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Activated dynamics and timescale separation within the landscape paradigm: signature of complexity, diversity and glassiness

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Abstract

The landscape paradigm has become a widespread picture within the realm of complex systems. Complex systems include a great variety of systems, ranging from glasses to biopolymers, which display a common dynamical behavior. Within this framework, the dynamics of a such a system can be envisioned as the search it performs on its (potential energy) landscape. This approach rests on the belief that the relaxation behavior depends only on generic features, irrespective of specific details and lies on the validity of a timescale separation scenario computationally corroborated but not properly validated yet form first principles.

In this work we shall show that the prevalence of activated dynamics over other kinds of mechanisms determines the emergence of complex dynamical behavior. Thus, complexity and diversity are not intrinsic properties of a system but depend on the kind of exploration of the landscape. We shall focus mainly on an ample generic context (complex hierarchical systems which have been used as models of glasses, spin glasses and biopolymers) and a specific one (model glass formers). For the last case we shall be able to reveal (in mechanistic terms) the microscopic rationale for the occurrence of timescale separation. Furthermore, we shall explore the connections between these two up to now mostly unrelated contexts and the relation to a variational principle, and we shall reveal the conditions for the applicability of the landscape approach.

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1. Introduction

Complex systems are systems made up of many strongly interacting units and which posses a wide range of intrinsic relaxation timescales. Systems very diverse from a structural standpoint such as biopolymers, glasses and spin glasses are included within this broad realm [1,2]. These systems exhibit a rather universal dynamical behavior suggesting that the underlying physics might only be sensitive to nonspecific details. A common feature exhibited by these systems is the occurrence of nonexponential relaxation laws (known as Kohlrausch laws) which have been related to an inhomogeneous scenario for the relaxation. Diversity is another attribute of complex systems: the existence of significantly different states that do not necessarily differ in energy. This concept, more familiar in biophysics, is also relevant to other complex systems.

The dominant description for the relaxation of complex systems is the Landscape Paradigm [3]. This framework reflects the constraints imposed on the dynamics by the potential energy surface (PES) and has been articulated by two main approaches (mostly unrelated up to date): by means of direct exploration of realistic PES via molecular dynamics simulations and quenching procedures, the inherent dynamics approach [3], and by making use of phenomenological models for the relaxation dynamics (hierarchical systems) [1,2]. The landscape paradigm originates in the fact that the potential energy of a complex system is a function of the positions of the different

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particles, constituting a complicated multidimensional surface ($3N+1$ coordinates for a system of N particles with no internal degrees of freedom). Accordingly, conformation space is made up of many minima or valleys separated by large energy barriers (which in turn may be arranged hierarchically) [1,2,4]. Thus, the existence of metastable states within a broken ergodicity scenario is implied. The relaxation dynamics of a complex system can therefore be mapped in the search the system performs of its potential energy surface. This landscape approach rests on a tenet introduced long ago (recently computationally corroborated but not yet properly validated from first principles): the timescale separation hypothesis [3]. This assumption entails the fact that local events are fast enough compared to long-range non-local ones to achieve local thermal equilibrium. The large scale events might thus be treated as activated events or defects, governing the long time dynamics.

From the above expounded picture it becomes evident that the study of the role of activated events in complex systems is a key factor to understand the dominant mechanisms for relaxation. Additionally, the knowledge of the specific ways in which different complex systems explore their PES (the mechanisms by which they perform the conformational search and that distinguishes them as structure seekers or glass formers) is a central question related to paramount issues as the protein folding problem and the glass transition [5].

In this work we shall focus on both implementations of the landscape paradigm (the broken ergodicity construction of hierarchical systems and the inherent dynamics or topographic approach, the latter being applied to the PES of a simple glass former) and we shall relate them to a variational principle. We shall demonstrate that in both contexts the onset of timescale separation, which determines the prevalence of activated dynamics, is the signature of complex behavior. In the more specific context we shall also reveal the microscopic foundation of timescale separation.

2. Relaxation in hierarchical systems

The landscape paradigm has been instrumented in a phenomenological picture grounded on the hierarchical nature of phase space and the idea of broken ergodicity, which has been applied to many complex systems like biopolymers and glasses [1,2]. This approach is based on phenomenological models of relaxation which lack any details of the interactions that give rise to the landscape. To place it in quantitative terms (and to fully relate it to the inherent dynamics approach) would demand an exhaustive characterization of the PES, which is only possible for small systems like small clusters [5] and simplified model biopolymers [6] with the construction of disconnectivity graphs. This description implies the fact that the hilly or rugged nature of phase (or conformation) space implies a broken ergodicity scenario [1,2]: at each observational timescale, conformation space can be decomposed in components or clusters of sates which are surrounded by (free) energy barriers, provided the probability to escape is smaller than certain arbitrarily small value. Components are internally ergodic but represent metastable states where the system is effectively confined within such timescale. As the observational timescale increases, different components merge into bigger ones in a hierarchical manner. In this way, the number of components into which conformation space is decomposed decreases as relaxation proceeds, until the globally-ergodic time is reached. Thus, the time evolution of the system generates a connectivity tree where the number of components at any observational timescale is given by the number of branches of the tree present at that time. Such hierarchical construction has been qualitatively validated for biopolymers and small clusters [4–6].

A simple caricature of such picture is constituted by ultrametric spaces [1,2], which were motivated by the discovery that the ground state of the Sherrington–Kirkpatrick (SK) spin glass model is endowed with an ultrametric topology in the mean-field description. An example of an ultrametric model of complex system is given in Fig. 1 which shows the tree structure of the ultrametric space for a hierarchical system. This is a Cayley tree or Bethe lattice in which only the upper level represents the states and the rest of the tree indicates connectivity. The tree of Fig. 1 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 $W(m)=\exp[-B(m)/R\ T]$. Walks are defined at the upper level ($m=0$) and initially, the autocorrelation function is $P_0(t=0)=1$, while $P_k(t=0)=0$ for any other state k. This simplified model is representative of a conformation space hierarchically structured in components or clusters of states as ergodicity is developed in time: at $t=0$ the system is confined to one of the states (labeled from 0 to 7 in the schematic Fig. 1; in this case, state 0). When the observation time is enough on average to surmount a barrier $B(m=1)$, the states separated by an ultrametric distance $m=1$ cluster together reflecting the fact that such portion of conformation space has become accessible and the corresponding cluster is internally ergodic at such timescales. This

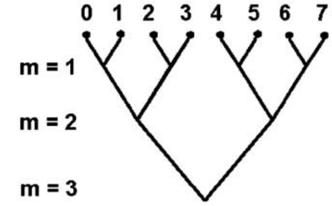

Fig. 1. Schematic representation of a hierarchical ultrametric system. The tree structure of the ultrametric space is regular and has branching ratio $K=2$.