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

G.A. Appignanesi*, L.M. Alarcón, J.A. Rodríguez Fris, M.A. Frechero, R.A. Montani

Departamento de Química, Universidad Nacional del Sur (UNS), Av. Alem 1253 (8000) Bahía Blanca, Argentina

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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

* Corresponding author. Tel.: +54 2914595110; fax: +54 2914595160.
E-mail address: appignan@criba.edu.ar (G.A. Appignanesi).

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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

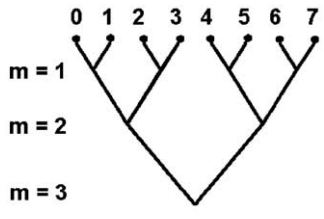

Fig. 1. Schematic representation of a hierarchical ultrametric system. The tree structure of the ultrametric space is regular and has branching ratio $K=2$.

clustering process continues as observation time is increased, since smaller clusters merge into bigger ones when the barrier which separates them is surmounted. That is, the surmounting of a barrier of height m clusters together the corresponding $s=K^m$ states. Finally, beyond certain observation time t_{erg} the whole conformation space becomes ergodic. This description is also equivalent to a one dimensional array of energy barriers of size $B=B(m)$, separating the corresponding states [2]. The lowest relevant timescale of this system is the one dictated by the lowest barriers, that is, the ones that separate states one hierarchical ultrametric level apart (states 0 and 1, states 2 and 3, . . .).

There exists a correspondence between this ultrametric system and a model of hierarchically constrained dynamics [7] in which Ising-type spins are arranged in hierarchical levels and constraints are transferred between the different levels. Constrained dynamics models have gained attention recently, mainly by the introduction of the concept of dynamic facilitation for glasses [8].

The dependence of the height of the energy barriers with the ultrametric distance, $B=B(m)$, represents the key feature in this model since a variety of relaxation behaviors are obtained depending on the particular choice [1,2]. If the barriers scale logarithmically with m, $B=\Delta \ln m$, the resulting relaxation behavior conforms to the usual phenomenology in complex systems: $<R(t)>=m(t)\sim t^{RT/\Delta}$; $P_0(t)\sim e^{-(\ln K)t^{RT/\Delta}}$ where $<R(t)>$ is the distance traveled in the random walk, R is the gas constant and $P_0(t)$ is the probability of return to the origin (state 0), estimated as the inverse of the number of states accessible within time t, and K is the branching ratio (in this case $K=2$ and is regular). The sum of probabilities does not converge for values of $RT>\Delta$, and thus, $0<RT<\Delta$. At $RT=\Delta$, the relaxation behavior is the fastest possible and implies a Debye exponential law. For lower temperatures, the resulting relaxation is given by Kohlrausch law with exponent $0<\beta<1$. Thus, at $RT=\Delta$ we obtain the limit of convergence of the dynamics or fastest relaxation regime yielding a stable random walk. We demonstrated [2] that this limit is prescribed exactly by a brachistochrone or least overall relaxation time (this variational principle had been inspired by the relaxation behavior of natural biopolymers, specifically ribonucleic acid molecules [9]). *That is, the brachistochrone corresponds to the transition from an activated dynamics regime to a diffusive one (where the barriers have been overlooked by thermal energy). Thus, for this system there exists a transition between two dynamical regimes dictated by the onset of activated dynamics, which constitutes the signature of complex behavior*.

At this point we shall place a question which will also be stated in the other specific context (the model glass formers we shall study in next section): what is the origin of this onset of activated dynamics and thus, of glassy behavior?. To answer this question we calculate the time employed to move a distance m apart: $t\sim e^{-B(m)/RT}=m^{\Delta/RT}$. Thus, for $RT=\Delta$ we find that the different hierarchies are equally time spaced. Accordingly, the timescales of any pair of hierarchically contiguous components differ in a value that is equal to the lowest relevant timescale of the system (the one dictated by the size of the lowest barriers). Thus, the limit of convergence of the dynamics entails the fact that the timescales of long range and short range events become comparable, implying the limit of validity of timescale separation. Moreover, should the dynamics be faster than this limit, components would be no more internally ergodic: fast local equilibration prior to nonlocal transitions would no longer hold, as required by the timescale separation hypothesis. *Thus, the main lesson from these models is that timescale separation is the marker of complex behavior*.

This result is also valid in situations where deviations from ultrametrcity are taken into account, since the relaxation law has been found to be robust with respect to such deviations [2]. Furthermore, the hierarchical structure is the relevant feature since completely disordered systems (a one dimensional array of energy barriers, but with the barriers randomly placed: chosen from an exponential, uniform or any other kind of distribution [2]), also posses on average the same hierarchical structure (as defined by the clustering process $s=K^m$, where m is now the hierarchical level and not the ultrametric distance). Thus, this kind of systems displays qualitatively the same relaxation behavior [1,2].

The ultrametric system considered above also presents another relevant dynamical limit, namely, the limit of compact exploration (the requirement, stronger than local ergodicty, to visit all the states comprised by a given component before performing a jump to a hierarchically higher component) [1,2]. This limit is relevant to the diffusion on fractal systems. The relaxation law that emerges (it arises from the fastest scaling law for the barriers $B=\Delta m$, thus implying a change in the structure of the portion of conformation space explored, as signed by higher barriers) is the slower power law decay [1,2]: $P_0(t)\sim t^{-\gamma}$, with $0<\gamma=RT/\Delta<1$. This limit implies a slower exploration of conformation space and is also given exactly by the variational principle [2].

2.1. Relaxation dynamics within the topographic approach

The topographic approach [3] is based on the notion that at low temperatures the dynamics of the system on its PES, the multidimensional surface generated while considering potential energy as a function of particle coordinates, can be decomposed in fast vibrations around and transitions between different energy minima or ‘basins of attraction’ called inherent structures (IS’s, in which configuration space is partitioned by potential energy minimizations). Thus, this fact implies a timescale separation scenario that allows to coarse grain the dynamics at the IS level. Nevertheless, whilst this timescale separation hypothesis has been recently computationally corroborated for a binary LJ system [3], the microscopic rationale behind it has not been elucidated.

A system which has been extensively studied by Molecular Dynamics (MD) and the topographic approach is a simple fragile glass-former: a binary Lennard–Jones system (LJ) [3,10,11]. MD simulations of this system at temperatures, T, close to T_C (the mode-coupling temperature) have demonstrated a dynamically heterogeneous nature, since "mobile" particles have been found not to be homogeneously distributed within the sample but to organize themselves in clusters [10,11]. In turn, these clusters have been shown to be made up of smaller string-like clusters of particles [10,11]. These string like movements have been shown to occur localized in narrow time windows and at different timescales from each other [11]. These string motions are consistent with a defect-diffusion mechanism as implied in the dynamics facilitation scenario [8] (grounded on ideas from constrained dynamics models [1,2,7] which are related to the hierarchical models of the previous section).

From the study of the Inherent dynamics, it was found that this system presents three distinct regimes of exploration of the PES depending on temperature [3], a point which resembles the situation above expounded for the ultrametric systems. Above certain T the system presents a free diffusion regime (in which the mean energy of the IS's visited is constant for the whole T range) characterized by an exponential Debye relaxation law, while at lower temperatures it presents an activated-dynamics or "landscape influenced" regime yielding Kohlrausch law. Thus, the onset of glassy dynamics, signed by Kohlrausch nonexponential relaxation, corresponds to a change in the kind of exploration of the PES. In turn, at temperatures below T_C the dynamics is even slower and is termed "landscape dominated". However, in this regime the relaxation law has not been determined so far. It is in fact slower than Kohlrausch law and also a change in the structure of the PES explored has been observed around T_c, when the system is confined to the lower minima [3]. In particular, the size of the barriers has also been found to increase as the system goes down in energy. The existence of such distinct exploration regimes has been related to the degree of complexity the conformational search is confronted to at different temperatures: the portion of conformation space visited is more complex as T is lowered [12].

Within this context, we shall here provide a microscopic rationale for the occurrence of timescale separation by studying the temperature behavior of the timescales corresponding to events of different range. Thus, a timescale separation scenario implying the dominance of activated dynamics will enable a mechanistic picture of relaxation in which ballistic string like movements shall be identified as two state relevant events in the PES exploration.

We performed a series of MD simulations for the binary Lennard–Jones system [10,11] consisting of a three-dimensional mixture of 80% of A and 20% of B particles, the size of the A particles being 10% larger than the B ones (we used the NPT ensemble with a step size of 0.0025 and a total number of particles N=500; see [11] for details). The particles interact by a Lennard–Jones potential (truncated at r=2.5 σ_{AA}) characterized by: ε_{AA}=1.0, σ_{AA}=1.0, ε_{AB}=1.5, σ_{AB}=0.8, ε_{BB}=0.5 and σ_{BB}=0.88. The MSD plots show the typical ballistic, caging localization, as denoted by a plateau, and diffusive regime [10,11]. The extent of the plateau depends strongly on temperature, increasing considerably as T_C (estimated at 0.435 [10]) is approached. The dynamically heterogeneous nature of this system is obvious from its deviation from Gaussian behavior, which is measured by the "non-Gaussian parameter" $\alpha(t)$ [10,11]. The time when $\alpha(t)$ presents its maximum value, t^*, defines the time window [0, t^*] in which the behavior of the system is most dynamically heterogeneous. The value of t^* for this system depends strongly on temperature as T_c is approached from above, increasing by almost two orders of magnitude from T=0.55 to T=0.45 [10,11]. The height of the maximum in $\alpha(t)$, $\alpha(t^*)$, also increases as T decreases. We determined the time t^* for each temperature and for each run we identified the "mobile" particles as the ones whose displacement at time t^*, $\Delta r_i(t^*)=r_i(t^*)-r_i(0)$ (where $r_i(t)$ is the position of particle i at time t), was greater than the one predicted by Brownian motion at such T (from approximately 0.6 to 0.7 σ_{AA} depending on T for the range we employed). As expected, only a small percentage of particles results mobile (5–10%) and is clustered together in the sample. t^* constitutes a characteristic time for this system and corresponds to times in the late β–early α relaxation (the transition from localized to diffusive behavior) and to the lifetime of such global clusters of mobile particles [10,11].

Strings were dynamically characterized as in [10,11] for time intervals [0, t^*]. We carried out many MD simulation runs after equilibration for each of a series of temperatures in the range $0.45 \le T \le 0.55$. We calculated the distances $\Delta r_{i,j}(t^*)=r_i(t^*)-r_j(0)$ and recorded the cases when $\Delta r_{i,j}(t^*)<0.6$. This means that after t^* particle j has moved and particle i has occupied its place to within 0.6 σ_{AA} (represented as $i \rightarrow j$). Most of the mobile particles were organized in different strings. From the study of the time evolution of these strings, we found that long strings usually decomposed in more than one short substring movement of around 3 or 4 particles which move together in short time intervals. Thus, from now on we shall refer to these movements as string motions. *An important fact is that these string motions occur in a ballistic fashion*. That is, once a fluctuation in the cage of one of the particles occurs, the corresponding particle moves ballistically (a distance typically between 0.5 to 1 σ_{AA}) in order to fill this space, allowing thus for the movement of a neighbor particle, and so on. Fig. 2 displays an example of this kind of ballistic string motion. Preliminary results indicate that string motions which occur close in time are also close in space, in agreement with dynamics facilitation [8].

We shall define a ballistic time as the time it would take a particle to perform a ballistic displacement of 1 σ_{AA}. This time unit depends slightly on T and represents around 400

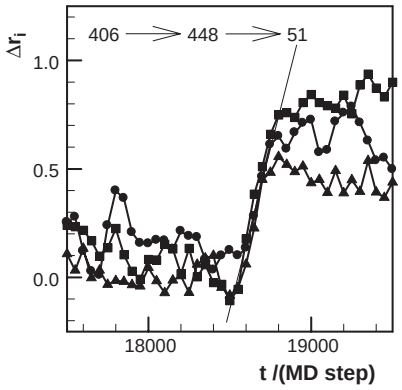

Fig. 2. Time evolution of the displacements of the particles of a string in the region where the string occurs for a MD run at the following conditions of temperature, pressure and density: T=0.469, P=2.296 and δ=1.176. The string is indicated by the particles taking part 406→448→51 (circles, squares and triangles, respectively). A line indicating perfect ballistic behavior (with velocity extracted from the mean kinetic energy) is drawn for comparison. Time is given in MD steps. Reduced time is obtained when dividing by 0.0025, the timestep used in the simulations.

MD steps for T=0.47. For low temperatures this ballistic time is small compared to t^* but for T=0.55 (since t^* decreases with T) these two timescales become comparable (we recall that for all the temperatures studied the number of mobile particles in [0, t*] was always 5–10% of the total number of particles and the mean squared displacements, MSD, at t^* did not differ appreciable, being around 0.1 σ_{AA}). Fig. 3 shows the temperature dependence of the ballistic time and of t^*. We also show the temperature behavior of the time when the MSD equals unity, $\tau_{MSD=1}$ (the average escape time of the particles from their cages). We can see that t^* (that decreases almost two orders of magnitude from T=0.451 to T=0.55) approaches the corresponding ballistic time at temperatures above T=0.55. The curve for $\tau_{MSD=1}$ displays a temperature dependence similar to t^* ($\tau_{MSD=1}$ is around an order higher than t^* for the different temperatures) and approaches the ballistic curve at a higher temperature. This relation between timescales corresponding to events of different range (the ballistic time corresponding to small string motions and t^* corresponding to large scale arrangements of global clusters) provides us, *for the first time, a microscopic rationale for the emergence of timescale separation*. This fact has important implications to the landscape approach, as we shall see below, since it marks its range of validity.

To study the Inherent dynamics of the system we performed periodical quenches of configurations obtained in a given real MD trajectory by means of potential energy minimizations using the conjugate-gradient method. This procedure maps each configuration to its corresponding Inherent Structure (IS). To locate transitions between IS's or jumps, we could monitor the inherent structure energy. Instead, we used another quantity, namely the mean squared displacement between successive IS's (this quantity represents a better measure in terms of diversity since structurally distinct IS's do not necessarily differ appreciably in energy): $\Delta R_{IS}(t) = \left(\sum_{j=1}^{N}\left(r_j^{IS}(t+\Delta t) - r_j^{IS}(t)\right)^2\right)^{1/2}$ where $r_j^{IS}(t)$ is the position of particle j in the IS that occurs at time t and Δt is the interval in MD steps between successive quenching minimizations. At each time the system performs a jump in the PES, the time evolution of ΔR_{IS} would produce a peak. This is so, since while vibrating around a given IS each minima would map (by the minimization procedure) to the bottom of its basin of attraction (the same IS) and ΔR_{IS} would be around zero. Thus, a peak would indicate an interbasin transition (that is, a transition between two different IS's).

We performed this study for different trajectories and at different temperatures. The $\Delta R_{IS}(t)$ curve for the MD trajectory that contains the string shown in Fig. 2 displays a series of peaks corresponding to transitions between successive IS's. Fig. 4 depicts the $\Delta R_{IS}(t)$ curve for the region where the string of Fig. 2 takes place. Similar results were found for other strings of this and other MD trajectories. A fact that can be learnt from such results is that at times where the real dynamics shows the occurrence of string movements, a peak is found in the $\Delta R_{IS}(t)$ curve. Additionally, most of the string movements entail a single peak in the $\Delta R_{IS}(t)$ curve, indicating that they occur between two consecutive IS's without the presence of intermediate IS's. Thus, *string movements represent well-differentiated two-state elementary processes without intermediate steps, corresponding to relevant events in the PES*

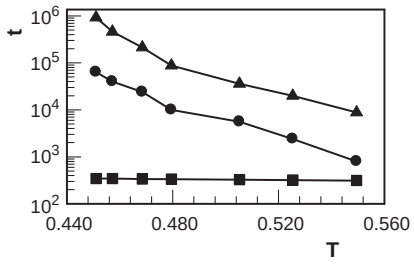

Fig. 3. Temperature dependence of the three relevant times, t: ballistic time (squares), t^* (circles) and $\tau_{MSD=1}$ (triangles).

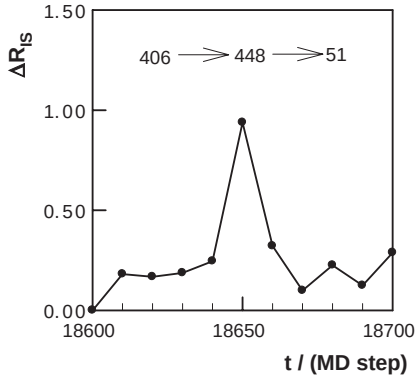

Fig. 4. Time evolution of ΔR_{IS} for the region where the string of Fig. 2 takes place.

exploration and making the relaxation process amenable of mechanistic description. This fact means that the ballistic time is related to the events responsible for transitions between IS's. On the other hand, t^* is located at the end of the β and at the beginning of the α relaxation. The α relaxation processes have been related to megabasin transitions (long range rearrangements involving the transition between groups of similar and related IS's). Thus, these two timescales would correspond to events to different range in the exploration of the PES. At sufficiently low T (when the ballistic time is much smaller than t^*) the different transitions between IS's (performed by means of string movements) are well separated in time from each other, thus allowing for local equilibration. This separation of timescales marks the onset of activated dynamics, concurrent with the appearance of nonexponential Kohlrausch laws characteristic of glassy dynamics. This fact is also reflected in the appearance of diversity (which is not intrinsic but depends on temperature and thus on the level of resolution of the conformational search). Thus, diversity is at the heart of the inhomogeneous nature of the relaxation. At high T, where the system has enough thermal energy to visit the whole conformation space, the sampled minima are high and shallow (as the great majority of the minima) [12]. At lower T deeper minima (which are scarce) separated by high barriers are explored and at even lower T the system becomes confined in the deepest minima. Thus, the portion of conformation space visited is more complex as T is lowered [12]. At high T all the minima are similar in which concerns dynamics (since thermal energy is enough to prevent confinement and the system does not spend much time around them). In fact, the liquid state does not present diversity since the sampled minima are all equally unimportant from a dynamical perspective. However, at lower T the system samples (and begins to be confined in) states very different from structural and dynamical standpoints (but not necessarily very different in potential energy), separated by high barriers. Since thermal energy is low, these minima begin to display their own distinct dynamical behavior (with their own activation barriers and relaxation timescales) implying the onset of an inhomogeneous relaxation scenario and, concurrently, the advent of diversity, complexity and glassiness.

3. Conclusions

We have examined the timescale separation scenario in two different implementation of the landscape paradigm, a widespread phenomenological picture in the realm of complex systems. These two approaches have been relevant to the study of the relaxation dynamics of a variety of complex systems, including from glasses to biopolymers. In this work the results in both schemes have been compared and related to a generic variational principle. We have emphasized the fact that the dominance of activated dynamics over other relaxation mechanisms marks the onset of complex behavior (including the occurrence of non-exponential Kohlrausch laws), of diversity and glassiness. The fact that complex behavior arises as a consequence of the separation of timescales between events of different range makes the relaxation process amenable of a (defect-dominated) mechanistic description. Additionally, for the specific context of a simple model glass-former we have demonstrated in this work the microscopic origin of timescale separation, the main tenet of the landscape paradigm.

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