

Multidimensional Transition State Theory and the Validity of Grote–Hynes Theory

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The Grote–Hynes theory of nonequilibrium solvation effects on reaction kinetics is examined using the perspective provided by multidimensional transition state theory. The analysis is performed for a model in which a solute reaction coordinate is bilinearly coupled to a harmonic solvent bath, and we derive intermediate quantities that shed light on the ability of Grote–Hynes theory to capture relevant physical features of the reaction dynamics. One example is a separatrix distribution, in particular, the distribution $P(r)$ of values of the solute reaction coordinate on the variationally optimized transition state dividing surface for the multidimensional model. Another example is the reactive probability density dp/dP_B on a trial transition state dividing surface orthogonal to the solute reaction coordinate. The model is seen to be capable of producing wide $P(r)$ distributions and bimodal dp/dP_B distributions. The bimodal distribution of the reactive probability density can exist on a trial transition state dividing surface transverse to the solute reaction coordinate even if there is no solvent barrier. The bimodality of the reactive probability density arises from the wings of the Gaussian solvent coordinate distribution in regions away from the saddle point. The model is in good agreement with recent simulations of Na^+Cl^- ion pair dissociation in water. The deviations from conventional transition state theory can be interpreted as arising from solvent friction or from the participation of the solvent in the reaction coordinate.

1. Introduction

The subject of nonequilibrium solvation effects on reaction kinetics in liquids is currently receiving considerable attention.¹ A recent paper in this journal by Geissler et al.² provides considerable insight into the problem by an elegant analysis of the dissociation of Na^+Cl^- ion pairs in water. The authors show that the reaction coordinate involves rearrangement of water molecules near the ion pair and that one-dimensional variational transition state theory (based on the maximum of the free energy of activation profile along the reaction coordinate) with the Na^+ -to- Cl^- distance, r , as the reaction coordinate overestimates the reaction rate by a factor of ~ 5 . The authors also observed that a solvent coordinate was required to define a transition state dividing surface based upon a dynamical criterion. Furthermore, they observed a fairly broad distribution of values of r for this dividing surface and a bimodal distribution of the probability for relaxing into the product valley from an ensemble with r constrained to the maximum of the free energy curve. On the basis of these observations, the authors concluded² that such a picture is inconsistent with the Grote–Hynes³ (GH) theory of the transmission efficient κ . We do not find these arguments compelling, and the purpose of this note is to provide further discussion because we believe it is important to place alternative viewpoints in a common perspective.

2. Theory and Model

Grote–Hynes theory may be derived using the long-time limit of the velocity autocorrelation function for a reaction coordinate

with a potential that is quadratic all the way to reactant and product stable state regions in the presence of memory friction,³ or, as a short-time approximation, by applying variational transition state theory (VTST) with a locally quadratic potential.^{4–6} In the latter case, one applies VTST in the multidimensional r, \mathbf{q} space, where \mathbf{q} denotes a set of solvent coordinates, with a coupling term bilinear in r and \mathbf{q} and rotating the transition state dividing surface to minimize the local one-way flux.^{4–6} Figure 1 provides simple examples of this picture in which \mathbf{q} is a one-dimensional coordinate q . The free energy contours in the figure are generated by

$$F_{\text{eff}}(r, q) = F_{\text{act}}(r) + (\mu\omega_b^2/2)[q - C(r - r^*)]^2 \quad (1)$$

where $F_{\text{act}}(r)$ is the free energy of activation for the one-dimensional problem and is given by

$$F_{\text{act}}(r) = W(r) - 2kT \ln(r/r^*) \quad (2)$$

where $W(r)$ is the radial potential of mean force for Na^+Cl^- association and is taken to be the sum of an exponential and asymmetric Eckart potential; k is Boltzmann's constant; T is temperature; both coordinates r and q are scaled to the NaCl reduced mass μ ; and the coupling constant C and bath frequency ω_b characterize the solvent friction. The parameters of this simple model were fitted to qualitatively reproduce the potential of mean force (PMF) and time-dependent friction of Smith and Dang for the RPOL potential.⁷ The function $W(r)$ was fitted to give a value for the magnitude of the imaginary barrier

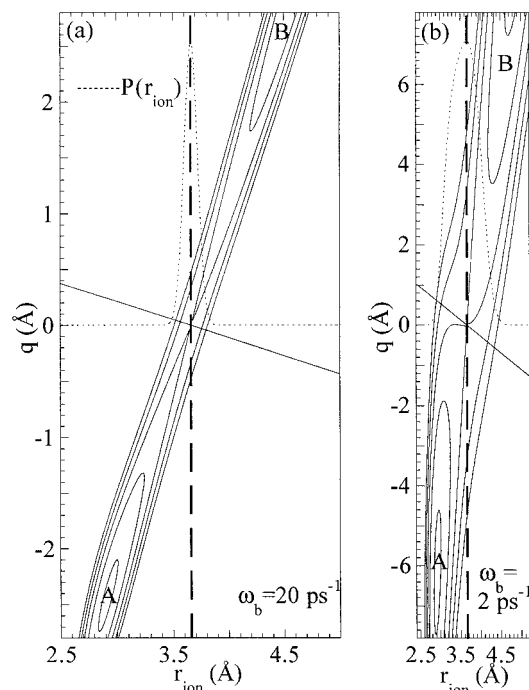


Figure 1. A two-dimensional model for reaction in a liquid. The plot shows contours of the effective free energy as a function of a solute coordinate r_{ion} and a solvent coordinate q . The reduced mass and length scale for each coordinate is the same so that classical dynamics can be imagined as a point mass moving on the surface. The long-dashed straight line is a possible transition state dividing surface; in particular, it is the conventional transition state choice for a one-dimensional theory if the reaction coordinate is r_{ion} . The solid straight line is the variational transition state dividing surface based on a quadratic approximation at the saddle point in the two-dimensional system. The short-dashed curve is the probability (from a 300 K Boltzmann distribution along the dividing surface) of the variational transition state having an ionic separation of r_{ion} . Parts a and b are for two sets of solvent potential parameters, but with the free energy of activation for the one-dimensional (r) problem the same. Parts a and b have bath frequencies of 20 and 2 ps^{-1} , respectively, with the coupling constant chosen in each case so that the GH value of κ is 0.3. In the figure, the $\text{Na}^+ - \text{Cl}^-$ distance r is denoted r_{ion} .

frequency, $|(d^2F_{\text{act}}/dr^2)|_{r=r^*}/\mu)^{1/2}$, of 15.5 ps^{-1} and a value of the barrier height of 1.9 kcal/mol. For the simple one-oscillator model, the friction is given by a single cosine term

$$\eta(t) = \mu\omega_b^2 C^2 \cos(\omega_b t) \quad (3)$$

where t is time. The friction computed by Smith and Dang has an initial short time decay over about 70 fs and a long time tail that extends to over 1 ps. Since a single cosine will not adequately fit this complicated behavior, we have chosen to consider two values for the bath frequency, 2 and 20 ps^{-1} , that imply time scales that are relevant to the dynamics of the system. The longer time scale (0.5 ps, corresponding to the former value of ω_b) is comparable to the range of time over which $\eta(t)$ contributes significantly to κ , and in particular it equals the time at which the plateau value of the transition rate is obtained in the calculation of Geissler et al. The shorter time scale (50 fs, corresponding to the latter value of ω_b) is comparable to the time scale of the initial decay of the friction of Smith and Dang. A different value of the coupling constant C is then chosen for each ω_b so that the Grote–Hynes value of κ calculated with a single time scale is 0.3, as calculated by Smith and Dang using GH theory based on the complete time dependence of the simulated $\eta(t)$. The transition state dividing surface for one-

dimensional VTST corresponds to $r = r^* = 3.66 \text{ \AA}$ and is depicted by a vertical long-dashed line in Figure 1. The multidimensional variational transition state dividing surface, as depicted by the solid line, is rotated so that $u_1(r - r^*) + u_2q = 0$, where u_1 and u_2 are determined variationally in the quadratic region around the saddle point, i.e., $F_{\text{act}}(r)$ is approximated by a parabolic barrier. It is visually clear that such a rotation can eliminate much of the recrossing.

Thus, although GH theory is often described as a one-dimensional motion along the reaction coordinate with friction (the buffeting of the solute by the solvent), the underlying physics is multidimensional, and it allows for the participation of the solvent in the reaction coordinate (which is the direction normal to the transition state dividing surface). In practice, the components of \mathbf{q} are generalized (collective) coordinates that represent solvent friction. The participation of solvent in the reaction coordinate does not invalidate GH theory. Conversely, the success of GH theory in explaining certain “frictional” recrossing phenomena in molecular dynamics simulations⁸ does not necessarily signal a breakdown of transition state theory. In fact, except where the agreement with simulations is fortuitous, the situation is just the opposite; it means that VTST with a suitable choice of solvent coordinate and an optimization of the orientation of the dividing surface does remove the recrossing. The multidimensional variational dividing surfaces, as depicted in Figure 1, also illustrate the fact that a distribution of values of interatomic distance is observed for this type of dividing surface. The distribution $P(r)$ in Figure 1b for this simple model is comparable in width to that observed by Geissler et al., so the observation of a distribution of r values of the dynamically determined transition state does not provide compelling evidence that GH theory is invalid for this system.

3. Calculation of a Reactive Probability Density

There is no doubt that realistic intermolecular potentials are not quadratic and critical couplings of solvent to solute are not linear. However, transition state dynamics is often determined in a limited region of space on a very short time scale, and it is still an open research question to learn to what extent critical solvent motions of various kinds can be usefully modeled as quasiharmonic variables linearly coupled to the solute during the time period that determines the reaction rate. A more compelling demonstration that the dynamics of ion pair dissociation (or any other reaction) is inconsistent with GH theory would be to show that one of the inherent approximations (such as linear response) is not valid. In fact, Geissler et al. focused on a related issue by calculating the probability density dp/dP_B of the probability P_B for phase points on the $r = r^*$ dividing surface to evolve to products (region B). Their conclusion that GH theory is too simple to explain ion pair dissociation in water is based primarily on their finding that this distribution is bimodal, which was interpreted as an inherent manifestation of nonlinearity. However, we will now show that this bimodality is not inconsistent with GH theory or linear response.

Geissler et al. define the probability density as follows. For a given initial configuration of the total system (including solvent molecules) with r constrained to r^* , P_B is defined as the fraction of trajectories initiated with random momenta which evolve to region B. The probability density was then determined as the probability that a value of P_B occurs in a sample of 1000 initial configurations. This distribution cannot be determined from GH theory by using the one-dimensional model with friction, since solvent coordinates and momentum are not explicitly treated in this approach, but are implicit in an averaged

sense in the friction and random force terms of the GLE. What can be obtained in this picture is the average of P_B over all initial solvent configurations, which should be $1/2$ by the arguments presented by Geissler et al. However, this averaged value of P_B should not be compared with the distribution dp/dP_B . Indeed, the near symmetry of the calculated dp/dP_B about $P_B = 0.5$ indicates that in the simulations the average of P_B over solvent configurations should also be approximately $1/2$. In contrast to the one-dimensional model with friction, if GH theory is viewed (as above) as a multidimensional variational transition state theory, then the quantity dp/dP_B can be directly calculated for comparison with the simulated curve. In the following paragraph, we provide a detailed derivation of the expressions for the probability P_B for phase points on the $r = r^*$ dividing surface to evolve to region B and for the probability density that a value of P_B occurs for Grote–Hynes theory in which the friction is approximated by a single harmonic oscillator.

The probability P_B that trajectories starting from $r = r^*$ and q will evolve to region B is given by

$$P_B(r=r^*, q) = \frac{\int_{-\infty}^{\infty} dp_r \int_{-\infty}^{\infty} dp_q \exp[-(p_r^2 + p_q^2)/2\mu kT] \theta[\lim_{t \rightarrow \infty} r(t) - r^*]}{\int_{-\infty}^{\infty} dp_r \int_{-\infty}^{\infty} dp_q \exp[-(p_r^2 + p_q^2)/2\mu kT]} \quad (4)$$

where p_r and p_q are the momenta conjugate to r and q , respectively, and θ denotes a Heaviside function. This expression can be most easily evaluated by transforming to normal coordinates \mathbf{z} defined by

$$\begin{pmatrix} r - r^* \\ q \end{pmatrix} = \begin{pmatrix} u_1 & -u_2 \\ u_2 & u_1 \end{pmatrix} \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} \quad (5)$$

where the matrix elements of the unitary transformation matrix are given by

$$u_1 = (\bar{\omega}^2 + \sqrt{\bar{\omega}^4 + C^2 \omega_b^4})[(\bar{\omega}^2 + \sqrt{\bar{\omega}^4 + C^2 \omega_b^4})^2 + C^2 \omega_b^4]^{-1/2} \quad (6)$$

$$u_2 = C \omega_b^2 [(\bar{\omega}^2 + \sqrt{\bar{\omega}^4 + C^2 \omega_b^4})^2 + C^2 \omega_b^4]^{-1/2} \quad (7)$$

and the harmonic frequencies are given by

$$|\omega_1|^2 = \frac{1}{2}[-|\omega^\ddagger|^2 + (1 + C^2)\omega_b^2] - (\bar{\omega}^4 + C^2 \omega_b^4)^{1/2} \quad (8)$$

$$\omega_2^2 = \frac{1}{2}[-|\omega^\ddagger|^2 + (1 + C^2)\omega_b^2] + (\bar{\omega}^4 + C^2 \omega_b^4)^{1/2} \quad (9)$$

where

$$\bar{\omega}^2 = \frac{1}{2}[|\omega^\ddagger|^2 + (1 - C^2)\omega_b^2] \quad (10)$$

and ω^\ddagger is the imaginary frequency for the unbound mode of the variational transition state computed from $F_{\text{act}}(r)$. For the parabolic model in the normal coordinates, the dynamics are easily solved to give

$$z_1(t) = z_1^0 \cosh(|\omega_1|t) + \frac{p_1}{\mu|\omega_1|} \sinh(|\omega_1|t) \quad (11)$$

$$z_2(t) = z_2^0 \cos(\omega_2 t) + \frac{p_2}{\mu\omega_2} \sin(\omega_2 t) \quad (12)$$

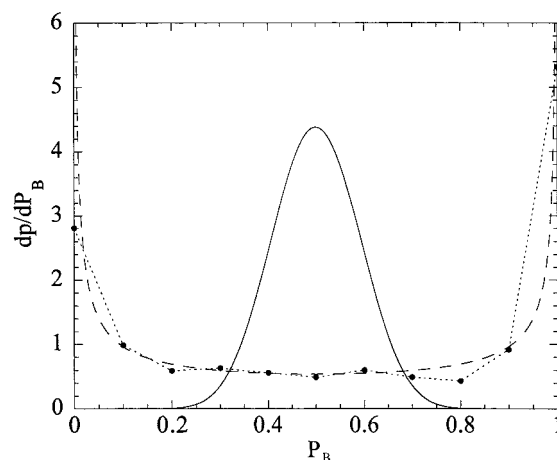


Figure 2. Probability density dp/dP_B of the probability P_B for phase points on the $r = r^*$ dividing surface to evolve to products (region B). The solid and long dashed lines are for the solvent model with bath frequencies of 20 and 2 ps^{-1} , respectively. The short dashed line with symbols is a reproduction of the simulated values of Geissler et al.

where z_1^0 , z_2^0 , and p_1 , p_2 are the initial coordinates and momenta for modes 1 and 2. Using eqs 11 and 12 with the transformation in eq 5, the long time limit of $r(t)$ is dominated by the behavior of the unbound normal mode so that

$$\lim_{t \rightarrow \infty} r(t) - r^* = u_1 \left(z_1^0 + \frac{p_1}{\mu|\omega_1|} \right) \frac{\exp(|\omega_1|t)}{2} \quad (13)$$

for initial geometries constrained to $r = r^*$, $z_1^0 = u_2 q$. Therefore, P_B can be written in the normal coordinates as

$$P_B(r=r^*, q) = \frac{\int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \exp[-(p_1^2 + p_2^2)/2\mu kT] \theta\left(u_2 q + \frac{p_1}{\mu|\omega_1|}\right)}{\int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \exp[-(p_1^2 + p_2^2)/2\mu kT]} \quad (14)$$

$$= \frac{1}{2} \text{erfc}\left(-\sqrt{\frac{\mu}{2kT}} |\omega_1| u_2 q\right) \quad (15)$$

where $\text{erfc}(x)$ is the complementary error function. The probability density dp/dP_B is the probability that P_B occurs when averaged over the probability density dp/dq of a solvent configuration q , which is given by

$$\frac{\partial P}{\partial q}(r=r^*, q) = \left(\frac{\mu\omega_b^2}{2\pi kT}\right)^{1/2} \exp\left(-\frac{\mu\omega_b^2 q^2}{2kT}\right) \quad (16)$$

The probability density dp/dP_B is then obtained as

$$\frac{dp}{dP_B}(P_B^*) = \int_{-\infty}^{\infty} dq \frac{\partial P}{\partial q} \delta[P_B^* - P_B(r=r^*, q)] \quad (17)$$

$$= \frac{\omega_b}{u_2 |\omega_1|} \exp\left[-\frac{\mu}{2kT} (\omega_b^2 - u_2^2 |\omega_1|^2) q_0 (P_B^*)^2\right] \quad (18)$$

where δ is the Dirac delta function, and $q_0(P_B^*)$ is defined by $P_B(r=r^*, q_0) = P_B^*$. Equation 18 is plotted in Figure 2.

We note that $P_B(r=r^*, q)$ increases monotonically from 0 to 1 as q increases from negative to positive. However, the Boltzmann distribution, dp/dq ($r=r^*, q$), is a Gaussian curve centered at $q = 0$. For large ω_b , P_B accomplishes most of its

rise near $q = 0$, and dp/dq is narrow. For smaller ω_b , if the coupling constant C is increased to maintain a fixed GH prediction of κ equal to 0.3, P_B rises more gradually (broader curve), but the Boltzmann distribution broadens much more rapidly, thereby giving more weight to the values of P_B near to 0 and 1 at the expense of those near to 0.5.

4. Discussion

The probability P_B for phase points on the $r = r^*$ dividing surface to evolve to region B from an initial solvent configuration (q) is given in the two-dimensional GH theory by eq 15, and the probability density $dp/dP_B(P_B^*)$ is given by eq 18. Figure 2 shows dp/dP_B for the two choices of the bath frequencies. Equations 15 and 18 and Figure 2 clearly show that GH theory does *not* predict $P_B \approx 1/2$ for all configuration atop the barrier ($r = r^*$). Furthermore, for one physically reasonable choice of the solvent parameters, GH theory reproduces the main qualitative feature (the bimodal distribution) of the dp/dP_B curve that was accurately calculated by Geissler et al. This result is easily understood from Figure 1b. An appreciable fraction of the statistically significant points on the dashed line that lie above the variational dividing surface (the solid line) have $P_B \approx 1$. The slight asymmetry in the accurate distribution is not seen in the simple model, and this feature may be due to anharmonicity, but the bimodal distribution is clearly not a signature that anharmonic effects are important or that GH theory is invalid for this system.

It has been emphasized elsewhere that GH theory is limited by its assumptions, such as quadratic potentials, bilinear coupling, and classical mechanics.^{1,9} But the two ways of deriving GH theory provide an illustration of the fact that the frictional picture and the picture of solvent participation in the reaction coordinate may provide two complementary (but—in a limit—equivalent) ways of looking at the same phenomenon rather than mutually exclusive scenarios. Often one tends to think of solvent dynamics as providing a fictional drag on solute motion when one does not understand the mechanism of the solvent effect at the atomic level. If one can identify the physical nature of the effect, e.g., slow adjustment of solvent reorientational polarization or motion of solvent molecules into the first coordination shell, it is often more fruitful to explicitly include those solvent degrees of freedom and find the variational transition state in the extended space.¹⁰ The importance of GH theory is that it is the simplest example of coupling a reaction

coordinate to a bath mode. The analysis of Geissler et al. is important in that it can help us to understand the nature of the relevant solvent motions so they can be modeled more effectively. In fact, they find that the important solvent motion in the reaction coordinate involves changes to the Na^+ ion coordination which requires solvent center-of-mass motion rather than just orientational changes in the solvent that are often assumed to be important for processes involving changes in charge distributions. Time correlation functions for center-of-mass motion in water typically have much longer decay times (e.g., 500 fs) than those for orientational motion (e.g., 10–20 fs). The role of the center of mass motion is consistent with our finding that the smaller frequency (longer time scale) provides a better model of the dynamical observation of Geissler et al.

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