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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 understanding self-organized matter. Although this approach 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, it 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 of 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

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1. Introduction

Matter grows and self-assembles to produce complex structures such 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 rests on a 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 performing back-of-the-envelope, pen-and-paper calculations.

Here, we perform a simple exercise. Take any book on phase transitions or statistical mechanics and attempt to understand why water becomes ice at $T = 0\text{ C}$ and $P = 1\text{ atm}$. 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 will 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].

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 a 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 insufficient energy by the surface generated by $E(\{q_j\})$. As the temperature decreases, the system can only explore lower basins of the landscape and sometimes jump from one basin to the other. The coordinate that 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 have been used to determine folding paths [16]. However, 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 does the energy landscape gradually show 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 straightforwardly predict 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], and 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 is not the primary choice when tackling such problems. This paper will provide some reflections on this matter, but first, a foreshadowing of the answer: self-organization often necessitates non-equilibrium conditions, and at first glance, it appears that Kerner's method assumes equilibrium. As will be demonstrated 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, even if the bath temperature changes with time*.

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 to make a short summary of how it works and then its interpretation in terms of the energy landscape paradigm.

2. Richard Kerner Agglomeration Model

The method is based on finding the probability of forming certain structural motifs at a certain time from those of the previous step of agglomeration [2]. The motifs in the melt are not necessarily monomers but can be clusters as well [31]. The method is almost self-explained by giving a simple example. As seen in Figure 1, 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 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 a small x . In fact, before RK applied his method [28], the explanation of the thousand-year-old Phoenician 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 arrived at the same conclusion [32–35]. Eventually, this led to other advancements, such as a universal topological law for glass relaxation [36,37] or in the description of liquid glassy melts [38,39] and the 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].

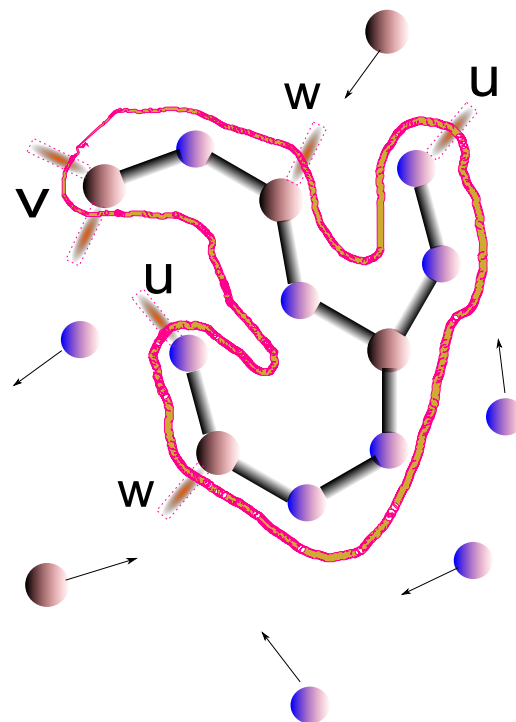


Figure 1. Agglomeration model of $Se_{1-x}As_x$ glass. A cluster made of *Se* atoms, with coordination $z_{Se} = 2$ and *As* atoms, with coordination $z_{As} = 3$ as indicated by the curve. The unsatisfied bonds at the rim of the cluster are indicated by dotted edges bonds. The three kinds of surface 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 temperature T is a function of time t . Usually, $T(t) = T_0 - Rt$ where T_0 is the initial temperature and R is 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. As seen in Figure 1, it will contain unsaturated Se bonds with one free bond, called 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,

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

where,

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

and $\mathbf{M}(t)$ is a 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. This will be discussed in 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 four entries of the physical input list, i.e., the elements of $\mathbf{M}(t)$ are,

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

and all other 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 conducted several works in which the calculations were made for several systems by hand, i.e., by performing the agglomeration steps, computing probabilities and sometimes 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, and 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.

3. Translation to the Energy Landscape Paradigm and Path Integrals

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

1. The method is too simple to work. For example, real systems encompass electronic and mechanical stress stabilization contributions [45–49].
2. Topology is taken into account in a very simplistic way, just by counting the number of bonding possibilities. Additionally, dealing with the complex structure of the melt can be challenging [50–53], and fixing coordination numbers may pose risks [54,55].
3. The transition elements of the stochastic matrix use Boltzmann factors, but agglomeration is usually a non-equilibrium process [56–58]. No general principles, such as thermodynamics, allow for a complete understanding of all non-equilibrium situations [59].

Point 1 of the previous list is not a problem per se and, in fact, according to Occam's razor, is a benefit when considering a pen-and-paper effort. In upcoming sections, we will discuss in more detail the guidelines to know if a system is suited to be studied under the RK perspective.

Point 2 has experimental support; for example, the boiling temperature of isomers depends upon the coordination number [60]. However, the reality is not as simple as depicted in the previous section. In the melt, several assembled structural units coexist [61], influenced by factors such as pressure, temperature, thermal history, etc. [45,62–65]. Furthermore, substantial reformation of the structural motifs is often observed, resulting from events such as bond breaking in the liquid state [61]. Even melts of elements in the same column of the periodic table, such as Te and Se, exhibit notably different behaviors [66–79] and, therefore, present totally different abilities to form glasses [80]. Elements can also have different coordination numbers. In molecular compounds of the type P_nS_m and As_nS_m , S can form double bonds with P, so that the composition of the molecular chalcogenides varies from [81] P_4S_3 to P_4S_{10} . The coordination numbers vary, 3 and 4 for P and 1 and 2 for S. The term “hyper-valence” is used when an element has larger coordination numbers than those given by the valence bond theory [55].

Another well-documented example is the case of B_2O_3 glass. Therein, several borate ion structures coexist [81]. Experimental conditions change its relative concentrations, as confirmed by looking at the structure of the B_2O_3 high-pressure crystal [82]. Ab initio molecular-dynamic simulations of liquid B_2O_3 further confirm the existence of different coordination structures at normal- and high-pressure conditions [51,52]. Such structures contribute to the atomic diffusion [51,52]. Furthermore, in principle, the RK model only includes the solidification reaction, $cluster(j) + monomer \rightarrow cluster(j+1)$, but not the decomposition reaction, $cluster(j+1) \rightarrow cluster(j) + monomer$ or the rearrangements of the cluster surface, $cluster(j) \leftrightarrow cluster(j)$. Some of these problems can be somehow mitigated using different strategies. For instance, the catalog of units in the melt can be extended to encompass various structural entities beyond monomers [31]. This expansion leads to renormalized coordinations that correspond to assembled clusters in the melt [31]. Such a strategy was used to improve the results in several chalcogenide glasses [31]. As explained in the conclusions, in principle, one can also expand the stochastic matrix to include the reverse solidification reactions. A simplified two-level model allows the capturing of such effect in a very crude way [83]. From all these considerations, it is clear that the RK method requires a careful study of the possible structural motifs, in many cases aided by looking at the available melt experimental data [84].

Point 3 is the most difficult to answer, but to be fair, it also turns out to be controversial for the energy landscape paradigm, as we will discuss. For the moment, 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 Equation (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 $\{q_1, q_2, \dots, q_{3N}, \Pi_1, \Pi_2, \dots, \Pi_{3N}\}$. 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 $V(q_1, q_2, \dots, q_{3N})$. When compared with the entries of the RK method, the situation looks hopeless. However, in most physical cases, the states are grouped in basins that 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 [85].

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

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

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 Equation (3) is,

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

Notice that a “time order operator” $\mathcal{T}$ was introduced. It takes into account the non-commutative nature of the operator $\mathbf{W}(t)$ at different times. This path integral is akin to the time evolution of a quantum mechanical system [86]. If the linear cooling protocol $T(t)$ is used where $T(t_0) = T_0$, we can define the path integral in temperature,

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

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 $q_1, q_2, \dots, q_{3N}$, are held fixed or frozen. This intuitive idea has been confirmed by using an automated approach based on self-organizing neural nets [87]. The result: “the conformational information from 30,000 samples from the full trajectories was retained in relatively few resultant clusters” [87].

4. 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 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 is 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 [88].

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 [85,89,90]. 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 Equation (3) can be locally written as,

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

where $1 - p(t)$ is the low energy, set to $E_0 = 0$ for convenience, 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 .

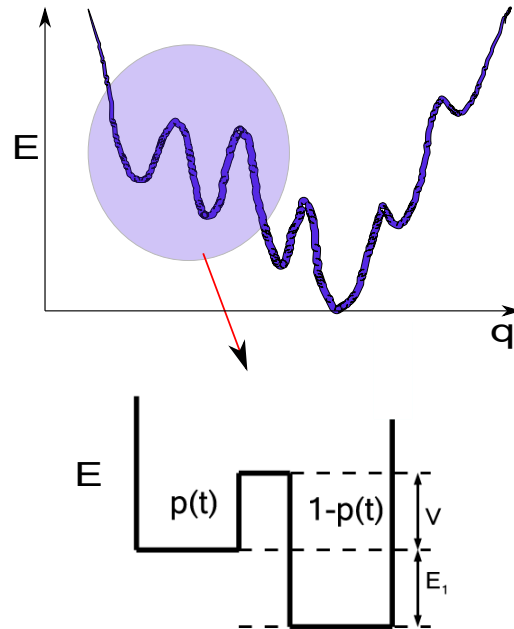


Figure 2. A funnel energy landscape E as a function of the reaction coordinate q . The circle indicates that in a certain energy range, locally, the system can be seen as the two-level model depicted below the landscape. In this reduced two-level model, we indicate the barrier height V and the energy 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 tunnelling [89,91], $\Gamma_{\uparrow\downarrow}(t) = e^{-\frac{E_1}{T(t)}} \Gamma_{\downarrow\uparrow}$ 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 appears not due to thermal equilibrium but is instead a property derived from the contact with a bath, which has a well-defined temperature [91]. 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.

Assuming thermal equilibrium here means 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 $p^e(T) = p^e(T(t))$,

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

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

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

where,

$$f(t, p) = \Gamma_0 e^{-\frac{V}{T(t)}} [(1 - p(t))e^{-\frac{E_1}{T(t)}} - p(t)]. \quad (9)$$

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,

$$\left. \frac{\partial f(t, p)}{\partial p} \right|_{p=p^e(t)} = -\Gamma_0 e^{-\frac{V}{T(t)}} [e^{-\frac{E_1}{T(t)}} + 1] < 0 \quad (10)$$

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 in Equation (9) is the equilibrium condition, while the term $\Gamma_0 e^{-\frac{V}{T(t)}}$ plays the role of an inverse relaxation time τ . For $V \ll T(t) = T_0 - Rt$, 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 local barriers V along the reaction coordinate are expected to be $V \ll T$ during the agglomeration process. Note that this does not necessarily imply that the potential barriers on the other coordinates are small when compared with T . In fact, the RK method implies that many coordinates are held fixed or frozen, and thus, such barriers are much higher than T . This is especially true for chalcogenide glasses, as the topology in real space is related to the energy barriers via the constraint (rigidity) theory [39,92–95]. Therefore, the lack of atomic constraints means that there is a thermodynamic finite amount of channels in configurational space where the present approach can be used [39,96]. 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 to be constant. This can be seen by writing Equation (6) as,

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

using the definitions,

$$x = \exp(-V/T), \mu = E_1/V \quad (12)$$

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 power 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,

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

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

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

For $x \gg x_b$, $x \approx 1$ and $\mathbf{W}(x)$ become 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.

Finally, the RK Markov state mode not only gives the activation energy $E(i, j)$ between states i and j , but also the activation entropy $S(i, j)$. The matrix elements of $\mathbf{W}(T(t))$ can be obtained according to $W_{ij} = \exp[-E(i, j)/T + S(i, j)]$, where $E(i, j)$ and $S(i, j)$ are separated from the temperature dependence. The equilibrium energy difference E_1 is obtained by considering the reverse reaction and by $E(i, j) = E_1 + V$; $E(j, i) = V$. Experimentalists have been using this method to analyze the chelate reactions [97]. The effect of the entropy term in two-level models has been proven to be essential to recovering sharp crystalline phase transitions and a glass transition depending on the cooling speed [83].

5. Conclusions

In this work, a short review of Richard Kerner's path integral approach was presented with the aim of understanding the self-organized matter agglomeration. It was shown how it can be translated into the energy landscape kinetics paradigm as the RK method identifies the most probable clusters and the state of their 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 barrier along the reaction coordinate of the energy landscape is not very high when compared with the thermal energy, as happens in funnel-like energy landscapes. This does not imply that other barriers are necessarily small compared to V .

All these considerations raise the question of guidelines for determining when this method can be applied. The requirement that the reaction coordinate barriers should be $V \ll T$ indicates that the system must have a well-defined hierarchy of forces. For example, in chalcogenide glasses, there are non-directional forces, such as ionic or Van der Waals bonding, and directional covalent bonding. As covalent bonds are much stronger, this implies that the energy landscape pathways are defined by such directional bonds. In fact, when such a hierarchy is present, the available entropy is just renormalized by one of the contributions from the ideal case [79]. Therefore, the RK method is well-suited to studying systems with well-defined directional bonding, as is the case with carbon compounds or network glass formers. Metallic or colloidal systems, for example, are not well-described, as the interactions are mainly non-directional, and their energy landscapes lack clear pathways [9,98,99]. These conclusions suggest that the RK method may be relevant for studying numerous newly discovered families of two-dimensional materials, such as silicene, borophene, and hexagonal BN. These materials exhibit directional forces, and many questions in their study remain open [100,101].

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Abbreviations

The following abbreviations are used in this manuscript:

RK Richard Kerner

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