

Rate constant and transmission coefficient in the diffusion theory of reaction rates

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(Received 18 September 1979; accepted 4 March 1980)

The diffusion theory of reaction rates, originally described by H. A. Kramers, is extended and new results are derived. It is shown that valuable information can be gained by using backward diffusion equations (equations in which the initial values are independent variables), in addition to the Fokker-Planck equation. Three theoretical formulations of the rate constant are described. The first formulation uses transition state theory. The second formulation uses a modification of Kramers's theory. In the third formulation, the rate constant is defined to be the reciprocal of the mean time to cross a given energy barrier. The three formulations of the rate constant are compared with each other and with Monte Carlo experiments. By using the backward equation, it is possible to calculate the transmission coefficient. The theoretical results are compared with Monte Carlo experiments.

I. INTRODUCTION

H. A. Kramers formulated a Brownian motion model for the calculation of reaction rates¹ in which molecules undergo a diffusion process in reaction space while moving in physical space. Kramers worked exclusively with the Fokker-Planck (or forward) equation and compared his results with the then new transition state theory. He tried to estimate the inaccuracies in transition state theory. The literature spawned by the original paper of Kramers is now quite large, and some representative examples are Refs. 2-11. Although the literature is large, the development of this field has been unbalanced. For example, almost all workers have used the Fokker-Planck equation, in which the independent variables are final time and position. However, the backward equation, in which the independent variables are initial time and position, can also be used to provide information about the reaction process. Kramers' original concept of the reaction rate as the eigenvalue of a diffusion equation has been used extensively. There are, however, other ways to define the rate constant, e.g., as the reciprocal of a mean time to cross an energy barrier, which may be more natural definitions.

In this paper, three theoretical formulations of the rate constant are compared with each other and with Monte Carlo experiments. The formulations use transition state theory, the Kramers theory, and the mean time theory. The relationship between these three formulations is clarified. It will be seen that transition state theory is off by about an order of magnitude from either the Kramers or mean time theories. The Kramers theory is the asymptotic form, for large barrier heights, of the mean time theory. Also, in this paper, the backward equation is used to calculate the transmission coefficient.

In Sec. II, the diffusion model is described. The work of Il'in and Khasminskii⁴ is followed, since they give a rigorous derivation of the diffusion equations. The two types of diffusion equations—forward (or Fokker-Planck) and backward—are discussed. When these equations are written in nondimensional form, a small parameter (ϵ) arises. This parameter is the ratio of $k_B T$ to the energy barrier Q that must be crossed.

Thus, when $\epsilon \ll 1$ the energy barrier is large.

In Sec. III, the three formulations of the rate constant are presented. Transition state theory uses the equilibrium solution of the Fokker-Planck equation to calculate the rate constant. The Kramers theory uses the lowest eigenvalue of the Fokker-Planck equation. The last theoretical formulation uses the mean time to cross the energy barrier. This time satisfies a backward equation, and the rate constant is the reciprocal of the mean time to cross the barrier. In Sec. IV, the transmission coefficient is calculated. The transmission coefficient is the probability that a molecule near the peak of the barrier becomes a product, rather than a reactant. The theoretical results are compared with Monte Carlo experiments.

The calculations in Secs. III and IV assume that the viscosity is high, so that the Fokker-Planck and backward equations simplify. The assumption of high viscosity is relaxed in Sec. V, where the rate constant and transmission coefficient are calculated for arbitrary viscosity but large barrier heights (i.e., small ϵ).

II. THE DIFFUSION MODEL OF REACTION RATES

Consider the following reaction model, which is similar to that used by Kramers. Let \tilde{x} denote the reaction coordinate in a large molecule of mass M . This molecule is immersed in bath of lighter molecules (mass $m \ll M$) which are distributed according to a Maxwell-Boltzmann distribution. It is assumed that, when there are no collisions with bath molecules, $\tilde{x}(t)$ obeys classical mechanics in a potential $V(x)$. The potential is assumed to have a local minimum at x_0 and a maximum at \hat{x} , where $x_0 < \hat{x}$. The energy barrier Q is defined as the difference $V(\hat{x}) - V(x_0)$. When $x > \hat{x}$, there are two possibilities to consider. In the first case, roughly corresponding to an irreversible reaction, $V(x)$ goes to 0 as $x \rightarrow \infty$. In the second case, roughly corresponding to a reversible reaction, there is a second minimum at some point $x_1 > \hat{x}$.

The collisions of the large molecule with the bath molecules are assumed to follow a Poisson process with mean rate of collisions equal to α . Then a friction

coefficient η can be defined as

$$\eta = 2am. \quad (2.1)$$

Let \tilde{v} be the velocity defined by $d\tilde{x}/dt$ and let $f(x, v)$ be an integrable function on the (x, v) phase space. Set

$$u(x, v, t) = \langle f(\tilde{x}(t), \tilde{v}(t)) | \tilde{x}(0) = x, \tilde{v}(0) = v \rangle. \quad (2.2)$$

In Eq. (2.2), the angle brackets denote the ensemble average, conditioned on the initial values of $\tilde{x}(0)$ and $\tilde{v}(0)$. In order to study the behavior of the phase space function $u(x, v, t)$, the theory of Il'in and Khasiminskii is used.⁴ They consider the case in which $m \rightarrow 0$ (very light molecules), $a \rightarrow \infty$ (very rapid collisions), such that η is constant. They prove that $u(x, v, t)$ satisfies the following equation:

$$\begin{aligned} \frac{\partial u}{\partial t} = & v \frac{\partial u}{\partial x} + \frac{F(x)}{M} \frac{\partial u}{\partial v} \\ & + \eta \frac{k_B T}{M^2} \frac{\partial^2 u}{\partial v^2} - \frac{\eta}{M} v \frac{\partial u}{\partial v}. \end{aligned} \quad (2.3)$$

The initial value for $u(x, v, t)$ is obtained from Eq. (2.2). Setting $t=0$,

$$u(x, v, 0) = f(x, v). \quad (2.4)$$

Equation (2.3) is an exact diffusion equation (cf. Refs. 1, 8, and 12) and is a backward diffusion equation, since it depends upon $\tilde{x}(t)$ and $\tilde{v}(t)$ at $t=0$.

Equation (2.3) can be simplified further by using the high viscosity or Einstein-Smoluchowski approximation.¹ In this approximation, one assumes that $M/\eta \approx 0$ while F/η is nonzero. Equation (2.3) is transformed to an equation for a new phase function $u(x, t)$ which is independent of velocity.⁴ The equation for $u(x, t)$ is

$$\frac{\partial u}{\partial t} = \frac{k_B T}{\eta} \frac{\partial^2 u}{\partial x^2} + \frac{F(x)}{\eta} \frac{\partial u}{\partial x}. \quad (2.5)$$

The transition from Eqs. (2.3) to (2.5) reduces the number of independent variables and simplifies the problem. This type of transformation was used by Kramers and is also discussed in Refs. 4, 5, and 8. Although a rigorous demonstration of the validity of the high viscosity limit is difficult,^{1,4} the underlying physical idea is easy to demonstrate. To explain this physical idea, the stochastic differential equations corresponding to Eqs. (2.3) and (2.5) are used.²¹ The stochastic differential equation corresponding to Eq. (2.3) is

$$\left. \begin{aligned} \frac{dx}{dt} &= v, \\ M \frac{dv}{dt} &= F(x) - \eta v + \sqrt{2\eta k_B T} \xi(t). \end{aligned} \right\} \quad (2.6)$$

In Eq. (2.6), $\xi(t)$ is Gaussian white noise²¹; it is the formal derivative of Brownian motion. In order to obtain the high viscosity approximation, one divides the second equation in Eq. (2.6) by η , yielding

$$\frac{M}{\eta} \frac{dv}{dt} = \frac{F(x)}{\eta} - v + \sqrt{\frac{2k_B T}{\eta}} \xi(t). \quad (2.7)$$

As mentioned above, in the high viscosity limit one assumes that M/η approaches zero much faster than any of the terms on the right hand side of Eq. (2.7). Setting

the left hand side of Eq. (2.7) equal to zero gives an equation for v ; this equation is

$$v = \frac{F(x)}{\eta} + \sqrt{\frac{2k_B T}{\eta}} \xi(t). \quad (2.8)$$

When Eq. (2.8) is substituted into the first equation in Eq. (2.6), one obtains

$$\frac{dx}{dt} = \frac{F(x)}{\eta} + \sqrt{\frac{2k_B T}{\eta}} \xi(t), \quad (2.9)$$

which is the stochastic differential equation corresponding to the diffusion equation (2.5). In order to obtain Eq. (2.9), one needs to assume that M/η is so small that the product $(M/\eta)dv/dt$ is approximately zero. The physical meaning is that the velocity relaxes to the "steady state" given by Eq. (2.8) on a time scale that is much faster than the time scale characterizing changes in reaction coordinate. Since the initial value of the velocity is arbitrary, there will be a small time interval, an initial layer,¹³ in which the approximation leading to Eq. (2.9) is not valid. In that time interval, Eq. (2.6) must be used. The length of the initial layer depends upon M and η but generally it is about 10^{-12} sec,¹⁴ and Eq. (2.5) will be good approximation for times much longer than 10^{-12} sec.

The next step in the formulation of the diffusion model is the introduction of dimensionless variables, so that the diffusion equations become nondimensional. Let x_c , t_c , and Q_c be characteristic length, time, and energy scales, respectively,^{13,14} and define dimensionless variables by $x_c = x/\bar{x}$, $v = (x_c/t_c)\bar{v}$, $V(x) = Q_c \bar{V}(\bar{x})$, and $\epsilon = k_B T/Q_c$.

The nondimensional form of Eq. (2.3), with the understanding that t , x , $V(x)$, and v are now dimensionless, is¹⁴

$$\frac{\partial u}{\partial t} = \epsilon \frac{\partial^2 u}{\partial v^2} + F(x) \frac{\partial u}{\partial v} + v \frac{\partial u}{\partial x} - v \frac{\partial u}{\partial v} \quad (2.10)$$

and the nondimensional form of Eq. (2.5) is

$$\frac{\partial u}{\partial t} = \epsilon \frac{\partial^2 u}{\partial x^2} + F(x) \frac{\partial u}{\partial x}. \quad (2.11)$$

In general, $Q \gg k_B T$ so that $\epsilon \ll 1$, and Eqs. (2.10) and (2.11) are singular perturbation problems, since a small term multiplies the highest order derivative. The singular nature of Eqs. (2.10) and (2.11) will be exploited in later sections.

The equations discussed so far are the backward equations. The Fokker-Planck equation can be obtained directly from the backward equation.¹⁵ Let $p(x, v, t)$ be the probability density for $(\tilde{x}(t), \tilde{v}(t))$, namely,

$$p(x, v, t) dx dv = \text{Prob}\{x \leq \tilde{x}(t) \leq x + dx, v \leq \tilde{v}(t) \leq v + dv\}. \quad (2.12)$$

This density satisfies the Fokker-Planck equation, which is the formal adjoint of Eq. (2.10):

$$\frac{\partial p}{\partial t} = \epsilon \frac{\partial^2 p}{\partial v^2} - \frac{\partial}{\partial v} [p(F(x) - v)] - v \frac{\partial p}{\partial x}. \quad (2.13)$$

In a similar fashion, one can consider the density $p(x, t)$ in the high viscosity limit; $p(x, t)$ will satisfy the equation

tion that is the adjoint of Eq. (2.11):

$$\frac{\partial p}{\partial t} = \epsilon \frac{\partial^2 p}{\partial x^2} - \frac{\partial}{\partial x} [F(x)p] . \quad (2.14)$$

Finally, note that initial conditions are needed for Eqs. (2.13) and (2.14) and boundary conditions are needed for all the partial differential equations discussed in this section. It will be seen that a good deal of information about the reaction process can be gained by choosing the initial and boundary conditions appropriately.

III. THREE FORMULATIONS OF THE RATE CONSTANT

In this section, formulations of the rate constant using transition state theory, the Kramers theory, and mean time theory are given. The theoretical results are compared with each other and with Monte Carlo experiments. By rate constant, we mean the rate at which particles reach \hat{x} from x_0 .

A. Rate constant in transition state theory

According to transition state theory, the equilibrium solution of the Fokker-Planck equation (2.13) is used to calculate the rate constant.^{6,14} The equilibrium density, obtained by setting the left hand side of Eq. (2.13) equal to zero, is

$$p(x, v) = c \exp \left\{ -\frac{1}{\epsilon} \left[\frac{v^2}{2} + V(x) \right] \right\} , \quad (3.1)$$

where c is a normalization constant. The rate constant is then calculated according to the following algorithm:

- (1) Find the flux of particles $J(\hat{x})$ across \hat{x} with $d\hat{x}/dt > 0$.
- (2) Find the number of particles N_0 in the potential well around x_0 . This number is obtained by integrating $p(x, v)$ over the well.
- (3) The rate constant is $k = J(\hat{x})/N_0$.

When ϵ is small, Laplace's method¹⁷ can be used to simplify the integral which gives N_0 . When Laplace's method is used, $V(x)$ is replaced by its second order Taylor expansion around the point x_0 . The result of this calculation is^{6,14,18}

$$k = \frac{[V''(x_0)]^{1/2}}{2\pi} \exp \{ -[V(\hat{x}) - V(x_0)]/\epsilon \} . \quad (3.2)$$

In Eq. (3.2), $V''(x_0) = (\partial^2 V / \partial x^2)|_{x=x_0}$ can be interpreted as a frequency factor and $V(\hat{x}) - V(x_0)$ is the activation energy of the reaction, since it is the energy barrier that must be crossed.

B. Rate constant in the Kramers theory

In the high viscosity limit, the Fokker-Planck equation of interest is Eq. (2.14). Kramers proposed that the rate constant can be found according to the following algorithm:

- (1) Assume that $p(x, t)$ has the eigenfunction expansion

$$p(x, t) = \sum_{m=0}^{\infty} \sigma_m(x) e^{-\lambda_m t} . \quad (3.3)$$

- (2) Find the smallest eigenvalue λ_0 where the eigenfunction $\sigma_0(x)$ is subject to the following boundary conditions:

$$\left. \begin{aligned} \sigma_0(\hat{x}) &= 0 , \\ \frac{\partial \sigma_0}{\partial x} \Big|_{x_0} &= 0 . \end{aligned} \right\} \quad (3.4)$$

- (3) The rate constant is $k \approx \lambda_0$.

The second boundary condition in Eq. (3.4) is chosen to correspond with Kramers' approach to the problem (Ref. 1, p. 292). There may be other choices of boundary conditions which are more appealing (e.g., a constant flux at x_0), but Eq. (3.4) is used to keep accord with Ref. 1. The physical idea is that so few particles leave that the density around x_0 remains approximately constant.

The eigenvalue problem of interest is

$$-\lambda_0 \sigma = \epsilon \frac{\partial^2 \sigma}{\partial x^2} - \frac{\partial}{\partial x} [\sigma F(x)] . \quad (3.5)$$

Kramers gave a solution of this problem, valid for small ϵ , but his derivation is difficult to follow. Other derivations of the solution, which are easier to understand, are in Refs. 19 and 20. The result of the eigenvalue calculation is

$$\lambda_0 \sim \frac{2}{\pi} [V''(x_0) |V''(\hat{x})|]^{1/2} \exp \{ -[V(\hat{x}) - V(x_0)]/\epsilon \} . \quad (3.6)$$

Equation (3.6) is valid for small ϵ ; note that the curvature of the potential near the peak \hat{x} appears in this theory.

C. Rate constant in the expected time formulation

The last formulation of the rate constant is based on the average time to cross the barrier at \hat{x} . For the model described above, consider an ensemble of particles that start at x_0 . As time progresses, the Brownian forces drive the particles across the barrier at \hat{x} ; each particle crosses \hat{x} at a different time. If T is the average time that it takes a particle to reach \hat{x} , then a reasonable definition of the rate constant is that k is the reciprocal of T , namely, define $T(x)$ by

$$T(x) = \langle \min t : \tilde{x}(t) \geq \hat{x} | \tilde{x}(0) = x \rangle \quad (3.7)$$

and the rate constant by

$$k = \int [g(x)/T(x)] dx . \quad (3.8)$$

In Eq. (3.8), $g(x)$ is the initial distribution of phase points in the well around x_0 .

Since $T(x)$ depends upon the initial value of $\tilde{x}(t)$, it will satisfy a backward equation.¹⁵ In the high viscosity limit, the equation for $T(x)$ is an ordinary differential equation (rather than partial differential equation) and the equation that $T(x)$ satisfies is

$$-1 = \epsilon \frac{d^2 T}{dx^2} + F(x) \frac{dT}{dx} . \quad (3.9)$$

Equation (3.9) is derived by differentiating Eq. (2.11) with respect to t , multiplying by t , integrating from $t = 0$ to $t = \infty$, and observing that the probability of even-

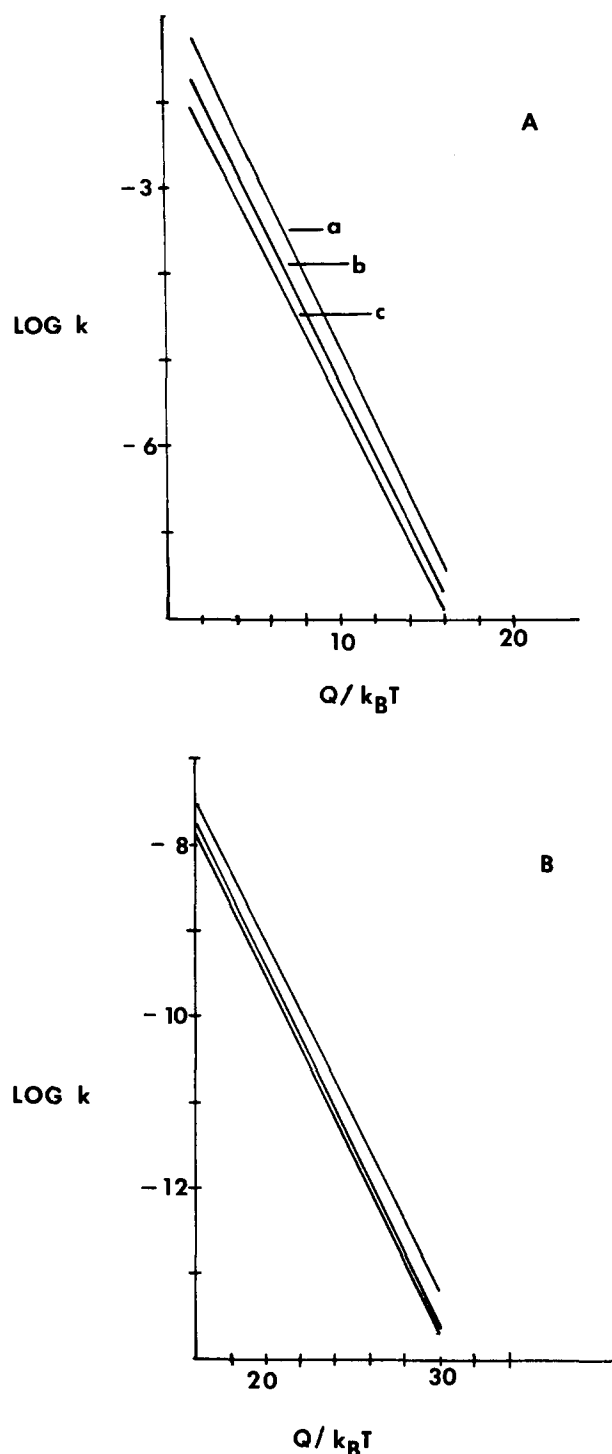


FIG. 1. A comparison of the numerical results using TST (line *a*), the Kramers formulation (line *b*), and the expected time formulation (line *c*). (A): $2 \leq Q/k_B T \leq 20$. (B): $16 \leq Q/k_B T \leq 30$. As the energy barrier increases, the lines come together.

tually reaching \hat{x} is 1 (in Refs. 10, 11, 14, and 21 the derivation is discussed in detail).

Since the mean time to reach \hat{x} starting at \hat{x} is zero, set $T(\hat{x}) = 0$. As the second boundary condition,

$$\lim_{x \rightarrow -\infty} \frac{dT}{dx} = 0 \quad (3.10)$$

is used. The solution of Eqs. (3.9) and (3.10) is

$$T(x) = \frac{1}{\epsilon} \int_x^{\hat{x}} e^{V(s)/\epsilon} \int_{-\infty}^s e^{-V(y)/\epsilon} dy ds. \quad (3.11)$$

Suppose that $g(x) = \delta(x - x_0)$, where $\delta(v)$ is the Dirac delta function. The rate constant given by Eq. (3.8) becomes

$$k = \epsilon \left(\int_{x_0}^{\hat{x}} e^{V(s)/\epsilon} \int_{-\infty}^s e^{-V(y)/\epsilon} dy ds \right)^{-1}. \quad (3.12)$$

Equation (3.12) is exact, and can be simplified by using Laplace's method on each of the integrals. When this is done¹⁴ one gets

$$k \approx \frac{2}{\pi} [V''(x_0) |V''(\hat{x})|]^{1/2} \exp\{-[V(\hat{x}) - V(x_0)]/\epsilon\} + O(\epsilon), \quad (3.13)$$

which is the same as Eq. (3.6). Thus, Kramers' result is the leading term in the asymptotic expansion of the solution (3.12). The asymptotic expansion used in Kramers' theory is valid for small ϵ . When ϵ is not small, the result given by Kramers is not valid, but the solution using the mean time formulation will still be valid.

When the high viscosity limit is not valid, the calculations used in the mean time formulation are more difficult. The calculations in the case of general viscosity are given in Sec. V.

D. Comparison with Monte Carlo experiments

In Fig. 1, the three theoretical rate constants are compared with each other as $Q_c/k_B T$ varies between 2 and 30. The formulations based on the Kramers theory and the mean time theory converge as ϵ decreases.

Transition state theory gives about the right order of magnitude for the rate constant, but is off by a factor of 2 to 5. The theoretical results are compared with Monte Carlo experiments in Fig. 2. In order to do the Monte Carlo experiments, the stochastic differential corresponding to Eq. (2.11) is solved. This stochastic differential equation is

$$\left. \begin{aligned} dx &= F(x) dt + \sqrt{2\epsilon} dW, \\ x(0) &= x_0. \end{aligned} \right\} \quad (3.14)$$

In Eq. (3.14), dW is the increment in Brownian motion, and is normally distributed with mean zero and variance dt . For the results presented in Fig. 2, the potential used is $V(x) = -\frac{1}{3}x^3 + \alpha x$; the force $F(x)$ is then $F(x) = x^2 - \alpha$. For this potential, $x_0 = -\sqrt{\alpha}$ and $\hat{x} = \sqrt{\alpha}$ and the barrier $Q = V(\hat{x}) - V(x_0)$ is $(\frac{2}{3})\alpha^{3/2}$.

For the points shown in Fig. 2, an ensemble average of 500 experiments is used. The rate constant shown in Fig. 2 is the reciprocal of the average time to reach \hat{x} . This experimental definition of the rate constant favors the theory based on the mean time. The rate constant computed with the mean time theory agrees most closely with the experiments. The Kramers theory is good for small ϵ ; but breaks down for large ϵ . Considering the assumptions that go into the derivation, transition state theory gives a remarkably good value for the rate constant.

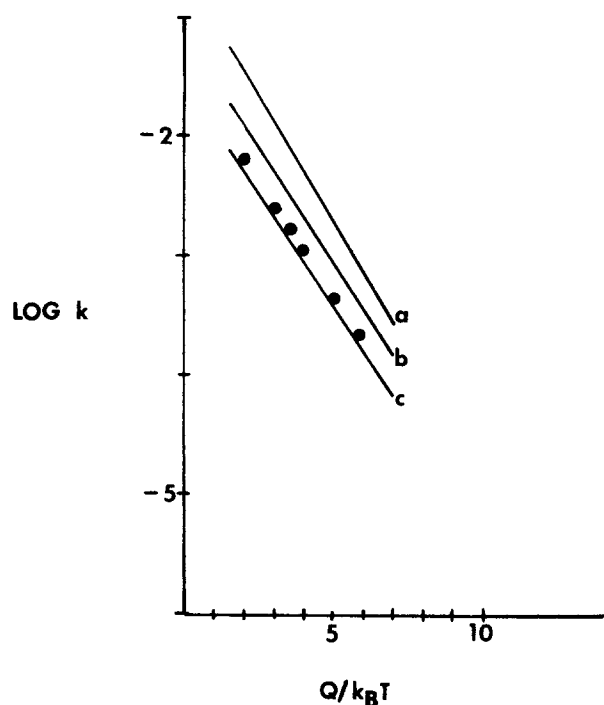


FIG. 2. Comparison of TST (line a), Kramers (line b), and expected time (line c) formulations with Monte Carlo experiments (circles).

IV. TRANSMISSION COEFFICIENT

A particle near \hat{x} does not necessarily become a product. Instead, it could return to the reactant state, namely, it could approach x_0 . The transmission coefficient can be defined as the probability that a particle starting at \hat{x} reaches some point $x_1 \gg \hat{x}$ before it reaches x_0 . The transmission coefficient can be calculated by using quantum mechanics,^{22,23} but the diffusion theory can also be used to calculate the transmission coefficient. In order to do the calculation, define

$$u(x) = \text{Prob}\{\tilde{x}(t) \text{ crosses } x = x_1 \text{ before } x = x_0 \mid \tilde{x}(0) = x\} \quad (4.1)$$

so that the transmission coefficient is $\kappa = u(\hat{x})$.

In the high viscosity limit, $u(x)$ satisfies the backward equation^{14,21}

$$0 = \epsilon \frac{d^2 u}{dx^2} + F(x) \frac{du}{dx}. \quad (4.2)$$

From the definition (4.1), it is clear that the boundary conditions must be $u(x_1) = 1$ and $u(x_0) = 0$. Using these boundary conditions when solving Eq. (4.2) gives

$$u(x) = \int_{x_0}^x e^{\int_{x_0}^s V(s)/\epsilon ds} ds / \int_{x_0}^{x_1} e^{\int_{x_0}^s V(s)/\epsilon ds} ds \quad (4.3)$$

and the transmission coefficient is

$$\kappa = \int_{x_0}^{\hat{x}} e^{\int_{x_0}^s V(s)/\epsilon ds} ds / \int_{x_0}^{x_1} e^{\int_{x_0}^s V(s)/\epsilon ds} ds. \quad (4.4)$$

If $|V''(\hat{x})|$ is bounded away from zero, then it's easy to show that $\kappa \approx \frac{1}{2} + O(\epsilon)$. If the potential is not symmetrical about \hat{x} , κ could differ significantly from $\frac{1}{2}$. In Table I, the theoretical result (4.4) is compared with the result

of Monte Carlo experiments, using the potential described in the previous section.

V. THE CASE OF ARBITRARY VISCOSITY

The results presented so far have exploited simplifications that arise when the viscosity is large. There are two reasons for studying the case in which the viscosity is not large. First, there are some problems, as Kramers noted, in which the viscosity is not large. Second, the behavior of a reacting system for short times can not be described by the high viscosity case. For arbitrary viscosity, Eqs. (2.10) and (2.13) have to be used instead of Eqs. (2.11) and (2.14) and the analysis becomes much harder. In this section, a simple model problem is studied, to show how some of the ideas discussed in the previous sections generalize. The analysis used in this section is developed in Ref. 24.

In the general case, the entire (x, v) phase space must be used. A simple model system, corresponding to the potential used in the previous sections, but not corresponding to any physical system, is

$$\left. \begin{aligned} \frac{dx}{dt} &= v, \\ \frac{dv}{dt} &= x^2 - \alpha - \gamma v + \sqrt{2\epsilon} \frac{dW}{dt}. \end{aligned} \right\} \quad (5.1)$$

In Eq. (5.1), γ is a damping coefficient. A sample phase portrait is shown in Fig. 3. In the general case, an entire deterministic trajectory, the separatrix S , plays the role that \hat{x} plays in the high viscosity case, namely, the separatrix separates phase points that are attracted to $(x_0, 0)$ from phase points that approach ∞ .

A. Transmission coefficient

In the high viscosity case, the transmission coefficient was calculated by considering points starting near \hat{x} and calculating the probability of approaching x_0 or x_1 . In the general case, points near the separatrix S must be considered. To describe the behavior of the phase points, introduce two curves parallel to S . One of these curves is located between $(x_0, 0)$ and the separatrix, and will be called S_1 . The other curve is located between the separatrix and ∞ , and will be called S_2 . In Fig. 4, the separatrix and the new curves are shown. Proceeding as in the previous section, define

$$u(x, v) = \text{Prob}\{[\tilde{x}(t), \tilde{v}(t)] \text{ crosses } S_2 \text{ before } S_1 \mid \tilde{x}(0) = x, \tilde{v}(0) = v\}. \quad (5.2)$$

TABLE I. A comparison of the theoretical transmission coefficient with Monte Carlo experiments.

Q (in units of $k_B T$)	\hat{x}	κ (Theory)	κ (MC) ^a
3	1.31	0.58	0.59
13	2.14	0.53	0.54
23	2.58	0.52	0.52

^a2500 Monte Carlo simulations were performed.

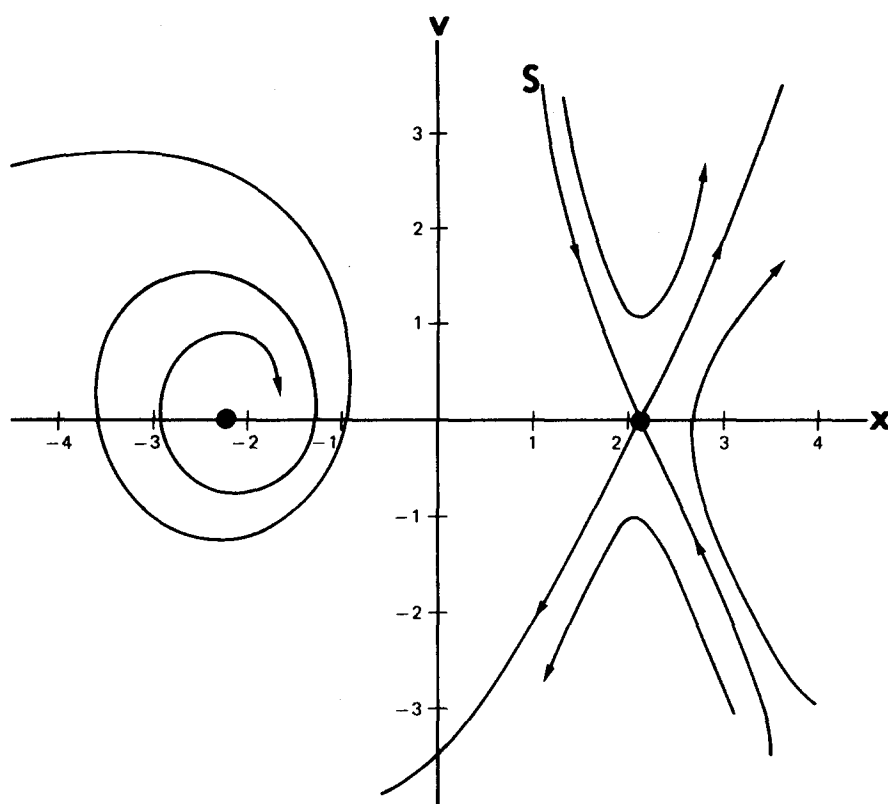


FIG. 3. Phase plane for the dynamical system $dx = v dt$, $dv = (x^2 - \alpha - \gamma v) dt$. $\alpha \cong 4.56$, $\gamma = 0.1$.

The definition of the transmission coefficient is no longer clearcut, but a reasonable definition is $\kappa = u(\hat{x}, 0)$. The function $u(x, v)$ satisfies the backward equation^{14,24}

$$0 = \epsilon \frac{\partial^2 u}{\partial v^2} + v \frac{\partial u}{\partial x} + [F(x) - v] \frac{\partial u}{\partial v} \quad (5.3)$$

and associated boundary conditions

$$\left. \begin{aligned} u(x, v) &= 0, \quad (x, v) \in S_1, \\ u(x, v) &= 1, \quad (x, v) \in S_2. \end{aligned} \right\} \quad (5.4)$$

Equation (5.3) is harder to solve than Eq. (4.2) because Eq. (5.3) is a partial differential equation. In Ref. 24, it is shown that the solution of Eq. (5.3) can be written as

$$u(x, v) \approx g(x, v) \int_{Z_0/\sqrt{\epsilon}}^{\psi(x, v)/\sqrt{\epsilon}} e^{-s^2/2} ds + \sqrt{\epsilon} h(x, v) \exp[-\psi(x, v)^2/2\epsilon] + O(\epsilon), \quad (5.5)$$

where $g(x, v)$, $\psi(x, v)$, $h(x, v)$, and Z_0 are chosen so that $u(x, v)$ defined by Eq. (5.5) asymptotically (for small ϵ) satisfies Eqs. (5.3) and (5.4). It can be shown that $\psi(x, v)$ satisfies the first order equation²⁴

$$v \frac{\partial \psi}{\partial x} + [F(x) - v] \frac{\partial \psi}{\partial v} - \psi \left(\frac{\partial \psi}{\partial v} \right)^2 = 0, \quad (5.6)$$

with initial data $\psi = 0$ on S . Equation (5.6) can be solved by the method of characteristics.¹⁶ The functions $g(x, v)$ and Z_0 are shown to be constants, which are determined as follows: Suppose that S_1 and S_2 are chosen so that they are level curves of $\psi(x, v)$; say $\psi = \psi_1$ on S_1 and $\psi = \psi_2$ on S_2 . It can be shown that²⁴ $Z_0 = \psi_1$ and

$$g = \left(\int_{\psi_1/\sqrt{\epsilon}}^{\psi_2/\sqrt{\epsilon}} e^{-s^2/2} ds \right)^{-1}. \quad (5.7)$$

The function $h(x, v)$ satisfies the equation

$$v \frac{\partial h}{\partial x} + [F(x) - v] \frac{\partial h}{\partial v} + g v \frac{\partial \psi}{\partial v} - \psi \frac{\partial \psi}{\partial v} \frac{\partial h}{\partial v} - h \frac{\partial}{\partial v} \left(\psi \frac{\partial \psi}{\partial v} \right) = 0, \quad (5.8)$$

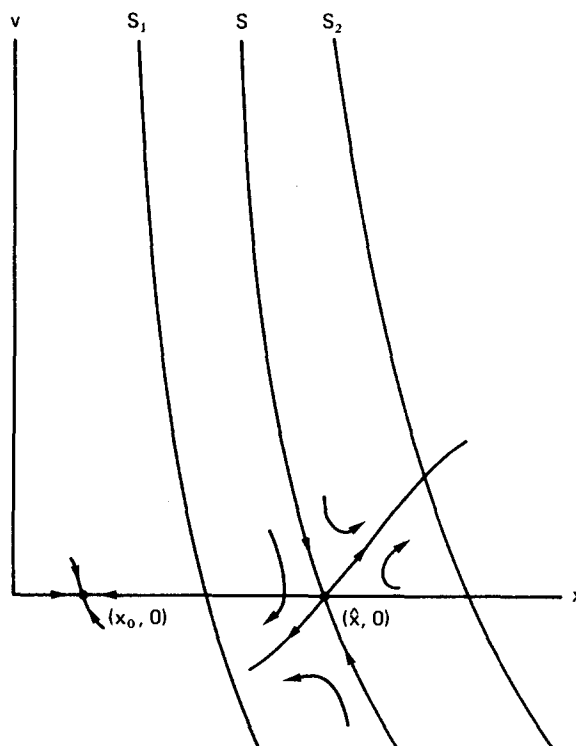


FIG. 4. Boundaries for the calculation of the transmission coefficient. The transmission coefficient is the probability that a particle starting in (S_1, S_2) exits through S_2 .

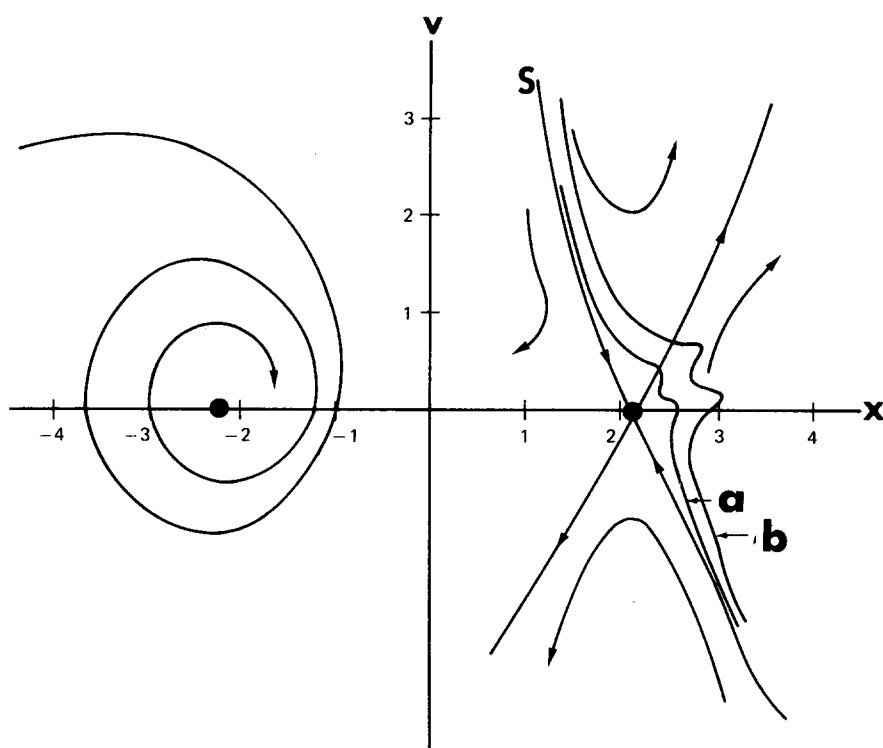


FIG. 5. Contours of the transmission coefficient, for $\epsilon = 0.01$. (a) 0.89 contour; (b) 0.99 contour.

which is a first order equation and can be solved by the method of characteristics.^{16,24}

In Fig. 5, two contours of $u(x, v)$ are shown for the system (5.1) with $\alpha = 4.56$, $\gamma = 0.1$, and $\epsilon = 0.01$. There is a dip in the level curve as the saddle point is approached.

B. Rate constant

In the case of arbitrary viscosity, the rate constant calculated according to the prescription of transition state theory is similar to the one in Sec. III A, since transition state theory uses the equilibrium solution of the Fokker-Planck equation. When the Kramers theory is used to calculate the smallest eigenvalue of the Fokker-Planck equation, a result very similar to λ_0 given by Eq. (3.6) is obtained.^{1,14}

In order to use the mean time theory of the rate constant, define

$$T(x, v) = \langle \text{mint} : [\tilde{x}(t), \tilde{v}(t)] \text{ has crossed } S \\ \text{going towards } S_2 | \tilde{x}(0) = x, \tilde{v}(0) = v \rangle. \quad (5.9)$$

Then a reasonable definition of the rate constant is

$$k = \iint \rho_0(x, v) / T(x, v) dx dv, \quad (5.10)$$

where $\rho_0(x, v)$ is the density for the initial position and velocity of phase points.

It can be shown²⁴ that $T(x, v)$ satisfies the backward equation

$$-1 = \epsilon \frac{\partial^2 T}{\partial v^2} + F(x) \frac{\partial T}{\partial v} + v \frac{\partial T}{\partial x} - v \frac{\partial T}{\partial v}. \quad (5.11)$$

With associated boundary conditions

$$\left. \begin{aligned} T(x, v) &= 0, \quad \text{for } (x, v) \in S, \\ \lim_{|v| \rightarrow \infty} T(x, v) &< \infty, \quad \lim_{x \rightarrow \infty} T(x, v) < \infty. \end{aligned} \right\} \quad (5.12)$$

An asymptotic solution of Eqs. (5.11) and (5.12) valid for small ϵ can be obtained by modifying the technique used to calculate the transmission coefficient. The details of the calculation are more complicated, and are presented in Ref. 24.

ACKNOWLEDGMENTS

I thank Dr. R. Snider and Dr. D. Ludwig for a number of discussions about this problem and Dr. Snider and Dr. J. Keizer for reading various versions of the manuscript.

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