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Richard Kerner's Path Integral Approach Aims to Understand the Self-Organized Matter Agglomeration and Its Translation into the Energy Landscape Kinetics Paradigm

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Abstract: Matter grows and self-assembles to produce complex structures such as virus capsids, carbon fullerenes, proteins, glasses, etc. Due to its complexity, performing pen-and-paper calculations to explain and describe such assemblies is cumbersome. Many years ago, Richard Kerner presented a pen-and-paper path integral approach to understand self-organized matter. Although successfully addressed many important problems including the yield of fullerene formation, the glass transition temperature of doped chalcogenide glasses, the fraction of boroxol rings in B_2O_3 glasses, the first theoretical explanation for the empirical recipe of window and Pyrex glass and the understanding of virus capsid self-assembly, still is not the primary choice when tackling similar problems. The reason lies in the fact that it diverges from mainstream approaches based on the energy landscape paradigm and non-equilibrium thermodynamics. In this context, a critical review is presented, demonstrating that the Richard Kerner method is, in fact, a clever way to identify relevant configurations. Its equations are simplified, common physical sense versions to those found in the energy landscape kinetic equations. Subsequently, the utilization of equilibrium Boltzmann factors in the transition Markov chain probabilities is analyzed within the context of local two-level energy landscape models kinetics. This analysis demonstrates that their use remains valid when the local energy barrier between reaction coordinate states is small compared to the thermal energy. This finding places the Richard Kerner model on par with other more sophisticated methods and, hopefully, will promote its adoption as an initial and useful choice for describing the self-agglomeration of matter.

Keywords: self-assemble; matter agglomeration; glasses; quasicrystals; carbon fullerenes; graphene; virus structures; nanotechnology; energy landscape; path Integrals

0. Introduction

Matter grows and self assemble to produce complex structures as virus capsids, carbon fullerenes, proteins, glasses, crystals, quasicrystals, liquid crystals, nanotubes, two dimensional materials, etc.[1–3]. Atomic interactions and external thermodynamical constraints are responsible for such an amazing behavior [4]. Our understanding of how it happens rest on few general principles. The catch here is that in real systems the basic principles have limited prediction powers due to the complexity involved [5–7], especially when doing back of the envelope, pen and paper calculations.

Let's perform a simple exercise. Take any book on phase transitions or statistical mechanics and attempt to understand why water becomes ice at $T = 0$ C and $P = 1$ atm. Try to predict the crystalline structure of ice and the most important property that distinguishes water from ice—its flow. Although the book will help you identify some properties of the phase diagram, the order parameter, analogies with the Van der Waals equation, and more, from a practical standpoint, you'll find that obtaining concrete answers can be challenging. Numerical calculations are often necessary, but even at this level, the phase diagram of water is still beyond the capabilities of current computers and interaction models [8].

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Another example is the process of protein folding in which a protein chain transforms into its native three dimensional form [9,10]. Any failure to do so is associated with many diseases [11]. A simple statistical mechanics calculation in which all possible conformations are explored leads to the well known Levinthal's paradox, i.e., the time to fold would be much longer than the age of the universe [12]. Most proteins fold in milliseconds. The solution to such paradox is that, folding follows a sequence in which only a bunch of self assembled, prominent structures have a significant role. This was revealed by a mathematical analysis of a simple model[13]. Later on, such scenario was confirmed by using computers and the energy landscape paradigm [14]. Therein the energy $E(\{q_j\})$ is a function of the configuration denoted by the set of all generalized coordinates $\{q_j\}$. Thus all accessible states are bounded by below in energy by the surface generated by $E(\{q_j\})$. As the temperature goes down, the system can only explore lower basins of the landscape, and sometimes, jump from one basin to the other. The coordinate which has the lower "mountain pass" between basins is known as the reaction coordinate. Therefore, the problem of self assembly is somewhat similar to railway localization in a given topography. When Levinthal's paradox was solved the verdict was that the energy landscape has the shape of a funnel [9,13] as was suggested before by the simple model. The precise shape of the funnel or the most important configurations are in general tasks left for computers [15]. Nowadays, artificial intelligence and collective computation has been used to determine folding paths [16]. Yet and in a surprising turn of fate, history balances again toward simple models. Using single-molecule magnetic tweezers, individual transitions during the folding process were recorded for a single talin protein [10]. It turns out to be very well described in an uncomplicated two-state manner. Only after many days the energy landscape shows gradually signatures of its complexity [10]. For the cosmologic landscape predicted by string theory the verdict is still unknown [17].

Based on all the previous discussions, it appears cumbersome to predict in a straightforward manner the temperature and yield of fullerene formation, comprehend the impact of doping on the glass transition temperature, or propose a viable approach to cure viral diseases by inhibiting the self-assembly of virus capsids. In this context, years ago Richard Kerner proposed a simplified approach[2,18–21]. It entails incorporating common-sense inputs and integrating them with a path integral-like approach to identify the most significant clusters, determine the state of their surfaces, and explore agglomeration paths, all in a manner akin to a saddle-point approximation [2,18–21].

This unique combination yielded impressive results through pen-and-paper calculations. It led to successful predictions, including the yield of fullerene formation [20,22], the glass transition temperature, viscosity, and specific heat of doped chalcogenide glasses [19,21,23–25], the fraction of boroxol rings in B_2O_3 glasses [26,27], all of which matched experimental data. Remarkably, the method provided the first theoretical explanation for the empirical recipe of window and Pyrex glass, a milestone in the understanding of glassy materials [2,28]. Later on, the method was applied to understand the self-assembly of virus capsids [29].

Considering the method's potency and intuitiveness, one might wonder why it isn't the primary choice when tackling such problems. In this paper, I will provide some reflections on this matter, but let me foreshadow the answer: self-organization often necessitate non-equilibrium conditions, and at first glance, it appears that Kerner's method assumes equilibrium. As I will demonstrate here, this is not the case. Kerner's path approach can be translated into energy landscape kinetic equations without assuming thermodynamical equilibrium. The only condition is to assume *contact with a thermal bath with a well defined temperature*.

The method has been described by Richard Kerner himself in an excellent book [2]. Another book that provides a description of the method was published quite some time ago by R. Aldrovandi. [30]. My intention here is not to repeat the method but instead, make a short summary of how it works and then its interpretation in terms of the energy landscape paradigm.

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1. Richard Kerner agglomeration model

The method is based in finding the probability of forming certain structural motifs at a certain time from those of the previous step of agglomeration [2]. The method is almost self-explained by giving a simple example. Here we will consider the case of a chalcogen element, say Se, doped with a concentration x of another element with well defined coordination, say As. Chalcogen atoms belong to the group VI of the periodic table and tend to form large chains, i.e., the coordination of Se atoms is $z_{Se} = 2$. The coordination of As is $z_{As} = 3$. Experimentally, at the time that RK was working on this compound, it was known that the glass transition temperature (T_g), viscosity (η) and specific heat jump (Δc_p) were a function of x. Only phenomenological theories were available and it was recognized as an important problem because T_g changes dramatically with small x. In fact, before RK applied his method [28], the explanation of the thousand years old phoenicians recipe for doping sand with certain concentrations of impurities to obtain window glasses remained elusive. It was also clear that network topology played an important role as the bonding energies between impurities and chalcogens were not able to explain the experimental data [18,21,23,31]. At that time, other scientists that arrived to the same conclusion [32–35]. Eventually, this leads to other advancements like a universal topological law for glass relaxation [36,37] or in the description of liquid glassy melts [38,39] and Boson peak [40–42]. These advances eventually proved crucial in describing, designing, and producing over 400 different types of glasses, including those used in tablets, smartphones, and other devices [43].

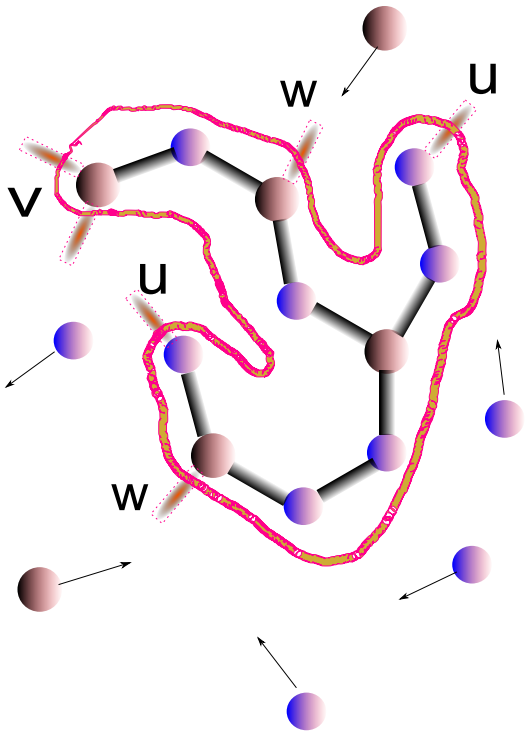

Figure 1. Agglomeration model of $Se_{1-x}As_x$ glass. A cluster made of Se atoms, with coordination $z_{Se} = 2$ and As atoms, with coordination $z_{As} = 3$ is indicated by the curve. The unsatisfied bonds at the rim of the cluster are indicated by dotted edges bonds. The three kinds of surface sites u,v,w are indicated. Free atoms in the melt are indicated with arrows that indicate the velocity vector.

Assuming that the system is melted at high temperatures, to form a glass the system is cooled down with a certain protocol, i.e., the temeprature T is a function of time t. Usually, $T(t) = T_0 - Rt$

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where T_0 is the initially temperature and R the cooling rate. At a certain time, the atoms will begin to interact with a nucleation center and form bonds. Each bond has a definite energy, ϵ for Se-Se bonds, η for Se-As bonds and α for As-As bonds. However, the probability of forming bonds, according to RK depends on,

1. The number of ways in which a bond can be made.
2. The Bond Energy;
3. The concentration of atomic species
4. The temperature

These are clearly very common sense physical inputs. Now consider a nucleation center. It will contain unsaturated Se bonds with one free bond, call them sites of type u, and As atoms with two and one available free bonds, called v and w sites respectively. The different possible terminations of the rim can be considered as possible states of a vector $|p(t)\rangle$ which encodes the probability of states on the rim. The probabilities after a new step of agglomeration are then obtained as in a Markov process, i..e, by applying a transition matrix to the rim state vector that contains the probability of making a new bond, i.e., we have,

$$|p(t+dt)\rangle = \mathbf{M}(t)|p(t)\rangle \tag{1}$$

where,

$$|p(t)\rangle = (p_u, p_v, p_w)^T \tag{2}$$

and $\mathbf{M}(t)$ is an stochastic matrix as each column must be normalized to one in order to ensure probability normalization at each step. The elements of $\mathbf{M}(t)$ are called the transition probabilities and as we will discuss later on, are the source of the debate. I will leave its discussion to a separate section. RK proposed that such transition probabilities of attaching Se or As into sites of type u,v or w on the cluster surface were given by taking into account in its simplest way all the four entries of the physical input list, i.e., the elements of $\mathbf{M}(t)$ are,

- u+Se; $M_{11}(t) = \frac{z_{Se}(1-x)e^{-\epsilon/T}}{Q_1(t)}$
- u+As; $M_{21}(t) = \frac{z_{As}xe^{-\eta/T}}{Q_1(t)}$
- v+Se; $M_{31}(t) = \frac{z_{Se}(1-x)e^{-\epsilon/T}}{Q_2(t)}$
- v+As; $M_{22}(t) = \frac{2z_{As}xe^{-\epsilon/T}}{Q_2(t)}$
- w+Se; $M_{31}(t) = \frac{z_{Se}(1-x)e^{-\epsilon/T}}{Q_3(t)}$
- w+As; $M_{32}(t) = \frac{z_{As}xe^{-\epsilon/T}}{Q_3(t)}$.

and all others elements are zero. Here $Q_1(T), Q_2(T), Q_3(T)$ are the normalization factors that ensure column normalization of $\mathbf{M}(t)$. Note that here we used the most powerful version of the method [24,27] that was made after RK made several works in which the calculations were made for several systems by hand, i.e., by performing the agglomeration steps, computing probabilities and sometime discarding some low probability configurations [20,22]. At a certain point, a self-consistent equation was found that defined the temperature at which the cluster was able to grow.

In terms of Markov chains, the solution is easy. As $\mathbf{M}(t)$ is stochastic, it has an eigenvector with eigenvalue one which will dominate others after successive applications of $\mathbf{M}(t)$ onto any given state vector [44]. Therefore, we compute the eigenvector with eigenvalue one and from it, obtain the stationary state of the rim. The glass transition temperature can be found for example by looking for a jump in the specific heat [27]. The method is well documented in many papers. It was able to find the concentration of boroxol rings, viscosity, specific heat [27] of B_2O_3 glass and even the modified empirically observed Gibbs-DiMarzio equation for chalcogenide glasses [24]. In the following section, we will discuss some controversial issues and their relationship in terms of the energy landscape kinetics picture and path integrals.

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2. Translation to the energy landscape paradigm and path integrals

Some objections have been raised against the RK and the stochastic matrix method. The main criticism are,

1. The method is too simple to work.
2. Topology is taken into account in a very simplistic way, just by counting the number of bonding possibilities.
3. The transition elements of the stochastic matrix use Boltzmann factors, but agglomeration is usually a non-equilibrium processes.

Point 1 of the previous list is not a problem per se and in fact, according to the Occam's razor, is a benefit. Point 2 has huge experimental support, as for example, the boiling temperature of isomers depend upon such number [45]. Point 3 is the most difficult to answer, but to be fair, it turns out to be controversial also for the energy landscape paradigm.

Let us now build the connection between the RK method and the energy landscape. Consider that any thermodynamical system evolves in the energy landscape exactly as given by eq. (1). The differences are in the details. $|p(t)\rangle$ represents a probability vector in which each component gives the probability of the system to be in a state, say j, with energy E_j and mechanical coordinates $\{q_1, q_2, ..., q_{3N}, \Pi_1, \Pi_2, ..., \Pi_{3N}\}$. q_l are the generalized space coordinates and Π_l the generalized momenta of N atoms [5,9,14,15]. The interaction is given by a potential $V(q_1, q_2, ..., q_{3N})$. When compared with the entries of the RK method, the situation looks hopeless. However in most physical cases the states are grouped in basins which evolve around inherent, dominant configurations. As an example, we already cited the case of proteins which although very complex are described by two level systems [10]. In molecular simulations, the phase space is partitioned in parcels and the size of $|p(t)\rangle$ is dramatically reduced to a bunch of configurations as in the RK method [46].

Now the connection between RK method, the energy landscape and a path integral approach is much clear. By writing eq. (1) as,

$$\frac{d}{dt}|p(t)\rangle = \mathbf{W}(t)|p(t)\rangle \tag{3}$$

where $\mathbf{M}(t) \equiv \mathbf{W}(t)dt + 1$ and dt is the time interval, the evolution after time t can be obtained from a recursive application of $\mathbf{W}(t)$ and the formal solution of eq. (3) is,

$$|p(t)\rangle = \mathcal{T} e^{\int_{t_0}^{t} \mathbf{W}(t)dt} |p(t_0)\rangle \tag{4}$$

Notice that a "time order operator" $\mathcal{T}$ was introduced. It takes into account the non-conmmutative nature of the operator $\mathbf{W}(t)$ at different times. This path integral is akin to the time evolution of a quantum mechanical system [47]. If the linear cooling protocol $T(t)$ is used where $T(t_0) = T_0$, we can define the path integral in temperature,

$$|p(T)\rangle = \mathcal{T} e^{-\frac{1}{R}\int_{T_0}^{T} \mathbf{W}(T)dT} |p(T_0)\rangle \tag{5}$$

Notice that here R plays the role of the Planck constant $\hbar$ when compared with the quantum case. Thus we see that the RK method relies on a clever way of identifying the states that play a prominent role. Agglomeration centers represent states in which a certain subset of generalized coordinates, denoted as $q_1, q_2, \ldots, q_{3N}$, are held fixed or frozen. This intuitive idea has been confirmed by using an automated approach, based on self-organizing neural nets [48]. The result: "the conformational information from 30,000 samples from the full trajectories was retained in relatively few resultant clusters" [48].

3. Transition probabilities of the agglomeration process

As we observed in the previous section, there are no major issues or problems with the RK method when compared to the energy landscape model. The primary distinction lies in the manual

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identification of relevant states, a process that is often facilitated by the computational power available in more complex studies [9,14,15]. As mentioned earlier, the main concern revolves around computing the elements of the matrix $\mathbf{M}(t)$, which has been addressed here in the context of $Se - As$ glasses. However, it's important to note that this is not a unique problem specific to the RK method. Markov state modeling has often been considered more of an art than a science [49].

To understand the Boltzmann factors of the RK method, we consider that locally in a certain energy range, the energy landscape can be seen as a typical two level energy landscape model [46,50,51]. Figure 2 presents a sketch of such idea. The system is not at equilibrium but is in thermal contact with a bath at a temperature $T(t)$ that varies with time. The energy landscape kinetic equation Eq. (3) can be locally written as,

$$\frac{d}{dt}\begin{pmatrix} -p(t) \\ p(t) \end{pmatrix} = \begin{pmatrix} -\Gamma_{\uparrow\downarrow}(t) & \Gamma_{\downarrow\uparrow}(t) \\ \Gamma_{\uparrow\downarrow}(t) & -\Gamma_{\downarrow\uparrow}(t) \end{pmatrix}\begin{pmatrix} 1-p(t) \\ p(t) \end{pmatrix} \tag{6}$$

where $1 - p(t)$ is the low energy, set to $E_0 = 0$ for conviencience, state probability occupation, and $p(t)$ is the same quantity but for the high energy state with energy E_1 (see Figure 2). These states are separated by a potential barrier of height V.

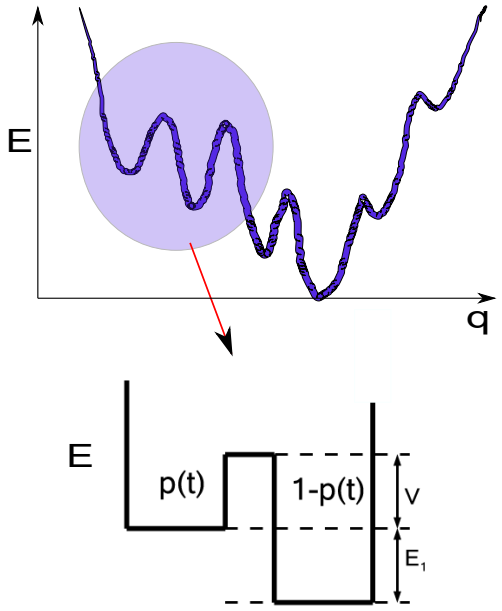

Figure 2. A funnel energy landscape E as a function of the reaction coordinate q. The circle indicates that in a certain energy range, locally the system can be seen as the two level model depicted below the landscape. In this reduced two-level model, we indicate the barrier height V and the energy E_1 of the high-energy states and $E_0 = 0$ of the local ground state.

The element $\Gamma_{\uparrow\downarrow}(t)$ is the transition rate from the lower to high energy state, and the inverse process has rate $\Gamma_{\downarrow\uparrow}(t)$. According to non-equilibrium thermodynamics and neglecting quantum tunelling [50,52], $\Gamma_{\uparrow\downarrow}(t) = e^{-\frac{E_1}{T(t)}}\Gamma_{\downarrow\uparrow}$ and $\Gamma_{\downarrow\uparrow}(t) = \Gamma_0 e^{-\frac{V}{T(t)}}$. Γ_0 is the oscillation frequency on each energy well and gives a natural time-scale for the problem $\tau_0 \equiv \Gamma_0^{-1}$. Now we see that the Boltzmann factor appear not due to thermal equilibrium, instead, is a property derived from the contact with a bath which has a well defined temperature [52]. The price paid is the factor that contains V, which is the potential barrier separating both states. To see this, we show how for the system in equilibrium, V disappears from the picture.

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Assuming thermal equilibrium means here a quasistatic cooling, obtained by setting $d|p(t)\rangle/dt \approx 0$. As the temperature can be considered fixed, from the eigenvector with eigenvalue one of $\mathbf{M}(t)$ we obtain the equilibrium population $p^e(T) = p^e(T(t))$,

$$p^e(T) = \frac{\Gamma_{\uparrow\downarrow}(T(t))}{(\Gamma_{\uparrow\downarrow}(T(t)) + \Gamma_{\downarrow\uparrow})(T(t))} = \frac{e^{-\frac{E_1}{T}}}{1 + e^{-\frac{E_1}{T}}}, \tag{7}$$

which reproduces the result obtained from an equilibrium partition function, without any final reference to V. Let us now discuss the non-equilibrium cooling. Eq. (6) reduces to one equation,

$$\frac{dp(t)}{dt} = f(t,p) \tag{8}$$

where,

$$f(t,p) = \Gamma_0 e^{-\frac{V}{T(t)}}[(1-p(t))e^{-\frac{E}{T(t)}} - 1]. \tag{9}$$

The equilibrium population $p^e(T)$ is recovered from the roots of $f(p,T)$. For a fixed time, the nature of the stability around the equilibrium solution is given by the sign of the derivative with respect to p evaluated at equilibrium,

$$\left.\frac{\partial f(t,p)}{\partial p}\right|_{p=p^e(t)} = -\Gamma_0 e^{-\frac{(V+E_1)}{T(t)}} < 0 \tag{10}$$

showing that indeed the solutions are stable and converge to $p^e(T)$. By looking at $f(t,p)$, we see that the term in square brackets is the equilibrium condition while the term $\Gamma_0 e^{-\frac{V}{T(t)}}$ plays the role of an inverse relaxation time τ. For $V << T(t) = T_0 - Rt$, the relaxation time is constant $\tau \approx \tau_0 = \Gamma_0^{-1}$ and we can use the local equilibrium Boltzmann factors. In a funnel landscape along the coordinate reaction direction, the barriers V are expected to be $V << T$ during the agglomeration process. This is specially true for chalcogenide glasses, as the topology in real space is related with the energy barriers via constraint, rigidity theory [39,53–56]. So the lack of atomic constraints means that there is a thermodynamic finite amount of $V \approx 0$ channels in configurational space where the present approach can be used [39,57]. Therefore, the use of Boltzmann factors by the RK theory appears to be well justified, explaining the striking agreement when compared with experimental data. Once the solid is formed, the approximation breaks down as the relaxation time can no longer be supposed constant. This can be seen by writing Eq. (6) as,

$$\delta\frac{dp(x)}{dx} = \frac{1}{(\ln x)^2}[-x^\mu + (1+x^\mu)p(x)] \tag{11}$$

using the definitions,

$$x = \exp(-V/T), \mu = E_1/V \tag{12}$$

where $\delta = RV/\Gamma_0 T_0$ is an adimensional cooling rate. For $\delta = 0$ it is easy to see that the equilibrium case is recovered. A power series expansion in powers δ reveals a divergence in the first order in a region of size determined by $x_b = \delta(\ln x_b)^2$ associated with temperatures in which the system is frozen in the upper state, indicating a glassy, solid, behavior. The evolution can also be written in terms of the path integral,

$$|p(x)\rangle = \mathcal{T} e^{-\frac{1}{\delta}\int_{x_0}^{x}\mathbf{W}(x)dx}|p(x_0)\rangle \tag{13}$$

with initial condition $x_0 = \exp(-V/T_0)$ and $\mathbf{W}(x)$ given by,

$$\mathbf{W}(x) = \frac{1}{(\ln x)^2}\begin{pmatrix} -x^{1+\mu} & x \\ x^{1+\mu} & -x \end{pmatrix}. \tag{14}$$

For $x >> x_b$, $x \approx 1$ and $\mathbf{W}(x)$ becomes a constant matrix. What we observe here is that the departure from the equilibrium case results in a renormalization of the weights, due to the presence of a barrier V, with respect to the Boltzmann factor.

4. Conclusions

In this work I made a short review of the Richard Kerner's path integral approach aims to understand the self-organized matter agglomeration. It was shown how it can be translated into the energy landscape kinetics paradigm as the RK method identifies most probable clusters and the state of its surface. Then a revision was made concerning the transition matrix elements of the associated stochastic matrix. As it was discussed, the most controversial issue is the use of Boltzmann factors. However, such issue disappears if the transition barriers along the reaction coordinate of the energy landscape are not very high when compared with the thermal energy as happens in funnel-like energy landscapes.

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Abbreviations

The following abbreviations are used in this manuscript:

RK Richard Kerner

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