Transition State in a Noisy Environment

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(Received 21 February 2005; published 25 July 2005)

Transition state theory overestimates reaction rates in solution because conventional dividing surfaces between reagents and products are crossed many times by the same reactive trajectory. We describe a recipe for constructing a time-dependent dividing surface free of such recrossings in the presence of noise. The no-recrossing limit of transition state theory thus becomes generally available for the description of reactions in a fluctuating environment.

Chemical reaction rates are determined by what happens in a very small fraction of phase space: Such is the premise of transition state theory (TST). It revolves around the concept of the transition state (TS), also known as the activated complex, that is defined by the dividing surface that best separates "reactant" and "product" regions in phase space. Actually, the TS is a general structure found in all dynamical systems that evolve from reactants to products. In addition to chemical reaction dynamics [1], it also determines rates in many other interesting systems such as asteroid capture [2], mass transport through the solar system [3], the rearrangements of clusters [4], the ionization of atoms [5], conductance due to ballistic electron transport through microjunctions [6], and diffusion jumps in solids [7].

TST is central to the understanding of chemical reactions because its radical simplification captures the physics involved in a pictorial way, but its accuracy hinges on the so-called "no-recrossing" requirement: If reagents and products are separated by an abstract hypersurface in phase space, the rate will be exact if each reacting trajectory crosses this surface once and only once. Recrossings will lead to an overestimate of the rate, a problem that occupied Wigner in the early days of TST [8,9]. While in low-dimensional systems a solution has been known for a long time [10], enforcing the no-recrossing condition in more than 2 degrees of freedom has been an open problem until very recently [11–13]. It is even more difficult to uphold for reactions in randomly fluctuating environments (such as chemical and biological processes in liquids) where the noise causes the particle to move randomly back and forth, so that it will typically cross any fixed dividing surface in phase space many times [14]. To solve this long-standing problem, many approximate TS structures have been suggested in the literature [15–21]. Martens [21], in particular, constructed a stationary stochastic separatrix (the collection of all phase-space points for which the reaction probability is $1/2$) that foreshadows the time-dependent structures to be described here. In some cases, infinite-dimensional representations of the Langevin equation [18,22,23], in which the system is coupled to a bath of harmonic oscillators, have been used to obtain approximate infinite-dimensional dividing surfaces that lead to excellent approximations to the rate [18,24,25].

In this Letter, an exact transition state in a noisy environment is constructed as a dividing surface which moves so as to avoid recrossings. For each instance of the noise, there is a unique trajectory that remains in the vicinity of the barrier for all time. This trajectory serves as the origin of a moving coordinate system to which the geometric structures of the noiseless phase space are attached. The result is a moving dividing surface, free of recrossings, that describes a reaction influenced by noise in the same way as a static dividing surface does in conventional TST. This construction goes beyond the geometric approach of [21] by fully taking into account the time-dependence of the fluctuating force. Indeed, the moving separatrices introduced here determine with certainty if a trajectory will or will not react.

We illustrate our findings on a reactive system described by the Langevin equation [26]

$$\ddot{\vec{q}}_\alpha(t) = -\nabla_{\vec{q}} U(\vec{q}_\alpha(t)) - \boldsymbol{\Gamma}\dot{\vec{q}}_\alpha(t) + \vec{\xi}_\alpha(t). \qquad (1)$$

The vector $\vec{q}$ denotes a set of N mass-weighted coordinates, $U(\vec{q})$ the potential of mean force governing the reaction, $\boldsymbol{\Gamma}$ a symmetric positive-definite friction matrix, and $\vec{\xi}_\alpha(t)$ a fluctuating force assumed to be Gaussian with zero mean. The subscript α represents randomness by labeling different instances of the fluctuating force. The latter is related to the friction matrix $\boldsymbol{\Gamma}$ by the fluctuation-dissipation theorem [26]

$$\langle \vec{\xi}_\alpha(t)\vec{\xi}_\alpha^{\mathrm{T}}(t')\rangle_\alpha = 2k_B T \boldsymbol{\Gamma} \delta(t - t'), \qquad (2)$$

where the angular brackets denote the average over the instances α of the noise.

The reactant and product regions in configuration space are separated by a potential barrier whose position is marked by a saddle point $\vec{q}_0^\ddagger = 0$ of the potential $U(\vec{q})$. The reaction rate is primarily determined by the dynamics in a small neighborhood of $\vec{q}_0^\ddagger$ [1,16–20], so that the deterministic force can be linearized around the saddle

point to yield the equation of motion

$$\ddot{\vec{q}}_\alpha(t) = \boldsymbol{\Omega}\vec{q}_\alpha(t) - \boldsymbol{\Gamma}\dot{\vec{q}}_\alpha(t) + \vec{\xi}_\alpha(t) \qquad (3)$$

with a symmetric matrix $\boldsymbol{\Omega}$ given by $\Omega_{ij} = -(\partial^2 U/\partial q_i \partial q_j)_{\vec{q}=\vec{q}_0^\ddagger}$. Coordinates can always be chosen so that $\boldsymbol{\Omega}$ is diagonal. It must have one positive eigenvalue ω_b^2 equal to the squared barrier frequency and $N-1$ negative eigenvalues $-\omega_i^2$, where ω_i are the frequencies of transverse oscillations. Including velocity-dependent forces from, e.g., a magnetic field [5] in this setup would be straightforward. Note that no restriction on the dimensionality of the configuration space is imposed.

Our aim in the following is to construct a recrossing-free surface for Eq. (3). The difference,

$$\Delta\vec{q}(t) = \vec{q}_\alpha(t) - \vec{q}_\alpha^\ddagger(t), \qquad (4)$$

of two trajectories under the influence of the same fluctuating force, which describes the location of the trajectory $\vec{q}_\alpha(t)$ relative to the moving origin $\vec{q}_\alpha^\ddagger(t)$, satisfies a deterministic equation of motion. Since this difference is independent of noise, there is no need to refer to α in $\Delta\vec{q}(t)$. Thus, invariant manifolds and a no-recrossing surface can be specified for the relative dynamics. These geometric objects in the noiseless phase space can then be regarded as being attached to the reference trajectory $\vec{q}_\alpha^\ddagger(t)$ while being carried around by it. They define randomly moving invariant manifolds and a moving no-recrossing surface in the phase space of the original, noisy system.

The construction outlined above can be carried out for any reference trajectory $\vec{q}_\alpha^\ddagger(t)$ and leads to a multitude of no-recrossing surfaces, but only one specific surface is relevant to the reaction dynamics: The crossing of this surface should signal the transition of the trajectory $\vec{q}_\alpha(t)$ from the reactant side to the product side of the barrier. If the reference trajectory is chosen arbitrarily, it will typically descend into either the reactant or product wells over time. However, only a reference trajectory that remains in the vicinity of the barrier can carry a no-recrossing surface that actually describes the reaction. Indeed, as shown here, for each instance of the noise there is a unique reference trajectory with this property. It represents, in mathematical terms, an invariant measure of the noisy dynamical system [27]. We call it the transition state trajectory and henceforth restrict the notation $\vec{q}_\alpha^\ddagger(t)$ to this privileged reference trajectory.

We solve Eq. (3) by rewriting it as a first-order equation in $2N$-dimensional phase space with coordinates $\vec{x} = (\vec{q}, \vec{v})$, with $\vec{v} = \dot{\vec{q}}$, and diagonalizing its linear part. Equation (3) then decomposes into a set of $2N$ independent scalar equations

$$\dot{x}_{\alpha j}(t) = \epsilon_j x_{\alpha j}(t) + \xi_{\alpha j}(t), \qquad (5)$$

where ϵ_j are the eigenvalues of the linear part, $x_{\alpha j}$ the

components of $\vec{x}$ in a basis of eigenvectors, and $\xi_{\alpha j}$ the corresponding components of $(0, \vec{\xi}_\alpha(t))$.

The components $\Delta q_j(t)$ of the relative coordinate (4) satisfy a noiseless version of (5) with $\xi_{\alpha j} = 0$. They grow or decay exponentially, depending on whether the eigenvalue ϵ_j has a positive or negative real part. In $N = 1$ degree of freedom there is one positive and one negative real eigenvalue. The phase portrait of the dynamics is shown in Fig. 1. The eigenvectors span one-dimensional stable and unstable manifolds of the saddle point. They act as separatrices between reactive and nonreactive trajectories. The knowledge of the invariant manifolds allows one to determine the ultimate fate of a specific trajectory from its initial conditions. It is also easy to identify lines in the quadrant of reactive trajectories that are surfaces of no recrossing. Clearly, the half line $\Delta q = 0$, with $\Delta\dot{q} > 0$ serves this purpose.

In multiple degrees of freedom, transverse damped oscillations must be added to the phase portrait in Fig. 1. Their presence manifests itself through $N-1$ complex conjugate pairs of eigenvalues ϵ_j. For strong damping, some of the transverse modes can become overdamped, so that further eigenvalues become negative real. In any case, there is exactly one positive real eigenvalue which corresponds to the particle sliding down the barrier. In all other directions, the dynamics is stable. The eigenvector corresponding to the smallest negative eigenvalue together with the unstable eigenvector span a plane in phase space in which the dynamics is given by the phase portrait of Fig. 1. The separatrices between reactive and nonreactive
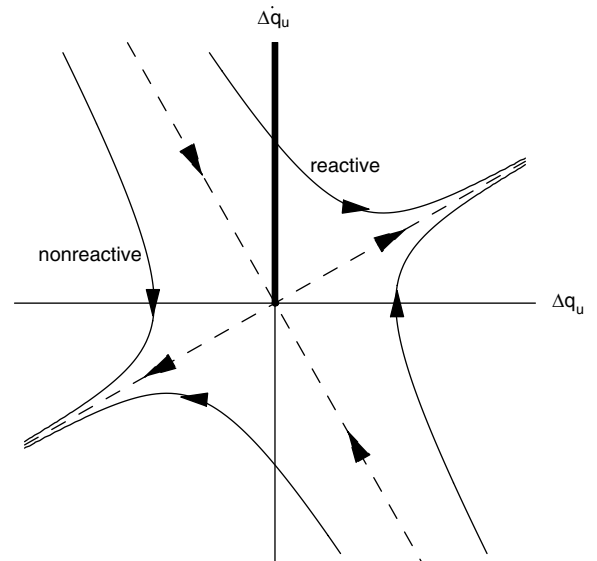

FIG. 1. Phase portrait of the one-dimensional noiseless damped dynamics corresponding to Eq. (3). The thick line indicates a possible choice for the no-recrossing surface. The simple relative dynamics illustrated here is exemplified by the trajectories in Fig. 2(a).
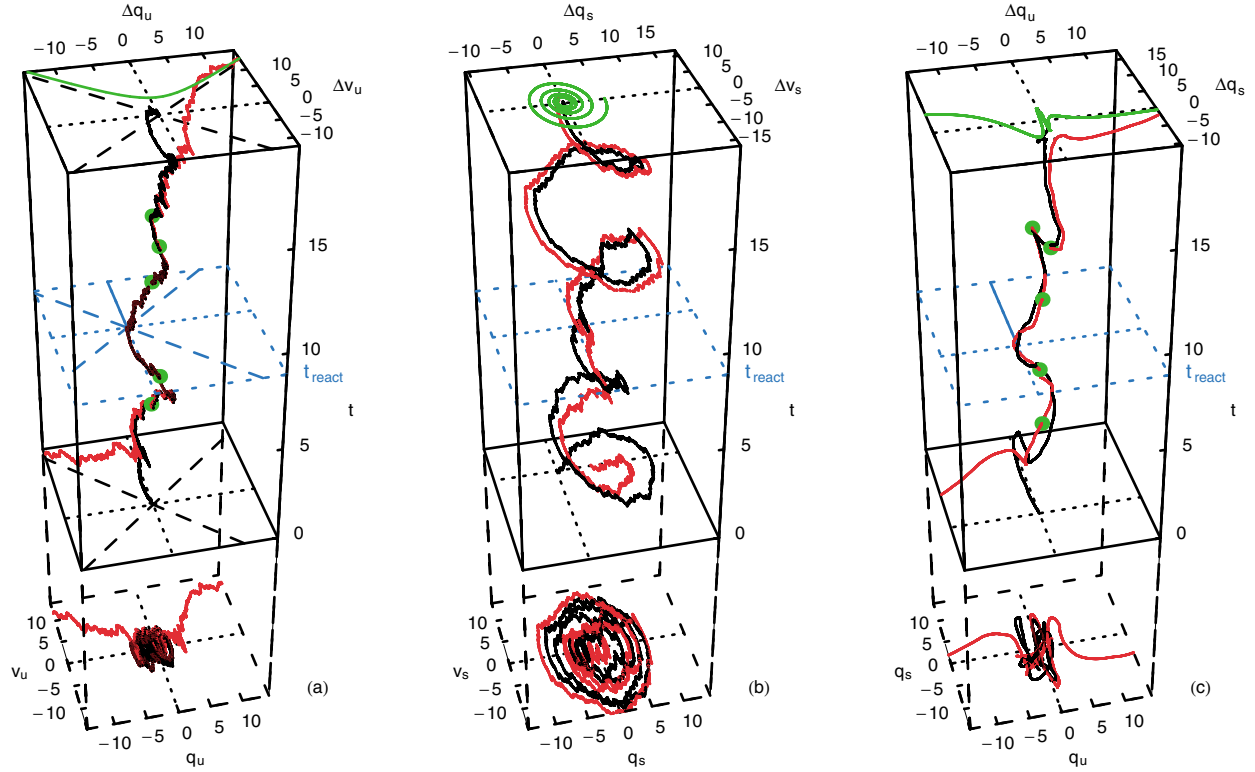
FIG. 2 (color).   A random instance of the TS trajectory (black) and a reactive trajectory (red) under the influence of the same noise in a system with $N = 2$ degrees of freedom: the unstable reactive coordinate q_u and the stable transverse coordinate q_s. The potential is $U(q_u, q_s) = -\frac{1}{2}\omega_b^2 q_u^2 + \frac{1}{2}\omega_s^2 q_s^2$. Trajectories are projected onto (a) the reactive degree of freedom, (b) the transverse degree of freedom, and (c) configuration space. Units are chosen so that $\omega_b = 1$ and $k_B T = 1$. The transverse frequency is $\omega_s = 1.5$, and the friction is isotropic, $\boldsymbol{\Gamma} = \gamma \mathbf{I}$, with $\gamma = 0.2$. The bottom of each column shows the projected trajectories in the corresponding space. Above this, their time evolution is illustrated using the same axes. The blue cut marks the unique reaction time $t_{react} = 8.936$ when the moving TS surface is crossed. Dotted lines in this cut, at $t = 0$, and at $t = 20$, indicate the moving coordinate axes centered on the TS trajectory. These axes are labeled explicitly only at the top face. Dashed lines in the cuts of column (a) show the moving invariant manifolds. No TS is indicated in column (b) because the $q_s - v_s$ subspace lies entirely within the moving TS surface. Thick green dots indicate repeated crossings of the stationary TS surface $q_u = 0$. Green lines in the top face of all three columns show the reactive trajectory in relative coordinates $\Delta \vec{q}$, $\Delta \vec{v}$ [not to scale in (a), for graphical reasons]. The typical behavior of a reactive trajectory shown in Fig. 1 is visible in the top face of column (a).

trajectories that were identified for the one-dimensional dynamics together with the stable transverse subspace form separatrices in the high-dimensional phase space. In a similar manner, a no-recrossing surface in the full phase space is spanned by a no-recrossing curve in the plane and the transverse directions.

Using the Green function technique and assuming $\mathrm{Re}\,\epsilon_j < 0$, we find a particular solution

$$x_{\alpha j}^{s\ddagger}(t) = \int_{-\infty}^{0} e^{-\epsilon_j \tau} \xi_{\alpha j}(t + \tau)d\tau \qquad (6)$$

of Eq. (5). The general solution consists of (6) plus an exponential term that must be suppressed to keep the solution bounded as $t \to -\infty$. Similarly, for unstable components with $\mathrm{Re}\,\epsilon_j > 0$, the only solution to (5) that remains bounded for $t \to +\infty$ is

$$x_{\alpha j}^{u\ddagger}(t) = -\int_{0}^{\infty} e^{-\epsilon_j \tau} \xi_{\alpha j}(t + \tau)d\tau. \qquad (7)$$

Eqs. (6) and (7) specify all the phase-space components of the unique random trajectory—viz. the TS trajectory—that remain bounded in the remote future as well as in the distant past. Its configuration-space representation is obtained by transforming back to position and velocity coordinates. Because the components $\xi_{\alpha j}$ of the fluctuating force are Gaussian random variables with zero mean, so are the components (6) and (7) of the TS trajectory. Their joint probability distribution can readily be specified through the explicit calculation of their cross-correlation function by insertion of the correlation function (2) of the noise.

As described above, the TS trajectory serves as the origin of a moving coordinate system to which the geometric structures in the noiseless phase space are attached.

This is illustrated in Fig. 2 for $N = 2$ degrees of freedom. The phase space is four-dimensional and already exhibits all the salient features of the dynamics in arbitrarily high dimensions. The figure compares a TS trajectory with a reactive trajectory under the influence of the same noise. The trajectory approaches the TS trajectory from the reactant side $q_u < 0$, remains in its vicinity for a while, and then wanders off to the product side. Because the moving invariant manifolds of the TS trajectory are known, it can be predicted already at time $t = 0$ that the trajectory actually will lead to a reaction instead of returning to the reagent side of the saddle.

The reactive trajectory crosses the space-fixed TS surface $q_u = 0$ several times before it finally descends on the product side. The moving TS surface $\Delta q_u = 0$, by contrast, is crossed only once, at the reaction time t_{react} indicated by blue lines. That this is actually the case can be seen from the curves in the top faces of each column, which indicate the noiseless relative motion $\Delta \vec{q}(t)$, $\Delta \vec{v}(t)$ between the TS trajectory and the reactive trajectory. The relative coordinates show, as expected, the hyperbolic motion known from Fig. 1 in the unstable degree of freedom, a damped oscillation in the stable transverse degree of freedom, and a superposition of the two in the configuration-space projection in Fig. 2(c).

The derivations presented here are based on the assumption (2) of white noise. If the noise were correlated, the friction would contain memory and the dynamics would consequently be significantly more complicated [26]. The construction of the TS trajectory can be carried out nonetheless. It leads to integral formulas similar to (6) and (7), with the eigenvalues ϵ_j given by the Grote-Hynes equation [18,28]. These generalizations will be presented in a forthcoming publication.

In recent simulations [29,30], ensembles of transition paths, i.e., trajectories connecting reactants to products, have been shown to be useful in computing rates even for high-dimensional systems. Our identification of the TS trajectory provides additional insight into the geometry of reaction dynamics that complements the transition path ensemble method. While the TS trajectory introduced here is not itself a transition path, it carries a dividing surface that is transverse to all transition paths and is crossed once and only once by each of them. It is no harder to compute than a typical trajectory. This is to be contrasted with most TST approaches in which finding a no-recrossing dividing surface requires the onerous solution of a highly nonlinear problem.

In summary, to generalize the formalism of TST to reactive systems driven by noise, a moving surface has been constructed that is crossed once and only once by each transition path. This surface is therefore suited to take over the role of the well-known and widely applied static dividing surface of conventional TST in a broader time-dependent setting.

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