SURVIVAL PROBABILITY FOR DIFFUSION ON A PERCOLATION CLUSTER*

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(Received March 12, 1997)

One of possible models of conformational transition dynamics in native proteins is diffusion on fractal lattices, in particular on percolation clusters. In this paper a theoretical model of reactions involving proteins with intramolecular dynamics of this kind is studied. It is assumed that the transition state of the reaction is reduced to a single conformational substate (a lattice site representing the gate) and that the initial state is also reduced to a single site. The latter can coincide with the gate or not. Despite the fact that the considered reaction is an activated process, computer simulations indicate that the pre-exponential stage of the reaction can be the most important one. In this stage after a short initial period strongly dependent on the location of the initial state the reaction proceeds according to the algebraic power law. There is no direct relation between the value of the power law exponent α in this stage and the spectral dimension $\tilde{d}$ of the lattice. The value of this exponent was estimated to be in the range 0.25 to 0.4. The rate of the final exponential decay is determined by two components — the characteristic reconstruction time of the transition state equilibrium occupation and the characteristic time predicted by the transition state theory.

PACS numbers: 87.15. He, 87.15. Rn, 05.40. +j

1. Introduction

An impetuous progress in experimental studies of native protein dynamics requires that more and more adequate theoretical models be worked out. In the time scale larger than 10^{-11}s this dynamics is reduced to purely stochastic conformational transitions. One class of models of conformational transition dynamics within native proteins are protein-glass type

* Presented at the IX Symposium on Statistical Physics, Zakopane, Poland, September 23–28, 1996.

models [1–3], in which the dynamics is assumed to look alike in every time-scale, *i.e.* the spectrum of corresponding relaxation times has self-similarity symmetry. For this kind of models time scaling originates either from a hierarchy of barrier heights in the potential energy landscape or from a hierarchy of bottlenecks in the network representing conformational states of the protein. Two conformations are connected in this network if and only if a direct transition between them is possible. Scaling properties are observed for diffusion on fractal lattices of spectral dimension less than 2 [4–7]. An example of such a lattice is the percolation cluster which will be the focus of this paper. In this case the bottlenecks can be identified as connections joining state groupings (clusters) of increasing magnitude (Fig. 1).

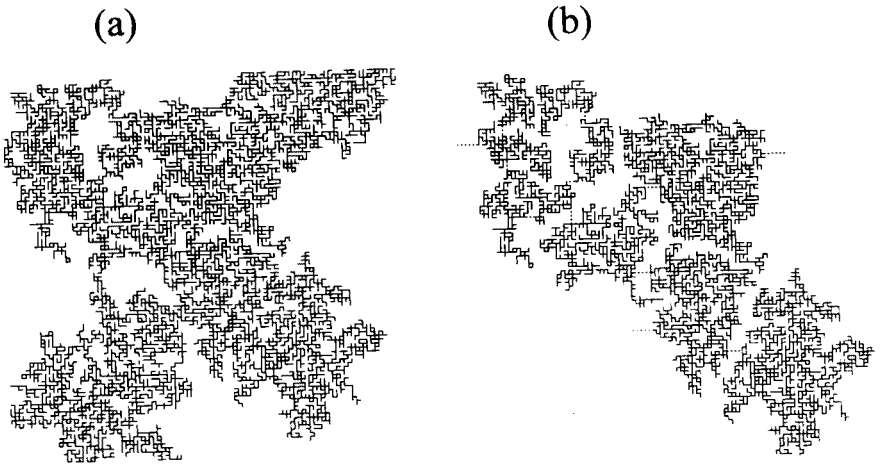

Fig. 1. (a) The largest connected subset of a percolating lattice obtained from a square lattice. The missing bonds were removed stochastically with critical probability 0.5. (b) A percolation cluster obtained from the same lattice by breaking 3 bonds connecting it with the rest of the lattice. Its 5 subclusters of the greatest order have been moved apart and connected with dashed lines. One of them has been further subdivided into 6 subclusters *etc.* The number of bonds connecting a subcluster with other subclusters of the same order is random, approximately in the range 3 to 7.

In the available literature there are many papers in which target or trapping problems of modeling reaction dynamics are considered [7–9]. In the present paper, however, another problem, namely that of gated reaction is studied. A reaction is called a gated reaction if its transition state is reduced to a single conformation (a selected site on the lattice). Such a conformation has the meaning of a gate. Because of numerous experimental realizations we consider mainly the case of diffusion on a percolation cluster with the gate being simultaneously the initial state [3].

Since the percolation cluster corresponds in the above sense to the conformational state space of the protein molecule, it is essential to require that its size be finite. In order to achieve that we imposed reflective or periodic boundary conditions. Finite size effects introduce a lower and upper limit into the reciprocal relaxation time spectrum. Moreover, in our context the form of the cluster is expected to be specific to a given protein thus no configurational averaging over different cluster realizations should be considered. We shall focus on the properties of one of the most essential variables in this process, namely the survival probability.

So far no analytical solutions for many diffusion problems on fractal lattices are known and computer experiments are the only tool that could be used to solve those problems. We present results of direct simulations of diffusion on percolation clusters. These results indicate that after an initial stage the reaction proceeds according to the algebraic power law stage and afterwards it enters the final exponential decay stage.

2. Random walk on a lattice in discrete time

In general, a stochastic Markov process of discrete vectorial values (lattice sites) in discrete time (steps) is described by the set of recurrent equations [10]

$$P_{n+1}(l|l_0) = \sum_{l'} W(l|l') P_n(l'|l_0), \tag{1}$$

with the initial condition

$$P_0(l|l_0) = \delta_{l\,l_0}, \tag{2}$$

$P_n(l|l_0)$ being the probability that a random walker starting from site l_0 occupies site l after n steps. Probabilities $W(l|l')$ of transition from site l' to l in a single step obey the condition

$$\sum_{l} W(l|l') = 1 \tag{3}$$

due to which Eq. (1) can be rewritten in the form of difference master equation

$$P_{n+1}(l|l_0) - P_n(l|l_0) = \sum_{l'} [W(l|l')\, P_n(l'|l_0) - W(l'|l) P_n(l|l_0)]. \tag{4}$$

There are three important quantities in the theory. The first is the probability $F_n(l|l_0)$ that a random walker starting from l_0 reaches l for the first time after n steps ($n > 0$); it is related to $P_n(l|l_0)$ by the equation

$$P_n(l|l_0) = \sum_{m=1}^{n} P_{n-m}(l|l) F_m(l|l_0). \tag{5}$$

The second is the mean number $S_n(l_0)$ of distinct sites visited in n steps by a random walker starting from l_0, defined by the equation

$$S_n(l_0) = 1 + \sum_{l}{}' \sum_{m=1}^{n} F_m(l|l_0) \tag{6}$$

(prime denotes summation with $l = l_0$ omitted). And the third quantity is the probability $C_n(l|l_0)$ that a random walker starting from l_0 did not reach l in the first n steps,

$$C_n(l|l_0) = 1 - \sum_{m=1}^{n} F_m(l|l_0). \tag{7}$$

If the random walk is assumed to cease once it reaches the state l (such a state, when excluded from the lattice, is referred to as a *limbo state* [3]), then C_n has the meaning of *survival probability* or (in chemical context) molar fraction of the decaying reagent in an irreversible reaction [3]. Upon denoting the limbo state as $*$, Eq. (4) should be rewritten for it as

$$P_{n+1}(*|l_0) = \sum_{l} W(*|l) P_n(l|l_0). \tag{8}$$

In the following sections we shall consider only systems for which $W(l|l')$ does not vanish only if $l = l'$ or l and l' are each other's nearest neighbours.

3. Simulation procedure

All simulations were performed on square lattices with bond percolation (critical concentration $p_c = 0.5$). Since finite size effects were of interest and computing resources were limited, the chosen lattices were fairly small (in the range 5×10^3 to 10^6 sites). The largest connected subset of sites was determined algorithmically; for systems of small size (*e.g.* $N \approx 5 \times 10^3$ sites) it was possible to find the percolation cluster of the highest order interactively. This procedure involved finding and breaking a few bonds connecting the chosen cluster with the rest of the lattice, which is equivalent to imposing reflecting boundary conditions. For larger systems periodic boundary conditions were introduced prior to the bond removal procedure and thus the largest connected cluster was obtained directly. Both approaches are equivalent for our problem. Indeed, clusters prepared according to the above presented methods differ in terms of self-similarity properties only when subclusters of the greatest order are considered, therefore discrepancies in the time evolution of the walker concentration could be observed only in

the long-time limit, that is for times comparable with the characteristic relaxation times of those subclusters. But in that time regime the finite-size effects determine the evolution.

For $l \neq l'$ the transition probability $W(l'|l)$ was assumed to be constant, $W(l'|l) = W$, and independent of the number of neighbours z because otherwise the equilibrium occupation probability of a given site would have been dependent on z and thus the time evolution of the system would have been considerably influenced by the local properties of absorption centres. But in order to satisfy Condition (3) it was necessary to allow non-zero values of $W(l|l)$, as well. Changing the value of $W(l|l')$ leads only to a rescaling of the time unit for the diffusion process but no other side-effects are observed.

Partly in order to test the simulation procedures we tried to determine the spectral dimension $\tilde{d}$ of the systems. For $\tilde{d} \leq 2$ the asymptotic relation [7]

$$S_n \propto n^{\tilde{d}/2} \tag{9}$$

holds (the value of S_n is asymptotically independent of the choice of the initial site l_0). If N denotes the number of lattice sites and the initial spatial distribution of walkers is assumed to be uniform, the *average* survival probability

$$\overline{C}_n = 1 - N^{-1} \sum_{l_0} \sum_{m=1}^{n} F_m(*|l_0). \tag{10}$$

Assuming that the diffusion process is on average symmetrical with respect to exchanging the initial point and the final one, $F_m(l/l') = F_m(l'/l)$, and

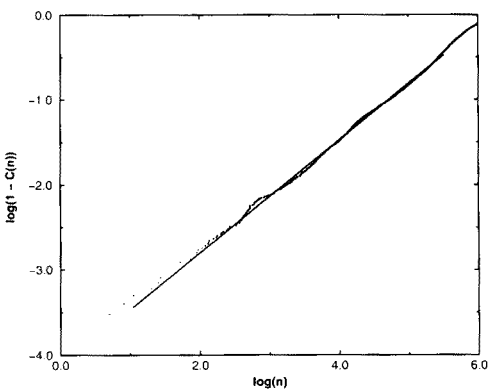

Fig. 2. Intermediate time period scaling behaviour of the "extinction" probability $1 - C_n$ for 10^4 walks on a percolation cluster of order 5 ($N \approx 5 \times 10^3$). The initial spatial distribution of walkers was uniform; n denotes the number of steps.

taking into account Eq. (6) one obtains

$$\overline{C}_n = 1 - \frac{1}{N}(S_n - 1), \tag{11}$$

thus in our case

$$1 - \overline{C}_n \propto n^{\tilde{d}/2}. \tag{12}$$

The quantity $1 - \overline{C}_n$ was calculated from some 10^4 simulations performed on a percolation cluster of size $N \approx 5 \times 10^3$ and the result is shown in Fig. 2. It is clearly seen that in the intermediate time period the simulated points are located along a straight line. Its inclination amounts to ca. 0.664 which is in good agreement with the Alexander–Orbach conjecture $\tilde{d} = 4/3$ ([4]).

4. Results

We studied the time evolution of the survival probability $C(*|l_0)$ for systems in which the random walk starts from one specific site l_0 and proceeds until it reaches the limbo state $l = *$. In our case the site corresponding to this state has only one neighbour $l = 0$. The latter is of course the only gate to exit the lattice and thus the transition state of the reaction. An activation barrier was introduced into the system by specifying that a random walker occupying site 0 can move over to one of the neighbouring sites with transition probability W, disappear from the lattice (fall into the limbo state) with transition probability V, smaller than the probability W or stay at 0 with probability $1 - zW - V$, where z is the number of neighbours of site 0.

The reciprocal relaxation time spectrum of our system differs from the spectrum of diffusion on an ideal percolation cluster because it has an upper bound (resulting from the fact that there exists the smallest size of the subcluster, corresponding to our site) and a non–zero lower bound (since the system is finite). Adding the limbo state results in adding a new value

$$k = P_0^{\mathrm{eq}}(V^{-1} + U^{-1})^{-1} \tag{13}$$

to the spectrum [3]. It has the meaning of the long time decay rate of the survival probability C. In Eq. (13), $P_0^{\mathrm{eq}} = 1/N$ is the equilibrium occupation probability of the site 0 (it has a non–zero value only for finite clusters) and U^{-1} denotes the longest relaxation time. The latter is a function of W and lattice size. The value of k is smaller than any other value belonging to the spectrum.

The ratio

$$a \equiv V/W \tag{14}$$

has the meaning of the absorption coefficient. If it is small enough, the population decay rate k is expected to be determined mainly by the time

the system spends waiting for opening of the gate to the limbo state, like in the transition state theory [11], where the reaction rate is determined mostly by the height of the activation barrier:

$$k^{\mathrm{TST}} = V/N. \tag{15}$$

For a large value of V, however, the time needed to find the transition state and reconstruct its equilibrium population determines the value of k:

$$k^{\mathrm{REC}} = U/N. \tag{16}$$

Unless expressly stated otherwise, the presented results were obtained for $l_0 = 0$ as there exist numerous physical realizations of this case [3]. Fig. 3 shows the time evolution of $C(*|0)$ obtained from four groups of two simulation series for various locations of the gate 0. The initial behaviour of $C_n(*|0)$ depends very strongly on the choice of 0, especially on the number of its neighbours. But in the limit of large n the evolution of C_n is not affected by this choice and an exponential decay is observed, which is of course a finite-size effect, *cf.* Eq.(13).

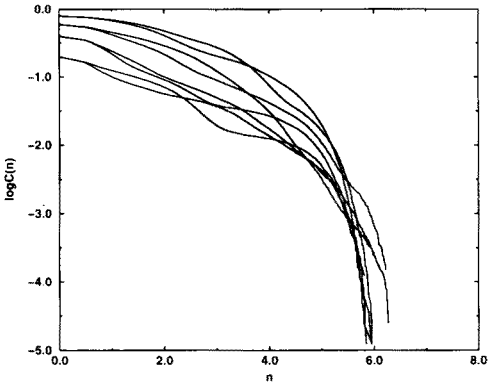

Fig. 3. Log-log plot of the time evolution of the survival probability C obtained from 4 groups of 2 simulation series with different starting sites 0. In these groups the number of l_0's nearest neighbours is equal to 1 (the smallest value of the population at the beginning), 2, 3 and 4 (the largest value).

The exponential stage of the reaction can be identified as a straight line decrease on the lin-log plot in Fig. 4 where the time evolution of $C_n(*|0)$ is shown for different values of the absorption coefficient a. The fastest exponential decay is observed for $a = 1$. In this case the characteristic time of the reaction predicted by the transition state theory $1/k^{\mathrm{TST}} \approx 0.25 \times 10^4$ is two orders of magnitude shorter than the estimated value $1/k \approx 0.40 \times 10^6$

thus the reaction rate is determined by the time the system requires to reconstruct the equilibrium population of the state 0. The longest relaxation time U^{-1} can be therefore easily found to amount to 0.8×10^2. Decreasing the value of a ten times does not influence the rate of this process (not shown). When $a = 0.01$, k^{TST} becomes comparable with k^{REC}, therefore a significant slowdown is observed ($1/k \approx 0.8 \times 10^6$).

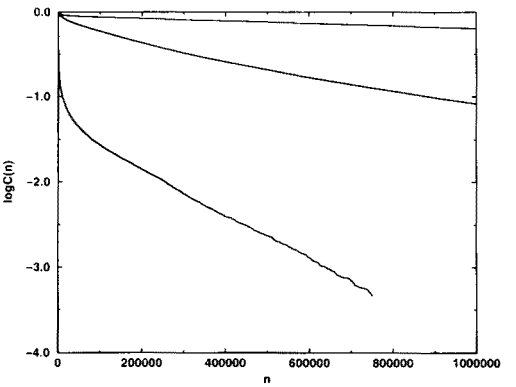

Fig. 4. Time evolution of the survival probability C for various values of the absorption ratio $a = 1.0$ (the fastest, the corresponding curve on the plot has the steepest slope), 10^{-2} and 10^{-3}. Number of lattice sites, $N \approx 5 \times 10^3$.

Selected results for series of simulations with different, although situated close to each other sites l_0 and 0 are shown in Fig. 5. It is clearly seen that the population at which the exponential decay starts is affected by the choice of l_0 and 0 whereas the decay rate appears to be independent of it.

The above presented results were obtained for percolation clusters of relatively small size. The time evolution of C_n in this case can be reasonably divided into two stages — the initial period and the exponential decay period — it is therefore determined by the properties of the initial state and the size of the lattice. In fact similar results could have been obtained for systems with no self–similarity symmetry at all. Only for larger values of N a new stage can be clearly seen. A typical result for $N \approx 5 \times 10^5$ is presented in Fig. 6. After the initial period the system enters a non–exponential stage in which the decay follows an algebraic power law

$$C_n \propto t^{-\alpha} \tag{17}$$

with exponent α apparently in the range 0.25–0.4. This scaling behaviour is a result of the scaling properties of the percolation cluster. Presumably the value of this exponent does not depend neither on the fractal dimension of the system nor its spectral dimension yet it does not depend on the value of the absorption coefficient a.

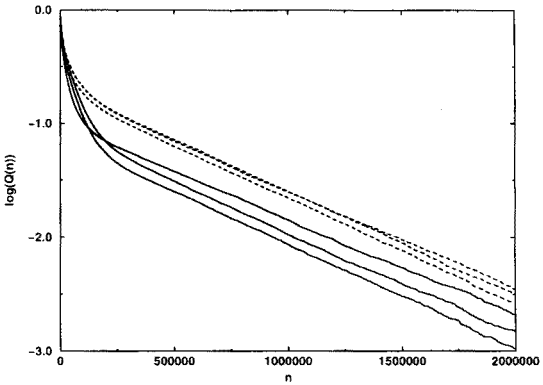

Fig. 5. Lin-log plot of the time dependence of the survival probability C obtained from 2 groups of 3 simulation series. In each group the simulations were obtained for the same location of l_0 but different locations of the gate 0.

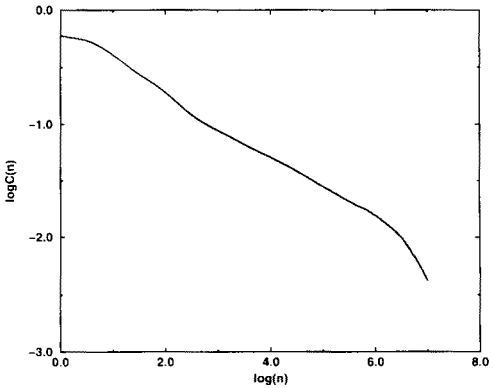

Fig. 6. Time evolution of the survival probability C on a cluster of size $N \approx 5 \times 10^5$. Three stages of reaction can be seen: the initial stage, the algebraic decay stage and the exponential decay stage.

5. Summary

The evolution of the survival probability of the investigated system proceeds in three stages. The behaviour of the system in the first stage depends on the choice of the initial state, especially on the number of this site's nearest neighbours. The intermediate power law decay stage appears only for sufficiently large values of N at least 5×10^5. In the last stage the population decays exponentially and the rate of this process is determined by two components — the characteristic reconstruction time of the transition state equilibrium occupation $1/k^{\mathrm{REC}}$ and the characteristic time predicted

by the transition state theory $1/k^{\mathrm{TST}}$. The above presented methods can be used to determine the longest relaxation time U^{-1} of the system. In case of systems where $l_0 \neq 0$ an upward shift can be observed on the population vs. time plot but the exponential decay rate is independent of the choice of l_0. The scaling behaviour of the process in the intermediate time period is a result of the self-similarity symmetry of the system. The relation of the scaling exponent to the systems' fractal and spectral dimension is currently being investigated.

The study has been supported by the Polish State Committee for Scientific Research (project 2 P03B 053 09). M.K. wishes to acknowledge additionally the earlier support of the Alexander von Humboldt Foundation.

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