PHYSICAL REVIEW
LETTERS

VOLUME 51 25 JULY 1983 NUMBER 4

Theory of Activated Rate Processes: Bridging between the Kramers Limits

Benny Carmeli and Abraham Nitzan
Department of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel
(Received 13 December 1982; revised manuscript received 28 February 1983)

The Kramers theory for the escape rate of a Brownian particle moving in a potential well is generalized to account for the full viscosity range. An expression for the escape rate, which is valid for all values of the friction and yields the Kramers results in the appropriate limits, is obtained.

PACS numbers: 05.40.+j, 05.60.+w

The Kramers approach to the theory of activated rate processes,[1] using a model of a Brownian particle moving in a one-dimensional potential well, has played a central role in many areas of science. The starting point is the Fokker-Planck equation for the probability distribution $P=P(x, v, t)$,

$$\frac{\partial P}{\partial t}=\frac{1}{m}\frac{dV(x)}{dX}\frac{\partial P}{\partial v}-v\frac{\partial P}{\partial X}+\gamma\left(\frac{\partial}{\partial v}(vP)+\frac{kT}{m}\frac{\partial^2 P}{\partial v^2}\right), \tag{1}$$

where m, v, and x are the mass, velocity, and position of the particle moving in the potential $V(x)$, T is the temperature, γ is the friction, and k is the Boltzmann constant. The objective is to find the steady-state escape rate (r) out of the potential well. Kramers has obtained different limiting results for this rate:

$$r=\begin{cases}(\omega_0\omega_B/2\pi\gamma)\exp(-E_B/kT) & (\gamma\to\infty), \quad (2a)\\ \gamma(E_B/kT)\exp(-E_B/kT) & (\gamma\to 0), \quad (2b)\end{cases}$$

where ω_0 and ω_B are the frequencies associated with the second derivative of the potential at the bottom of the well and at the barrier top, respectively, and where E_B (assumed to be much greater than kT) is the depth of the well. Kramers has also derived an expression which is supposedly appropriate for "intermediate" values of γ:

$$r=\frac{\omega_0}{2\pi\omega_B}\left\{\left[\left(\tfrac{1}{2}\gamma\right)^2+\omega_B^2\right]^{1/2}-\tfrac{1}{2}\gamma\right\}\exp\left(-\frac{E_B}{kT}\right). \tag{3}$$

This expression yields (2a) for $\gamma\gg\omega_B$ while for $\gamma\to 0$ it goes to the transition-state-theory (TST) rate

$$r_{TST}=(\omega_0/2\pi)\exp(-E_B/kT). \tag{4}$$

Even though these results have long been discussed and used in the literature, a unified theory for r as a function of γ that yields the forms (2)–(4) as limiting cases has never been provided. (For recent attempts to construct such a theory see Skinner and Wolynes[2] and Matkowsky, Schuss, and Ben-Jacob.[3]) In this work we derive for the first time a general expression for $r(\gamma)$ that reduces to the forms (2) and (3) in the appropriate limits. This in turn enables us to identify ranges of the friction for which the different results are valid.

Our approach is based on a picture which divides the particle phase space into two (assumed overlapping) regions. In the first, for low energies, the variation of the phase is assumed to be much faster than that of the energy (i.e., $\gamma\ll\omega$) so that a Smoluchowski equation for the energy

(or the action J) is valid. Then in action-angle space, $P(J, \varphi, t) = (1/2\pi)P(J, t)$ and[1]

$$\frac{\partial P(J,t)}{\partial t} = \gamma \frac{\partial}{\partial J}\left[\frac{J}{\omega(J)}\left(kT\frac{\partial}{\partial J} + \omega(J)\right)P(J,t)\right]. \quad (5)$$

In the second, at higher energies Kramers barrier dynamics[1] [leading to Eq. (8) below] holds.[4] This picture does not cover the situation where the motion is overdamped ($\gamma > \omega$) for all energies. However, in this case the escape rate is governed by the barrier dynamics and any assumption concerning the well motion is of no consequence.

Kramers's result (3) is obtained by joining together a steady-state (SS) solution of Eq. (1) near the barrier top with an *equilibrium* solution in the well. This procedure disregards the possibility that for low friction the well motion is not in equilibrium. Instead, we join, at a point (x_1, J_1) determined below, using appropriate continuity conditions, SS solutions of Eqs. (1) and (5) and thus obtain a unified expression for the SS current that reduces to all the different Kramers limits under the proper conditions.

Considering first the motion in the well we note that a general SS solution of (5) is given by[5]

$$P_{SS}^{(W)}(J) = \exp\left(-\frac{E(J)}{kT}\right)\left[A_1 + A_2\int_J^{J_1} dJ'\,\frac{\omega(J')}{\gamma J'}\exp\left(\frac{E(J)}{kT}\right)\right]. \quad (6)$$

(Note that the upper limit of the integral can be chosen arbitrarily and was assigned the value J_1 for convenience.) This solution corresponds to a SS current on the action axis,

$$j_{J,SS}^{(W)} = -\gamma\frac{J}{\omega(J)}\left(kT\frac{d}{dJ} + \omega(J)\right)P_{SS}^{(W)}(J) = kTA_2. \quad (7)$$

Turning to the SS solution $P_{SS}^{(B)}$ near the barrier top, the Kramers function

$$P_{SS}^{(B)}(x, v) = B\exp\left(-\frac{\frac{1}{2}mv^2 + V(x)}{kT}\right)\int_{-\infty}^{v-(\alpha+1)\gamma x} dz\exp\left(-\frac{\alpha m z^2}{2kT}\right), \quad (8)$$

where

$$\alpha = \tfrac{1}{2}\{[1 + (2\omega_B/\gamma)^2]^{1/2} - 1\}, \quad (9)$$

provides a suitable solution, corresponding to the net SS current $j_{x,SS}^{(B)}$ on the x axis given by [with $j_{x,SS}^{(B)} = \int_{-\infty}^{\infty} dv\, v P_{SS}^{(B)}(x, v)$]

$$j_{x,SS}^{(B)} = B\left(\frac{kT}{m}\right)^{3/2}\left(\frac{2\pi}{\alpha+1}\right)^{1/2}\exp\left(-\frac{E_B}{kT}\right). \quad (10)$$

Kramers has determined the coefficient B of (8) by matching the distribution (8) with a Boltzmann distribution (BD) in the well. This leads to expression (3) for the rate. However, for small γ the barrier distribution (8) should go over to the distorted distribution (6) in the well.

To proceed we have to assume that the distributions (6) and (8) overlap in some region of phase space. This is supported for chemical reaction models by the observation that for a reasonable choice of potential and friction parameters, the action equation (5) provides a good approximation up to $E \simeq 0.9E_B$.[6] However, since the function (8) cannot describe a phase-independent distribution, it follows that this function is valid only in a region near the potential well. Referring to Fig. 1 we assume that there exists at least one point $(x_1, v_1 = 0)$ corresponding to the action $J = J_1$ so that the distribution (6) is valid for $J \leq J_1$ while (8) is valid for $x \geq x_1$. Next we determine the parameters A_1, A_2, J_1, and B so that the two distributions match at $(J_1, v_1 = 0)$ so as to satisfy essential continuity conditions.

First, noticing that the Jacobian for the (J, φ) to (x, v) transformation is just the mass m, we

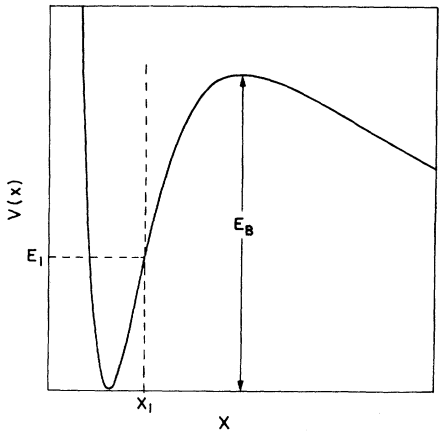

FIG. 1. The potentials used in the calculations of Fig. 2.

get $(m/2\pi)P_{SS}^{(W)}(J_1) = P_{SS}^{(B)}(x_1, v=0)$, which leads to

$$A_1 = (2\pi/m)B\int_{-\infty}^{(\alpha+1)\gamma|x_1|} dz \exp(-\alpha m z^2/2kT). \tag{11}$$

Secondly, we notice that at SS the molecular flux crossing the line $J = J_1$ must be equal to that crossing the line $x = x_1$. Therefore [with Eqs. (7) and (11)]

$$A_2 = \frac{B}{m^{3/2}}\left(\frac{2\pi kT}{\alpha+1}\right)^{1/2}\exp\left(-\frac{E_B}{kT}\right). \tag{12}$$

Finally, we require that at the matching point ($x = x_1, v=0$) the distributions (6) and (8) represent the same amount of distortion relative to a BD, namely,

$$\left[\frac{\partial}{\partial E}\ln(P_{SS}^{(B)}e^{E/kT})\right]_{E_1, v=0} = \left[\frac{\partial}{\partial E}\ln(P_{SS}^{(W)}e^{E/kT})\right]_{E_1}. \tag{13}$$

Equations (11)–(13) lead after some algebra to an equation for the matching energy E_1:

$$\exp\left(-\alpha\frac{E_B - E_1}{kT}\right) = \frac{kT}{(\alpha+1)\gamma J_1}\left(\alpha\frac{E_B - E_1}{\pi kT}\right)^{1/2} \tag{14}$$

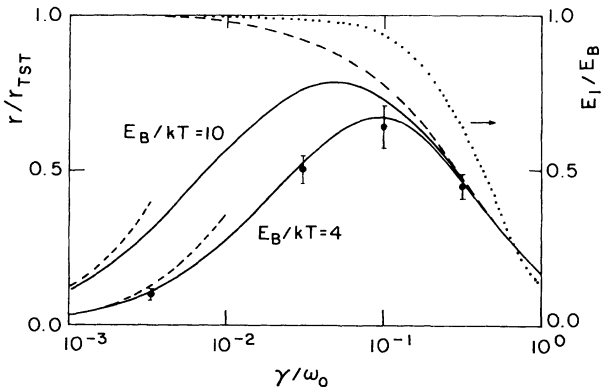

FIG. 2. Matching energy E_1 (dotted line) and escape rate r as functions of friction. The full lines are results based on Eq. (17). The dashed lines are results based on the Kramers equations (2b) (rising lines) and (3) (descending line). The points with error bars are results of numerical simulations based on the Langevin equation equivalent to Eq. (1).

which has a solution $0 < E_1 < E_B$ (see Fig. 2). We note again that the importance of determining the proper matching point stems from the fact that the solution (6) fails near the barrier top while (8) fails near the bottom so that these functions are expected to overlap only in a limited range near E_1.

The SS rate is obtained by dividing the current [(7) or (10)] by the total number of particles $N = \int_{E\le E_B} P_{SS}$ in the well. Here we adopt the following approximate expression for N:

$$N \simeq \int_0^{J_1} dJ\, P_{SS}^{(W)}(J) + \int_{-\infty}^{x_B} dx \int_{-\infty}^{\infty} dv\, P_{SS}^{(B)}(x,v)\,\theta(\tfrac{1}{2}mv^2 + V(x) - E_1), \tag{15}$$

where $\theta(x) = 0$ for $x \le 0$ and $\theta(x) = 1$ otherwise. The approximation lies in using $P_{SS}^{(B)}$ to calculate the contribution from the phase-space region $(E > E_1, x < x_1)$. This may be justified for deep wells by noticing that for large γ this part of phase space is described well by $P_{SS}^{(B)}$ while for small γ its contribution is negligible relative to that from $E < E_1$. As a further approximation we may (for similar reasons) replace $P_{SS}^{(B)}$ in the second contribution to N in (15) by P_{BD}, the limiting Boltzmann distribution obtained from (6) or (8) for $\gamma \to \infty$. This leads to

$$N = A_1\int_0^{J_B} dJ \exp\left(-\frac{E(J)}{kT}\right) + A_2\int_0^{J_1} dJ \exp\left(-\frac{E(J)}{kT}\right)\int_J^{J_1} dJ\, \frac{\omega(J')}{\gamma J'}\exp\left(\frac{E(J)}{kT}\right). \tag{16}$$

By use of (7), (9), (11), (12), and (16) [Eq. (15) could be used instead of (16) for a slightly more accurate but less transparent result], we finally get (erf is the error function)

$$r = \left(\frac{1+\mathrm{erf}\{[(\alpha+1)(E_B - E_1)/kT]^{1/2}\}}{2}\, r_K^{-1} + \tau_1\right)^{-1}, \tag{17}$$

where r_K is the Kramers rate given by Eq. (3) and where

$$\tau_1 = (\gamma kT)^{-1}\int_0^{J_1} dJ\, \frac{\omega(J)}{J}\exp\left(\frac{E(J)}{kT}\right)\int_0^{J} dJ' \exp\left(-\frac{E(J')}{kT}\right) \tag{18}$$

is just the mean first passage time to reach from $J=0$ to $J=J_1$. To obtain this result we have used $\int_0^{J_B} dJ \exp[-E(J)/kT] \simeq kT/\omega_0$ and have transformed the double integral of Eq. (16) to the form in (18) by using integration by parts.

For large γ, $E_1 \to 0$ (Fig. 2) and $\tau_1 \to 0$. At the same time the error function in (17) becomes 1 and $r \to r_K$ which behaves as γ^{-1} for $\gamma \to \infty$. For $\gamma \to 0$, $E_1 \to E_B$ and $\tau_1 \to \tau_B$. τ_B, the mean first passage time to reach the barrier energy [in a dynamics described by Eq. (5)], becomes the dominant contribution in (17) and $r \to \tau_B^{-1}$. It is easy to show[1,3,6] that in this limit τ_B^{-1} is given (for a truncated harmonic oscillator) by Eq. (2b). The dependence of r, Eq. (17), on γ is displayed in Fig. 2. To produce this graph we have used the potential $V(x) = D[\exp(-x/a) - \exp(-x/b)]^2$ shown in Fig. 1, where we chose $a/b = 20$ (leading to $E_B/D = 0.658$ and $\omega_0/\omega_B = 5.236$). Also shown in Fig. 2 are results of numerical simulations based on the Langevin equation

$$m\ddot{x} + dV(x)/dx + \gamma\dot{x} = R(t);$$

$$\langle R \rangle = 0, \quad \langle R(0)R(t)\rangle = 2\gamma mkT\,\delta(t),$$

which is equivalent to Eq. (1). Excellent agreement with the analytical results is obtained.

We see, as intuitively expected, that deviations from TST are larger for shallower wells, and that low-friction behavior (operationally defined as the range where r increases with γ) is expected for $\gamma/\omega_0 < 10^{-1} - 10^{-2}$ depending on the well depth. We note that the present derivation is valid for a single-well model. For double well, the small-γ behavior is affected also by trajectories returning from the second well.[7]

The result (17) [with Eq. (14) for E_1] provides, for the first time, a derived expression for the SS escape rate in the Kramers model valid for all $0 \leq \gamma \leq \infty$. The Kramers theory has been recently extended to include memory effects in the particle-thermal-bath interaction [generalizing *separately* the Kramers equations (2b)[6] and (3)[8]]. Extending the present theory to the non-Markoffian case will be the subject of a future publication.[7]

[1]H. A. Kramers, Physica (Utrecht) 7, 284 (1940).

[2]J. L. Skinner and P. G. Wolynes, J. Chem. Phys. 72, 4912 (1980).

[3]B. J. Matkowsky, Z. Schuss, and E. Ben-Jacob, to be published; P. B. Visscher, Phys. Rev. B 14, 347 (1976); R. S. Larson and M. D. Kostin, J. Chem. Phys. 72, 1392 (1980).

[4]We make the usual (see Ref. 1) deep-well assumption which is necessary for the steady-state escape rate to be physically meaningful by insuring separation between the thermal relaxation and the exit time scales. This also makes it possible for the two dynamic regions introduced here to overlap in many situations. Numerical work based on stochastic classical trajectories (B. Carmeli and A. Nitzan, to be published) show that this holds well for $E_B \gtrsim 3kT$.

[5]Note that the point $J=0$ is a singular point of this distribution. Problems arising from this singularity can be remedied by supplementing Eq. (5) with a source term at some small J (see Visscher, Ref. 3). This turns out not to affect the results obtained here.

[6]R. W. Zwanzig, Phys. Fluids 2, 12 (1959); R. F. Grote and J. T. Hynes, J. Chem. Phys. 77, 3739 (1982); B. Carmeli and A. Nitzan, Phys. Rev. Lett. 49, 423 (1982); B. Carmeli and A. Nitzan, to be published.

[7]Carmeli and Nitzan, Ref. 4.

[8]R. F. Grote and J. T. Hynes, J. Chem. Phys. 73, 2715 (1980); P. Hanggi and F. Mojtabai, Phys. Rev. A 26, 1168 (1982).