Shortcomings of current theories of non-Markovian activated rate processes[a)]

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The calculation of barrier crossing rate constants is an important problem in chemical physics. Recent work has focused on the non-Markovian effects where a particle (of unit mass) is described by a generalized Langevin equation[1-7]

$$\ddot{x} = -\frac{\partial U(x)}{\partial x} - \int_0^t dt'\, \zeta(t-t')\dot{x}(t') + R(t), \qquad (1)$$

where the random force $R(t)$ satisfies the fluctuation–dissipation theorem and $U(x)$ is a symmetric double well potential with energy barrier βQ in units of $k_B T$.

If the dynamics in the *intermediate and overdamped regime* is solely determined by the potential near the top of the barrier one can approximate the potential by an inverted parabola. As first shown by Grote and Hynes[1,2] the rate constant for this case is

$$k_{\mathrm{GH}} = k_{\mathrm{TST}} \frac{\lambda}{\omega_B}, \qquad (2)$$

where ω_B is the barrier frequency, $k_{\mathrm{TST}} = (\omega_0/2\pi)e^{-\beta Q}$ is

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the transition state rate constant, ω_0 is the well frequency, and λ is the largest positive root of

$$\lambda^2 + \lambda\hat{\zeta}(\lambda) = \omega_B^2, \tag{3}$$

where $\hat{\zeta}(s)$ is the Laplace transform of the time dependent friction kernel $\zeta(t)$.

In the *underdamped regime* the energy diffusion mechanism becomes rate limiting [3–5] and the rate constant is approximately given by

$$k_{ED} \simeq \mathrm{Re}\,\hat{\zeta}(-i\omega_0)\frac{\beta Q}{2}e^{-\beta Q}. \tag{4}$$

It has been argued recently[4,5] that only these two mechanisms contribute so that the overall rate constant k should be well approximated by the stable states formula[1,4]

$$k^{-1} \simeq k_{GH}^{-1} + k_{ED}^{-1} \tag{5}$$

or similar relations.[5]

Given the importance of these ideas we have decided to test their validity against full stochastic simulations. In this study we focus on a simple exponential friction kernel with Laplace transform

$$\hat{\zeta}(s) = \frac{\gamma}{1+\tau_c s}; \quad \tau_c = \alpha\gamma, \tag{6}$$

where γ is the static friction and τ_c is the correlation time. This friction kernel resembles closely the frequency dependent part of the hydrodynamic friction studied in the theory of reaction rates[6] if τ_c is proportional to the damping γ. We thus take $\tau_c = \alpha\gamma$.

We study this problem numerically by considering the system[7]

$$\begin{aligned} \dot{x} &= v, \\ \dot{v} &= -\frac{\partial U(x)}{\partial x} + z, \\ \dot{z} &= -\frac{1}{\alpha\gamma}z - \frac{1}{\alpha}v + \xi. \end{aligned} \tag{7}$$

Elimination of the variable z yields Eq. (1) with the friction kernel [Eq. (6)]. The spectral density of the white Gaussian noise $\xi(t)$ is adjusted to reproduce the correct random force of Eq. (1). Numerical integration of Eq. (8) is achieved using an Adams–Moulton predictor–corrector algorithm[8] and the random force is approximated by a constant during one integration step.[9] The rate constant is determined using the rapid absorbing boundary method.[9]

In this Communication we report results for a symmetric piecewise harmonic double well potential [5,10] ($\beta Q = 20$ and $\omega_B/\omega_0 = 2$). The static friction coefficient γ is varied at fixed $\omega_B^2\alpha = 4/3$. The rate constant k_{GH} of Grote–Hynes theory, Eq. (2), [see Fig. 1 (---)] approaches a constant ($k_{GH}/k_{TST} \to 1/2$) for large γ since the correlation time $\tau_c = \alpha\gamma$ increases with γ. The energy diffusion rate constant k_{ED} was evaluated numerically from exact expressions presented elsewhere.[3] One finds that Eq. (5) is accurate to within a few percent in this particular case. As shown in Fig. 1 (— —) k_{ED} increases initially with γ but since the correlation time also rises k_{ED} goes through a maximum (not shown in Fig. 1) and decreases like $1/\gamma$ for large γ. Note that for our particular choice of parameters one remains in the weak to moderate friction regime for all γ. If the overall rate constant

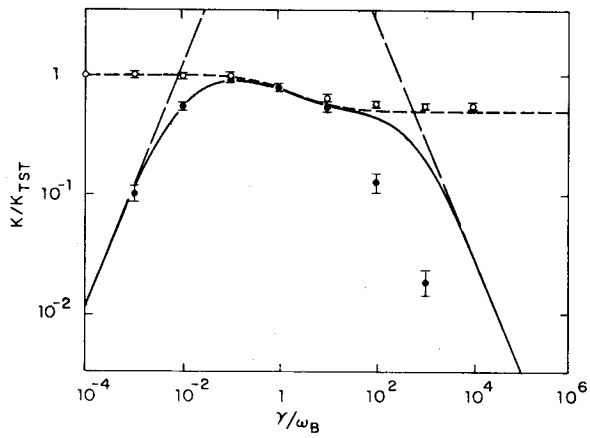

FIG. 1. Barrier crossing rate constants vs the static friction γ for a non-Markovian bath. The prediction of the Grote–Hynes theory [Eq. (2) (---)], the energy diffusion mechanism [Eq. (4) (— —)], and the overall rate constant Eq. (5) (—) within this model. Dots are simulation data (with 95% confidence intervals) for the symmetric double well potential (●) and the inverted parabola (○).

k is given by Eq. (6) [see Fig. 1 (—)] the Grote–Hynes theory should be rate limiting over a wide range of γ.

The simulation data (●) in Fig. 1 agree well with Eq. (6) at low γ. Surprisingly, however, for large γ the simulations show a much faster decrease (roughly as $1/\gamma$) in complete disagreement with the Grote–Hynes theory.

As a check, another stochastic simulation was run using the inverted parabolic barrier instead of the double well potential. For this potential the Grote–Hynes theory should be correct and should give the same results as the simulation. Indeed, for this case our simulation data shown in Fig. 1 (○) agree well with the Grote–Hynes theory (---).

In conclusion we have demonstrated that a simple interpolation formula [Eq. (6)] which is based solely on the Grote–Hynes theory and energy diffusion mechanism can fail by orders of magnitude in the intermediate regime. In this regime the rate constant is very sensitive to anharmonicities in the potential. This can be most clearly seen by comparing the simulation data for the double well (●) with those for the corresponding parabola (○) in Fig. 1. The Grote–Hynes theory, while correct for the inverted parabola, cannot generally be applied to evaluate rate constants for double well potentials. For this reason we question earlier interpretations of weak viscosity dependence of isomerization rate data[6] which were based on the application of Grote–Hynes in the intermediate regime.

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