

Reply to Comment on: Diffusion theory of multidimensional activated rate processes: The role of anisotropy

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The problem of two dimensional overdamped anisotropic diffusion is governed by two small parameters, (i) the thermal energy $\epsilon \equiv k_B T / \Delta V$, where ΔV is a reference activation energy (e.g., the height of the saddle point above the bottom of the reactant well), and (ii) the anisotropy parameter $\delta \equiv \eta_x / \eta_y$, where η_x and η_y are the two damping coefficients (assuming the friction tensor is diagonal). Therefore the two limits, (a) first $\epsilon \rightarrow 0$, then $\delta \rightarrow 0$, and (b) first $\delta \rightarrow 0$, then $\epsilon \rightarrow 0$, must be considered separately, because it is not *a priori* clear that they are interchangeable. Indeed, there are cases when they are not, as correctly pointed out in Ref. 2.

It should be pointed out however that the analysis presented in Ref. 1 is concerned with the limit (a). The limit (b) is considered there only for the case $A > 0$, for which the limits (a) and (b) are indeed interchangeable (here $A \equiv V_{xx}$ at the saddle point). The results for the case $A \leq 0$ in Ref. 1 are valid only in the limit (a), so that the comment "the cases $A \leq 0$ can be handled in a similar manner" is misleading, as correctly pointed out in Ref. 2.

Unfortunately, some of the statements, as well as the result

$$\kappa = \frac{|V_{\text{eff}}^*(y_r) V_{\text{eff}}^*(y_b)|^{1/2}}{2\pi\eta_y} e^{-\Delta V_{\text{eff}}/k_B T}, \quad (1)$$

presented in Ref. 2, are not correct. First, the effective potential

$$V_{\text{eff}}(y, \epsilon) \equiv -\epsilon \ln \int_{-\infty}^{\infty} e^{-V(x,y)/\epsilon} dx, \quad (2)$$

which governs the motion of the slow variable y , does not necessarily form a double well, as claimed in Ref. 2. Consequently (1) [that is, formula (2) in Ref. 2] is not correct in general. Even in the case that $V_{\text{eff}}(y, \epsilon)$ does form a double well, while the exponential part of (1) may be correct, the preexponential factor in (1) is not. For although the reduced one-dimensional problem appears to be identical to that treated in Ref. 3 (the so-called Smoluchowski problem), in fact it is not. The effective potential (2) is almost sharp, its curvature at the top is $O(1/\epsilon)$, and its slopes at a distance $O(\epsilon)$ on either side of the point y_M where it achieves its local maximum, are $O(1)$ and have opposite signs. Therefore Laplace's expansion of integrals, which is the basis for the results of Ref. 3, and hence of (1), is inapplicable.

Instead, we present a different formula for the rate in the limit (b), for the case $A < 0$. We assume that the potential $V(x, y)$ has two local minima at (x_A, y_A) and

(x_B, y_B) , and that V_{eff} is a double well potential. We also assume, for simplicity of presentation, that $V(x, y_M)$, as a function of x , has two wells of equal depth. We find that the escape rate is then given by

$$\kappa = \frac{\delta \sqrt{\mathcal{H}}}{2\pi \int_{y_A}^{y_B} e^{V_{\text{eff}}(t)/\epsilon} dt} e^{V(x_A, y_A)/\epsilon}, \quad (3)$$

where $\mathcal{H} = |V_{xx}(x_A, y_A) V_{yy}(x_A, y_A) - V_{xy}^2(x_A, y_A)|$. Evaluating the integral in the denominator of (3) for $\epsilon \ll 1$ we obtain

$$\begin{aligned} \kappa \approx & \delta \frac{\sqrt{\mathcal{H}} |V'_L| (\omega_R + \omega_L)}{\pi \sqrt{2\pi\epsilon\omega_L\omega_R}} \left(\frac{\omega_R}{\omega_L}\right)^{\omega_R/(\omega_L + \omega_R)} \\ & \times \sin \frac{\pi\omega_L}{\omega_L + \omega_R} e^{-\Delta V_{A,M}/\epsilon}, \end{aligned} \quad (4)$$

where

$$\begin{aligned} V'_L & \equiv V_y[x_L(y_M), y_M], \\ \omega_{L,R} & \equiv \sqrt{V_{xx}[x_{L,R}(y_M), y_M]}, \\ \Delta V_{A,M} & \equiv V[x_L(y_M), y_M] - V(x_A, y_A). \end{aligned} \quad (5)$$

In the very special case that the potential $V(x, y)$ is so symmetric that $\omega_L = \omega_R \equiv \omega_M$, we find that (4) reduces to

$$\kappa \approx \delta \frac{\sqrt{2\mathcal{H}} |V'_L|}{\pi \sqrt{\pi\epsilon\omega_M}} e^{-\Delta V_{A,M}/\epsilon}. \quad (6)$$

It can be readily seen that the dimensional form of (3), and even of (6), differ from (1).

The problem of anisotropic diffusion in the case $A < 0$ has much more structure than indicated in both Ref. 2 and references therein, and in Ref. 1. Some elementary notions, such as the geographical location of the stochastic separatrix in the (x, y) plane, that is, the location of the transition region, the time scales on which changes occur, the relative sizes of the first two nonzero eigenvalues, and so on, have to be clarified before definite statements about the activation process can be made. To clarify the notion of activation in the strongly anisotropic case, the reactant and product wells should be defined in a way that reflects the sojourn times of the stochastic trajectories in various parts of the (x, y) plane. As pointed out in Ref. 1, the ridge R of the potential does not partition the plane into two parts which are characterized by long sojourn times. It is rather the *stochastic separatrix* S that accomplishes this partition. It is defined as the locus of initial points of stochastic trajectories which are equally likely to end up near the bottom

of one well as they are to end up near the other. In certain cases S is the deterministic separatrix Γ , e.g., if $A > 0$ (see Ref. 1). However, if $A < 0$, it can be shown that for an extremely anisotropic system S tends to the line $y=y_M$. The point y_M can be located practically anywhere on the y axis, depending on the structure of the two wells. Therefore R , Γ , and the saddle point are not directly relevant to the definitions of the reactant and product wells nor to the activation process. Rather, reactant and product are determined by S .

We observe that the partition into reactant and product wells determined by S , reflects what is actually measured in, e.g., single bond rotational isomerization reactions (see, e.g., Refs. 4 and 5). That is, observationally one measures and distinguishes between populations on either side of S , rather than R or Γ .

These and related issues will be considered in detail, in a paper which is in preparation.

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