Trajectory analysis of a kinetic theory for isomerization dynamics in condensed phases[a),b)]

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We use an exact microscopic formalism to study the implications of a stochastic model of isomerization dynamics in liquids. In the model, a reaction coordinate moves in a multistable potential and is coupled to a thermal bath via random collisions which occur with a specified average collision frequency. The nonlinear dynamics for this system is solved numerically. It is found that the usual linear rate law for isomerization is valid for any nonzero collision frequency if the activation barrier to reaction is sufficiently high. The reasons for this behavior are discussed at length. With appropriate parameter choices, we can draw conclusions concerning the *trans–gauche* isomerization of *n*-butane in liquids. Transition state theory is found to overestimate the rate constant by at least a factor of 2 to 3 at any collision frequency. The collisional contribution to the volume of activation is calculated. At 1 atm, the result is an order of magnitude larger in size than the transition state theory activation volume. Furthermore, this collisional contribution has a strong pressure dependence that should be observable experimentally.

I. MOTIVATION

A fundamental problem in chemical kinetics is the connection between the microscopic dynamics in a reacting fluid and the phenomenological description of the reaction by a chemical rate law. Recently, one of us has provided a theoretical framework for the analysis of this connection in a discussion of isomerization dynamics in classical liquids.[1]

Consider, as the simplest possible model of a two state system, the bistable potential of Fig. 1, representing the potential $V(q)$ corresponding to motion along the internal coordinate q of some hypothetical molecule. The two internal states A and B are specified by a dividing point $q=r_c$. The usual linear rate equation for two-state isomerization assumes that the nonequilibrium average numbers of A and B isomers present at time t, i.e., $\langle N_A\rangle_{ne}(t)$ and $\langle N_B\rangle_{ne}(t)$, respectively, obey

$$\frac{d}{dt}\langle N_A\rangle_{ne}(t)=-k_{AB}\langle N_A\rangle_{ne}(t)+k_{BA}\langle N_B\rangle_{ne}(t) \qquad (1.1)$$

for a closed system $[N_A(t)+N_B(t)=N=\text{constant}]$. The fluctuation of $\langle N_A\rangle_{ne}(t)$ away from its equilibrium value $\langle N_A\rangle$ therefore satisfies

$$\frac{d}{dt}\langle\delta N_A\rangle_{ne}(t)=-\tau_{rxn}^{-1}\langle\delta N_A\rangle_{ne}(t)\ , \qquad (1.2)$$

with

$$\langle\delta N_A\rangle_{ne}(t)=\langle N_A\rangle_{ne}(t)-\langle N_A\rangle\ , \qquad (1.3)$$

and

$$\tau_{rxn}^{-1}=k_{AB}+k_{BA}\ . \qquad (1.4)$$

Equations (1.1) and (1.2) are alternative statements of the same rate law.

Two important questions are at the core of our subsequent discussion: (1) Under what conditions does the rate law (1.1) provide a valid description of the behavior of the system? and (2) under what conditions are the rate constants k_{AB} and k_{BA} correctly given by classical transition state theory? These questions can be formulated at the molecular level with the aid of linear response theory. In particular, from the fluctuation-dissipation theorem, it is known that for small deviations from thermal equilibrium, $\langle\delta N_A\rangle_{ne}(t)$ will decay to zero in precisely the same way that spontaneous fluctuations $\delta N_A(t)=N_A(t)-\langle N_A\rangle$ regress in an equilibrium system. The relaxation of the spontaneous fluctuations is determined by the correlation function

$$C(t)=\langle\delta N_A\delta N_A(t)\rangle\ , \qquad (1.5)$$

where $\delta N_A=\delta N_A(0)$, and the equilibrium ensemble average is over initial conditions. As emphasized in Ref. 1, the microscopic analysis of the rate equation is most conveniently discussed in terms of the time derivative of $C(t)$ rather than the function itself. It was shown there that

$$k(t)=-\frac{1}{N}\frac{dC(t)}{dt} \qquad (1.6)$$

$$=\langle v_1\delta(q_1-r_c)H_B[q_1(t)]\rangle\ . \qquad (1.7)$$

Here, $q_1(t)$ and $v_1(t)=\dot{q}_1(t)$ are the position and velocity of the internal degree of freedom of a tagged particle at time t, the initial conditions are $q_1(0)=q_1$, $v_1(0)=v_1$, and the function $H_B(q)$ is $\theta(q-r_c)$, where $\theta(x)$ is unity for $x>0$ and zero otherwise. Equation (1.7) counts the fraction of particles crossing into state B at time zero that are still in state B at time t. Thus, $k(t)$ is the reactive flux across the barrier.

Figure 1 shows how $k(t)$ will behave for two different situations. First, imagine that $q_1(t)$ is not affected by

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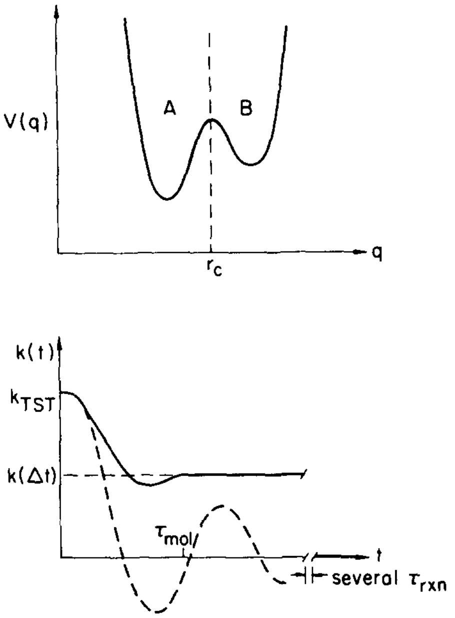

FIG. 1. A one-dimensional bistable model potential and the function $k(t)$. The dashed curve illustrates the oscillatory behavior of $k(t)$ when there is no dissipation. The solid curve illustrates the behavior of $k(t)$ when there is coupling to a heat bath, producing the plateau behavior discussed in the text.

any other degrees of freedom. The delta function in $k(t)$ places $q_1(0)$ at the transition state r_c. Given this initial condition, any trajectory will send $q_1(t)$ back and forth. In the absence of coupling to other degrees of freedom, there will be no dissipation, and the reaction coordinate $q_1(t)$ will sample each stable state for short periods of time. This behavior leads to the oscillatory behavior shown by the dashed line in Fig. 1.

The more physically relevant situation corresponds to $q_1(t)$ being coupled to a large number of degrees of freedom. Let us assume that this "bath" is at (or near) thermal equilibrium. Further, let us assume that the potential barrier separating the two potential minima is large compared to the thermal energy k_BT. Then, after $q_1(t)$ leaves the transition state and passes over one of the stable wells, the kinetic energy for the reaction coordinate will be large compared to that of a typical degree of freedom in the bath. Hence, the coupling between $q_1(t)$ and the other degrees of freedom will lead to dissipation, i.e., the bath will take energy from the reaction coordinate, and $q_1(t)$ will be rapidly trapped in one of the wells, and it will remain trapped for a long period of time. This behavior leads to the plateau value shown in Fig. 1. The time to trap the particle is denoted by τ_{mol} (a molecular relaxation time), and the time it takes to activate the reaction coordinate so it is no longer trapped is roughly τ_{rxn} (the average time between reactions).

In Ref. 1, it was shown that if the phenomenological rate law is correct, then the plateau value behavior will be found for times $t=\Delta t$, where $\tau_{mol} < \Delta t \ll \tau_{rxn}$. Furthermore, the average frequency of reaction τ_{rxn}^{-1} is given by

$$\tau_{rxn}^{-1} = (x_A x_B)^{-1} k(\Delta t) , \tag{1.8}$$

where x_A and x_B denote the equilibrium mole fractions of species A and B, respectively. It is also a straightforward matter to prove that the existence of the plateau value with $\tau_{mol} < \Delta t \ll \tau_{rxn}$ guarantees the correctness of the phenomenological rate law near equilibrium. Thus, for processes occurring in systems at or near macroscopic equilibrium, *the plateau value behavior of $k(t)$ is equivalent to the rate law, and the rate constant is determined by the value of $k(t)$ in the plateau region.*

One way to appreciate the importance of the separation in time scales is to note that according to the rate law $C(t)$ is given (in a coarse grained sense) by

$$C(t) \cong \langle (\delta N_A)^2 \rangle \exp(-t/\tau_{rxn}) . \tag{1.9}$$

Therefore, from Eq. (1.7)

$$\tau_{rxn}^{-1} = (x_A x_B)^{-1} k(\Delta t) [1 + O(\Delta t/\tau_{rxn})] . \tag{1.10}$$

Thus, for any nonzero value of τ_{mol}/τ_{rxn}, Eq. (1.8) is an approximate expression for τ_{rxn}^{-1} rather than an exact one, as we have neglected terms of order $\Delta t/\tau_{rxn}$ in the expansion of the exponential $\exp(-\Delta t/\tau_{rxn})$. It is also important to note that this same quantity $\Delta t/\tau_{rxn}$ provides a measure of the validity of the phenomenological rate law, as mentioned earlier. This is made clearer physically by a consideration of the reactive flux $k(t)$. The quantity $\Delta t/\tau_{rxn}$ is proportional to the area under $k(t)$ in the transient region, which is a measure of the transport over the barrier by the transient (non-steady state) flux, i.e., $\Delta t/\tau_{rxn}$ measures the fraction of reactions which do not obey the rate law.

A somewhat different approach has been taken by Widom.[2] Classically, Widom's argument is as follows: The phase space distribution function $f(qv;t)$ obeying some (unspecified) kinetic equation is written as

$$f(qv;t) = \sum_n a_n \psi_n(qv) \exp(-\lambda_n t) \tag{1.11}$$

in terms of the eigenfunctions $\psi_n(qv)$ and eigenvalues λ_n of the kinetic equation. The number of isomers in state A is given by

$$\langle N_A \rangle_{ne}(t) = \int dq \int dv f(qv;t) H_A(q) , \tag{1.12}$$

$$= \sum_n b_n \exp(-\lambda_n t) , \tag{1.13}$$

where $H_A(q)$ stands for $\theta(r_c - q)$, and

$$b_n = a_n \int dq \int dv\, \psi_n(qv) H_A(q) . \tag{1.14}$$

Note that $b_0 = \langle N_A \rangle$ and $\lambda_0 = 0$ (equilibrium state). Widom immediately makes the identification $\tau_{rxn}^{-1} = \lambda_1$ (if the eigenvalues are ordered $0 = \lambda_0 < \lambda_1 < \lambda_2 < \cdots$), and thereby reduces the problem to determining the spectrum of a kinetic operator and asserts that the rate law will be valid if $\lambda_2 - \lambda_1 \gg \lambda_1$. We have two comments on this approach. First and most important, it is very difficult in practice to find the spectrum of a kinetic equation corresponding to a realistic system (Widom has done it only for idealized models), whereas it is not difficult to calculate $k(t)$ for a realistic model. Indeed, it is convenient to analyze computer simulations in terms of

$k(t)$. Our second comment is that, while it is clear the condition $\lambda_2 - \lambda_1 \gg \lambda_1$ is necessary for the rate law description to be valid, it is not obviously sufficient, as Eq. (1.13) shows. It is conceivable that even if $\lambda_2 - \lambda_1 \gg \lambda_1$, for some system, b_1 and b_2 may be of comparable magnitude. In that case, a considerable fraction of reactants would not obey the rate law (1.1). Stated another way, the condition $\lambda_1 - \lambda_2 \gg \lambda_1$ guarantees that some variable, namely, $\psi_1(qv)$, the eigenfunction with eigenvalue λ_1, does obey a simple linear rate law. However, it is not obvious for the general case that the integral over v of this eigenfunction is exactly or approximately the concentration of the reactant or product. If it is not, then the concentration will not obey a rate law even if the gap in the eigenvalue spectrum exists.

The correlation function $k(t)$ is especially well suited to a consideration of our second important question, the validity of transition state theory.[1,3] In the context of our model, transition state theory says that once a particle has crossed r_c into the product region of the potential, it remains there (until another reaction occurs). Mathematically, this means that $H_B[q_1(t)]$ is replaced by the Heaviside function $\theta(v_1)$ in Eq. (1.7), giving

$$k_{\mathrm{TST}} = s(r_c)\langle v_1\theta(v_1)\rangle = (1/2)\langle |v_1|\rangle s(r_c)\ , \tag{1.15}$$

with

$$s(r_c) = \exp[-\beta V(r_c)] \Big/ \int_{-\infty}^{\infty} dq \exp[-\beta V(q)]\ , \tag{1.16}$$

where β^{-1} is the temperature times Boltzmann's constant k_BT. Equation (1.15) does not depend on dynamical behavior, only on the shape of the potential, and is therefore constant in time. Note that the replacement of $H_B[q_1(t)]$ by $\theta(v_1)$ is correct at very short times [short enough that the particle has experienced no collisions with other particles or rebounds from the repulsive wall of $V(q)$]. Therefore, for any system, $k(t) \to k_{\mathrm{TST}}$ as $t \to 0+$ (see Ref. 1). We also mention that, while Eq. (1.8) and (1.10) are independent of the precise location of r_c, Eq. (1.15) depends crucially on it. The usual choice is the location of the maximum of the potential barrier.

Another way of viewing transition state theory was also described in Ref. 1. Suppose we imagined that the rate law was valid at all time scales. Then the exponential in Eq. (1.9) would be valid not only in a coarse grained sense but even for times shorter than τ_{mol}. Since $\dot{C}(0+) = -k(0+) = -k_{\mathrm{TST}}$, the assumption of pure exponential behavior fixes τ_{rxn} at k_{TST}^{-1} and thus yields transition state theory for the rate constant. Of course, no one should expect such strong adherence to phenomenology on short time scales.

To see what we should expect, we analyze in this article a simple kinetic theory for motion of a particle in a bistable potential coupled via collisions to a heat bath. This model is solved for various potentials and couplings of interest and the results are interpreted in the context of the preceding discussion.

II. KINETIC THEORY

A. Model kinetic equation and formal solution

We present now a simple kinetic theory for the phase space distribution function $f(qv;t)$ due originally to Bohm and Gross.[4] Assume that $f(qv;t)$ obeys the local kinetic equation (classical master equation)

$$\left(\frac{\partial}{\partial t} + L\right) f(qv;t) = \int dv' \int dq' \times [w(q'v', qv) f(q'v';t) - w(qv, q'v') f(qv;t)] \tag{2.1a}$$

and take the probability $w(q'v', qv)$ going from the state $q'v'$ to the state qv as

$$w(q'v', qv) = \alpha\phi(v)\,\delta(q - q')\ , \tag{2.1b}$$

where α is a parameter (the mean collision frequency), $\phi(v)$ is the Boltzmann distribution for velocities, and L is the Liouville operator

$$L = v\,\frac{\partial}{\partial q} + m^{-1}F(q)\,\frac{\partial}{\partial v}\ , \qquad F(q) = -\frac{\partial V(q)}{\partial q}\ , \tag{2.2}$$

which generates the free streaming motion of a single particle in the potential $V(q)$. If the initial value of $f(qv;t)$ is taken as

$$f(qv;0) = s(q)\,\phi(v)\,\delta(q - q')\delta(v - v')\ , \tag{2.3}$$

then Eq. (2.1) describes the time evolution of the phase space correlation function

$$f(qv, q'v';t) = \langle \delta[q - q_1(t)]\,\delta[v - v_1(t)]\,\delta(q' - q_1)\delta(v' - v_1)\rangle\ . \tag{2.4}$$

Here, q, v, q', and v' are field variables; q_1, v_1, $q_1(t)$, and $v_1(t)$ are the position and velocity of a tagged particle at time zero and time t, respectively. $s(q)$ is the spatial distribution function defined in Eq. (1.16). The indices q' and v' will subsequently be suppressed unless explicitly needed.

This kinetic equation describes a model in which a test particle streams freely in the potential $V(q)$ between instantaneous collisions (of average frequency α) which randomize the particle's velocity without changing its position. The stochastic nature of the dynamics will be made more precise in subsequent discussion.

It is not difficult to obtain a formal solution to Eq. (2.1). The Laplace transform $\tilde{f}(qv;s)$ given by

$$\tilde{f}(qv;s) = \int_0^{\infty} dt \exp(-st) f(qv;t) \tag{2.5}$$

satisfies

$$[s + \alpha + L]\tilde{f}(qv;s) = \alpha\phi(v)\int dv'\,\tilde{f}(qv';s) + s(q)\,\phi(v)\,\delta(q - q')\,\delta(v - v')\ . \tag{2.6}$$

Solving for $\tilde{f}(qv;s)$ gives

$$\tilde{f}(qv;s) = [s + \alpha + L]^{-1}\,[s(q)\phi(v)\delta(q - q')\delta(v - v') + \alpha\phi(v)\int dv'\,\tilde{f}(qv;s)]\ . \tag{2.7}$$

Integrate both sides over v and v', define $\tilde{C}(q, q';s)$ by

$$\tilde{C}(q, q';s) = \int dv \int dv'\,\tilde{f}(qv, q'v';s)\ , \tag{2.8}$$

and Eq. (2.7) becomes

$$\tilde{C}(q,q';s)=\tilde{C}^{(0)}(q,q';s+\alpha)+\alpha\int dv[s+\alpha+L]^{-1}\times\phi(v)\,\tilde{C}(q,q';s)\ , \tag{2.9}$$

$$=\tilde{C}^{(0)}(q,q';s+\alpha)+\alpha\int dq''\int dv\times[s+\alpha+L]^{-1}\phi(v)\delta(q-q'')\tilde{C}(q'',q';s) \tag{2.10}$$

$$=\tilde{C}^{(0)}(q,q';s+\alpha)+\alpha\int dq''\tilde{C}^{(0)}(q,q'';s+\alpha)\times\tilde{C}(q'',q';s)\,s(q'')^{-1}\ . \tag{2.11}$$

Iteration of Eq. (2.11) gives a formal expansion for the correlation function

$$\tilde{C}(q,q';s)=\tilde{C}^{(0)}(q,q';s+\alpha)+\alpha\int dq''\tilde{C}^{(0)}(q,q'';s+\alpha)\tilde{C}^{(0)}(q'',q';s+\alpha)s(q'')^{-1}$$
$$+\alpha^2\int dq''\int dq'''\tilde{C}^{(0)}(q,q''';s+\alpha)\tilde{C}^{(0)}(q''',q'';s+\alpha)\,\tilde{C}^{(0)}(q'',q';s+\alpha)s(q''')^{-1}s(q'')^{-1}+\cdots \tag{2.12}$$

in terms of the ideal gas (collisionless) correlation function

$$\tilde{C}^{(0)}(q,q';s)=\int dv[s+L]^{-1}\phi(v)s(q)\delta(q-q')\ . \tag{2.13}$$

$k(t)$ and $C(t)$ are related to $C(q,q';t)$ by

$$C(t)=N\int dq\int dq'\ H_A(q)H_A(q')C(q,q';t)\ , \tag{2.14}$$

and

$$k(t)=\frac{-1}{N}\ \frac{dC(t)}{dt}\ , \tag{2.15}$$

and therefore can in principle be calculated from Eq. (2.12), but this is quite difficult, in practice. The difficulty arises because the computation of $\tilde{C}^{(0)}(q,q';s)$ requires the solution of a difficult nonlinear classical mechanics problem for any interesting bistable potential. However, approximate solutions may be found analytically in several limiting cases.

B. Limiting behavior

1. $\alpha T \ll 1$

Let T represent the average period for a particle to traverse the entire bistable potential. Then the condition $\alpha T \ll 1$ means physically that a particle on the average will rebound from the repulsive walls of $V(q)$ many times before suffering a collision. Skinner and Wolynes[5] have shown that, for symmetric potentials,

$$\tau_{\rm rxn}^{-1}=2\alpha\int_{-V^{-1}(Q)}^{0}dq\,s(q)\,[1-h(q)]h(q)+0(\alpha^2)\ , \tag{2.16}$$

where $V^{-1}(Q)$ is the value of q when $V(q)=Q$, Q is the value of $V(q)$ at the top of the potential barrier, and $h(q)=\mathrm{erf}(\{\beta[Q-V(q)]\}^{1/2})$. This result was obtained by an expansion of $\tilde{C}(s)^{-1}$ in powers of α, keeping only the lowest order term. Further discussion of this result will be given in connection with exact numerical solutions in Sec. III.

2. $\alpha/s \gg 1$ (Diffusion limit)

Equation (2.6) gives, for large α,

$$\tilde{f}(qv;s)=[s+\alpha+L]^{-1}[f(qv;0)+\alpha\phi(v)\,\tilde{C}(q;s)]\ , \tag{2.17}$$

$$=\left[\frac{1}{\alpha}-\frac{1}{\alpha^2}(s+L)+\frac{1}{\alpha^3}(s+L)^2+0(\alpha^{-4})\right]\times[f(qv;0)+\alpha\phi(v)\,\tilde{C}(q;s)]\ , \tag{2.18}$$

where the q' variable is suppressed for convenience. Integration of both sides over v and v' gives

$$0=C(q;0)-s\tilde{C}(q;s)+D\frac{\partial^2}{\partial q^2}\tilde{C}(q;s)$$
$$-\frac{1}{\alpha m}\ \frac{\partial}{\partial q}F(q)\tilde{C}(q;s)+0\left(\frac{1}{\alpha^2}\right)\ ,\quad D\equiv\frac{\langle v^2\rangle}{\alpha}\ , \tag{2.19}$$

using the identities

$$\int dv\,Lf(qv;0)=0 \tag{2.20}$$

and

$$\int dv\,L^2f(qv;0)=\langle v^2\rangle\ \frac{\partial^2}{\partial q^2}C(q;0)-\frac{1}{m}\ \frac{\partial}{\partial q}F(q)\,C(q;0)\ . \tag{2.21}$$

Equations (2.20) and (2.21) are derived by noting that L is an odd function whereas $f(qv;0)$ is even. Neglecting terms of order α^{-2}, Eq. (2.19) becomes, after inverse Laplace transformation,

$$\frac{\partial}{\partial t}C(q;t)=D\frac{\partial^2 C(q;t)}{\partial q^2}-\frac{1}{\alpha m}\ \frac{\partial}{\partial q}F(q)\,C(q;t)\ , \tag{2.22}$$

which is the Smoluchowski equation.[6] Thus, we have shown that our kinetic model tends to the correct Brownian motion limit in the limit of high collision rate. There are many discussions of the problem of passage over a barrier based on Eq. (2.22), the first being that of Kramers.[6,7] An especially comprehensive recent discussion is given by van Kampen,[8] and there are many more in the literature.[9] Kramers[7] was able to show, for a smooth potential with quadratic maxima and minima, that

$$\tau_{\rm rxn}^{-1}=\frac{\omega_A\omega_C}{\pi\alpha}\exp(-\beta Q)+0(\alpha^{-2})\ , \tag{2.23}$$

where $\frac{1}{2}m\omega_A^2$ and $\frac{1}{2}m\omega_C^2$ determine the curvatures of the well and barrier, respectively.

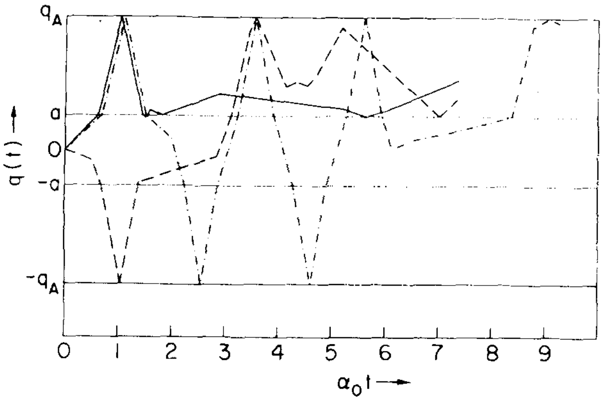

FIG. 2. Sample trajectories computed from the stochastic dynamics with the piecewise constant potential reference parameters listed in Table I. The trajectory — enters the products region and is trapped (a TST trajectory), whereas the trajectories --- and —•— demonstrate different types of non-TST behavior.

C. Stochastic dynamics

As mentioned previously, the formal solution (2.12) of the kinetic equation did not prove immediately useful for numerical calculations of the correlation functions $C(t)$ and $k(t)$. It is possible to expand $f(qv;t)$ in a series of orthogonal functions (e.g., Hermite polynomials) and numerically determine the expansion coefficient (as done by Visscher[10] and Blomberg[11] in discussions of the Fokker–Planck equation). However, the convergence of such a solution for our problem is uncertain. We preferred to develop a method more closely related to the physics of the kinetic equation.

Our approach is to calculate trajectories for a particle in a bistable potential using a stochastic dynamics corresponding to the collision operator in Eq. (2.1). If the stochastic trajectories are properly computed, then any dynamical property of the system calculated by ensemble averages over a sufficient number of trajectories should equal that calculated from the phase space distribution function satisfying the kinetic equation. The stochastic dynamics corresponding to Eq. (2.1) is specified by the following scheme:

(1) Sample a phase point (qv) from the canonical distribution $s(q)\phi(v)$;

(2) advance the phase point in time using the Liouville operator (2.2);

(3) at random intervals, "collisions" occur, which instantaneously randomize the velocity, leaving the position fixed;

(4) the times between collisions are sampled from an exponential distribution, with decay constant α;

(5) new velocities are sampled from the Boltzmann distribution $\phi(v)$.

By this algorithm, one may advance a trajectory in time as far as desired. This type of stochastic dynamics has been applied numerically by others to problems involving rotational motion.[12] Previous work[4,13] suggested to us that the algorithm would provide the same correlation functions as the solution to the kinetic equation. Indeed, the equivalence of the stochastic dynamics and the kinetic Eq. (2.1) can be established mathematically. This is demonstrated in the Appendix. The algorithm for the stochastic dynamics easily adapted for machine computation using standard numerical techniques to integrate the free motion and sample exponential and normal deviates. Figure 2 shows examples of trajectories computed by this procedure for a potential drawn in Fig. 3. The details of the calculation and the physical interpretation of the trajectories is given in the next section.

III. RESULTS

To make our results physically meaningful, our model bistable potentials are chosen to roughly approximate the barrier to internal rotation between *gauche* and *trans* states observed in n-butane.[14] We consider two functional forms: (1) a piecewise harmonic potential

$$V(q)=\begin{cases}\frac{1}{2}m\omega_A^2(q+q_A)^2\,, & q<-a\,,\\ Q-\frac{1}{2}m\omega_I^2q^2\,, & -a<q<b\,,\\ V_B+\frac{1}{2}m\omega_B^2(q-q_B)^2\,, & b<q\,,\end{cases}\qquad(3.1)$$

[Q, V_B, q_A, q_B, m, and ω_I are specified, and ω_A, ω_B, a, and b are chosen to ensure that $V(q)$ and $dV(q)/dq$ are continuous] and (2) a piecewise constant potential

$$V(q)=\begin{cases}\infty\,, & q<-q_A-d_A/2,\\ 0\,, & -q_A-d_A/2<q<-a\,,\\ Q\,, & -a<q<a\,,\\ V_B\,, & a<q<q_A+d_A/2\,,\\ \infty\,, & q_A+d_A/2<q\,.\end{cases}\qquad(3.2)$$

These potentials have the advantage that the free streaming motion can be solved exactly and that a small number of simple parameters specify their shape.

A set of reference potential parameters were chosen so that our calculations might be relevant to an actual physical process: the *trans*–*gauche* isomerization of n-butane. In going from the *trans* to the *gauche* state,

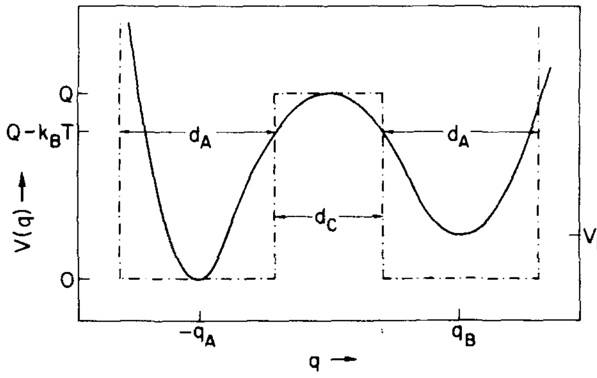

FIG. 3. The two model potentials described in the text. The solid line is the piecewise harmonic potential given by Eq. (3.1). The dashed line is the piecewise constant potential of Eq. (3.2).

TABLE I. Reference parameters.

Piecewise harmonic potential	Piecewise constant potential
$Q = 2.95$ kcal/mole	$Q = 2.95$ kcal/mole
$q_A = q_B = 1.57$ Å	$d_C = 2a = 1.30$ Å
$\omega_1 = 1.06 \times 10^{13}$ sec^{-1}	$q_A = 2.50$ Å
$V_B = 0.70$ kcal/mole	$d_A = q_A - a = 1.85$ Å
	$V_B = 0$
$k_B T = 0.60$ kcal/mole	
$\alpha = 3.0 \times 10^{12}$ sec^{-1}	
$m = 1.85 \times 10^{-23}$ g	

a CH_3 group in n-butane rotates through an angle $\Delta\phi = 2\pi/3$, which, for a carbon–carbon bond length of ~1.5 Å, means the CH_3 group has moved a distance of roughly 3.14 Å along a circular arc. To incorporate the essential elements of this motion in our one-dimensional model, we have performed our calculations for a particle of mass m equal to the reduced CH_3 mass in n-butane moving in a bistable potential whose minima are separated by 3.14 Å. The barrier height and well depths are adjusted to match those of the experimental Scott–Scheraga potential.[14] These considerations fix the parameters m, Q, V_B, q_A, and q_B of the piecewise harmonic potential (3.1). The parameter ω_1 is fixed by requiring the width of the barrier at energy $Q - k_B T$ to equal that of the Scott–Scheraga potential (see Fig. 3). The reference parameters that we have used for the piecewise constant potential (3.2) are chosen as shown in Fig. 3. The collision frequency α is really the frequency of collisions which couple to the reaction degree of freedom, rather than the actual collision frequency. Thus, imagining a n-butane molecule dissolved in liquid CCl_4, the reference value for α was taken to be 1/3 of the collision frequency in a rough hard sphere model of CCl_4.[15] A summary of the reference parameters is given in Table I. When describing variations in parameters, a subscript or superscript zero is frequently used in the text to indicate reference values for particular parameters.

We find that for $k(t)$ both the smooth and discontinuous potentials give qualitatively similar results, as illustrated in Fig. 4. The small differences are in the transient behavior; the behavior of the plateau value as a function of α is nearly the same for both potentials. Most calculations were done using the piecewise constant potential.

As our value for the effective collision frequency was only an estimate, calculations were performed for a range of α. In each case, a plateau was found in $k(t)$, from which τ_{rxn}^{-1} was determined. Figure 5 gives τ_{rxn}^{-1} as a function of α for the piecewise constant potential. Also shown in Fig. 5 are the results for small α [given by Eq. (2.16)] and Kramers' large α formula. The traditional Kramers' result (2.23) is valid for a harmonic potential like Eq. (3.1) rather than a piecewise constant one. However, it is not difficult to extend Kramers' argument to the case of a discontinuous potential,

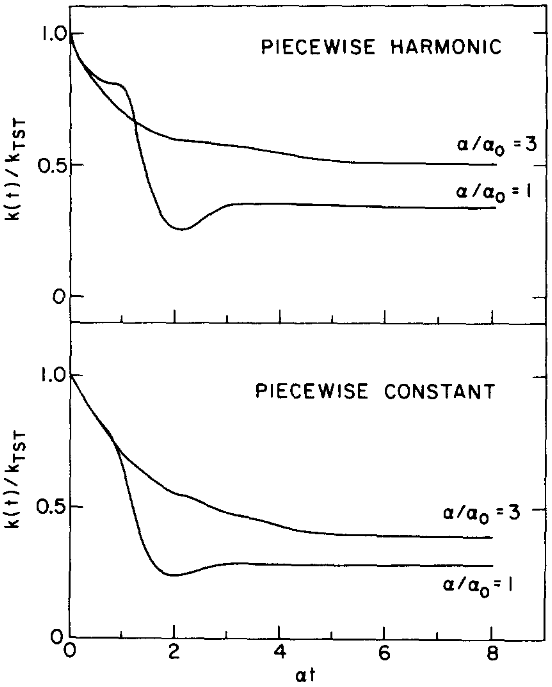

FIG. 4. A comparison of results for $k(t)$ found using the piecewise constant and piecewise harmonic potentials for two different collision frequencies and the reference parameters given in Table I.

and one obtains

$$\tau_{\mathrm{rxn}}^{-1}(\mathrm{Kramers}) = \exp(-\beta Q)\left[2\langle v^2\rangle/(d_A d_C \alpha) + 0(\alpha^{-2})\right] , \tag{3.3}$$

where d_A and d_C are the well and barrier width, respectively. It is this Kramers' formula which is plotted in Fig. 5. At small α, fair agreement with the small α result of Skinner and Wolynes[5] is obtained; excellent agreement with the Kramers' result is obtained at sufficiently large values of α. Note, however, that physically reasonable values of α are far smaller than those

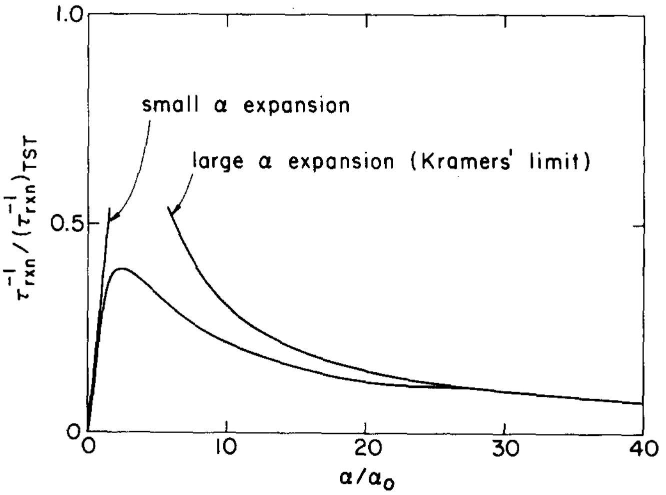

FIG. 5. τ_{rxn}^{-1} is as a function of α/α_0 for the piecewise constant potential. Here, α_0 is the reference collision frequency. All model parameters other than α are the reference parameters listed in Table I. With those values, $(\tau_{\mathrm{rxn}}^{-1})_{\mathrm{TST}} = 5.0 \times 10^{-3}\alpha_0$.

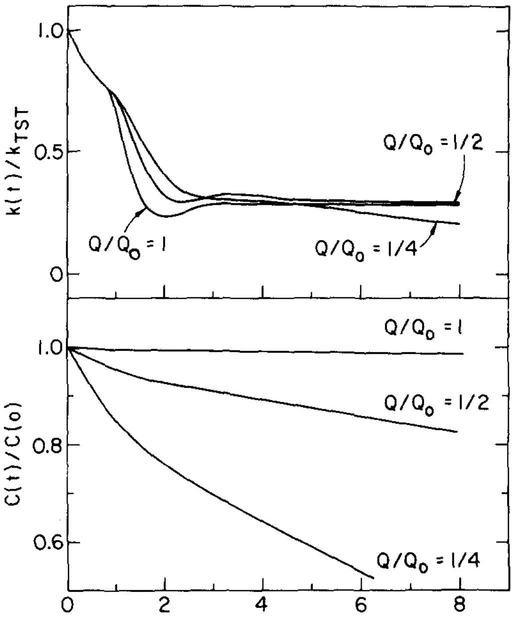

FIG. 6. $k(t)$ and $C(t)/C(0)$ for the piecewise constant potential at different barrier heights Q. Here, Q_0 is reference barrier height listed in Table I. Others parameters used are those given in Table I. From the graphs of $k(t)$, we estimate that for $Q/Q_0=1$ and $\frac{1}{2}$, the ratio $\tau_{\rm mol}/\tau_{\rm rxn}$ is 0.04 and 0.05, respectively. For $Q/Q_0=\frac{1}{4}$, no plateau is apparent.

for which the asymptotic Kramers result is valid. Figure 5 clearly shows that the transition state theory (TST) result (1.15) is never a good approximation to the actual rate, for any value of α.

There are enough parameters in this problem that a systematic exploration of all possible combinations is not feasible. We have, therefore, used our physical ideas to guide our parameter choices. One major objective of this work was to investigate the domain of of validity of the rate law (1.1). As discussed above, the validity of the rate law is controlled by the quantity $\tau_{\rm mol}/\tau_{\rm rxn}$, the rate law becoming exact as $\tau_{\rm mol}/\tau_{\rm rxn}\to 0$. The following argument shows that for our stochastic model the $\tau_{\rm mol}/\tau_{\rm rxn}$ is a strong function only of the barrier height Q. Consider *α small*: Since the collision operator samples the Boltzmann distribution $\phi(v)$, we may estimate $\tau_{\rm rxn}^{-1}$ by

$$\tau_{\rm rxn}^{-1}\approx\alpha\int_{\sqrt{2Q/m}}^{\infty}\phi(v)\,dv$$
$$=\alpha\,{\rm erfc}(\sqrt{\beta Q})\,. \qquad (3.4)$$

Another derivation of this result is given by Skinner and Wolynes.[5] The time at which the plateau value appears $\tau_{\rm mol}$ will be roughly the collision time α^{-1} (the time to trap the particle once it has crossed the barrier). Therefore,

$$\tau_{\rm mol}/\tau_{\rm rxn}\approx{\rm erfc}(\sqrt{\beta Q})$$
$$\sim\exp(-\beta Q)\quad(\beta Q\gg 1)\,, \qquad (3.5)$$

and clearly $\tau_{\rm mol}/\tau_{\rm rxn}$ is small if $\beta Q\gg 1$.

Consider *α large*: In the diffusion limit, the Kramers' result gives (with $d_C=d_A=d$)

$$\tau_{\rm rxn}^{-1}=\frac{2\langle v^2\rangle}{d^2\alpha}\exp(-\beta Q)\,. \qquad (3.6)$$

The time $\tau_{\rm mol}$ is roughly the time required for a particle to diffuse across the top of the barrier (as it is instantly trapped when it reaches the edge). It is a simple consequence of the diffusion Eq. (2.22) that this time satisfies

$$d^2=D\tau_{\rm mol}=\frac{\langle v^2\rangle}{\alpha}\tau_{\rm mol}\,,$$
$$\tau_{\rm mol}=\frac{\alpha d^2}{\langle v^2\rangle}\,, \qquad (3.7)$$

and therefore

$$\tau_{\rm mol}/\tau_{\rm rxn}\approx\exp(-\beta Q)\,, \qquad (3.8)$$

which, again, is small if $\beta Q\gg 1$.

From the limiting behaviors as α becomes large and small, we expect that, provided α is nonzero, the rate law will be valid if Q is large compared to k_BT. We have numerically studied the effect of changing the barrier height for a value of α between the limiting cases discussed above (corresponding to $\alpha d/\langle v^2\rangle^{1/2}=1$). Figure 6 shows the numerical results for $k(t)$ and $C(t)$ corresponding to different values of the barrier height Q. Also given is an estimate of $\tau_{\rm mol}/\tau_{\rm rxn}$, which shows quantitatively the errors in the rate law description as βQ becomes small. In Fig. 7, the barrier height Q is that given in Table I for the *trans-gauche* isomerization of *n*-butane (~5 k_BT at 300 °K), and $C(t)$ is shown for different values of α. The estimates of $\tau_{\rm mol}/\tau_{\rm rxn}$ demonstrate that the rate law description is valid over a wide

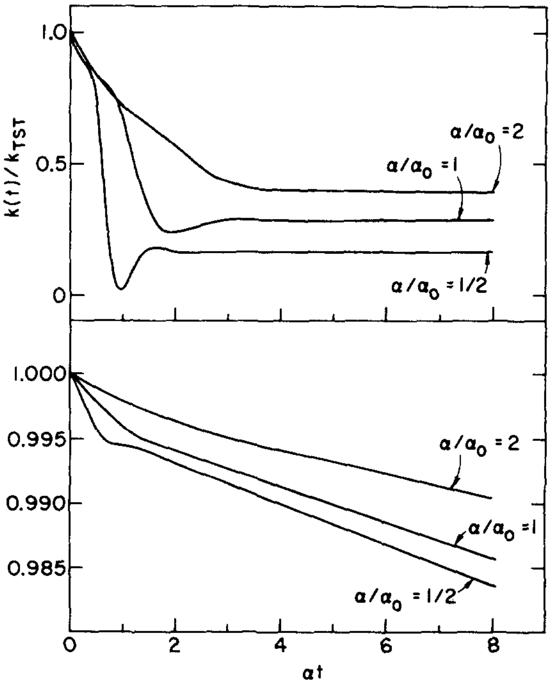

FIG. 7. $k(t)$ and $C(t)/C(0)$ for the piecewise constant potential at different collision frequencies α. Here, α_0 is the reference collision frequency. Other parameters used are given in Table I.

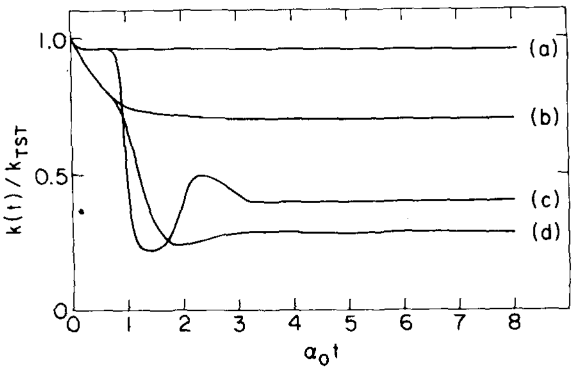

FIG. 8. $k(t)$ for piecewise constant potentials with parameters chosen to demonstrate the factors influencing the deviation from transition state theory. Curve (d) corresponds to $d_C/d_C^{(0)} = d_A/d_A^{(0)} = 1$. Curve (a) corresponds to $d_C/d_C^{(0)} = \frac{1}{10}$ and $d_A/d_A^{(0)} = 10$. Curve (c) corresponds to $d_C/d_C^{(0)} = \frac{1}{10}$. Curve (b) corresponds to $d_A/d_A^{(0)} = 10$. Here, $d_A^{(0)}$ and $d_C^{(0)}$ are the reference values given in Table I. Parameter values not specified above are taken from Table I.

range of α, as expected (only in the trivial limit $\alpha = 0$ would serious deviations be expected).

Numerical calculations have also been used to explore the validity of transition state theory (TST). As mentioned earlier, TST assumes that once a particle has crossed the potential barrier, it is trapped (until the next reaction occurs.) In the context of our model, we expect this to be a good approximation if (1) $\alpha d_C/\langle v^2\rangle^{1/2} \ll 1$ (essentially no collisions occur while the particle is crossing the barrier) and (2) $\alpha d_A/(2Q/m)^{1/2} \gg 1$ (many collisions occur while the particle is crossing the well of the potential, ensuring that it is trapped). Figure 8 illustrates the behavior of $k(t)$ for a potential satisfying both conditions above. Note that the transient period is very brief, and that $k(t)$ remains within 10% or so of k_{TST} in the plateau region. Figure 8 also shows the behavior obtained when condition (1) and (2) respectively are relaxed. Replacing condition (1) shows the deviations from TST that are due to collisions suffered on top of the barrier. Relaxing condition (2) shows deviations from TST that are due to rebounding from the walls of the potential before being trapped in one of the wells. To illustrate the kind of events that may occur, some sample trajectories (briefly mentioned earlier) are displayed in Fig. 2. Three trajectories are shown, one which crosses the barrier and is trapped (a TST trajectory), and two others demonstrating different types of non-TST behavior. Note that all trajectories begin at the midpoint of the barrier, as required by the delta function in Eq. (1.7).

While it is clear from our calculations that TST does not provide an accurate measure of the precise value of the rate constant, it is also important to assess whether TST provides a reliable estimate of the thermodynamic state dependence of the rate constants determined from our model. For this discussion, it is convenient to introduce the transmission coefficient κ defined by

$$k(\Delta t) = k_{TST}\kappa \ . \tag{3.9}$$

The transmission coefficient is a dynamical quantity (as opposed to the equilibrium k_{TST}) which measures the fraction of non-TST trajectories. A common approximation is to assume that κ is independent of thermodynamic state. If that approximation is accurate, then the activation energy and volume defined by

$$k_B T^2[\partial \ln k(\Delta t)/\partial T]_p = \Delta E^{\ddagger} \ , \tag{3.10}$$

and

$$-k_B T[\partial \ln k(\Delta t)/\partial p]_T = \Delta V^{\ddagger} \ , \tag{3.11}$$

respectively, can be replaced by the TST estimates

$$k_B T^2(\partial \ln k_{TST}/\partial T)_p = \Delta E^{\ddagger}_{TST} \tag{3.12}$$

and

$$-k_B T(\partial \ln k_{TST}/\partial p)_T = \Delta V^{\ddagger}_{TST} \ .$$

To see if these replacements are justified, we have applied our stochastic model to estimate the dependence of κ on the temperature T and the pressure p for the *trans–gauche* isomerization of n-butane in dissolved liquid CCl_4 and we have compared the dependence with that of k_{TST}.

For our choice of reference parameters, the thermodynamic state dependence of k_{TST} is contained primarily in the Boltzmann factor $\exp[-\beta V(r_C)]$. When an isomerization process occurs in a condensed phase, $V(r_C)$ is actually a free energy[1] and thus the Boltzmann factor depends on density (or pressure) as well as on temperature. By applying the theory for this density dependence due to Pratt *et al.*[16] and using the equation of state data of McCool and Woolf,[17] we estimate that for n-butane in liquid CCl_4

$$\Delta V^{\ddagger}_{TST} \approx -1.3 \text{ cm}^3/\text{mole} \ . \tag{3.13}$$

The temperature dependence is estimated more directly and one finds at room temperature

$$\Delta E^{\ddagger}_{TST} \approx Q \approx 5k_B T \ . \tag{3.14}$$

In our stochastic model (and presumably in nature as well), κ depends on thermodynamic state primarily through its dependence on the collision rate α. Consequently,

$$(\partial \ln\kappa/\partial T)_p = \frac{d\ln\kappa}{d\alpha}\left(\frac{d\alpha}{\partial T}\right)_p \tag{3.15}$$

and

$$(\partial \ln\kappa/\partial p)_T = \frac{d\ln\kappa}{d\alpha}\left(\frac{d\alpha}{\partial p}\right)_T \ . \tag{3.16}$$

Notice from Fig. 5 that $d\ln\kappa/d\alpha$ is not a constant; it even changes sign. As described earlier, we estimate that the value of α appropriate for n-butane in liquid CCl_4 is roughly 1/3 the hard sphere collision frequency obtained from the Carnahan–Starling formula[18]

$$\alpha \approx (4/\sigma)(k_B T/M\pi)^{1/2}\eta(2-\eta)/(1-\eta)^3 \ , \tag{3.17}$$

where M and σ denote the mass and hard sphere diameter for CCl_4, respectively, and η is the packing fraction for the liquid [i.e., $(\pi\sigma^3/6)$ times the molecular density]. The value of σ is taken from the rough hard sphere theory for CCl_4,[15] and η is determined from the

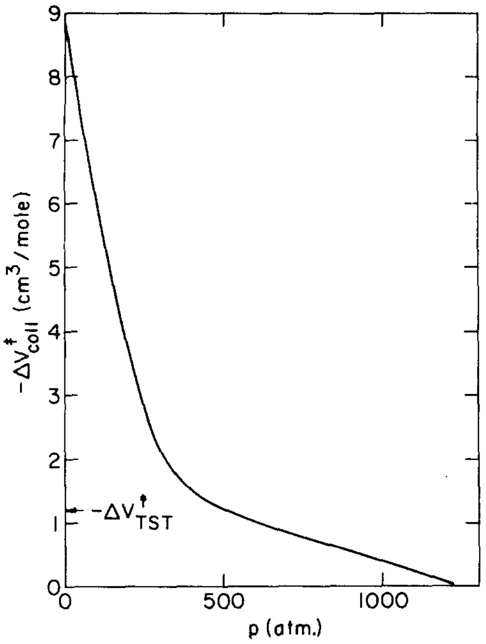

FIG. 9. The collisional contribution to the activation volume $-\Delta V^{\ddagger}_{\mathrm{coll}}$ for the *trans–gauche* isomerization of n-butane as a function of solvent (CCl_4) pressure. The transition state theory estimate of $-\Delta V^{\ddagger}$ is shown for comparison.

equation of state.[17] By combining this information with Eqs. (3.15)–(3.17) and our calculated results for $d\ln\kappa/d\alpha$ (see Fig. 5), we have estimated the collisional contributions to $\Delta V^{\ddagger}$ and $\Delta E^{\ddagger}$ for n-butane dissolved in liquid CCl_4. These quantities are defined as

$$\Delta V^{\ddagger}_{\mathrm{coll}} = -k_B T(\partial \ln\kappa/\partial p)_T \tag{3.18}$$

and

$$\Delta E^{\ddagger}_{\mathrm{coll}} = k_B T^2(\partial \ln\kappa/\partial T)_p\,, \tag{3.19}$$

respectively. At 1 atm pressure and room temperature, we find

$$\Delta E^{\ddagger}_{\mathrm{coll}} \approx 0.4 k_B T \tag{3.20}$$

and

$$\Delta V^{\ddagger}_{\mathrm{coll}} \approx -8.8 \text{ cm}^3/\text{mole}\,. \tag{3.21}$$

The collisional contribution to the activation energy is small compared to the TST value (3.14). However, $\Delta V^{\ddagger}_{\mathrm{coll}}$ is an order of magnitude larger in size than $\Delta V^{\ddagger}_{\mathrm{TST}}$. Thus, the pressure dependence of κ is far from negligible. Our results for $\Delta V^{\ddagger}_{\mathrm{coll}}$ at higher pressures are graphed in Fig. 9. The principal effect of increasing pressure is to increase α, which (see Fig. 5) leads to a sharp decrease in $d\ln k/d\alpha$ and hence the large decrease in $\Delta V^{\ddagger}_{\mathrm{coll}}$ shown in Fig. 9. Indeed, at even higher pressures, $\Delta V^{\ddagger}_{\mathrm{coll}}$ can change sign, as $d\ln k/d\alpha$ changes sign at large α. Thus, there are qualitative features that are missed if one assumes that κ is a constant and applies the simple transition state theory approximation. These effects should be observable in high pressure experiments and we hope such experiments will be performed in the near future.

IV. DISCUSSION

We have shown that trajectory studies of the reactive flux $k(t)$ provide a convenient means of analyzing both the validity of phenomenological rate laws and the behavior of rate constants. For the particular stochastic trajectories we have performed, we have drawn several important conclusions. First, the phenomenological description of an isomerization reaction seems correct provided the collision frequency (i. e., coupling to the bath) is nonzero, and $\exp(-\beta Q) \ll 1$. Indeed, for $\alpha > 0$, the activation energy Boltzmann factor $\exp(-\beta Q)$ is essentially the fraction of reactions that occur which do not obey the rate law.

Second, we have found that for physical processes like the *trans–gauche* isomerization of n-butane, transition state theory (TST) is not a good approximation to the rate constant. The equilibrium TST overestimates the value of the rate constant by a factor of 2 to 3. Further, the transmission coefficient is a sensitive function of the thermodynamic state. This dependence gives rise to a dynamical contribution to the activation volume which is far larger in size than that of TST. Perhaps this phenomenon is responsible for the experimental observation that, for many organic reactions occurring in solution, $\Delta V^{\ddagger}$ is larger in size than the partial molar volume change for the completed reaction.[19]

Third, we find that inertial effects play as significant a role in producing non-TST trajectorties as do collisional effects. Indeed, Fig. 8 shows that, for one particular physical model, roughly half of the non-TST trajectories (or roughly 1/3 of all trajectories) are due to recrossings produced by rebounding off of the wall which confines the stable product. This result implies that studies of isomerization dynamics based on the Smoluchowski limit (which neglects inertial terms in the Fokker–Planck equation) may overlook important physical processes.

Previous to this paper, most studies of stochastic motion in multistable potentials were based on the Smoluchowski or related limits and approximations.[6–8] Two investigations which do not employ this limit are those of Skinner and Wolynes,[5] and of Visscher.[10] As we have noted earlier, Skinner and Wolynes[5] study the same Bohm-Gross kinetic equation in the limit of small α. However, for larger collision frequencies, they adopt a different kinetic equation in which collisions randomize positions as well as velocities. While the rate constant for this strong collision model can be easily reduced to simple quadrature, it does not appear to be a physical model for isomerization reactions. In fact, in the limit of large α, the strong collision model yields transition state theory.

Visscher[10] studied escape from a monostable potential using the Fokker–Planck equation (including inertial terms). The particular potential he studied prohibits the study of the effects of the rebounding for trajectories with positive initial velocities. Nevertheless despite the differences in potential models, Visscher's calculations illustrate the type of nonmonatonic behavior we have also found for the rate constant as a function of the coupling to a bath. Unlike our calculations, Visscher did not analyze stochastic trajectories. Rather, he assumed a rate constant existed and he searched for a steady state solution of the Fokker–Planck equation employing basis set expansions.

The work we have presented differs from Visscher's and others in that we have investigated a wide range of potentials and numerous coupling constants. Further, by performing trajectory calculations for the reactive flux, we have illustrated how it is possible to analyze the validity of phenomenological rate equations as well as determine the value of rate constants (if they are well defined). This procedure is applicable to many body Hamiltonian systems, and it is not limited to stochastic trajectories. Thus, our methodology can play a useful role in the simulation of chemical reactions or other infrequent events[20] occurring in condensed phases.

ACKNOWLEDGMENT

While carrying out this research, we have benefited from numerous conversations with Philip Pechukas.

APPENDIX

We wish to derive a kinetic equation for the phase space density of a tagged particle which is coupled to a heat bath by the following dynamical scheme. Between collision events, the particle streams freely with its motion generated by the operator $\exp[L(qv)t]$. At random intervals, instantaneous collisions occur, during which the velocity of the particle is thermalized, i. e., its velocity is discontinuously changed to a new value sampled randomly from a Boltzmann distribution. The times between collisions are assumed to be Poisson distributed.

We define the Liouville operator $L(qv)$ by

$$L(qv)=v\,\frac{\partial}{\partial q}-\frac{1}{m}\,\frac{\partial V(q)}{\partial q}\,\frac{\partial}{\partial v} \tag{A1}$$

and note that, if $A(q_1v_1)$ is any function of the dynamical variables q_1 and v_1,

$$A(q_1v_1;t)=\exp[L(q_1v_1)t]A(q_1v_1)=A[q_1(t)v_1(t)] \tag{A2}$$

describes the time evolution of $A(q_1v_1)$ when we are considering the uninterrupted free motion of a single particle [possibly in some external field $V(q)$]. The time evolution of $A(q_1v_1)$ according to the stochastic dynamics described above is given by

$$A(q_1v_1;t)=\exp[L(q_{n+1}v_{n+1})(t-t_n)]\cdots\exp[L(q_1v_1)t_1]A(q_1v_1)\ , \tag{A3}$$

where $t_k=$ time at which kth collision occurs, $q_1=q_1(0)$, $v_1=v_1(0)$, $q_2=q_1(t_1)$, $v_2=v_1(t_1)$, $\ldots$, $q_{n+1}=q_1(t_n)$, and $v_{n+1}=v_1(t_n)$. Equation (A3) corresponds to a particular trajectory, where n collisions have occurred at times $t_1\cdots t_n$ (sampled according to the Poisson distribution) and the particles velocities after collision are $v_2\cdots v_{n+1}$ (sampled from a Boltzmann distribution). To obtain the ensemble averaged quantity $\langle A(q_1v_1;t)\rangle$, we must average the velocities $v_1\cdots v_{n+1}$ over the Boltzmann distribution $\phi(v)$, sum over all possible numbers of collisions, weighted by the Poisson distribution $P_n(t)=[(\alpha t)^n/n!]\exp(-\alpha t)$ ($\alpha=$ collision frequency), and average over the times of collision, i. e.,

$$\langle A(q_1v_1;t)\rangle=\sum_{n=0}^{\infty}P_n(t)\,\frac{n!}{t^n}\int_0^t dt_n\cdots\int_0^{t_2}dt_1\,\langle A(q_1v_1;t)\rangle_n\ , \tag{A4}$$

where

$$\langle A(q_1v_1;t)\rangle_n=\int dv_1\phi(v_1)\cdots\int dv_{n+1}\phi(v_{n+1})\int dq_1 s(q_1)A(q_1v_1;t) \tag{A5}$$

Now consider the phase space correlation function $f(qv,q'v';t)$, defined by

$$f(qv,q'v';t)=\langle\delta[q-q_1(t)]\,\delta[v-v_1(t)]\,\delta(q'-q_1)\delta(v'-v_1)\rangle \tag{A6}$$

$$=\exp(-\alpha t)\sum_{n=0}^{\infty}\alpha^n\int_0^t dt_n\cdots\int_0^{t_2}dt_1 f_n(qv,q'v';t)\ , \tag{A7}$$

$$\begin{aligned}f_n(qv,q'v';t)={}&\int dq_1 s(q_1)\int dv_1\phi(v_1)\cdots\int dv_{n+1}\phi(v_{n+1})\\&\times\delta(q'-q_1)\delta(v'-v_1)\exp[L(q_{n+1}v_{n+1})(t-t_n)]\cdots\\&\times\exp[L(q_1v_1)t_1]\,\delta(q-q_1)\delta(v-v_1)\end{aligned} \tag{A8}$$

from Eqs. (A3)–(A5). Since velocities are randomly sampled on collision, the time evolution of any function $B(v_1)$ of velocity only is given by

$$B(v_1;t)=\exp[L(q_{n+1}v_{n+1})(t-t_n)]\,B(v_{n+1})\ . \tag{A9}$$

Therefore, Eq. (A8) may be rewritten as

$$\begin{aligned}f_n(qv,q'v';t)={}&\int dq_1 s(q_1)\int dv_1\phi(v_1)\cdots\int dv_{n+1}\phi(v_{n+1})\delta(q'-q_1)\\&\times\delta(v'-v_1)\exp[L(q_{n+1}v_{n+1})(t-t_n)]\cdots\exp[L(q_1v_1)t_1]\,\delta(q-q_1)\delta(v-v_{n+1})\ .\end{aligned} \tag{A10}$$

Note that

$$\exp[L(q_{n+1}v_{n+1})(t-t_n)]\cdots\exp[L(q_1v_1)t_1]\,\delta(q-q_1)\delta(v-v_{n+1})=\exp[L(q_{n+1}v_{n+1})(t-t_n)]\,\delta(q-q_{n+1})\delta(v-v_{n+1})\ , \tag{A11}$$

$$=\exp[-L(qv)(t-t_n)]\,\delta(q-q_{n+1})\,\delta(v-v_{n+1})\ , \tag{A12}$$

and write Eq. (A10) as

$$f_n(qv,q'v';t)=\exp[-L(qv)(t-t_n)]\int dq_1 s(q_1)\int dv_1\phi(v_1)\cdots\int dv_{n+1}\phi(v_{n+1})\delta(q'-q_1)\delta(v'-v_1)$$
$$\times\exp[L(q_n v_n)(t_n-t_{n-1})]\cdots\exp[L(q_1v_1)t_1]\,\delta(q-q_1)\,\delta(v-v_{n+1})\,. \tag{A13}$$

Integrate Eq. (A13) over dv_{n+1} giving

$$f_n(qv,q'v';t)=\exp[-L(qv)(t-t_n)]\,\phi(v)\int dq_1 s(q_1)\int dv_1\,\phi(v_1)\cdots\int dv_n\,\phi(v_n)\delta(q'-q_1)\delta(v'-v_1)$$
$$\times\exp[L(q_n v_n)(t_n-t_{n-1})]\cdots\exp[L(q_1v_1)t_1]\,\delta(q-q_1) \tag{A14}$$
$$=\exp[-L(qv)(t-t_n)]\,\phi(v)\int dv\int dq_1 s(q_1)\int dv_1\phi(v_1)\cdots\int dv_n\phi(v_n)$$
$$\times\delta(q'-q_1)\delta(v'-v_1)\exp[L(q_nv_n)(t_n-t_{n-1})]\cdots\exp[L(q_1v_1)t_1]\,\delta(q-q_1)\delta(v-v_n)\,, \tag{A15}$$
$$=\exp[-L(qv)(t-t_n)]\,\phi(v)\int dv f_{n-1}(qv,q'v';t_n)\,,\qquad n\geq 1\,. \tag{A16}$$

We may now substitute Eq. (A16) into (A7) to get

$$f(qv,q'v';t)=\exp(-\alpha t)\left\{f_0(qv,q'v';t)+\sum_{n=1}^{\infty}\alpha^n\int_0^t dt_n\cdots\int_0^{t_2}dt_1\exp[-L(qv)(t-t_n)]\,\phi(v)\int dv f_{n-1}(qv,q'v';t_n)\right\}, \tag{A17}$$

where

$$f_0(qv,q'v';t)=\int dq_1 s(q_1)\int dv_1\phi(v_1)\delta(q'-q_1)\delta(v'-v_1)\exp[L(q_1v_1)t]\,\delta(q-q_1)\delta(v-v_1)\,, \tag{A18}$$
$$=\exp[-L(qv)t]\int dq_1 s(q_1)\int dv_1\phi(v_1)\delta(q'-q_1)\delta(v'-v_1)\delta(q-q_1)\delta(v-v_1)$$
$$=\exp[-L(qv)t]\,s(q)\phi(v)\delta(q-q')\,\delta(v-v')=\exp[-L(qv)t]f(qv,q'v';0)\,\,. \tag{A19}$$

Substitution of Eq. (A19) into (A17) and Laplace transformation (LT) gives

$$\tilde{f}(qv,q'v';s)=[s+\alpha+L(qv)]^{-1}\left\{f(qv,q'v';0)+\alpha\phi(v)\int dv\sum_{n=1}^{\infty}\alpha^{n-1}\,\mathrm{LT}\left[\exp(-\alpha t_n)\int_0^{t_n}dt_{n-1}\cdots\int_0^{t_2}dt_1 f_{n-1}(qv,q'v';t_n)\right]\right\}, \tag{A20}$$
$$=[s+\alpha+L(qv)]^{-1}\left\{f(qv,q'v';0)+\alpha\phi(v)\int dv\,\mathrm{LT}\left[\exp(-\alpha t_1)f_0(qv,q'v';t_1)\right.\right.$$
$$\left.\left.+\sum_{n=1}^{\infty}\alpha^n\exp(-\alpha t_{n+1})\int_0^{t_{n+1}}dt_n\cdots\int_0^{t_2}dt_1 f_n(qv,q'v';t_{n+1})\right]\right\}\,, \tag{A21}$$
$$=[s+\alpha+L(qv)]^{-1}\left\{f(qv,q'v';0)+\alpha\phi(v)\int dv\tilde{f}(qv,q'v';s)\right\}\,. \tag{A22}$$

Inverse Laplace transformation gives

$$\left[\frac{\partial}{\partial t}+L(qv)\right]f(qv,q'v';t)=\alpha\phi(v)\int dv f(qv,q'v';t)-\alpha f(qv,q'v';t)\,, \tag{A23}$$

which is the desired result.

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