The Influence of Dimensionality on the Rate of Diffusive Escape From an Energy Well

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A commonly used idealization when describing separation of a chemical bond between molecules is that of an energy well which prescribes the dependence of energy of interaction between the molecules in terms of a reaction coordinate. The energy difference between the peak to be overcome and the root of the well is the so-called activation energy, and the overall shape of the well dictates the kinetics of separation through a constitutive assumption concerning transport. An assumption tacit in this description is that the state of the bond evolves with only a single degree of freedom—the reaction coordinate—as the system explores its energy environment under random thermal excitation. In this discussion we will consider several bonds described by one and the same energy profile. The cases differ in that the energy profile varies along a line extending from the root of the well in the first case, along any radial line in a plane extending from the root of the well in a second case, and along any radial line in space extending from the root of the well in a third case. To focus the discussion we determine the statistical rate of escape of states from the well in each case, requiring that the profile of the well is the same in all three cases. It is found that the rates of escape each depend exponentially on the depth of the well but that the coefficients of the exponential vary with depth of the well differently in the three cases considered. [DOI: 10.1115/1.4005895]

Introduction

A number of models of material behavior rely on an understanding of the rate of separation of molecular bonds under random thermal excitation or due to stress induced bias. A perusal of textbooks that include discussion of this idea leaves the impression that such bonds can be characterized by a single generalized coordinate or degree of freedom, although several studies based on wells of higher dimension have been reported in the literature; for example, see [1] and [2]. While escape of a state from a one-dimensional well provides a useful framework for qualitative understanding of bond separation, the role of dimensionality on transition rates of a bond remains relatively unexplored. If the configurations of the bound molecules are represented by points, then three coordinates are needed to describe relative positions; for points with orientations, six coordinates are required to represent the state of the bond. The purpose here is to report on a study of the influence of dimensionality of bond state representation on a particular transition, namely, the so-called *off-rate* for a bond under random thermal excitation.

As a basis for proceeding, we adopt a particular profile for a bond well in any number of dimensions, say

$$U(r) = kT\hat{U}(r) = kT \begin{cases} -c_b \left(1 - \frac{r^2}{a^2}\right)^2, & r \leq a \\ 0, & r > a \end{cases} \quad (1)$$

where the nondimensional number c_b represents the well depth in units of kT and a is a measure of the well width. The coefficient kT is a product of the Boltzmann constant k and the ambient temperature in degrees Kelvin. Thus c_b is the well depth in units of kT , which has a value of about 4 pN nm at room temperature. The profile (1) is sketched in Fig. 1.

A one-dimensional bond for states along a line within $-a < r < a$ by reflection of the profile (1) with respect to $r = 0$, a bond for states within a circle of radius a in a plane is defined by rotating the profile about an axis through $r = 0$, and a three-dimensional bond is defined within a spherical region of radius a by assuming that the confining energy varies with distance according to the profile along every radial line emanating from the common point $r = 0$.

According to reaction rate theory, the off-rate η for a large number of nominally identical, noninteracting bonds is defined in the following way. If the number of intact bonds among them at time $t = 0$ is n_0 , and if no bond is reformed once separated, then the number n of intact bonds at time $t > 0$ is given by $n = n_0 e^{-\eta t}$. Equivalently, $\eta > 0$ is the ratio of the instantaneous rate of decrease in the number of intact bonds to the total number of instantaneously intact bonds. In the context of the present discussion, this is equivalent to the ratio of the net flux of bonds out of the energy well to the total number of bonds remaining within the well. This ratio is calculated here in terms of the properties of bond wells in one, two, or three dimensions, each with the profile (1). The calculation procedure for two dimensions is developed in some detail and results for the other two cases are stated by analogy.

A Confining Potential in Two Dimensions. As a representative case the state of a molecular bond is assumed to have two degrees of freedom and, consequently, all accessible states can be represented by the points in a plane. Any particular state can be identified by its plane polar coordinates r and θ , where r is the length of a radial line from the point of lowest bond energy to the point representing the current state and θ is the angular orientation of that line with respect to some arbitrary but fixed reference orientation.

The free energy of the bond state, here denoted by $\mathcal{U}$, is assumed to depend only on the current values of the coordinates r , θ that characterize the state. Specifically, the bond energy is zero when r assumes large values in some sense, indicating that the molecules are separated beyond each other's influence.

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Fig. 1 The profile of energy versus distance which provides the common basis for identification of energy bond wells on one, two, and three dimensions

Essentially, the polar coordinates are viewed as representing the position of one molecule of the bond pair with respect to the other molecule, but other interpretations are useful for some purposes.

When the molecules are fully bound, that is, at their minimum energy configuration, the state of the bond is identified with the origin of coordinates in the plane. All other accessible states of the bond are represented by means of a surface of elevation $\mathcal{U}(r, \theta)$ over the coordinate plane. This surface, which is assumed to be continuous and relatively smooth, has the properties that $\mathcal{U} \rightarrow 0$ as $r \rightarrow \infty$ and that it assumes its minimum value that $r = 0$.

An axisymmetric example of such a surface based on the profile (1) is

$$\mathcal{U}(r, \theta) = kT\hat{\mathcal{U}}(r, \theta) = kT \begin{cases} -c_b \left(1 - \frac{r^2}{a^2}\right)^2, & r \leq a, \quad 0 < \theta < 2\pi \\ 0, & r > a, \quad 0 < \theta < 2\pi \end{cases} \quad (2)$$

where c_b represents the maximum depth of the bond well as a multiple of the reference thermal energy kT ; as such, the parameter c_b is dimensionless.

The state of the bond at any instant of time corresponds to some particular point in the plane spanned by the coordinates (r, θ) . Because of its immersion in a thermal environment, the state of the bond varies randomly over points in the plane as a result of the fluctuations in position that it experiences. Consequently, the configuration of the bond is described in terms of the *probability* of being at any particular place at a certain instant of time. According to the central limit theorem, a very large number of noninteracting identical bonds will have an actual density of states identical to the probability distribution for the state of any particular bond. On this basis, attention is redirected to the study of the time evolution of the density of states of a large number of identical noninteracting bonds; this density of states is here denoted by $\rho(r, \theta, t)$.

A feature of a diffusive process is that the energy imparted to a state as a result of its immersion in a thermal environment, which appears in the form of fluctuations in state, is rapidly returned to that environment through small steps. In other words, the energy dissipation during microscopic motion is relatively rapid and the change in configuration or step size executed as a result of that excitation is very small on the scale of a . It follows that the escape of a state from the well is a rare event among all changes in configuration. Under such conditions, the evolution in time of the density of states ρ is essentially a continuous diffusion process.

The density of states in the plane evolves according to a local flux of states $\mathbf{j}(r, \theta, t)$ representing the fractional number of states

crossing a line in the plane that is perpendicular to the flux vector, measured per unit time and per unit length along that line. Local conservation of states requires that the rate of change of probability density at a point is balanced by the local divergence of the flux vector according to

$$\partial_t \rho + \nabla \cdot \mathbf{j} = 0 \quad (3)$$

The flux is driven by a gradient in chemical potential arising from both a gradient in density of states and a gradient in the confining potential. If it is assumed that the flux of states varies linearly with the chemical potential gradient and that the proportionality factor is the spatially uniform and isotropic diffusivity D , then

$$\mathbf{j} = -D(\nabla \rho + \rho \nabla \hat{\mathcal{U}}) = -D e^{-\hat{\mathcal{U}}} \nabla (\rho e^{\hat{\mathcal{U}}}) \quad (4)$$

The evolution of the density of states is then determined by solving the partial differential equations (3) and (4) throughout the relevant region of the plane, given an initial density of states and suitable conditions on the boundaries of the region considered. The second or alternate form of the transport equation (4) shows that the flux of states in everywhere normal to the level curves of the surface defined by the function of position $\rho e^{\hat{\mathcal{U}}}$ in the plane at any fixed time.

The Off-Rate for the Potential. The bond well (2) is rotationally symmetric. If the initial distribution of bonds in the well is also rotationally symmetric, then symmetry alone dictates that both the density of states $\rho(r, t)$ and the radial component of the flux of states $j_r(r, t)$ are independent of angular position θ and that the circumferential component of the flux j_θ is identically zero at all points of the plane. Therefore, the governing equations reduce to

$$\partial_t \rho + \frac{1}{r} \partial_r (r j_r) = 0, \quad j_r = -D(\partial_r \rho + \rho \partial_r \hat{\mathcal{U}}) \quad (5)$$

Once a solution of the differential equations is in hand, the off-rate is expressed in terms of $j_r(r, t)$ and $\rho(r, t)$ according to

$$\eta = \frac{2\pi a j_r(a, t)}{\int_0^a 2\pi r \rho(r, t) dr} \quad (6)$$

where $j_r(a, t)$ is the flux of states across the circle $r = a$ and the common factor 2π has been retained as an aid in interpreting the expression. In order to determine this flux, it is necessary to specify a boundary condition on a particular circular boundary, say $r = b$, that essentially identifies b as the *radius of no return* for any particular state. Once a state diffuses to a point beyond radius b , it will never again be found within the well. A common boundary condition that corresponds to this requirement is $\rho(b, t) = 0$. In the particular example developed here, it is assumed that the radius of no return is the crest of the well at $r = a$ and that the corresponding boundary condition is

$$\rho(a, t) = 0 \quad (7)$$

Situations for which $b > a$ can be examined by the same general approach as is introduced here, but transport conditions on the plane $\mathcal{U} = 0$ must be enforced throughout the annular region $a < r < b$. This feature is avoided here to keep the details as simple as possible. The off-rate is the specific quantity for which a value is sought in terms of the parameters c_b and a which characterize the bond well.

For any specific potential $\mathcal{U}(r)$, the partial differential equations (5) are linear but the coefficients of the gradient terms in the equations depend on the independent variable r . Consequently, a

closed form solution is not available in general. Therefore, we seek an approximate expression for the off-rate η in terms of c_b and a , and then make use of numerical or other methods to get a measure of the quality of that approximation. The approximation is obtained by means of a restatement of the governing equations in variational form, as described in the next section, based on a framework for doing so introduced by Needleman and Rice [3].

Variational Form of the Governing Equations. In this section the mathematical problem outlined in the previous section is restated in variational form; the reason for doing so is that the stationary property of a functional of the desired solution field provides a powerful basis for extracting approximate behavior of the governing differential equations introduced above. To this end, a functional defined over the range of all admissible flux vectors and stationary at an extreme value for the actual flux vector is identified. While equivalent to the partial differential equations already introduced, the variational principle has the added advantage that it provides a basis for finding accurate approximate solutions for mathematical problems of the type described in the preceding section. Although the discussion in the previous section was focused on describing physical phenomena in two space dimensions and time, the variational principle is stated in terms of an arbitrary number of space dimensions and time with a view toward its application to the study of a broader range of phenomena.

An observation that is important for understanding the statement of the variational principle follows from the conservation equation (3) in its general form, valid in any number of dimensions. Given an initial spatial distribution of the probability density, say $\rho(x, 0)$, the conservation equation can be integrated term by term to yield

$$\rho(\mathbf{x}, t) = \int_0^t \nabla \cdot \mathbf{j}(\mathbf{x}, \tau) d\tau + \rho(\mathbf{x}, 0), \quad 0 < t \quad (8)$$

This expression states that the current value of the density of states at a fixed value of x is determined by the initial value of density at that point and by the *history* of the flux of states at that point. In particular, for a given history of flux, the *current* value of the density of states is *independent* of the current value of flux throughout the range of x . As will be seen below, this observation is important for a proper statement of the variational principle.

We introduce the functional $\Phi[\mathbf{j}]$ for which a value can be determined for any admissible distribution of flux $\mathbf{j}(x, t)$ over some range of spatial coordinates x ; this range is identified by the symbol $\mathcal{A}$. In the two-dimensional configuration described in the preceding section; for example, $\mathcal{A}$ is that portion of the plane bounded by a circle of radius a centered at the origin. The boundary of $\mathcal{A}$ is identified by the symbol $\mathcal{C}$; in the context of the two-dimensional configuration above, $\mathcal{C}$ identifies the circle $r = a$. In the case of a spatial domain spanned by an arbitrary number of dimensions, the coordinates are represented symbolically by x , the domain spanned by x is again denoted by $\mathcal{A}$ and its boundary by $\mathcal{C}$.

The functional of interest is

$$\begin{aligned} \Phi[\mathbf{j}] = & \int_{\mathcal{A}} \left(\frac{1}{2} \mathbf{j}(\mathbf{x}, t) \cdot \mathbf{j}(\mathbf{x}, t) - D\rho(\mathbf{x}, t) \nabla \cdot \mathbf{j}(\mathbf{x}, t) \right) e^{\hat{\mathcal{U}}(\mathbf{x})} d\mathcal{A} \\ & + \int_{\mathcal{C}} D\mathbf{n} \cdot \left(\mathbf{j}(\mathbf{x}, t) \rho(\mathbf{x}, t) e^{\hat{\mathcal{U}}(\mathbf{x})} \right) d\mathcal{C} \end{aligned} \quad (9)$$

where $\mathbf{n}$ is a unit vector of appropriate dimensions that is normal to the boundary $\mathcal{C}$ and that is directed outward from $\mathcal{A}$. For a given past history of flux distribution, the actual flux distribution at the present instant of time is that for which the functional is stationary under small amplitude variations from that distribution. It is evident from (8) that, although the local value of the density of states depends on past history of the local flux distribution, it is inde-

pendent of the current value. Consequently, it is independent of any variation in the current value of flux. Straightforward application of the methods of the calculus of variations leads to the conclusion that the Euler-Lagrange partial differential equation arising as a necessary condition for the functional to be stationary is exactly the transport equation (4), a result which is expected. Although it is readily demonstrated that the functional takes on not only a stationary value but a *maximum* value for the particular flux distribution that satisfies the transport equation, only the stationary character is exploited here. The advantage offered by having the functional $\Phi[\mathbf{j}]$ in hand is that, due to its stationary character, it provides a basis for finding *approximate* solutions for a class of mathematical problems for which exact solutions are out of reach, in general. This is the point of view adopted below. Analysis of the transport process has been recast in a variational framework of the kind pursued here by Freund and Suresh [4].

For the particular case of the rotationally symmetric potential defined above, all physical fields depend on only one spatial coordinate r and time t . Consequently, the only nonzero component of the flux vector is the radial component $j_r(r, t)$. Furthermore, the density of states vanishes at $r = a$ according to (7). In this case, the functional Φ takes on the relatively simple form

$$\Phi[j_r] = \int_0^a \left(\frac{1}{2} j_r(r, t)^2 - D\rho(r, t) \frac{1}{r} \partial_r (r j_r(r, t)) \right) e^{\hat{\mathcal{U}}(r)} r dr \quad (10)$$

where the current value of density at any r is given in (8) in terms of the history of flux at that point as

$$\rho(r, t) = - \int_0^t r^{-1} \partial_r (r j_r(r, \tau)) d\tau + \rho(r, 0) \quad (11)$$

The result of requiring that the functional defined in (10) is stationary under variation among all possible admissible radial flux vectors leads to the partial differential equations stated in (5). The objective here is to adopt a relatively simple *approximate* form of the flux distribution and to use the requirement that the functional must be stationary under variations in flux to deduce the time dependence of that form.

An Example. A principal task when applying the variational principle to a particular situation is the selection of a suitable class of admissible flux distributions. In the present instance, the only strict requirement is that the net flux of states into or out of $r = 0$ is zero, so there is enormous flexibility in the choice of $j_r(r, t)$. For linear systems with constant coefficients, a common approach is the Ritz method whereby $j_r(r, t)$ is represented as a linear sum of a subset of a complete set of functions of r which are orthogonal over the appropriate range. The variational principle then makes it possible to determine the time-dependent coefficients of the series; see [5] for example. For more complicated systems of the type considered here, it is more common to choose a class of admissible functions on the basis of general expectations on the qualitative behavior of the system. The variational principle can then be used to identify the optimal choice from within this restricted class of behaviors. These steps are outlined next for the escape of states from the rotationally symmetric energy well described in (2).

The physical situation being considered here is the state of a molecular bond in a thermal environment represented by a point executing a random walk within an energy well. The local time scale is set by the time elapsed in executing a single step in the walk. On this scale, the mean time required for the state to escape from the well is extremely long. Based on this point of view, the density of states representing the collective evolution of an ensemble of a large number of nominally identical, noninteracting systems is nearly an equilibrium distribution. Guided by this feature of expected behavior, the density of states is presumed to be an equilibrium distribution for the parabolic profile corresponding

to the curvature of the energy well at its root $r=0$. In other words, it is assumed that

$$\rho(r, t) = \alpha(t) \left(e^{-\frac{1}{2}\kappa r^2} - e^{-\frac{1}{2}\kappa a^2} \right), \quad \kappa = \left(\partial_{rr} \mathcal{U}(r) \right)_{r=0} = 4 \frac{c_b}{a^2} \quad (12)$$

where the second term in the expression for density has been included to ensure that the form adopted satisfies the boundary condition (7). In effect, the spatial dependence of the density of states has been fixed but the amplitude of the distribution as represented by $\alpha(t)$ remains to be determined.

The density of states $\rho(r, t)$ and the radial flux $j_r(r, t)$ are related according to (8), from which it is readily determined that

$$j_r(r, t) = \frac{\alpha'(t)}{2\pi r} \left(e^{-\frac{1}{2}\kappa r^2} + \frac{1}{2}\kappa r^2 e^{-\frac{1}{2}\kappa a^2} - 1 \right) \quad (13)$$

The constant of integration that arises in extracting this expression for flux is selected so that the limit as $r \rightarrow 0$ is $rj_r(r, t) \rightarrow 0$ which ensures that no states are “lost” through the singular point at $r=0$. It is evident that the spatial dependence of the admissible flux is completely defined by (13). Consequently, the search among all admissible flux vectors involved in the application of the variational principle involves only a search among values of $\alpha'(t)$. Stated more simply, the variational principle leads directly to an ordinary differential equation governing the amplitude $\alpha(t)$. The differential equation must be augmented by an initial condition, and this is provided by the requirement that the probability of finding all states in the ensemble within the well at time $t=0$ is equal to one, that is,

$$2\pi \int_0^r \rho(r, 0) r dr = 1 \quad (14)$$

Straightforward calculation leads to the result that

$$\alpha(0) = \frac{2}{2 - (2 + a^2\kappa)e^{-a^2\kappa/2}} \quad (15)$$

If the flux $j_r(r, t)$ given by (13) and the corresponding density $\rho(r, t)$ given by (12) are substituted into the general expression (10) for the functional Φ , the result is the simple expression

$$\Phi[j_r] = \frac{1}{2} A_1 \alpha'(t)^2 + \frac{D}{a^2} A_0 \alpha'(t) \alpha(t) \quad (16)$$

where A_1 and A_0 are dimensionless system parameters defined by the integrals

$$A_1 = \frac{1}{2\pi} \int_0^1 \frac{1}{s} e^{-c_b(5+2s^2+s^4)} \left[e^{2c_b} (e^{2c_b s^2} - 1) - 2c_b s^2 e^{2c_b s^2} \right]^2 ds \quad (17)$$

$$A_0 = \frac{8c_b^2}{\pi} \int_0^1 e^{-c_b(5+2s^2+s^4)} (e^{2c_b} - e^{2c_b s^2})^2 ds \quad (18)$$

The dimensionless integration variable s over the range $0 < s < 1$ represents the ratio r/a over the range of the well $0 < r < a$. The integrands of the integrals that define A_1 and A_2 are well behaved and the integrals are clearly convergent. However, it appears that the integrals cannot be evaluated in terms of elementary functions. Nonetheless, the general properties of each, particularly the dependence on the fundamental system parameter c_b , can be extracted in an unambiguous way.

The variational principle introduced above requires that, for the actual flux, the functional $\Phi[j_r]$ must be stationary under admissible variations in the flux $j_r(r, t)$ for fixed time t . In the present case, the dependence of the flux on radial coordinate r is specified explicitly on the basis of expectations for the probability distribution $\rho(r, t)$ and the conservation of states. The only element of the flux

not specified *a priori* is the coefficient $\alpha'(t)$. Consequently, in this instance, variation of the flux in the sense of calculus of variations amounts to variation of the coefficient of the flux in the sense of continuous functions. Thus, the requirement that $\delta \Phi = 0$ under variation of the flux reduces to the condition that

$$\frac{\partial \Phi}{\partial \alpha'(t)} = 0 \quad (19)$$

Upon application of this requirement to the expression for Φ given in (16), we find that the history of $\alpha(t)$ must satisfy the ordinary differential equation

$$A_1 \alpha'(t) + \frac{D}{a^2} A_0 \alpha(t) = 0 \quad (20)$$

which is subject to the initial condition (15). It follows immediately that the approximation for the off-rate η implied by the variational principle is

$$\eta = A_0 D / a^2 A_1 \quad (21)$$

The coefficients A_0 and A_1 are dimensionless, D is a diffusivity with physical dimensions of length²/time, and a is a length. Consequently, η has the physical dimension of time⁻¹, as expected, and the focus here is on the nondimensional off-rate $\bar{\eta} \equiv \eta a^2 / D = A_0 / A_1$.

Evaluation of the Results. In this section the focus is on extraction of the dependence of the off-rate $\bar{\eta}$ on the depth of the bond well as represented by c_b ; the dependence of $\bar{\eta}$ on the other characterizing parameters of the well is explicit in the expression (21). We first extract analytic approximations of A_0 and A_1 valid for $c_b \gg 1$, and these are then compared to the corresponding off-rates for one-dimensional and three-dimensional energy wells described by the same “radial” dependence $\mathcal{U}(r)$. The coefficients are also evaluated numerically for a wide range of values of c_b to get a measure of the quality of the asymptotic approximation.

The integral defining A_0 in (18) can be evaluated in terms of the error function as defined in [6], where series representations of the error function are available. Adopting approximations valid for $c_b \gg 1$, it is readily demonstrated that

$$A_0 \approx \frac{2}{\pi} c_b e^{-c_b} \quad (22)$$

It appears that the integral defining A_1 in (17) cannot be evaluated in the same simple way. However, it is easily verified that the integrand is sharply peaked near $s=1$ and that its value decays rapidly to small values with increasing distance from that peak. This behavior suggests that a fruitful approach is to expand the natural logarithm of the integrand in powers of $(s-1)$ up to second degree, and then to integrate the quantity e raised to the power given by that expansion over $0 < s < 1$. Again, a result in terms of the error function is found, and it is a simple matter to show that the principal contribution to that result for $c_b \gg 1$ is

$$A_1 \approx \frac{1}{8\sqrt{\pi c_b}} \quad (23)$$

It follows that an estimate for the off-rate for this two-dimensional energy well is

$$\bar{\eta}_{(2)} \approx \frac{16}{\sqrt{\pi}} \sqrt{c_b} e^{-c_b} \quad (24)$$

where the subscript (2) has been added to make clear that the result is for the case of two degrees of freedom. In some respects, this result is consistent with the general form that might have been

Fig. 2 Plot of the dependence of the natural log of the nondimensional off-rate versus well depth c_b for the two-dimensional well. The curves show the behavior based on asymptotic (solid) and numerical (dashed) evaluation of the integrals defining the parameters A_0 and A_1 . The open circles show the results of solution of the partial differential equations by means of the numerical finite element method, while the open triangles show the results of discrete random walk analysis. Note that $\eta a^2/D = \bar{\eta}_{(2)} = A_0/A_1$.

anticipated at the outset. Finding the result, however, is not the main point of this discussion. Instead, the question is the following. Suppose that we consider escape of states from another energy well having precisely the same sectional profile as that considered above, as represented by $\mathcal{U}(r)$, but for which the spatial range of diffusion of states spans only one space dimension or perhaps three space dimensions or even n dimensions. How does the issue of dimensionality influence the off-rate, given that the sectional profiles are identical? This question is addressed in the next section.

This section is concluded by examining the quality of the approximations underlying the estimate of off-rate given by (24). This must be addressed at two levels. First of all, the result is obtained by approximating the solution of the differential equation (20) governing the amplitude $\alpha(t)$ under the assumption that $c_b \gg 1$; the consequence of invoking this approximation is examined first. After doing so, the validity of the assumed spatial dependence of the probability distribution $\rho(r, t)$ in (12) is considered.

As is evident from (21), the value of normalized off-rate implied by the variational principle is

$$\bar{\eta}_{(2)} = A_0/A_1 \quad (25)$$

The value of $\bar{\eta}_2$ for any value of c_b can be determined by direct numerical integration of the integrals (18) and (17) which define its value. Although having algebraically complicated integrands, there are no singularities and these integrals are convergent. Direct numerical evaluation leads to the result illustrated in Fig. 2. In this figure the solid line shows the computed dependence of $\bar{\eta}_{(2)}$ on c_b for values in the range $5 < c_b < 30$. For purposes of comparison, the dashed line is a plot of the asymptotic approximate given by (24). It is evident that the asymptotic result represents a good approximation for the off-rate over the entire range of values of c_b considered.

Additional Observations. It is evident from Fig. 2 that, in the case of two space dimensions and time, the results of a continuum finite element analysis of the transport and conservation equations yields results for the off-rate that are in good agreement with those determined by means of the variational principle for c_b less than about 15. However, for larger values of c_b , implying deeper energy wells, the results of finite element analysis diverge from the variational results in a direction of becoming insensitive to changes in value of c_b . The reason for this behavior is not evident from the results. However, there is a possibility that the accuracy of the estimate of off-rate is lost for larger values of c_b . This possi-

bility is suggested by the trend in the numerical values for the flux of states out of the well implied by calculations in that range; these values become very small and ultimately become too small to be accurately resolved in the calculation. Further study is required to identify the limit of accuracy in terms of the value of the parameter c_b .

It is also clear from Fig. 2 that, in the case of two space dimensions and time, the results of a discrete random walk analysis are in good agreement with those determined by the variational principle for values of c_b less than about 15. Beyond that value, the random walk results diverge sharply from those from the variational analysis as indicated in the figure. Closer examination of the results of the random walk calculation show that the flow of discrete states out of the well with time becomes too low to be considered either continuous or axisymmetric. While the number of random walkers assumed in these calculations ranged into the hundreds of thousands, it is possible that the number would have to be increased substantially in order to extend the range of agreement between the variational approach and the random walk approach.

The determination of the off-rate $\eta_{(2)}$ for the case of a two-dimensional bond well has been described in some detail in the foregoing sections. For purposes of comparison, the corresponding results for one dimension and three dimensions are

$$\eta_{(1)} = \frac{D 8\sqrt{2}}{a^2 \pi} c_b e^{-c_b}, \quad \eta_{(2)} = \frac{D 16}{a^2 \sqrt{\pi}} c_b^{3/2} e^{-c_b}, \quad \eta_{(3)} = \frac{D 32\sqrt{2}}{a^2 \pi} c_b^2 e^{-c_b} \quad (26)$$

These results have been obtained by precisely the same procedure as was demonstrated above, with only the details of the expressions varying from case to case.

In a comparison of the off-rate estimates for one, two, and three dimensions summarized in (26), it is clear that the magnitude in each case is dominated by the exponential dependence on well depth e^{-c_b} common to the three cases. The coefficients of the exponential factor vary in a systematic way from case to case. For example, the coefficients depend on well depth c_b according to $c_b^{(d+1)/2}$ where d is the dimension or number of degrees of freedom. The parameter c_b is the well depth in units of kT , as noted above. A typical value for the strength of a bond between biomolecules is about $25kT$. For such a case, the magnitudes of the coefficients of the exponential terms in (26) would vary with dimension according to 5^d where again d is the number of dimensions involved. In addition, the pure numbers appearing in the expression for off-rate increase with increasing number of spatial dimensions. Combining these observations, it is concluded that the chemical off-rate for a molecular bond increases significantly with the number of degrees of freedom assumed to characterize the bond, within the framework of the simple bond profiles considered here.

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