Transition state theory in liquids beyond planar dividing surfaces

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Abstract

The success of Transition State Theory (TST) in describing the rates of chemical reactions has been less-than-perfect in solution (and sometimes even in the gas phase) because conventional dividing surfaces are only approximately free of recrossings between reactants and products. Recent advances in dynamical systems theory have helped to identify the interconnected manifolds —"superhighways"— leading from reactants to products. The existence of these manifolds has been proven rigorously, and explicit algorithms are available for their calculation. We now show that these extended structures can be used to obtain reaction rates directly in dissipative systems. We also suggest a treatment for the substantially more general case in which the molecular solvent is fully specified by the positions of all its atoms. Specifically, we can construct effective solvent configurations for which the exact TST manifolds can be constructed and used to sample the rates of an open system.

Key words: Kramers Rate Theory, Activated Dynamics, Dissipation, Nonrecrossing Dividing Surfaces, Invariant Manifolds

1. Introduction

Chemistry is the science of change at the molecular level and beyond. Consequently, the questions at the core of chemistry are invariably concerned with how a reaction proceeds and how long it takes. The former is the is concerned with the mechanism of a reaction. In the limit of a single mechanistic reaction, it reduces to the problem of finding the reaction path along which the reaction proceeds. The latter is concerned with determining the time it takes for a reaction to proceed along this putative reaction path. Thus a complete reaction

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rate theory for chemical processes requires a long-time description of the multi-dimensional geometry of the molecular reaction. This is a difficult problem even when it is appropriate to assume that classical mechanics is sufficient[1], and that a rate exists.[2] If it is appropriate, then such a formalism is applicable well beyond chemistry because processes in many other fields are also determined by rare events—that is, those that go through bottlenecks along the reaction path. For example, the ionization of atoms,[3] the rearrangement of clusters,[4] conductance through microjunctions,[5] asteroid capture,[6] and even phase transitions in cosmology[7] all involve rare events traversing through bottlenecks.

The beauty of Transition State Theory (TST)[8–14] lies partly in that it addresses both the question of time and geometry in a single step. The bottleneck along the reaction path is identified as the transition state (TS) or activated complex. Intuitively, the crossing of the TS is the rate-determining step. The rate is calculated by obtaining the flux through this transition state divided by the reactant population.[10, 15, 16] The calculation of the instantaneous flux through the transition state side-steps the need to calculate the dynamics at any time, let alone long times. Meanwhile, there is no longer a question of identifying a *reaction path* because the only relevant geometry determining the rate is that of the transition state.

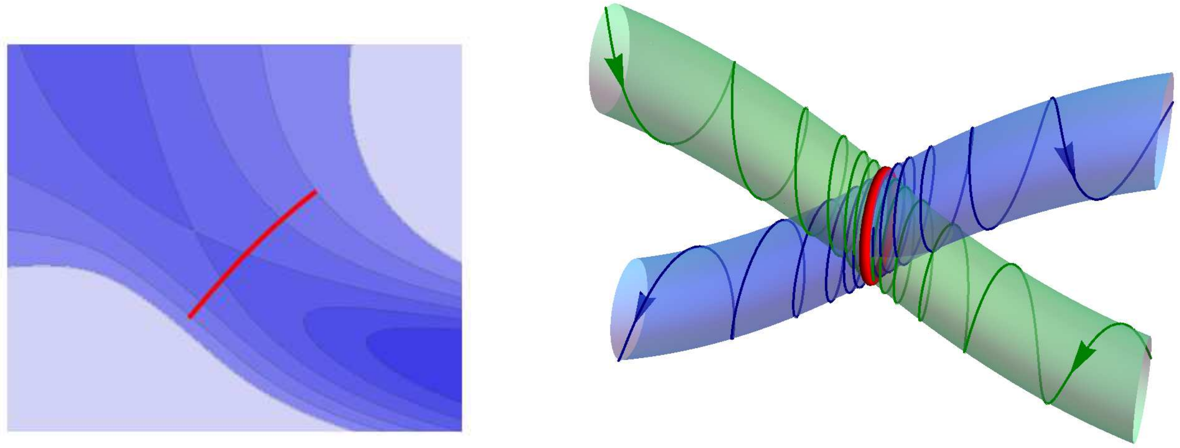
The value of this vast simplification hinges on the accuracy of TST and depends on the extent to which trajectories between reactants and products recross the identified transition state (dividing) surface. Indeed, if all of the trajectories can be shown to be strictly "non-recrossing" through the dividing surface, then the TST rate is exact.[17] That is, as one reduces the number of recrossings, the TST rate is improved.[1, 18] This is the basis of variational transition state theory.[11, 19–26] Ideally, one aims to construct a dividing surface that rigorously admits no recrossing trajectories. In two dimensional systems, this is precisely what was accomplished by Pechukas and Pollak[27, 28] in identifying dividing surfaces as periodic orbits that are strictly non-recrossing.[27–30] Analogous structures in higher-dimensional systems can be described explicitly if the transition is mediated by a parabolic barrier with a set of uncoupled transverse harmonic oscillators. As described in Section 2, the transition state can then be identified with a normally hyperbolic invariant manifold (NHIM), while the stable and unstable manifolds of the NHIM channel the reaction towards and away from the TS. [31] A critical result from the mathematical (nonlinear dynamics) community is the proof [32–36] that these manifolds persist under small perturbations of the Hamiltonian, so that they will survive if anharmonic corrections to the barrier dynamics are taken into account. [31] Moreover, they can be obtained approximately using canonical or Lie-transform perturbation theory to arbitrary order. [4, 31, 37–44]

In chemical processes, the construction of the exact nonplanar dividing surface is hampered by the fact that the multi-dimensional molecular potential is generally not known accurately over the entire domain of positions (although the calculation of gradients in the proximity of the naive transition state does allow for much improved estimates.[45–48]) Thus, although the non-recrossing TST rate of a chemical reaction is formally exact for isolated finite-dimensional reactions, it will in practice be limited by the extent to which the underlying potential energy surface is known globally.

This begs the question of whether a TST rate expression can be constructed that is exact for solvated chemical reactions. The difficulty of this problem has led many to introduce the strong simplifying assumption involved with representing the solvent forces as stochastic variables within the framework of the Langevin or generalized Langevin equations. [49–65] For example, within the time scale of a chemical reaction event, fluctuations of the environment will almost inevitably cause recrossings of the dividing surface[66], so that a naive TST rate calculation would yield a poor estimate of the rate. Indeed, Grote and Hynes showed that they could obtain a more accurate rate formula than that afforded by the naive TST theory—obtained in the frame of the reaction path—by extending the reactive flux calculation to longer times.[67] However, Pollak[68, 69] showed that the same rate expression can be obtained from TST if the Langevin equation is recast as a Hamiltonian system in which the subsystem is coupled to an infinite set of harmonic oscillators[52, 70] and a dividing surface is sought in the full space of the extended Hamiltonian. (It is worthwhile to point out that such a linearized approximation for the effect of solvation is not without error. Recent work[16, 71–74] has shown that in reduced dimensional subsystems, there is sometimes a need to include momentum corrections.) The dividing surface in the extended phase space is recrossing-free if the barrier can be approximated as parabolic. In order to do this more generally, many have resorted to the use of a variational transition state theory in the infinite-dimensional phase space following Keck.[19] These nonplanar dividing surfaces have been shown to lead to excellent estimates of the rate in various solvated reactions.[11, 19–26] A completely different approach is taken by the Monte-Carlo-based transition path ensemble scheme of Chandler and coworkers.[75] It bypasses the identification of a TS structure and focuses on the calculation of the entire long-time transition paths from the reactant to the product region instead. They avoid calculating non-reactive trajectories, and hence dramatically reduce the numerical effort required to address rare events. The approach, however, does not provide the rate determining transition state that is the hallmark of TST, and that limits its use in visualizing a chemical reaction.

The strategy in our recent work [76–81] has involved the recognition that from the frame of a reacting system, the environment plays the role of creating a time-dependent potential. If one can generalize the non-recrossing TST of isolated systems to such driven (or time-dependent) Hamiltonians, then one can presumably also address reactions in solutions. Such a generalization has indeed been accomplished.[79, 81] In the limit that the interaction between the reaction and the solvent is linear within the Langevin representation, the solvent is uncoupled to the reacting subsystem. Such decoupling leads to a tremendous simplification, as observed by Graham [82] and Martens [83]. In our previous work, we followed this further by constructing a dividing surface in a time-dependent frame in which the trajectories are strictly non-recrossing, albeit by constructing such a surface for each manifestation of the noise. The construction of this TS trajectory and its associated reaction geometry is summarized in Section 3. A central result of this work is the fact that this construction is formally also correct even if the interaction is nonlinear as long as the solvent response remains uncoupled to the reacting subsystem. The heuristic proof of this claim is presented in Section 4.

However, many solvents do not possess the simple structure that allows their effects to be modeled by the Langevin equation or generalized Langevin equation that were used to



(a) (b)

Figure 1: Schematic representation of TS structures in two degrees of freedom. (a) The configuration space view: A periodic orbit (red) acts as a recrossing-free dividing surface. It is superposed onto contours of the potential energy surface. (b) The phase space view: A periodic orbit (red) defines an opening through which the reaction proceeds. Stable (green) and unstable (blue) manifolds channel trajectories towards and away from the bottleneck. (Contrary to appearance, the stable and unstable manifolds do not intersect in the four-dimensional phase space.)

calculate the TS trajectory. [75, 84, 85]. Instead, they must be described in atomistic detail if their effects on the effective free energies (that is, the time-independent properties) and the solvent response (that is, the non-equilibrium or time-dependent properties) associated with the chemical reaction are to be modeled accurately. In so doing, the solvent is necessarily no longer uncoupled to the dynamics of the reacting subsystem. In section 5, we will outline a strategy for implementing the TS trajectory even in such a case. The main idea is the construction of an ensemble of time-dependent environment trajectories (TiDEs) self-consistently with a guiding trajectory of the reacting solvent. The dynamics of the subsystem can then be obtained by oversampling each TiDE with a swarm of subsystem trajectories. Such a system could then be addressed using numerical integration, or by constructing the corresponding non-recrossing moving transition state for each TiDE. In the latter case, the calculation of the rate is reduced to the sampling of the TiDEs.

2. TST in Isolated Systems

TST is traditionally based on the assumption that the reaction rate is determined by the dynamics in a small area of phase space and that in this "bottleneck," a dividing surface can be identified through which all reactive trajectories pass once and only once. If a unique surface with this property can be found, TST will yield the exact reaction rate (apart from quantum effects) [17]. For systems with two degrees of freedom, it was realized in the 70s that an ideal recrossing-free dividing surface is provided by an unstable periodic orbit close to the barrier top [17, 21, 86] that is often called the Liapunov orbit. Although the initial formulations of TST relied on dividing surfaces restricted to the configuration space, it is advantageous to study the corresponding structures in phase space[19] as illustrated in Fig. 1. The Liapunov periodic orbit then appears not as a dividing surface between reactants and products, but rather as a loop through which the reaction must proceed. The interior of this loop provides a recrossing-free dividing surface in phase space. Once a phase space view has been adopted, TST can be applied to systems without time-reversal invariance, e.g., in the presence of a magnetic field [3, 87].

In addition to a dividing surface, the phase space picture of TST contains the stable and unstable manifolds of the Liapunov periodic orbit. These are surfaces that contain all those trajectories that approach the Liapunov orbit and are therefore trapped on the barrier top in the infinite future or infinite past, respectively. Trajectories on the invariant manifolds neither cross the barrier nor return into the well from which they originate. The importance of the trapped trajectories was realized by Pollak and coworkers [86, 88, 89]: Being neither reactive nor non-reactive, these trajectories form the natural boundaries between reactive and non-reactive regions in phase space. Reactive trajectories are those that approach the barrier in the interior of the stable manifolds, which are cylinders in phase space. They form the reaction tubes described in [90–92].

It has been realized only relatively recently [4, 31, 35, 36, 38] that the phase space picture of non-recrossing TST, but not the configuration space picture, can be generalized to systems with many degrees of freedom. This approach provides a higher-dimensional analog of the Liapunov periodic orbit that is called a normally hyperbolic invariant manifold (NHIM). The NHIM forms the boundary of a dividing surface in phase space that is free of recrossings. It also possesses stable and unstable manifolds that separate reactive from non-reactive trajectories and thus provide reaction tubes which channel trajectories towards and away from the TS. Qualitatively, therefore, the dynamical framework of TST in many dimensions is the same in two degrees of freedom, with the exception that the phase space dividing surface does not project onto a recrossing-free dividing surface in configuration space.

All geometric objects of TST can be described explicitly [31] if the barrier is assumed to be parabolic and the bath modes are uncoupled harmonic oscillators. Anharmonic corrections will deform these structures, but not destroy them, as long as they are sufficiently weak. In the same way, the Liapunov periodic orbit in an anharmonic two-dimensional potential energy surface is deformed from a straight line across the saddle point, but not destroyed. Of course, it is known that the Liapunov orbit can undergo bifurcations for energies sufficiently high above the barrier, and the TS dynamics then becomes more complex than what was described above [21, 27]. One might expect that a higher-dimensional NHIM can also bifurcate at high energies, and indeed evidence for such bifurcations has recently been seen [93, 94].

For applications to specific systems, it is essential that we can calculate the NHIM and its associated invariant manifolds, for which we have so far only invoked existence theorems. Such calculations have successfully been carried out for a number of systems with the help of normal form theory [4, 31, 37–44].

The shift from a configuration-space to a phase space picture brings about not only a generalization to high-dimensional systems, which is its most obvious advantage, but also a subtle shift of emphasis in TST. The NHIM and its stable and unstable manifolds are invariant objects in phase space on which it is natural to focus one's attention. The dividing surface, in contrast, is not invariant under the flow (because trajectories must cross it) and is not even uniquely defined: Among all possible surfaces that are bounded by the NHIM, many will be recrossing-free, and all of these will yield the same reactive flux. Indeed, the flux across the TS can be determined as an integral over the NHIM alone, without any reference to a dividing surface at all [43]. In two degrees of freedom, the flux is given by the action integral along the Liapunov periodic orbit [86, 95]. The dividing surface itself, which has traditionally been at the heart of TST, thereby loses some of its importance (though it is still useful in many computational schemes). The NHIM and its invariant manifolds, which allow one to distinguish between reactive and nonreactive trajectories easily, now take center stage.

3. TST in Solvated Systems

The powerful techniques of geometric TST that were summarized in Section 2 are well adapted to the description of autonomous gas-phase reactions, but they must be extended if the physical insight and the computational efficiency offered by TST are to be retained for systems that are subject to the influence of a time-dependent environment. A detailed dynamical and geometrical picture of *exact* time-dependent transition state structures in phase space has recently begun to emerge.[76–81] In this work we constructed an exact transition state that avoids recrossings by moving stochastically in a noisy harmonic environment. Just as the TST for high-dimensional autonomous systems, the time-dependent TST is critically a phase space theory to which no analog can be constructed in configuration space. The trajectories within the invariant manifolds are trapped trajectories in the sense of Pollak and coworkers [86, 88, 89]. They separate reactive from nonreactive trajectories, and their knowledge enables one to predict the fate of a trajectory a priori.

The key to our solution is the observation that all the geometric structures that exist in the autonomous TST are attached to, and organized by, the saddle point, which is a fixed point of the dynamics. The generalization to driven systems depends on the identification of an analog of the saddle point. For each instance of the noise, we found that there exists a specific trajectory that never leaves the vicinity of the saddle point—viz. the naive transition state. This so-called TS trajectory is analogous to the dynamical fixed point and to the NHIM in the autonomous case. Whereas a time-independent system possesses an infinite family of NHIMs that are distinguished by the energy, energy is not conserved in a driven system, and the family of NHIMs collapses into a single TS trajectory.

The TS trajectory serves as the origin of a moving coordinate system to which the phase-space structures are attached. The result is a moving dividing surface that is free of recrossings and that therefore describes a reaction influenced by noise in the same way as a static dividing surface does in conventional TST. In addition, the TS trajectory possesses stable and unstable invariant manifolds. For systems with harmonic barriers, we described these manifolds in [76, 77] using an explicit solution of the equations of motion, through which they can be identified easily. In anharmonic systems, a more qualitative approach to characterizing invariant manifolds is required. The definition of stable and unstable manifolds that is used in autonomous systems can successfully be adapted to random dynamical systems. Let us consider the sets of all trajectories that approach the TS trajectory in the distant future or the remote past, respectively. These sets are invariant under the dynamics. It remains to be seen if these sets are indeed manifolds of the requisite dimension which partition the phase space into distinct regions with reactive and regions with nonreactive trajectories, respectively. If the nonlinearities are sufficiently weak, one can regard these sets as small deformations of the invariant manifolds in the harmonic system, and it appears plausible to expect that they should have the desired properties.[78] This can indeed be shown to be true. A thorough discussion of the underlying theory of random dynamical systems is contained in [96].

The practical advantages of our proposed approaches are not merely numerical. Our construction shows how rate-determining phase space structures (like the "superhighways" for mass transport in the solar system) move with the TS Trajectory. The most prominent of these structures are the impenetrable barriers in phase space [the stable and unstable manifolds of the so-called Normally Hyperbolic Invariant Manifold (NHIM) which act like scissors cutting the phase space into the hypervolumes of those initial conditions which lead to reactions and those which do not.[31, 39, 40] Once these manifolds are calculated, large-scale simulations of reactivity are no longer needed. Instead, one only needs to check on which side of these manifolds (known as "separatrices") the initial conditions lie because if their locations are known, the outcome of the calculation is also known! If these time-dependent structures exist numerically, then this begs the question of whether these approximate structures can be rigorously constructed. In work to date, these time-dependent geometric structures have been obtained numerically up to some order in an approximate expansion, but we have yet to prove rigorous conditions for their existence.

In the harmonic limit, the moving dividing surface attached to the TS trajectory is strictly free of recrossings, while in more general (nonseparable) cases it is approximately so. This surface (or one of its variants) 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. A further consequence of a Hamiltonian system-bath interaction is that the "bath modes" that we include in the system dynamics will be undamped, i.e. will have purely real frequencies. As shown in [79], this means that the corresponding components of the TS trajectory are not unique. It is not clear whether they are well defined if the interaction does not vanish at large times. Thus, even these advances are not sufficient to treat the full nonlinearity of many externally driven reactive systems such as chemical reactions in a liquid, and this is the subject of current work.

4. Rates in Langevin Baths

It is instructive to discuss the stochastic (Langevin) system in more detail. In the parabolic case, the general system takes of the form:

$$\dot{x} = Ax + g(t) \ , \qquad (4.1)$$

where $g(t)$ is the noise term, x is a n-vector, and A is an $n \times n$ matrix. Suppose that $\bar{x}(t)$ is any solution of this equation. We then consider the following change of variables:

$$x(t) = y(t) + \bar{x}(t) \ . \tag{4.2}$$

Substituting this into the equation gives the following equation for y:

$$\dot{y} = Ay \ . \tag{4.3}$$

Hence, the noise completely disappears. Therefore it is possible to construct explicit analytic expressions for the dividing surfaces for this equation, and transform them back to the original equations. In our earlier work [76, 77], we took the further step of choosing boundary conditions on $\bar{x}(t)$ that required it to always stay within the vicinity of the putative transition state. For every fixed realization of the noise, there is a unique trajectory that satisfies this condition. This Transition State trajectory $\bar{x}^{\mathrm{TST}}(t)$ then affords us the opportunity of using all of the geometric structure that we know from the time-independent setting. But can we actually do this for a nonlinear system? To frame an answer to this question, consider a general form for the non-parabolic system, i.e., a nonlinear first-order vector equation:

$$\dot{x} = f(x) + g(t) \ . \tag{4.4}$$

Here $g(t)$ is the noise, as before, and $f(x)$ is a nonlinear function of x. Assuming that the appropriate lesson from the derivation sketched above is to solve this equation for a special trajectory, $\bar{x}(t)$, and again make the same change of coordinates as in Eq. (4.2), obtaining

$$\dot{y} = \mathcal{D}f(\bar{x}(t))y + \mathcal{O}(|y|^2) \ , \tag{4.5}$$

where $\mathcal{D}f$ denotes the Jacobian matrix of f—i.e. the matrix of its partial derivatives—and $\mathcal{O}(|y|^2)$ represents the nonlinear terms in y with coefficients depending on $\bar{x}(t)$. If we were to stop here, then we would fail. Unlike in the parabolic case, we are now left with an equation that is no longer noiseless because the dynamics of the relative coordinate y is driven by the reference trajectory $\bar{x}(t)$. It is therefore no longer straight-forward to describe the transition state geometry of the relative dynamics.

We can obtain a clearer view of the difficulties if we decompose the deterministic terms

$$f(x) = Ax + \Delta f(x) \tag{4.6}$$

in Eq. (4.4) into a sum of linear (Ax) and nonlinear ($\Delta f(x)$) terms:

$$\dot{x} = Ax + \Delta f(x) + g(t) \ . \tag{4.7}$$

We now choose the reference trajectory $\bar{x}(t)$ to be a solution of the linearized equation (4.1)—usually, one would choose the TS trajectory $\bar{x}^{\mathrm{TST}}(t)$—and use this particular solution in the change of coordinates of Eq. (4.2) to obtain

$$\dot{y} = Ay + \Delta f\left(y + \bar{x}\right) \ . \tag{4.8}$$

By choosing a reference trajectory that follows the linearized dynamics instead of the full nonlinear dynamics, we have obtained an equation of motion for the relative coordinate that has a constant linear term. The nonlinear terms, however, still couple the relative dynamics to the reference trajectory. In Ref. [79], time-dependent normal form transformations were used to eliminate the coupling terms in a Hamiltonian system under time-dependent driving. This approach is also applicable to the present dissipative setting. It provides an explicit construction of the TS geometry in the transition region, not too far away from the saddle point.

In the opposite limit, one would like to study the dynamics in the reactant and product wells, far away from the transition region. In this case, if we choose $\bar{x}(t) = \bar{x}^{\mathrm{TST}}(t)$, we know that the reference trajectory will be confined to the vicinity of the saddle point, and therefore $\bar{x}(t) \ll y$ with high probability. We can therefore approximate the equation of motion (4.8) by

$$\dot{y} = Ay + \Delta f\left(y\right), \tag{4.9}$$

which is once again completely noiseless. Hence the geometry underlying this equation once more affords us a picture of the transition state and thereby the dynamics that flows through it. Only in the "interaction region" where y is comparable to $\bar{x}^{TST}(t)$ will the TS geometry be time-dependent in a manner that differs strongly from the simple shift given by (4.2). The problem of how to connect the time-dependent invariant manifolds of the barrier region to those in the well region across the interaction region is currently open. Nevertheless, the geometric structures associated with (4.9) divide the phase space into reactive and nonreactive regions, and they remain intact as long as the nonlinearity is sufficiently small.

The chemical reactive or reorganizing systems of interest are usually time-dependent[81] either because of some external time-dependent field (or fields), or because of interaction with a solvent. To generalize the exact limit of TST to reactive systems driven by noise, we have introduced a time-dependent dividing surface that is stochastically moving in phase space such that it is crossed once and only once by each transition path.[76, 77] This moving dividing surface can be used to identify reactive trajectories in harmonic or moderately anharmonic systems within solvents represented by stochastic noise with considerably lower numerical effort or even without any simulation at all.[78] The surprising accuracy of this approach, even at high anharmonicities, can now be understood from the arguments above. The geometric structure obtained from (4.9) persists to a reasonable approximation because $\bar{x}^{TST}(t)$ is close to the barrier and leads to small corrections in the time-dependent nonlinear terms. As such, the moving TS obtained from 4.9 is a good approximation to the moving TS for the exact dynamics leading to high accuracy in assigning which trajectories are reactive.

Two additional computer-enabled methods[80] for transition state theory (TST) rate calculations have also been developed by us to take advantage of these notions of the moving dividing surface and the associated moving separatrices: One is based on the flux-over-population approach and the other on the calculation of the reactive-flux. In particular, numerical simulations of harmonic and anharmonic systems have been used to calculate reaction rates based on the reactive flux calculation using the fixed and moving dividing surfaces so as to illustrate the computational advantages of the latter.

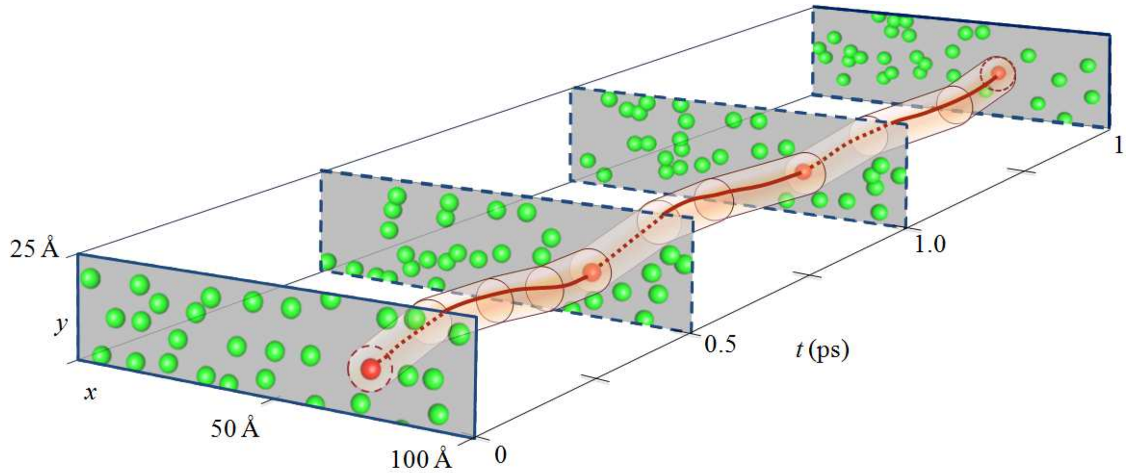


Figure 2: A schematic of a guiding trajectory and its associated moving TiDE is shown here for a very simple two-dimensional system consisting of Argon atoms whose pair-wise additive interactions are represented by the Lennard-Jones (6-12) potential. The third dimension illustrated above corresponds to time, and allows us to illustrate a series of time-slices of the particle positions. The red particle represents the subsystem which together with the TiDE can be evolved in time by integrating the classical equations of motion. Note that the TiDE consists of the trajectory of all the particles with the exclusion of the red (system) particle. Without the red particle there is a cavity at each time slice which is roughly defined by a disk centered at the position of the red particle going out to the nearest neighbor. This cavity (disk) evolved in time is illustrated by a tube. An oversampling of the subsystem dynamics can be taken by generating additional trajectories of particles that move within this tube, i.e. on the TiDE.

5. Rates in Atomic and Molecular Solvents

As seen above, the use of the TS trajectory to characterize the phase space geometry of a reaction hinges on the fact that the Langevin solvent does not depend on the dynamics of the reacting subsystem. That is, the critical assumption is not that the solvent is linearly coupled to to the reaction, but rather that its motion is independent of the reaction. Such a simplification is clearly not available when the reacting subsystem and solvent are specified atomically. In that case, the motion of the solvent atoms will be influenced by the instantaneous configuration of the solute. The presence of this feedback between the reacting subsystem and the solvent does not allow one to study an ensemble of solute trajectories that are subject to the same noise sequence, and the computational advantages offered by the moving TS structures are in danger of being lost. The problem is thus how to approximately construct an ensemble of reacting subsystems for a given solvent structure.

To formulate this problem precisely, we split the system into two sets of variables: the subsystem—which is the part that is undergoing a chemical change and can include solvent modes,— and the environment—which is the part that is not included in the subsystem. The conjectured algorithm involves the following steps: (1) We first calculate a trajectory for the subsystem and the environment. The trajectory in the subsystem variables is a guiding trajectory for the coordinates of the time dependent environment (TiDE). The latter is evidently associated with —coupled to— the guiding trajectory of the subsystem with which it was generated. In the context of reactions with rare events, we should generate the guiding trajectory and the TiDE by starting the subsystem at or near the putative transition state with no other bias. (2) The TiDE that is obtained with a given guiding trajectory of the subsystem can then be used as a reference for many independent trajectories of the subsystem. Of course, the subsystem dynamics for a fixed TiDE will usually not adequately sample all the dynamical possibilities of the subsystem. It is therefore likely that several TiDEs obtained from a sampling of differing subsystem trajectories will be required. (3) We then generate a Moving TST for a given specification of the TiDE. As noted in our earlier work,[78] an oversampling of the subsystem using the moving TST for a TiDE in the Langevin limit results in a more accurate estimate of the dynamics. Why should a TiDE generated self-consistently with a particular subsystem trajectory be compatible with another subsystem trajectory, let alone a family of such subsystem trajectories? In the limit of an uncorrelated random solvent, the construction of the TiDE is merely a recipe for constructing such a solvent in which all the molecular (and atomic) positions of the solvent are fully specified. Otherwise, this construction defines a family of subsystem trajectories that are consistent with the generating trajectory in the sense that they define a similar moving cavity through the solvent. The arguments made in Section 4 to treat nonlinear systems dissipated by Langevin forces will be generalized in future work to provide limits on the accuracy (and generality) of this approach. (4) If one TiDE suffices to describe the dynamics of the subsystem, then there's no need to iterate this procedure. Such could be the case if the subsystem dynamics are only weakly interacting with the environment. Otherwise we must sample over several TiDEs. The last step is critical as it reintroduces the non-linear coupling between the subsystem and the environment by way of sampling over sets in the dynamic ensemble space. The primary efficiencies gained here are that one need only generate enough TiDEs to obtain an accurate numerical estimate, *e.g.,* on the order of 10,000 to 100,000 trajectories, and this number doesn't need to scale with the size of the subsystem or the environment. Of course, the larger the overall system, the larger the calculation of each trajectory, but this is an effort that can't be avoided. Finally, rates can be obtained for this family of trajectories using the same techniques described at the end of Section 4 for the Langevin dissipated reactions.

6. Concluding Remarks

What is the practical benefit of the TS trajectory and its generalization to nonlinear (complex) systems described in Section 4? We see it as a first necessary step to generalizing the formalism of TST to reactive systems driven by noise. As in all TST formulations, merely knowing that there is a such a transition state allows an investigator to concentrate on that special part of phase space which corresponds to the critical configuration, paving the way for better and faster rate calculations than before. This numerical course of action has already been successfully followed for gas-phase reactions by Komatsuzaki and Berry,[41, 97–102] and could make a profitable research direction towards addressing time-dependent environments. As remarked above, we showed recently[78] that the moving dividing surface can be used, for example, to identify reactive trajectories in linear and nonlinear systems with considerably lower numerical effort or even without any simulation at all. This was illustrated using the simple chemical reaction of $H + H_2 \rightleftharpoons H_2 + H$ dissipated by a Brownian bath (as modeled by the Langevin equation.) Equally importantly, this exercise illustrates the advantage of cyber-enabled investigations even for implicit solvents. Namely, we were able to simulate a family of subsystem trajectories so as to see the extent to which they preserved the geometry of the linear reference even though we could not solve it analytically in the nonlinear case. Thus the simulations allowed us to confirm and view the geometry of the TS of the nonlinear system even when we had no proofs on the bounds of accuracy for the structure.

A very important open question concerns whether the moving TST dividing surface for a dissipative system could be extended to the quantum domain, thereby providing a new semi-classical version of TST. Indeed, the phase-space geometry of the integrated Hamiltonian —by way of successive Lie transformations of the expansion of the potential at the col of the potential energy surface— of a conservative system was originally exploited to construct highly accurate semiclassical transition state theory (SCTST).[37, 38, 45] In order to extend such an SCTST to a dissipated system, one could couple the reactive system to a Langevin bath. The latter in turn would then be rewritten into the Zwanzig Hamitonian—viz, the finite system bilinearly coupled to and infinite but countable harmonic oscillators for a specified spectral function.[52, 68] Such a system could then be transformed, via Lie transforms, to a normal form up to specified order with the actions connected to quantum numbers using the Bohr-Sommerfeld quantization rules as done in the small-dimensional case.[37, 38, 45] To our knowledge, this has yet to be published in the open literature.[103] Equally interesting would be the generalization of such a procedure using the moving TST discussed here. However it is not clear how one would identify the requisite good action angle-variables needed to connect to the corresponding quantum states within this time-dependent formalism. This is yet another open problem that awaits a solution.

The second result of this paper involves our conjectured strategy for generalizing this formalism to molecular dynamics representations of the reacting subsystem and its environment. There is a crucial difference between the TiDE scheme outlined here and the oversampling method used in [78, 80] because the interaction of the system with the TiDE provides the analogs of both the noise and the damping terms in the Langevin equation. In our earlier work, we fixed a noise sequence, but regarded the damping as part of the autonomous system dynamics. When the trajectory was changed, therefore, the damping force was allowed to adapt to the new trajectory immediately, while the noise was fixed. The interaction with the TiDE does not split into noise and damping (at least, not easily), and we will need to freeze all of the system-bath interaction. The TiDE oversampling will therefore be cruder than the oversampling in the Langevin equation.

In future work, we intend to use this strategy to address the unimolecular reorganization of LiCN and the bimolecular reaction of $H+H_2$ in argon baths. The latter reaction represents a simple model system for more general bimolecular reactions, and its parameterization was used as the basis for our earlier work in which the solvent is represented by implicit and stochastic forces.[78] The former reaction has recently been modeled [104] in argon baths using full molecular dynamics simulations under high temperature conditions. The latter condition is necessary because it speeds up the dynamics to a point in which brute-force calculations are accessible. Nevertheless, the results [104] indicate the existence of the so-called Kramers turnover in the rate as a consequence of changing the interaction between the reaction and the solvent. Implementation of our strategy should allow us go further by exploring substantially lower temperatures. An additional potential benefit of the implementation of the proposed methods will come from the resolution of the geometric structure of the putative transition paths of the environment of the system. That is, by analysis of the TiDEs that contribute most to the rate, we will be able to identify which geometric pathways of the system (coupled to the environment) are most important in each of these dynamical processes.

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