(7) dielectric materials(8–10) and biopolymers.(11) This "anomalously" slow relaxation law is fitted by a stretched exponential of the form:

$$q(t) = Q \exp[-(t/\tau)^{\beta}] \tag{1}$$

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where $q(t)$ represents a generic relaxation quantity with $Q = q(0)$, τ is a characteristic timescale and $0 < \beta \leqslant 1$. The limit case $\beta = 1$ corresponds to purely exponential or Debye relaxation. The universality of this law and the diversity of materials where it holds valid suggest that the underlying physics might only be sensitive to certain generic features shared by systems with highly degenerate ground states conforming a rugged free energy landscape with valleys separated by high barriers.

From a theoretical standpoint, such relaxation processes have been shown to be encompassed within the realm of dynamics in ultrametric spaces.[12–15] This approach was motivated by the ultrametric topology with which the ground state of the Sherrington–Kirkpatrick (SK) spin glass model[16] is endowed in the mean-field description.[17, 18, 3, 12] But this picture represents an extremely simplifying limit case for the relaxation of complex systems.[12] The existence of a rugged free energy landscape implies that the system breaks ergodicity and that phase space can be decomposed in a hierarchy of components or clusters of states,[19] but need not necessarily satisfy strictly the strong triangular inequality that determines a perfect ultrametric topology ($d(x, y) \leqslant \max[d(x, z), d(y, z)]$). This strong triangular inequality rules out the possibility for cooperative effects or the existence of locally preferred pathways (states z acting as intermediates for the transition from state x to state y). *This fact implies that the transition probability between any two given states depends only on their ultrametric distance, with no role left to correlated interactions.* Thus, ultrametricity translates in a free energy landscape with a fixed ruggedness.

Deviations from ultrametricity are expected in real systems with correlated interactions not accounted for in the mean-field SK model, and work has been done to characterize and quantify these deviations.[12, 20] Deviations from ultrametricity have been found to play a central role in the folding of random heteropolymers within a model with a locally connected correlated energy landscape,[21] and seem to have arisen in a study of overlaps between ribonucleic acid (RNA) secondary structures.[22]

In systems with correlated interactions, the deviations from ultrametricity must be reflected in the free energy landscape which must be rougher than the one originated in the ultrametric picture. Our aim is then to explore the connection between relaxation and the ruggedness of the free energy landscape beyond the ultrametric limit. More specifically, we shall identify the level of ruggedness directly responsible for the occurrence of Kohlrausch relaxation law in systems which would follow the Debye exponential law in the ultrametric limit. Furthermore, our results will display a qualitative dependence of Kohlrausch's exponent, β, on the ruggedness of the free energy landscape beyond the ultrametric limit in accord with experimental findings.[23, 24] This type of study demands dynamic simulations where the level of ruggedness may be altered selectively under controllable conditions.

The investigation of the relaxation behavior in rugged free energy landscapes requires that we make use of a model that deviates from the ultrametric tree of Fig. 1. We are only interested in the generic effect on the relaxation behavior of the ruggedness of the free energy landscape beyond ultrametricity, since we intend to address the common physical origin of this rather universal phenomenon. Thus, we shall implement a minimal model of rugged landscape which should be regarded as a precursor for a correlated system, and shall not be concerned with the physical origin of interactions giving rise to correlations.

As a limit for our rugged model we shall take the ultrametric model by Ogielski and Stein[15] (Fig. 1) with the choice $B(m) = RT \ln m$ for the scaling of the barriers with the ultrametric distance. This case leads to Debye exponential relaxation or, equivalently, to the limit $\beta = 1$ of Kohlrausch law, and represents the limit of convergence of the model. The dependence $B = B(m)$ represents the key feature in these models since a variety of relaxation behaviors is obtained depending on the particular choice performed.[15, 12] Moreover. the resulting relaxation law is robust, since it has been found not to be sensible to the shape of the ultrametric tree (the relaxation can be faster or slower, but the functional dependence and the exponent remain the same).[13, 25, 26] However, we must note that

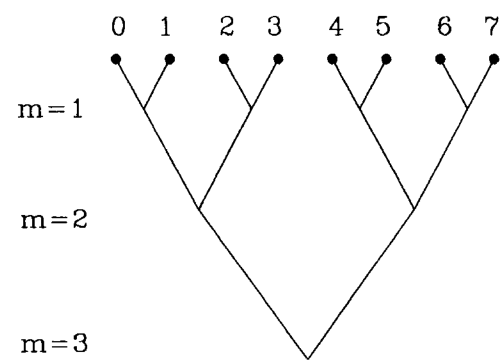

Fig. 1. Tree structure of the ultrametric space for a hierarchical system. The tree is regular and has branching ratio $K = 2$. The distance between any two given points is m, the level of their common ancestor, and the dynamics is generated by temperature-assisted hoppings over potential barriers $B = B(m)$ which are monotonically increasing functions of m. Thus, the probability of surmounting a barrier of level m, $W(m)$, is $W(m) = \exp[-B(m)/RT]$, where R is the gas constant and T is the absolute temperature. Walks are defined at the upper level ($m = 0$) and initially, the autocorrelation functions is $P_0(t = 0) = 1$, while $P_k(t = 0) = 0$ for any other state k.

this choice has been always made in an *ad hoc* manner, since no physical reason has been invoked to single out one particular dependence. In this case, our choice shall be justified later using a variational or least-action approach which will provide the physical grounds to our model by revealing that the favored pathway is not only the most economical at each step of relaxation but it also minimizes the over-all relaxation timespan.

In our paradigm model, the tree of Fig. 1 defines the connectivities and the distances. However, the barrier corresponding to a jump between states a distance m is chosen from a *distribution* centered at the value of $RT \ln m$. The mean of each distribution moves with m in the same way as B in the ultrametric limit case. The disorder built upon ultrametricity is quenched by constructing the transition probability matrix at the beginning of the process and fixing it throughout the simulation. As in the ultrametric case, once a jump of height m occurs, the walker lands with equal probability in any of its 2^{m-1} neighbors of the corresponding cluster (the transition probabilities for jumps of a given height m depend only on the initial state). In our present case of uniform distributions, the barriers were chosen from: $B = (\ln m)[1 + 2\alpha(0.5 - P)]$, with P a variable uniformly distributed in $[0, 1]$ and α, $0 \leqslant \alpha \leqslant 1$, a parameter that modulates the deviation. The results obtained are insensitive to the shape of the distribution used. Thus, the departure from Debye law due to the controlled increase in ruggedness built upon ultrametricity follows the same semi-empirical fit regardless of whether the distribution is gaussian or uniform. The role of the distributions is merely to provide a simple means of selectively introducing a variable and controllable ruggedness in the free energy landscape which should arise beyond the ultrametric limit. The microscopic physical origin of this picture is immaterial from a phenomenological standpoint, since we only intend to show the change in relaxation behavior as the system deviates from the ultrametric representation. The free energy landscape generated by this model has a ruggedness that increases with the value of α ($\alpha = 0$ corresponds to the ultrametric case). Thus, different pathways connect locally any two given states, thereby providing a richer picture than the ultrametric model. For example, the mean transition time from a given state to another placed at distance m is completely determined by the value of m in the ultrametric model. In our model, neighbors a distance m', with $m' < m$, may provide faster or slower pathways.

The relaxation behavior was studied by means of kinetically-controlled Monte Carlo simulations consistent with usual kinetic algorithms.[27] In our simulations, the walker starts at the origin and performs jumps of height m, landing with equal probability in one of the corresponding 2^{m-1} sites. The probabilities of performing jumps of given heights are proportional to the transition probabilities $W(m)$. The time for each Monte Carlo step or transition, t_{step}, is chosen as follows: $t_{step} = -\ln P / \sum_m W(m)$, where P is a variable uniformly distributed in $[0, 1]$. The number of levels accounted for in our model was 100 and thus, 2^{100} sites were included.

Figure 2 displays the time-dependence of $\langle R(t) \rangle$, the average distance traveled by the walker, in log–log scale. The straight line plots clearly indicate that we have reproduced the stretched exponential behavior, since $\langle R(t) \rangle$ is given by[15, 12]

$$\langle R(t) \rangle = \sum_k d(k, 0)\, P_k(t) \approx (t/\tau)^{RT/\Delta} \tag{2}$$

where $d(k, j)$ is the ultrametric distance between site k and site j, and $P_k(t)$ is the probability of finding the particle at site k at time t. This leads to an autocorrelation function that displays Kohlrausch relaxation

$$P_0(t) \approx \exp[-(\ln K)(t/\tau)^{RT/\Delta}] \tag{3}$$

with $RT \leqslant \Delta$ and $RT/\Delta = \beta$, once $P_0(t)$ is identified with $q(t)$ of Eq. 1.[15, 28] Debye or exponential relaxation behavior is obtained when $\Delta = RT$. The parameter K is the branching ratio, as indicated in the legend of Fig. 1.

We can see that the ultrametric case ($\alpha = 0$) shows exponential Debye relaxation. For all other values of α characterizing the level of ruggedness,

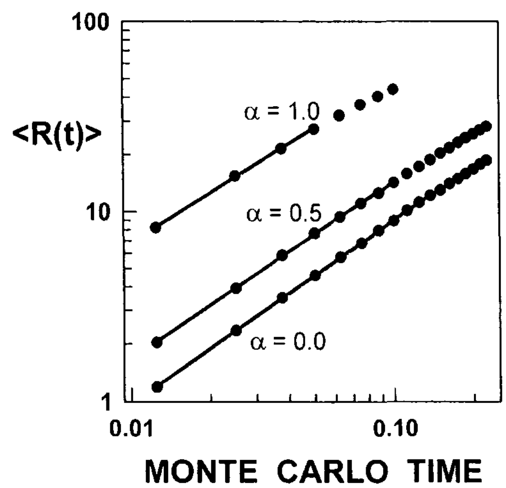

Fig. 2. Log–log plot for the time-dependent behavior of $\langle R(t) \rangle$ for selected values of α ($0 \leqslant \alpha \leqslant 1$). The values of β are obtained from the slopes of the straight lines well before the asymptotic regime is reached, as given by Eqs. 2 and 3. The existence of an asymtotic value for $\langle R(t) \rangle$ is due to the finite size of the system ($m = 100$) used in the simulations.

the relaxation is found to follow Kohlrausch law. This result reveals that departures from pure exponential behavior are due to deviations from ultrametricity which give rise to a rugged free energy landscape and makes the phenomenological exponent β computationally accessible.

Figure 3 depicts the dependence on α of the Kohlrausch exponent, β. From these results we learn that β decreases with the increase in the value of α. Thus, as intuition dictates, an increase in the level of ruggedness of the landscape leads to a slower relaxation behavior and, most importantly, the relaxation is invariably fitted to a Kohlrausch stretched exponential. A similar qualitative behavior has been found experimentally in the context of glassy ionic conductors where relaxation has been found to follow a Kohlrausch law with the exponent β nearly 1 (Debye or exponential law) when the mobile ion concentration is very small, and decreasing with an increment in the mobile ion concentration.[23, 24] This change in relaxation behavior cannot be explained by the ultrametric models since any choice in $B = B(m)$ leads to only one relaxation law. In accord with our results, the observed behavior may be due to correlations that make the system deviate from the ultrametric case with concomitant increase in the ruggedness. We conjecture that the mean-field ultrametric description captures the intrinsic disorder of the glassy material, but there exists an additional dynamic disorder built upon ultrametricity and due to correlated interactions between mobile ions.

At this point we state the variational principle that led us to make the choice in $B = B(m)$. As already pointed out, the choice in the scaling of

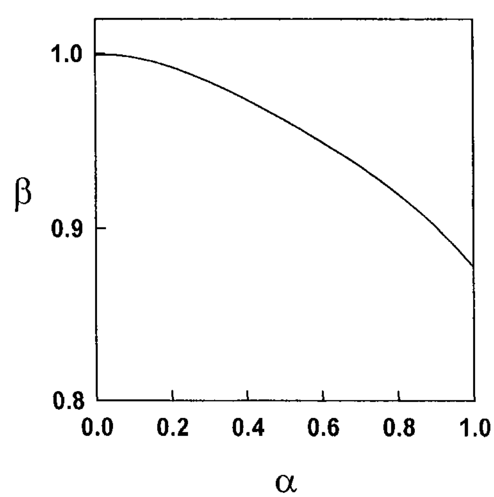

Fig. 3. The ruggedness dependence of relaxation: Kohlrausch exponent, β, as a function of α.

barriers with m represents the key feature in the problem of relaxation in ultrametric spaces, but has been always made in an *ad hoc* manner. We shall show that glassy relaxation is singled out by a brachistochrone, or least over-all relaxation pathway, thus suggesting the existence of a variational principle underlying the rather universal phenomenon of relaxation in rugged free energy landscapes. A Fermat-like variational principle of this kind has been stated by us in the context of the relaxation of disordered biopolymers.[29]

For mathematical convenience we shall concentrate in the ultrametric case ($\alpha = 0$). To place the system within a variational context, we define a generic relaxation coordinate X and attempt to single out a specific behavior $X = X(B)$. Without loss of generality, we shall focus on a generic situation in which the expected barrier $B = B(m)$ encountered at level m grows monotonically with m, as is the case when relaxation steps become increasingly difficult in time, and the progress of relaxation may be monitored by a single-valued function $X = X(B)$ which is monotonically increasing in time.

Under these tenets, the path integral giving the over-all relaxation time is:[29]

$$\int dt = f^{-1} \int_0^b \exp(B/RT)(1 + (X')^2)^{1/2}\, dB \tag{4}$$

where $X' = dX/dB$, $(1 + (X')^2)^{1/2}\, dB$ is the arc differential and $f^{-1} \exp(B/RT)$ is the reciprocal of the velocity for an activated process with barrier B and unimolecular rate constant f.[29–32] By solving the Euler–Lagrange equations associated to the action given by Eq. 4, we find the brachistochrone, that is, the relaxation pathway that minimizes the over-all time. This pathway is defined by the following equations:[29]

$$X = X(B) = RT \arctan[(\exp(2B/RT) - c^2 f^2)^{1/2}/(cf)] \tag{5}$$

$$B = B(t) = (RT/2) \ln[(Ft)^2 + (cf)^2] \tag{6}$$

$$X = X(t) = RT \arctan\left(\frac{t}{cRT}\right) \tag{7}$$

where $F = f/RT$ and c is an integration constant with dimensions of [time/energy]. Equation 5 reveals the scaling of barriers with X. We can verify that the growth of the expected barrier corresponds to the logarithmic growth of barriers with m, as in the particular case of the Ogielski–Stein model[15] we used as a limit for our rugged model ($\alpha = 0$). This is so since the ultrametric distance m ranges from zero to infinity, while here X is confined to the interval $[0, \pi/2]$. Thus, by introducing the transformation $Y = \tan(X/(RT))$, Eq. 5 yields the following relation:

$$B = B(Y) = (RT/2) \ln[(cf)^2 (1 + Y^2)] \tag{8}$$

which in the long time regime where $Y^2 \gg 1$, and fixing $cf = 1$ (as in the model by Ogielski and Stein), yields the desired proportionality $B(Y) \approx RT \ln Y$, in agreement with ref. 15 after the identification $Y = m$. This fact provides a physical justification to the choice of barrier growth made in the model introduced in this work. In turn this barrier growth results in a pure exponential or Debye relaxation law since:[12]

$$\begin{aligned} &\langle R(t) \rangle \approx Y(t) = t/(cRT) \\ &P_0(t) \approx K^{-R(t)} = K^{-t/(cRT)} = \exp - \left(\frac{\ln K}{cRT}\right) t; \quad \Delta = RT \end{aligned} \tag{9}$$

where $R(t)$ is the distance traveled in the random walk, and we have made use of the transformation $Y = \tan(X/(RT))$ in Eq. 7. That is, in the ultrametric description, the Debye exponential relaxation law is the signature of the brachistochrone if the time evolution of the system is monitored adopting the representation $Y = m$. This relaxation law is precisely the fastest relaxation regime yielding a stable random walk within the Ogielski–Stein ultrametric model[15] and points to the validity of the variational principle. Kohlrausch relaxation law should arise in real systems as a consequence of the increase in the ruggedness of the free energy landscape, as revealed by our simulations.

In this work we have demonstrated that a ruggedness of the free energy landscape built upon the ultrametric topology is a key factor to explain Kohlrausch relaxation law. In spite of its simplicity, our model may be viewed as a paradigm providing the theoretical underpinnings of complex relaxation behavior in more realistic contexts beyond the ultrametric limit. Our simulations also displayed a decrease in the exponent β of Kohlrausch law with the increase in the ruggedness of the free energy landscape in solid agreement with recent experimental probes.[23, 24] Finally, our results also reveal the existence of a variational principle underlying glassy relaxation and explain the expediency of experimentally-probed relaxation pathways.

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