Inter-basin dynamics on multidimensional potential surfaces. I. Escape rates on complex basin surfaces

Florin Despa and R. Stephen Berry
Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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In this report, we present a general prescription for computing the escape rate of the system from a basin with full consideration of the topographical fingerprint of that basin. The method is based on a solution of the reduced Fokker–Planck equation and built up to allow the separation of the inter-basin dynamics from that of the intra-basin motion. The main result is that when local well populations thermalize within a basin, local minima, especially those of higher energy, enhance the escape rate from the basin. Also, numerical analyses lead to the inference that kinetic traps of ''wrong'' structures are distinctive topographical patterns which may produce kinetic properties similar to those of the primary basin, i.e., that containing the global minimum, but lie in other basins. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1409955]

Related to the general question of characterization of the topography of a multidimensional potential surface (PS) are numerous examples in which seemingly it is convenient to classify the PS into basins of minima and saddles.[1–3] As defined previously,[4] a basin is formed by monotonic sequences of linked minima and saddles leading to the lowest local energy minimum. Two consecutive basins are separated from each other by a divide, that is, the top saddle of major height linking monotonic sequences of those basins. The basin containing the global minimum is called a primary basin (PB) and the others, which contain other locally stable forms are classified consequently as secondary basins, tertiary basins, and so on, according to the number of divides separating them from the primary basin.

In the present report, we focus on the dynamics of the system for the archetypal case of a steep basin surface. Particularly, we assume that along the downward direction of the monotonic sequences of minima, the differences between the saddle heights are small. These saddles may correspond to structural transformations of the system between almost similar conformational states. For example, in the protein folding case,[5–8] it may be useful to classify together all systems that have reached some state with the native physiological activity but have structural differences in parts of the system irrelevant to the protein's function. All such similar structures can be said to lie in primary basins. The overall topography of the basin may display, in this case, a (mild) steep surface with small potential barriers downhill, toward the lowest minimum. An extreme example is the $(KCl)_{32}$ cluster,[9] whose PS consists of many basins, at the bottoms of which are low-energy rocksalt structures (even with a few defects). These define a set of similar basins that can be classified together as primary. This generalization from a single primary basin to a set of primary basins for the global minimum becomes more and more useful as the clusters become larger. The interest here is in whether the system has found some fcc, hcp, icosahedral, or other type of structure, rather than in whether it has reached the global minimum. This question can be reformulated in more general terms: ''How do relatively small topographical differences among basin surfaces affect the capability of the system to relax preferentially only to one of them?''

We now ask whether there are circumstances under which the usual conceptual frames of the energy landscape theory can offer practical ways to understand the inter-basin transitions. Studying dynamics on multidimensional potential surfaces is a task complex enough that it demands finding a way to reduce the information about the topography of the PS to a statistical sample, for example as described previously.[4] This statistical sample should contain a significant number of minima and saddles to remain representative for the system. Certainly, the volume of the data sets does affect the efficiency of manipulation and extraction of useful informations. Unfortunately, there are not so many methods at hand to study efficiently the dynamics on the PS. Stochastic simulation may offer a practical approach to simulating and understanding dynamics on multidimensional potentials, at least it seems now, in contrast to the impracticability of any approach based on the full topography of the system. For example, the method of transition state theory (TST), at whatever level of accuracy is desired,[10,11] can be used to compute a matrix of well-to-well transition probabilities, and from this matrix, one can construct a master equation whose solutions reveals the intra-basin and inter-basin dynamics.[4] For many purposes, such as preparation of nanoscale materials, intra-basin dynamics are far less important than inter-basin motion. It is then useful to develop new theoretical tools to account for the inter-basin transitions, in a manner that shows the influence of the topography of the basins involved in transition. Any recipe for computation of these quantities has a key role in a stochastic approach to the system's dynamics. Any systematic way to compute the escape rate from one basin to another would be very valuable, as long as it could be implemented in a practical way.

In this report, we present a general prescription for accurately computing the escape rate of the system from a

steep basin that takes into consideration the topographical fingerprint of that basin. The method is based on a solution of a reduced Fokker–Planck equation[12–14] and is built up to allow us to separate the inter-basin dynamics from that of intra-basin motion. Specifically, we assume that all the individual locally stable states of the basin make their own independent contributions to the mean rate at which the system leaves the basin. Consequently the escape rate depends on the number of local minima and their relative positions from the lowest minimum.

The main result that emerges from the present approach is that when local well populations thermalize within a basin, local minima, especially those of higher energy, enhance the escape rate from the basin. The present approach not only offers a practical way to visualize the relation between the topography of the basin surface and the escape rate from that basin but has also the ability to make some interesting predictions. For example, on the basis of numerical analyses presented here, one can infer that basins of almost the same depth may have various escape rates if their topographical fingerprints are different. Moreover, we may predict that a complex basin surface, with more and higher energy local minima, promotes a faster escape of the system than a smoother potential basin of similar energy. Another interesting case which emerges from our study is one in which the escape rate from the primary basin (the basin which contains the global minimum) is in the same range as, or even higher than, the escape rates from other basins on the multidimensional PS. This case is particularly important for understanding the system's accessibility to different regions of the PS because it offers insight into the problem of kinetic traps.[15] Thus, in the frame of the present approach, these kinetic traps of ''wrong'' geometrical structures of the system may be seen as basins with distinct topographical patterns but with kinetic properties similar to those of the primary basin.

We start with the supposition that the motion of the system inside the basin PB (of a sort as displayed in Fig. 2 in a previous work[4]) consists primarily of oscillations determined by the local wells in the monotonic sequences of minima and saddles on the walls of the basin w_0 whose depth is E_b, at the bottom of which the frequency of harmonic oscillations is ω_0. These local wells give the effective potential many local variations with successive changes in slope. We treat these low-amplitude potential variations as a perturbation on the main contribution to the effective force acting on the system, which comes from the mean slope of the potential basin w_0. We assume that local well populations thermalize at the bottoms of these local wells. Therefore, basin dynamics is governed by energy accumulation and relaxation processes among the local wells of the basin. Consequently, the escape rate from the basin must be energy-dependent. Moreover, due to the change of curvature of the effective potential between the bottom and the top of each local well, the typical rate of energy exchange between the reaction mode and other modes may become comparable with the molecular vibrational period. Therefore, the intra-basin motion of the system along the reaction coordinate x (with the reactive mode ω) may be non-Markovian and can be described by a generalized Langevin equation (GLE)

$$\ddot{x}=-\frac{1}{M}\frac{\partial V_{\mathrm{eff}}}{\partial x}-\int_0^t d\tau Z(t-\tau)\dot{x}(\tau)+\frac{1}{M}F(t). \tag{1}$$

Here M is the mass associated with the reaction coordinate $x,\dot{x}$ is the velocity, $V_{\mathrm{eff}}(x)$ is the potential energy part of the total energy $E(x,\dot{x}),F(t)$ is the (stationary Gaussian) fluctuating force associated with the coupling to the thermal bath, and $Z(t)$ is the memory function. The second term in the right-hand part of the equation represents the friction force that describes the extent and nature of mode–mode coupling that engages the reaction coordinate x. It gives the contribution to the motion of the system of all the other nonreactive modes, which constitute a thermal bath.

Equation (1) is the starting point for a full-system dynamics in numerical simulations. In the following we set up the stochastic analogs of Eq. (1), namely, the reduced Fokker–Planck equation which gives the probability distribution $p(J,t)$ for the action variable J as[14]

$$\frac{\partial p}{\partial t}=\frac{\partial}{\partial J}\left[\mu(J)\left(k_BT\frac{\partial p}{\partial t}+\omega(J)\right)\right]. \tag{2}$$

Here, μ stands for the energy diffusion coefficient given by

$$\mu(J)=2M\sum_{n=1}^{\infty}n^2|x_n(J)|^2\,\mathrm{Re}[\hat{Z}_n[\omega(J)]], \tag{3}$$

where x_n is the nth coefficient of the Fourier expansion of the deterministic motion [given by Eq. (1) without the Z and F terms] within the representation $x=x(J,\varphi)$ (φ is the angle variable), and $\hat{Z}_n$ stands for the nth Fourier–Laplace component of the memory function $Z(t)$. The function $\omega(J)$ is the (action-dependent) frequency which is determined by the effective potential function.

A steady state solution of Eq. (2) has the form

$$p_{ss}=F(J)\exp\left(-\frac{E(J)}{k_BT}\right), \tag{4}$$

where $F(J)$ is the ''correction function.'' In a strict sense, the system cannot achieve a steady state because the number of particles in the basin decreases as particles escape. Mathematically, to obtain an approximate steady state situation, the escape rate must be negligible relative to the other rate scales in the system; to represent this, we impose a boundary condition on Eq. (2). We assume that the distribution p_{ss} is of a Boltzmann form on the action interval $0\leqslant J\leqslant J_s$

$$p_{ss}(J)=A\exp\left(-\frac{E(J)}{k_BT}\right), \tag{5}$$

which is equivalent to saying that a source is provided at or near the bottom of the basin to prevent the depletion of the particle number. A is a constant to be determined.

It is a simple matter to convert the above results to energy language via the action-energy relation $dE/dJ=\omega(E)$. Accordingly, the energy diffusion coefficient $\mu(J)$ transforms to $\mu(E)\equiv\omega(E)\mu(J(E))$. In the following, we use the energy-dependent formalism instead of the action J. We also denote $1/k_BT$ by β.

Equation (2) implies the following expression for the escape rate from a potential well[16]

$$k_{\mathrm{PB}}=\left[\int_0^{E_b} dE_s p_{ss}(E_s)\tau(E,E_s)\right]^{-1}, \tag{6}$$

which is the average of the mean first passage time $\tau(E,E_s)$ to reach a point E starting from a point E_s over the steady state distribution p_{ss}. The above equation is a result of the general approach to the first passage time problem (see, for example, Weiss[16]): If we consider a space **A** that can be decomposed into two nonoverlapping subspaces **B** and **C** and it will be assumed that initially the random variable of interest lies in the subspace **B** then, the first passage time is defined to be the time elapsing before passage to **C** for the first time. We note in passing that Eq. (6) is based on the assumption that all trajectories with $E>E_b$ exit out of the well; otherwise, it may be thought that the result of Eq. (6) should be multiplied by some number of order 1/2 to account, roughly, for the trajectories which start at the critical energy E_b and are expected to go back into rather than up and out of the well. For a system with not so many degrees of freedom, the fraction of trajectories that enter the region of regularity[17,18] that then cross the dividing surface can still be evaluated exactly in the frame of the Komatsuzaki–Berry approach[17,19] to transition state theory. For simplicity, we ignore here this correction and, instead of this, impose the condition that τ include only trajectories that cross E_b with $E>0$.

Under circumstances we will show in the following, Eq. (6) may be used also to describe the escape rate from the basin. The main requirement to be imposed on Eq. (6) is to account specifically for the ''escape channels'' which carry the system over the barrier of height E_b. In our case, these ''escape channels'' are all uphill trajectories which start from local minima of the basin.

To that end, we use Eq. (6) as the template for computing the escape rate from the basin and propose a picture of the energy landscape founded on two postulates. First, the steep basin surface must have potential barriers leading downward, toward the lowest energy minimum, that are lower than the corresponding upward barriers. This assumption is almost a trivial consequence of geometry. We then assume that the system rapidly achieves a thermal equilibrium in the well of its the starting point E_s so that the steady state distribution $p_{ss}(E_s)$ may be approximated by the Boltzmann distribution given by Eq. (5)

$$p_{ss}(E_s)\simeq \frac{e^{-\beta E_s}}{\beta(1-e^{-\beta E_b})}. \tag{7}$$

The above steady state distribution Eq. (7) remains a good approximation as long as the local well is deep enough. All effects that result from a deviation from this equilibrium distribution are neglected. Second, the secondary minima of the basin surface do establish an effective value of the mean first passage time $\tau(E_s,E_b)$. Therefore we need to replace $\tau(E,E_s)$ in Eq. (6) by $\tau_{\mathrm{eff}}(E_b,E_s)$, which is defined as an average over all the ''escape channels'' which lead the system to reach the critical point E_b from the starting point E_s. In other words, all the individual states $w_i(i=0,N)$ of the basin are expected to have their own independent contributions to $\tau_{\mathrm{eff}}(E_s,E_b)$. These contributions are denoted by τ_i and averaged as

$$\frac{1}{\tau_{\mathrm{eff}}(E_s,E_b)}=\sum_{i=0}^{N}\frac{1}{\tau_i(E_s,E_b)}\vartheta(E_{i,i+1}-E_s), \tag{8}$$

where ϑ stands for the unit-step function and $E_{i,i+1}$ is the position on the energy spectrum of the saddle between the minima w_i and w_{i+1}, uphill. According to this equation, only those trajectories that go up and out of the basin contribute to the value of the effective mean first passage time, as discussed above.

We now need to compute all the contributions τ_i to the average Eq. (8). The mean first passage time τ_i (Ref. 16) along each ''escape channel'' can be expressed in the frame of the non-Markovian dynamics theory as a function of the energy-dependent frequency $[\omega_i(E)]$, which is determined, in turn, by the local potential and by the energy diffusion coefficient $\mu_i(E)$

$$\tau_i(E_s,E_b)=\int_{E_s}^{E_b} dE\,\frac{\exp(\beta E)}{\mu_i(E)}\int_0^E dE'\frac{\exp(-\beta E')}{\omega_i(E')}. \tag{9}$$

Equation (3) shows that the diffusion coefficient $\mu_i(E)$ follows from the deterministic motion of the system which depends also on the local potential. In addition, $\mu_i(E)$ includes properties of the thermal environment.

As can be seen from above, Eq. (8) contains all the requisite information about the main properties of the pattern of the topography, particularly the relative positions of minima and saddles along the monotonic sequences. Moreover, the content of Eq. (9) relates τ_{eff} to the form of the local effective potential and the contact with the thermal bath. In this context, the escape rate Eq. (6), which now becomes

$$k_{\mathrm{PB}}=\left[\int_0^{E_b} dE_s p_{ss}(E_s)\left(\sum_{i=0}^{N}\frac{\vartheta(E_{i,i+1}-E_s)}{\tau_i(E_s,E_b)}\right)^{-1}\right]^{-1}, \tag{10}$$

preserves in detail the topographical fingerprint of the basin surface. This is our final general result.

To further investigate the dependence of the escape rate k_{PB} on the parameters characterizing the basin surface, we have applied the approach to analyze a specific example. For simplicity, we employ a model of a basin surface with a monotonic sequence of only four local minima $w_i\,(i=1,4)$ linked by a single reaction coordinate, leading to the global minimum w_0; however, the present theory, as can be seen from the above, is not limited by computational strictures.

In order to compute the contributions of all the individual minima of the basin surface to the effective value of the mean first passage time $\tau_{\mathrm{eff}}(E_s,E_b)$, we need to know the vibrational frequency functions $\omega_i(E)$ and the corresponding energy diffusion coefficients $\mu_i(E)$ for each minimum w_i. The frequencies are derived from the specific form of the potential V_{eff} in the region of each minimum. We approximate the motion of the reaction coordinate around each minimum with the model of the harmonic oscillator. Consequently, the key frequencies are

$$\omega_i(E)=\omega_{0i}, \tag{11}$$

where ω_{0i} is the frequency of harmonic oscillation in the minimum w_i. The main ingredient required to compute the energy diffusion coefficient $\mu_i(E)$ is the time-dependent friction $Z(t)$. Since $Z(t)$ is probed at high frequencies, we apply the usual Gaussian model[13]

$$Z(t)=\frac{\gamma}{\tau_c\sqrt{\pi}}\exp\left(-\frac{t^2}{4\tau_c^2}\right), \tag{12}$$

with the spectral density

$$\hat{Z}(\omega)=\gamma\exp(-\omega^2\tau_c^2). \tag{13}$$

The time parameter τ_c entering the above equations is the frictional relaxation time which provides the time scale for their decay to zero and γ is the damping rate of the thermal bath [the zero frequency friction constant, $\hat{Z}(\omega)=\gamma$]. The bath model has long exponential time decays, as predicted by the phenomenological theory of the Brownian motion, and shows the required physically realistic feature that it has rapidly diminishing spectral density at high frequencies [see Eq. (13)]. Typically, $Z(\omega)$ is far smaller than the zero frequency friction constant γ.

The energy diffusion coefficient corresponding to each local minimum in the basin PB, $\mu_i(E)$, is given by

$$\mu_i(E)=\frac{E\gamma}{\beta\omega_{0i}}\exp(-\rho_i^2), \tag{14}$$

where

$$\rho_i=\omega_{0i}\tau_c. \tag{15}$$

We now are in the position to compute the escape rate k_{PB} for this particular model of the topography of a basin surface. The critical (barrier) energy E_b is set at $10\,k_BT$, the global minimum w_0 is at the origin of the energy axis and, the energies of the saddles are as follows: $E_{0,1}=3k_BT$, $E_{1,2}=4k_BT$, $E_{2,3}=6k_BT$, $E_{3,4}=8k_BT$. We make the approximations $\rho_0\simeq 1$ and $\rho_i\simeq 0.9\,(i=\overline{1,4})$, respectively.

By using the present theoretical approach we obtain an escape rate of the system from this basin of $k_{\mathrm{PB}}=2.39\times10^{-2}$, in units of $\gamma(\sim 10^{13}\,\mathrm{s}^{-1})$. (All the numerical results of the escape rates are given in units of the damping rate γ.) In the following extension of the analysis, we would now like to see how the number of secondary minima in the monotonic sequence and their energies relative to the global minimum affect the escape rate. To this end, we now drop the minimum w_4 from the previous monotonic sequence, keep the others at the same energies and compute the escape rate corresponding to the topographical pattern (w_0, w_1, w_2, and w_3). In this case, we get $k'_{\mathrm{PB}}=1.88\times10^{-2}$, somewhat smaller than in the previous case. By proceeding in the same manner and eliminating successively the other minima from the monotonic sequence, the escape rate becomes smaller and smaller. The result of the escape rate obtained for a smooth potential well of the same depth as above ($10\,k_BT$, $\rho_0\simeq 1$), with no other secondary minima, is $k_w=0.42\times10^{-2}$. That is about one order of magnitude lower than k_{PB}.

Not only the number of the local minima in the monotonic sequence is important in determining the escape rate; their relative positions with respect to the global minimum are also important. For example, an alternate situation to the case of the monotonic sequence (w_0, w_1, w_2, and w_3), which has been evaluated above, is that in which w_4 is kept up and w_1 is dropped. We compute the escape rate corresponding to the monotonic sequence (w_0, w_2, w_3, and w_4), and obtain $k''_{\mathrm{PB}}=1.9\times10^{-2}$, higher than k'_{PB}, as expected, but still lower than k_{PB}.

The number of secondary minima in the monotonic sequences and their energies relative to that of the global minimum are the main factors which compete with each other to determine the escape rate of the system from that basin. These parameters are measures of the kinetics on the complex pattern of topography of the basin surface. Some interesting aspects emerge from these results. Of two basins of the same depth but with different topographical fingerprints, the corresponding escape rates will differ: the basin with more high energy secondary minima can be expected to have the higher escape rate. The escape rate can be expected to increase with the number of secondary minima in the monotonic sequences and with the increase of their relative energies above the basin's minimum. One might encounter the situation in which the escape rate from the PB is in the same range as, or even higher than, the escape rates from other basins on the multidimensional PS. This case would be particularly important in the context of understanding the system's accessibility to different regions of a complex PS. For example, it offers insight into the problem of the kinetic traps.[15] Thus in the frame of the present approach, these kinetic traps of ''wrong'' geometrical structures of the system may be seen as basins with distinct topographical patterns but with kinetic properties similar to those of the primary basin. This inference deserves a special attention as it enables one to diagnose and interpret these kinetic traps.

We have presented a general prescription for averaging over all mean first passage times along the ''escape channels'' that carry a system over the basin rim when the system starts from a specified local well of the basin. This method yields an effective mean first passage time. This quantity contains implicitly the requisite information about the topography of the potential surface, particularly the relative positions of minima and saddles along the monotonic sequences. Our approach allows a direct separation of the inter-basin dynamics from that of the intra-basin motion and produces the escape rate of the system from a basin as it depends on the topographical fingerprint of that basin. In addition, the present theory allows one to treat a system that undergoes nonideal stochastic processes (non-Markovian behavior) in its exploration of its configuration space. Therefore by treating the system as non-Markovian, we obtained here a direct connection between the thermal bath properties and the ability of the system to escape from a steep basin. The latter is increasingly important in modeling real systems and annealing schedules.

The above method provides a practical method for computing escape rates from steep basins. Other archetypal en-

ergy landscapes must be treated appropriately and will be the objects of forthcoming reports.

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