

Relaxation dynamics in the presence of unequally spaced attractors along the reaction coordinate

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Abstract. We show how reaction coordinate path lengths affect the relaxation efficiency of a complex system. To this purpose, we consider the metric contributions to the transition rates. These metric contributions contain information about the system's change of geometry at the barrier crossing and, therefore, are directly related, differentially, to the path lengths. The results of this work can enrich the accuracy with which we describe how complex systems relax to preferential structures.

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There is, currently, considerable interest in how the topographies and topologies of multidimensional potential surfaces of polyatomic molecules, clusters and nanoscale particles govern the dynamics and phaselike behavior of these systems; for reviews, see [1–3] and the references therein. As a result, a new manner of interpreting their energy landscapes is emerging which enhances our understanding in this pressing issue. Despite the enormous power available now to do computations and the many methods for extracting useful information about these surfaces, the problem of relating potential surfaces of complex systems to their relaxation is far from a complete solution.

For complex systems, development of better potential functions still remains clearly a priority. We can say that, at least, starting from available expressions for the interaction between and among the system constituents, accurate potential energy surfaces (PES) may be constructed for many systems. Finding minima and saddles on potential surfaces has become a straightforward matter by employing some of the most widely used algorithms or combinations thereof [4–7]. The problem has shifted from asking how to find minima efficiently to asking how to find and describe the connections between the topography and the dynamics on the surface. Statistical methods [8–10], especially that based on the topographic diagnosis procedure [8], achieved considerable success, carrying the study of complex systems to the point where one can begin to infer dynamics of flow on the surface from the general characteristics of the topography. A serious shortcoming of the available dynamical studies, however, has to be pointed out: virtually, all of them describe the thermally activated barrier crossing rate by the traditional transition state theory (TST) rate model which deals only with the height of the barrier and the densities of initial and

saddle states [11]. No information about the geometrical structures of the initial and saddle sites enter into this approach. This simplification imposes a limit to the precision with which we can characterize the relaxation of complex systems, *e.g.* of how some systems relax preferentially to one or only a very few geometrical structures from among the vastly larger variety that the system might exhibit. However, there are other ways to compensate for this lack of information. It was shown, for example, that the topographical properties of the potential energy surface (PES) determine the extent to which the system is either glass-forming or structure-seeking [2, 8, 12]. In addition, qualitative interpretations of the interplay between structure and dynamics have been made of the path length distributions between connected minima along the reaction coordinate [12, 13].

For a better understanding of dynamics, it is now useful to investigate the relation between the variety of path lengths between neighboring minima along the reaction coordinate of a specific PES and the flow of probability between those minima. We attempt in the following to get more insight into this particular aspect by invoking a generalization of transition-state theory (TST) to express the transition rates on the PES [14]. To this end, we include the metric contributions to the transition rates and demonstrate their influence on the flow along the reaction coordinate paths. We work out a simple three-level system with a model surface based on a “nearest-neighbor” connection pattern and focus on the ability of the system to find the global minimum under the assumption of unequal path lengths between connected minima.

Let x denote the reaction coordinate of a complex system with N degrees of freedom whose dynamics is governed by an appropriate potential surface. The reaction coordinate x is a function of all the degrees of freedom $x = x(q_1, \dots, q_N; p_1, \dots, p_N)$, where q_i stands for the i th

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configuration coordinate and p_i for its momentum. In the following, we restrict our considerations to a small region of the PES containing two locally-stable states, Θ_1 and Θ_2 , for which the reaction coordinate takes the particular values x_1 and x_2 with the corresponding energy levels E_1 and E_2 , respectively. In general, these two domains of attraction might be separated by barriers containing one or possibly more saddle points, possible unstable limit cycles, or even more complex unstable attractors, including combinations thereof. For most of the following we shall restrict our discussion of the theory to the situation in which two adjacent attracting basins are separated by a single, simple saddle of rank 1. In the present case, we assume that between the local minima Θ_1 and Θ_2 there is a transition state at $x_{(1-2)} \equiv x_a$.

Generally, the forward TST rate w_{1-2} is given by [15]

$$w_{1-2} = \frac{\langle \delta(x - x_a) \dot{x}(a) \theta[\dot{x}(a)] \rangle}{\langle \theta(x_a - x) \rangle}, \quad (1)$$

where δ and θ are the usual δ - and step functions. Here, the average $\langle \dots \rangle$ denotes an equilibrium average over the canonical probability density. The integration over the momenta is straightforward and leads to

$$w_{1-2} = (2\pi\beta)^{-1/2} \frac{[\delta(x - x_a) |\nabla_Q(x)|]}{[\theta(x_a - x)]}, \quad (2)$$

where $|\nabla_Q(x)|^2 = \sum_i (\partial x / \partial Q_i)^2$ and Q_i are the mass-weighted coordinates ($Q_i = q_i m_i^{1/2}$). The brackets [...] indicate an average over the coordinates only. Further simplifications in (2) can be achieved by integrating over the coordinates of the center-of-mass position R and all orientations Ω relative to a reference configuration of the system. This follows the coordinate transforming $(Q_1, \dots, Q_N) \rightarrow (R, \Omega; f_1 \dots f_m)$, where \mathbf{f} are the internal coordinates (in number, $m = N - 6$). The internal coordinates allow us to describe forces acting in the system in terms of the potential function $U(\mathbf{f})$. For example, the number of particles in the well $[\theta(x_a - x)]$ can be written after suitable integrations as

$$[\theta(x_a - x)] = \int df_1 \dots df_m J(\mathbf{f}) \theta(x(\mathbf{f})) \exp\left(-\frac{U(\mathbf{f})}{k_B T}\right). \quad (3)$$

$J(\mathbf{f})$ is the Jacobian of the coordinate transformation (integrated over center-of-mass and orientation angle coordinates) and comprises the determinant of the metric tensor times the volume of the system and factors resulting from those integrations over the orientational degrees of freedom.

In the low temperature limit ($\beta U(\mathbf{f}) \gg 1$, with $\beta = 1/k_B T$), eq. (2) can be evaluated by a Gaussian steepest-descent approximation. The procedure requires expanding the effective potential $U_{eff}(\mathbf{f}) = U(\mathbf{f}) - k_B T \ln J(\mathbf{f})$ to second order at the saddle point (a) and at the local minimum (Θ_1). After some simple algebra, the final formula

for the TST forward rate can be given in the form

$$w_{1-2} \simeq \frac{|\mathbf{M}^{-1/2}|}{2\pi} \left(\frac{J_a}{J_1} \right) \frac{\prod_{i=1}^m \lambda_i^{(1)}}{\prod_{i=1}^{m-1} \lambda_i^{(a)}} \exp(-\beta E_{1-a}). \quad (4)$$

Note that in the case of multiple transitions states we have to count each contribution separately and write the rate as a sum over pathways [8]. The \simeq sign is used instead of the equality sign because of terms of order $O(1/\beta\mathbf{f})$ compared to unity have been neglected in above. \mathbf{M} is the mass matrix and the indices (a) and (1) indicate that the corresponding quantities are evaluated at the saddle point and the local minimum 1, respectively. E_{1-a} measures the barrier height for the forward transition. The λ_i are the eigenvalues of the force constant matrix, that is the *covariant* second derivatives of the energy. The Jacobians $J_{1,a}$ in eq. (4) contain information about the volume, bond lengths and orientations of the system at the local minima Θ_1 and the saddle point, respectively. Equivalently said, the metric contributions $J_{1,a}$ are directly related to the values of the reaction coordinate at these particular sites the system is visiting in the evolution through the configuration space. Under these circumstances, the above contributions modify the rate constant by a multiplicative factor. This factor is the ratio of the two Jacobians corresponding to the atomic arrangements at the saddle point and at the position of the initial well, respectively, all taken in the same reference frame. Within the Gaussian steepest-descent approximation for integrations in the phase space, this Jacobian ratio can be taken constant. for any set of coordinates employed. The backward rate w_{2-1} may be obtained straightforwardly by replacing J_2 and E_{2-a} for J_1 and E_{1-a} , respectively.

In the following we shall apply the TST rate formula to a simple landscape case in which the two higher-energy states of local stability Θ_1 and Θ_2 are connected sequentially to the global minimum, Θ_3 . The global minimum has the energy E_3 ($E_3 < E_{1,2}$) and lies at x_3 along the reaction coordinate. A barrier at $x_{(2-3)} \equiv x_b$ separates the global minimum from its nearest-neighbor attractor Θ_2 . All the considerations regarding Θ_1 and Θ_2 apply equally to the forward (w_{2-3}) and backward (w_{3-2}) transitions between the attractors Θ_2 and Θ_3 . These can be constructed by using the parameters J_b , $J_{2,3}$, $\lambda_i^{(b,2,3)}$ and $E_{2-b,3-b}$.

The general procedure describing the dynamics on the PES relies in practice on the explicit knowledge of a master equation governing the time dependence for the single-event probability $P_i(x_i, t)$ of the reaction coordinate. For the PES described above, the system of master equations has the form

$$\begin{aligned} \frac{\partial P_1}{\partial t} &= w_{2-1} P_2(x_2) - w_{1-2} P_1(x_1) \\ \frac{\partial P_2}{\partial t} &= -(w_{2-1} + w_{2-3}) P_2(x_2) \\ &\quad + w_{1-2} P_1(x_1) + w_{3-2} P_3(x_3) \\ \frac{\partial P_3}{\partial t} &= w_{2-3} P_2(x_2) - w_{3-2} P_3(x_3). \end{aligned} \quad (5)$$

The problem we address is determining the extent to which the dynamics of the system is affected by the metric

contributions J to the corresponding TST rates w_{i-j} ($i, j = \overline{1, 3}$). To do so, we must solve the kinetic equations, with a set of initial conditions given. For simplicity, let us assume that at the initial moment ($t = 0$) the system is in the domain of attraction Θ_1 with the probability $P_1(t = 0) = 1$. The evolution of the population distribution is thus relaxation along the reaction coordinate through the configuration space, starting with the population all at $x = x_1$.

Analytic solutions of eqs. (5) are available for this simple system:

$$\begin{aligned} P_1(t) &= \alpha \left[1 + \frac{g_1 S_6}{2S_5 S_2} \phi \left(\frac{2 + \chi}{\chi} \frac{\varphi}{\phi} e^{-\omega_1 t} - \frac{2 + \psi}{\psi} e^{-\omega_2 t} \right) \right], \\ P_2(t) &= \alpha g_1 \left[1 + \frac{S_6}{2S_2} \left(\frac{2 + \chi}{\chi} e^{-\omega_1 t} - \frac{2 + \psi}{\psi} e^{-\omega_2 t} \right) \right], \\ P_3(t) &= \alpha g_1 g_3 \left[1 + \frac{1}{2S_2} \left[(2 + \chi) e^{-\omega_1 t} - (2 + \psi) e^{-\omega_2 t} \right] \right], \end{aligned} \quad (6)$$

which were obtained in terms of eigenvalues and eigenvectors of the characteristic system of equations. The (nontrivial) eigenvalues are given by $\omega_{1,2} = \frac{w_{2-1}}{2} (S_1 \pm S_2)$ with $S_1 = 1 + g_1 + g_2 + g_3$, $S_2 = \sqrt{(1 + g_1 - g_2 - g_3)^2 + 4g_3}$, $g_1 = \frac{w_{1-2}}{w_{2-1}}$, $g_2 = \frac{w_{3-2}}{w_{2-1}}$ and $g_3 = \frac{w_{2-3}}{w_{2-1}}$. All the other constants entering eq. (7) are given by $\chi = S_4 - S_2$, $\phi = S_2 + S_3$, $\varphi = S_2 - S_3$, $\psi = S_4 + S_2$ and $\alpha = \frac{S_5}{S_6} \left[\left(g_1 + \frac{S_3 - S_2}{2} \right) \frac{S_4 - S_3}{S_6} + \left(g_1 - \frac{S_3 - S_2}{2} \right) \right]^{-1}$ with $S_{3,4} = 1 \mp g_1 \pm g_2 + g_3$, $S_5 = S_3^2 - S_2^2$ and $S_6 = S_2^2 - S_4^2$.

The energy levels corresponding to the minima Θ_1 , Θ_2 and Θ_3 of the simple potential energy surface employed in the present study lie along a slope or funnel, in the sequence $E_1 > E_2 > E_3$. Each transition state connecting two adjacent minima lies an energy l_i above the nearest uphill minimum. Therefore, one sets $E_{2-a} - E_{1-a} = l_1 > 0$ and $E_{3-b} - E_{2-a} = l_2 > 0$, respectively. We assume in our first version of this model that the potential energy barrier opposing the escape from the global minimum back to Θ_2 is higher than that opposing the escape from the minimum Θ_2 towards the minimum Θ_1 , ($E_{3-b} > E_{2-a}$). We also assume that the energy barrier from Θ_2 towards the global minimum is energetically lower than that for uphill escape E_{2-a} , ($E_{2-a} - E_{2-b} = l_3 > 0$). In our computation $\lambda^{(1-3)}$ denote the vibrational frequencies of the reaction coordinate in the corresponding minima and we shall keep them at constant values. As for the mean vibrational frequency of the transition state, we make the usual assumption [9], that its absolute value is the geometric mean of the vibrational frequencies of the two minima it connects, $\lambda^{(a)} = \sqrt{\lambda^{(1)} \lambda^{(2)}}$ and $\lambda^{(b)} = \sqrt{\lambda^{(2)} \lambda^{(3)}}$, respectively.

By using probability distributions P_i ($i = 1, 2, 3$) as derived above, we have investigated the relaxation of this ‘‘complex’’ system with various choices for reaction coordinate paths. In simulating the distribution of path lengths we specifically explore the relation between the Jacobian

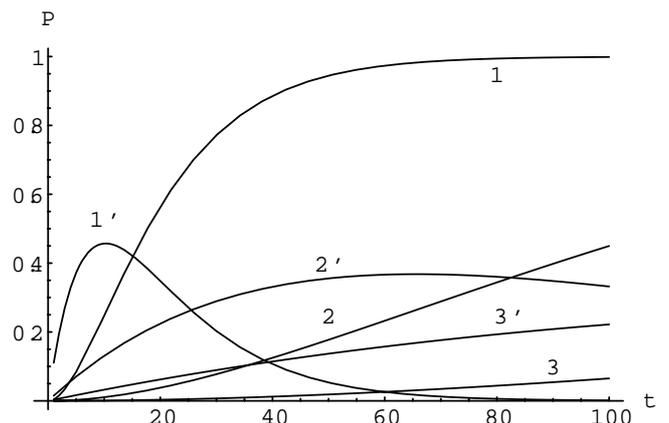


Fig. 1. Time evolution of the probability P_3 (curves 1, 2 and 3) and P_2 (curves 1', 2' and 3') for three different sequences of path lengths between connected minima. The initial population in the highest minimum was assumed equal to unity, $P_1(t = 0) = 1$. For explanation, see the text.

$J(\mathbf{f})$ and the reaction coordinate, as can be seen below. The results are displayed in Fig. 1.

Going back to the purpose of the present paper, we focus on the role the metric contribution plays in the relaxation behavior of the system and first assign to the Jacobians J_1, J_2, J_3, J_a and J_b the following sequence of numbers $J_1:J_2:J_3 \equiv 1:2:3$, $J_a:J_b \equiv 4:5$. Roughly, these numbers should correspond to a distribution of path lengths along the reaction coordinate with increasing step sizes towards the global minimum. The pictorial correspondence in nuclear configuration space is therefore characterized by sizeable rearrangements of the system’s components as it relaxes toward its ground state. The values of the parameters l_{1-3} have been tuned to achieve rapid saturation on a scale of 100. The time evolution of the probability P_3 is displayed in Fig. 1 (see the curve labeled (1)). The population of the ground state and the corresponding probability P_3 increase rapidly and soon reach a plateau.

We now modify the metric contributions to the relaxation rates by setting $J_1 \equiv J_2 \equiv J_3 \equiv A J_a \equiv B J_b = 1$, which corresponds to an equally spaced distribution of minima along the reaction coordinate. All the other parameters remain at their original values. Fig. 1, curve 2, shows that the accumulation in the global minimum is much slower in this case. The time evolution of the probability P_3 does not reach saturation on the same time scale. This indicates that the backward rates of escape from domains of local minima are higher for this second case than in the first, and that the system spends considerably more time now moving uphill on the PES. The geometric structures corresponding to minima Θ_1 and Θ_2 attract the system at rates comparable to that of the ground state potential well even though the latter is energetically more favorable. This balance could be turned around if the numbers of pathways towards Θ_1 and Θ_2 , respectively, were large enough to compensate the energy gaps by entropic contributions [8].

The efficiency of relaxation towards the global minimum can be reduced even more dramatically by inverting the numbers in the sequence $J_1:J_2:J_3$ from those assumed in the first example. This becomes $J_1:J_2:J_3 \equiv 3:2:1$, and the pictorial correspondence of the PES may be that of a steeper funnel with a wide step at the top, between the minima Θ_1 and Θ_2 and a narrow one at the bottom, between the minima Θ_2 and Θ_3 . (We assume $J_a:J_b \equiv 1$, for the present case.) Fig. 1, curve 3, shows that the probability P_3 of accumulation in the global minimum is even slower than that of the second case. In turn, a narrow barrier between the global minimum Θ_3 and adjacent local minimum Θ_2 combined with a broader one between Θ_2 and Θ_3 should result in a longer survival of the system in the well around energy level E_2 . This is demonstrated by curve 3' in Fig. 1 which shows that the accumulation in the domain of attraction Θ_2 is still rising over the entire time scale for the above values of the metric contributions. This behavior contrasts with the two previous situations; see curves 1' and 2' in Fig. 1. There, after an initial increase in population, the attractor Θ_2 starts, more or less suddenly, to depopulate.

In conclusion, we can say that the efficiency of relaxation towards the global minimum can be much affected by the metric contributions to the transition rates. The metric contributions are directly related by the Jacobians to the distribution of the differential path lengths. Therefore these play, in concert with the barrier heights, a non-negligible role in determining how we classify the archetypal energy landscapes in terms of the dynamics they determine [2, 3, 8, 12]. In addition, we can say that incorporating the metric contribution to the TST rate is the appropriate way to combine the height of the barrier and the densities of initial and saddle states with the differential path length corresponding to the transition of the system between these specific stationary points.

The present approach allows the TST rate to be related implicitly to the geometric structure changes in each min-saddle-min transition of the system. We intend to use the information so obtained to identify a way to enrich the precision with which we can characterize the ability of complex systems to relax, preferentially, to only a limited number of geometrical structures from the vastly larger variety that the system might exhibit.

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