Energy diffusion in many-dimensional Markovian systems: The consequences of competition between inter- and intramolecular vibrational energy transfer[a]

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We examine the dynamics of barrier crossing using a two-dimensional Langevin equation in the low friction regime. We find that as the friction on the nonreactive mode is increased there is a transition from two-dimensional Markovian dynamics to one-dimensional non-Markovian dynamics resulting in a qualitative change in the behavior of the rate constant as a function of friction. This result supports the conclusion that existing theories which predict rates for energy activation in Markovian and non-Markovian systems have limited ranges of validity and are not as general as had previously been supposed. A method is proposed which analyzes the eigenvalues of the full system and provides a criterion for the validity of the various theories. These ideas are then used to interpret the results of a recent experimental study. In the Appendix we discuss, in some detail, the role of a random force in aiding intramolecular energy transfer.

I. INTRODUCTION

In a recent paper, Borkovec, Straub, and Berne studied the rate constant of a two degree of freedom system for strong collision models like the implusive BGK collisional model.[1] They found that the rate constant at a particular collision frequency was very sensitive to the coupling between the intramolecular degrees of freedom. When the coupling was weak, RRKM theory[2] overestimated the rise in rate with increasing collision frequency. For strong coupling, the rate approached the RRKM prediction. In this paper we examine the effect of coupling between intramolecular degrees of freedom on the predictions of weak collision models.

Weak collision models can be formulated using the one-dimensional Langevin equation

$$\dot{x} = -\frac{\partial V(x)}{\partial x} - \gamma \dot{x} + R(t) , \qquad (1)$$

where x is the system variable (which may represent the internuclear separation of two reacting atoms or the dihedral angle of an isomerizing molecule), $V(x)$ is the internal potential experienced by x, γ is the damping coefficient, and $R(t)$ is the fluctuating force representing all other system coordinates which are not treated explicitly. The fluctuating force and damping coefficient satisfy the second fluctuation dissipation theorem

$$\langle R(0)R(t)\rangle = 2kT\gamma\delta(t) \qquad (2)$$

which requires $R(t)$ to be a white noise which fluctuates such that the average thermal energy of the bath is kT. It is usually assumed that $R(t)$ is a Gaussian stochastic process. Equations (1) and (2) are predicted on the assumption that the bath coordinates relax very quickly compared to the system variable so that motion of the system is uncorrelated with that of the bath.

Kramers[3] used Eq. (1) to calculate rate constants for the escape of a particle from a well in the presence of a thermal bath. He looked at two limiting cases, the underdamped limit where γ is very small and where the rate limiting process is energy activation in the well, and the overdamped limit where γ is very large and where the rate limiting process is spatial diffusion across the barrier top.

In the underdamped limit, γ is small and the probability that a particle will gain energy much greater than kT is small. However, once the particle is activated, having enough energy to cross the barrier top, it will feel little damping and be able to oscillate freely and leave the reactant well. In the case of a symmetric double well potential for large energy barriers $Q \gg kT$, where the well is approximated by a harmonic oscillator, the rate constant for energy activation is given by

$$k_{\text{ED}} \sim \tfrac{1}{2}\beta Q\gamma e^{-\beta Q} , \qquad (3)$$

where the factor of $\tfrac{1}{2}$ indicates that once the particle is activated it will oscillate many times before being trapped and have equal probability of being trapped in either well.

The two most obvious limitations of the Kramers' model are (i) $x(t)$ is a Markov process so that memory effects one might expect in a condensed phase are neglected and (ii) Eq. (1) is one-dimensional so that systems which have degrees of freedom strongly coupled to the reaction coordinate are not accurately treated. Recent work has extended the result of Eq. (3) to both one-dimensional non-Markovian systems[4] and Markovian[5] and non-Markovian[6] systems of many dimensions.[7]

To *include memory effects* Grote and Hynes used the non-Markovian generalized Langevin equation

$$\ddot{x} = -\frac{\partial V(x)}{\partial x} - \int_0^t dt'\, \zeta(t-t')\dot{x}(t') + R(t) , \qquad (4)$$

where $\zeta(t)$ is a time-dependent friction kernel and $R(t)$ is the fluctuating force which satisfies the second fluctuation dissipation theorem

$$\langle R(0)R(t)\rangle = kT\zeta(t) . \qquad (5)$$

Equation (1) is a special case of Eq. (3) where $\zeta(t) = 2\gamma\delta(t)$.

For the case of a one-dimensional symmetric double well potential, with energy barrier $Q \gg kT$, the rate for energy activation is given by[4]

$$k_{\mathrm{ED}} = \frac{1}{2}\left[\int_0^Q dE\,\frac{e^{\beta E}\omega(E)}{D(E)}\int_0^E dE'\,\frac{e^{-\beta E'}}{\omega(E')}\right]^{-1} , \qquad (6a)$$

where $\omega(E)$ is the oscillator frequency at energy E and $D(E)$ is the energy diffusion coefficient. In the case where the well may be assumed harmonic to a good approximation,[4]

$$k_{\mathrm{ED}} \sim \tfrac{1}{2}\beta Q\,\mathrm{Re}\,\hat{\zeta}(-i\omega_0)e^{-\beta Q} , \qquad (6b)$$

where $\mathrm{Re}\,\hat{\zeta}(-i\omega_0)$ is the real part of the Fourier transform of $\zeta(t)$ taken at the well frequency ω_0. This result is exactly Eq. (3) where the constant damping term γ has been replaced by the friction felt by a particle moving at the frequency of the well.

To extend Eq. (3) to many dimensional systems in the Markovian limit Borkovec and Berne used the multidimensional Langevin equation

$$\ddot{x} = -\nabla V(x) - \gamma\cdot\dot{x} + \mathbf{R}(t) \qquad (7)$$

which is the obvious generalization of Eq. (1) to more dimensions. They took an N-dimensional system consisting of a bistable reaction coordinate linearly coupled to $N-1$ nonreactive coordinates where the coupling is such that equipartitioning of energy between the N degrees of freedom is fast compared to the rate for activation in the well and the full phase space is chaotic. If the energy barrier $Q \gg kT$, in the harmonic approximation the rate for energy activation is found to be[5]

$$k_{\mathrm{ED}} \sim \tfrac{1}{2}\frac{(\beta Q)^N}{N!}\sum_{i=1}^N \gamma_{ii}e^{-\beta Q} , \qquad (8)$$

where γ_{ii} is the ith diagonal element of the friction tensor γ. For $N = 1$, Eq. (8) reproduces the one-dimensional result of Eq. (3). The fundamental difference between the higher dimensional result and the one-dimensional result of Eq. (3) is that the prefactor in Eq. (8) depends strongly on the dimension of the system. The factor $(\beta Q)^N/N!$ comes from the density of states for the N-dimensional harmonic well. This indicates that as the number of states in the well at energy βQ increases so does the probability of reaching that total energy. A result similar to Eq. (8) has been found for multidimensional non-Markovian systems.[6]

II. A PARADOX AND ITS RESOLUTION

The Langevin equations for N linearly coupled harmonic oscillators may be exactly reduced to a one-dimensional generalized Langevin equation whose time dependent friction kernel will depend on the frequency, friction, and coupling parameters of the eliminated coordinates. Similarly, the generalized Langevin equation, Eq. (4), may be transformed into a system of linearly coupled Markovian equations.[8] The number of resulting equations will, in general, depend on the time-dependent friction kernel used. A Gaussian kernel results in an infinite set of equations. An expon-

ential kernel requires three equations and is not isomorphic with a Markovian Langevin equation. However, certain kernels do lead to an equivalence between Eqs. (4) and (7).

It is obvious that whether one chooses to model the reaction system with N coupled Langevin equations or the equivalent one-dimensional generalized Langevin equation, the results must be identical. However, the energy activation rate constants corresponding to these two models, given by Eqs. (8) and (6b), respectively, are certainly *not* the same. They most obviously differ in their prefactors, which show a different dependence on βQ, and their frictional dependence, where Eq. (8) is a monotonically increasing function of the friction while Eq. (6b) is capable of more complicated behavior. This implies that while the transformation from N linearly coupled Langevin equations to a one-dimensional generalized Langevin equation is exact, the application of the corresponding theories for energy diffusion rates must be restricted.

The derivation of Eq. (6a) for the rate of energy activation has as its basic equation of motion the Zwanzig equation for energy diffusion.[9,10] In the derivation of this equation, one assumption is that all those coordinates not treated explicitly, corresponding to those coordinates eliminated from the N dimensional Langevin equation, must relax much faster than those coordinates treated explicitly.[11] At any point in time the eliminated coordinates must be distributed according to their equilibrium thermal averages. The Zwanzig equation, and therefore Eq. (6a), will be valid only when those coordinates which were eliminated from the corresponding set of coupled Langevin equations are overdamped.[12] We define N_{ISO} to be the total number of coordinates which are actively coupled to the internal potential in the isolated molecule. When all coordinates are underdamped and the full phase space is chaotic, Eq. (8) will accurately predict the rate of energy activation where $N = N_{\mathrm{ISO}}$. As the damping on N_E of the N_{ISO} coordinates increases, to the point where they may be eliminated, the result is an $N_{\mathrm{EFF}} = N_{\mathrm{ISO}} - N_E$ dimensional generalized Langevin equation where the rate for energy activation will be given by the appropriate non-Markovian theory.[6]

When the phase space is not fully chaotic, the prefactor in Eq. (8) will be reduced by the portion of regular phase space which does not contribute reactive trajectories.[1] In the limit where the friction goes to zero the random force fluctuations are very small and the rate reduces to Eq. (8) multiplied by $X^{\neq}$ which is the measure in phase space of reactive trajectories.[1,14] For larger frictions and temperatures the random force fluctuations are larger and may lead to an increase in $X^{\neq}$. This is discussed further in Sec. VII and the Appendix.

III. A MODEL SYSTEM

To make these ideas more concrete we examine the two-dimensional system

$$\ddot{x}_1 = -\frac{\partial U(x_1)}{\partial x_1} - \epsilon x_2 - \gamma_1\dot{x}_1 + R_1(t) , \qquad (9a)$$

$$\ddot{x}_2 = -\omega_2^2 x_2 - \epsilon x_1 - \gamma_2\dot{x}_2 + R_2(t) . \qquad (9b)$$

A similar set of equations has been studied for weak coupling

in both the underdamped and overdamped limits.[13] The authors transformed Eq. (9) into the corresponding generalized Langevin equation by elimination of x_2 and obtained

$$\ddot{x}_1 = -\frac{\partial U_{EFF}(x_1)}{\partial x_1} - \int_0^t dt' \, \zeta(t-t')\dot{x}_1(t') + R(t) \,, \tag{10}$$

where the Laplace transform of $\zeta(t)$ is

$$\hat{\zeta}(s) = \gamma_1 + \frac{\epsilon^2}{\omega_2^2}\frac{s+\gamma_2}{s^2+s\gamma_2+\omega_2^2} \tag{11}$$

and the effective potential is

$$U_{EFF}(x_1) = U(x_1) - \frac{\epsilon^2}{2\omega_2^2}x_1^2 \,. \tag{12}$$

They concluded that when the nonreactive mode x_2 relaxed very quickly the time-dependent friction kernel of Eq. (11) could be replaced by its zero frequency value resulting in a one-dimensional Markovian Langevin equation whose rate for energy activation would be given by Eq. (3) where

$$\gamma = \gamma_1 + \frac{\epsilon^2}{\omega_2^4}\gamma_2 \,. \tag{13}$$

For the case where x_2 does not relax quickly, the one-dimensional non-Markovian result similar to Eq. (6b) was applied over a large range of coupling where they found that the dependence of the rate constant on the activation energy, or temperature, was *not* affected by the mode–mode coupling.

In contrast to these results, our discussion implies that only for the case when the nonreactive mode relaxes quickly may Eq. (6a), corresponding to the one-dimensional generalized Langevin equation, be used. When the nonreactive mode is underdamped we must use the two-dimensional result of Eq. (8) which, as we have mentioned, has a different temperature dependence than does Eq. (6a).

IV. SIMULATION RESULTS

The transition state theory normalized rate constants were calculated using the rapid absorbing boundary version of the reactive flux.[15] The runs were performed on an FPS-264 attached processor. The equations of motion were solved using an Adams–Moulton predictor–corrector algorithm.[16] The random force was taken to be a constant during each integration step.[15] An average calculation using 1000 trajectories required several hours of CPU time.

The transition state theory rate is defined as[17]

$$k_{TST} = \frac{1}{X_A Q}\int d\Gamma \, \dot{x}\Theta[\dot{x}(0)]e^{-\beta H(\Gamma)}\delta(x-x_{TST}) \,, \tag{14}$$

where $x = x_{TST}$ defines the transition state surface, Θ is the Heaviside step function which is 1 for $\dot{x}(0) > 0$ and 0 otherwise, $H(\Gamma)$ is the Hamiltonian for the isolated system, $Q = \int d\Gamma \exp[-\beta H(\Gamma)]$, and X_A is the equilibrium mole fraction for the reactant well. Thus, k_{TST} is simply the equilibrium flux across the transition state surface assuming that (i) a constant thermal population of reactant states exists in the well with energy βQ and (ii) that these particles cross the transition state surface and are trapped in the product well.

To define the total rate constant k for all friction we use the connection formula[6,18,20]

$$k^{-1} \simeq k_{ED}^{-1} + k_{GH}^{-1} \,, \tag{15}$$

where k_{ED} is the appropriate energy diffusion rate, and k_{GH} is the Grote–Hynes rate constant for crossing the saddle,[6,18–20]

$$k_{GH} = k_{TST}(\lambda/\omega_B) \,. \tag{16}$$

λ is the largest positive root of the Grote–Hynes relation

$$\lambda^2 + \lambda\hat{\zeta}(\lambda) = \omega_B^2 \,, \tag{17}$$

and $\hat{\zeta}(s)$ is the Laplace transform of the total friction projected on the reaction coordinate, Eq. (11), and ω_B is the frequency of the unstable mode of the saddle.

We wish to examine this system when the rate for energy transfer to the reaction coordinate is relatively slow. To do this we set $\gamma_1 = 0$ in Eq. (9a) so that the bath acts directly only on the nonreactive coordinate x_2 and the equations of motion are

$$\ddot{x}_1 = -\frac{\partial U(x_1)}{\partial x_1} - \epsilon x_2 \,, \tag{18a}$$

$$\ddot{x}_2 = -\omega_2^2 x_2 - \epsilon x_1 - \gamma_2 \dot{x}_2 + R_2(t) \,. \tag{18b}$$

We first examine the dynamics for the quartic reactive coordinate potential

$$U(x_1) = x_1^4 - \left(2 - \frac{\epsilon^2}{2\omega_2^2}\right)x_1^2 \,. \tag{19}$$

To determine N_{ISO} we characterized the isolated system by examining Poincaré surfaces of section for various values of the coupling strength ϵ (Fig. 1). We found that there is no strong, or first order, transition to chaos in this system.
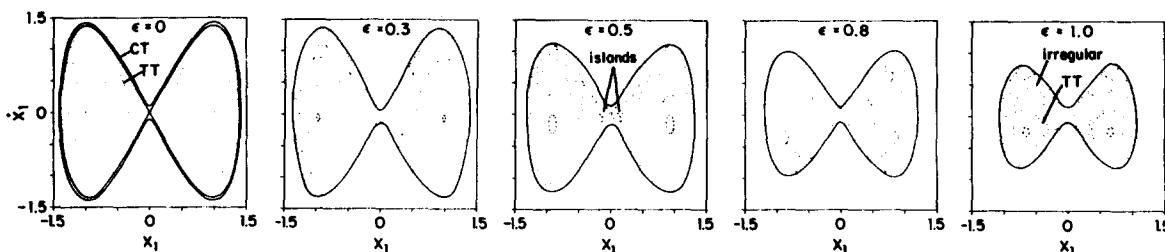

FIG. 1. Schematic diagram describing the qualitative behavior of the transition to chaos in the bistable potential of Eq. (19) in terms of the Poincaré surface of sections for the reactive coordinate x_1. The surface of sections are shown for energy $E = 1.01$ and coupling strength (indicated for each figure) which increases from left (no coupling) to right. For no coupling the phase space is fully regular with trapping tori (TT) and crossing tori (CT). As the coupling is increased there is the destruction of TT and the formation of primary islands. At the strongest coupling there is a large measure of phase space which is irregular while TT still exist.

However, there is a sizable portion of phase space which is irregular for $\epsilon \gtrsim 0.85$, while those portions which are regular often contain resonance tori which contribute to sizable resonant energy exchange between x_1 and x_2. This is supported by the results of critical point analysis[21] which indicates that the global inversion symmetry of the potential is important in stabilizing the diverging trajectories in the saddle region. It is possible that in the presence of collisions the condition that the isolated system be chaotic for there to be equipartitioning in the dissipative system is too strong. Collisions coupled with resonant energy exchange may often be sufficient to partition energy between modes effectively. This idea will be discussed in greater detail in the Appendix.

We compare the simulation results with the theoretical predictions in Fig. 2 for the case of large ϵ leading to intermediate coupling. For large γ_2 the rate is accurately predicted by the one-dimensional theory.[22] This is the adiabatic limit. As γ_2 is decreased there is a gradual approach towards the two-dimensional Markovian theory. This is expected, as for smaller γ_2 the rate for energy transfer between x_1 and x_2 becomes comparable to the rate for energy activation and so a larger portion of phase space contributes reactive trajectories leading to an increased initial slope.

For the case of isotropic friction, corresponding to Eq. (9) with $\gamma_1 = \gamma_2$, the reaction coordinate x_1 directly experiences a friction and random force. In Fig. 3 the simulation results are compared with theoretical predictions. The predicted rate for one-dimensional energy diffusion is much faster than the anisotropic case above. For very large γ_2, the rate is limited by spatial diffusion across the saddle. For small ϵ and weak coupling, Fig. 3(a) shows the rate constants are accurately predicted by the one-dimensional theory over the full range of γ_2 simulated. For large ϵ and intermediate coupling, Fig. 3(b) shows that at large γ_2 the rate is accurately predicted by the Grote–Hynes theory [Eq. (16)] while for smaller friction the simulation results approach the two-dimensional theory.

V. ADIABATIC ELIMINATION

We would like to be able to predict when the transition from two- to one-dimensional dynamics occurs as the fric-
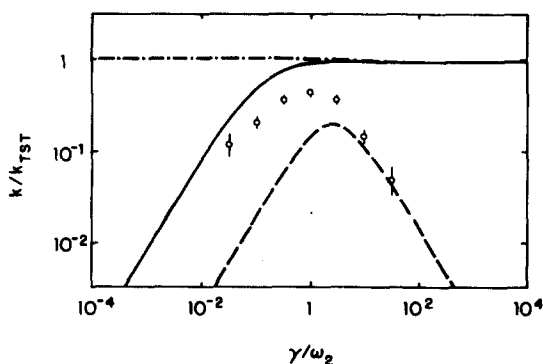

FIG. 2. Rate constants for the potential of Eq. (19) as a function of the static friction $\gamma = \gamma_2$ for $\beta Q = 5$, $\omega_2 = 0.75$, $\gamma_1 = 0$, and $\epsilon = 1.0$. The simulation data with error bars (Ref. 33) are represented by circles. The theoretical predictions are represented by lines: Grote–Hynes theory for saddle crossing Eq. (16) (——), and the overall rate using the interpolation formula of Eq. (15) for one (– – –) and two (——) dimensions, using k_{ED} from Eqs. (6a) and (8), respectively.
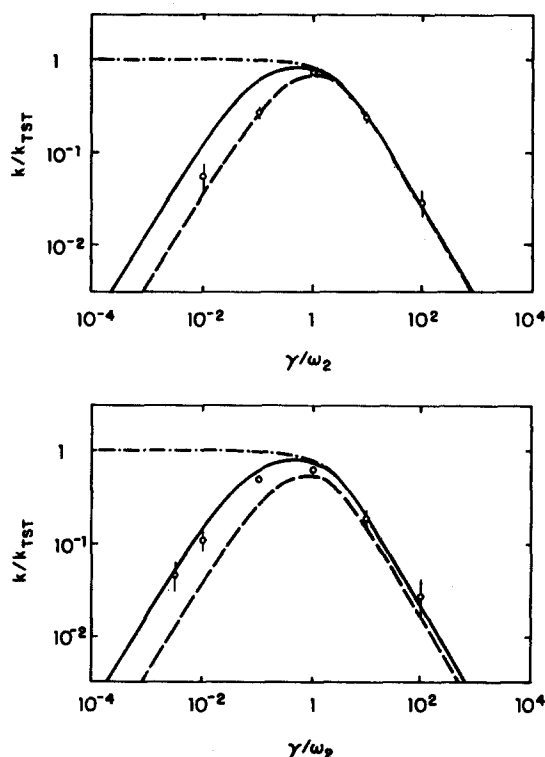

FIG. 3. Rate constants for the potential of Eq. (19) as a function of the static friction $\gamma = \gamma_2$ for $\beta Q = 5$, $\omega_2 = 0.75$, $\gamma_1 = \gamma_2$ for (a) $\epsilon = 0.3$ and (b) $\epsilon = 1.0$. The simulation data with error bars are represented by circles. The theoretical predictions are represented by lines and described in the caption of Fig. 1.

tion is increased. We concentrate on the case where $\gamma_1 = 0$ (Fig. 2). We define a transition value of γ_2 as the *approximate* value of γ_2 separating the two- and one-dimensional dynamics. The theory of "slaving," or adiabatic elimination of variables,[23] predicts that when γ_2 is large, so that x_2 is overdamped, one may set $\ddot{x}_2 = 0$ in Eq. (18b). We may then integrate in time to get x_1 in terms of x_2 and substitute in Eq. (18a) to find an equation similar to Eq. (10) with

$$\hat{\zeta}_{AE}(s) = \frac{\epsilon^2}{\omega_2^2} \frac{\gamma_2}{s\gamma_2 + \omega_2^2}. \tag{20}$$

If we use Eq. (20) in Eq. (6a) we find as expected that for small γ_2 the result differs dramatically from the result using the exact friction kernel of Eq. (11). However, as γ_2 is increased, after some $\gamma_2 \gtrsim \omega_2$ the adiabatic result agrees well with the exact result. *The transition value from adiabatic elimination, γ_{AE}, would be roughly that γ_2 where the adiabatic result is approximately equal to the result from full elimination.*

In Fig. 4(a) we have indicated the value of γ_{AE} on the abscissa. Comparison with Fig. 2 shows that the transition occurs at $\gamma_2 < \gamma_{AE}$ so that this criterion is too strong. We therefore need a criterion which is more sensitive to the internal dynamics of the system.

VI. EIGENVALUE ANALYSIS

Another possibility lies in analyzing the behavior of the system eigenvalues as a function of γ_2.[24,25] If we first linearize Eq. (18) about the well minima and then Laplace trans-
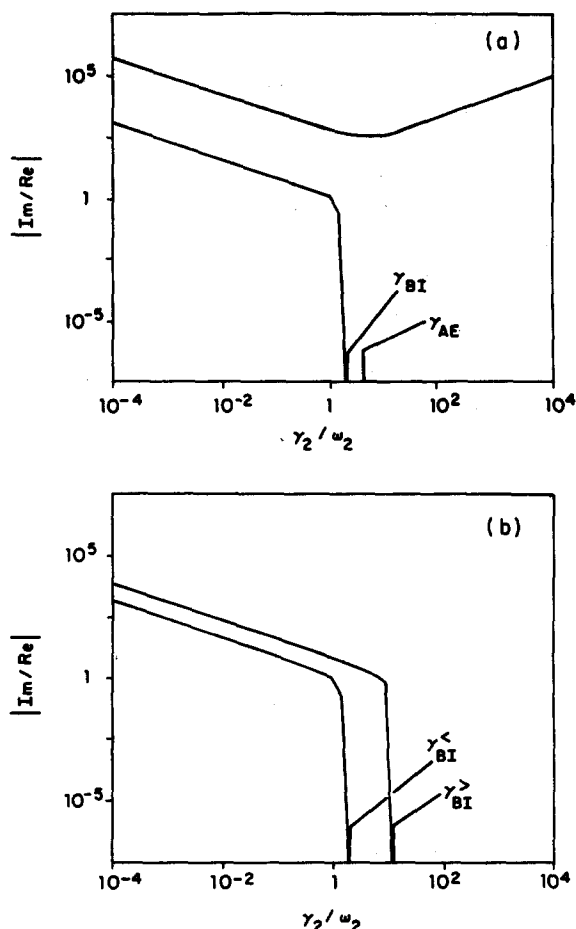
FIG. 4. Diagram describing the quantitative behavior of the ratio of the imaginary to real parts of the system eigenvalues for (a) the anisotropic system of Fig. 2 and (b) the isotropic system of Fig. 3(b). The various approximations for the transition value for γ_2 are marked on the abscissa.

form, disregarding initial condition terms and fluctuating forces, we find the equation for the Laplace variable s:

$$s^4 + \gamma_2 s^3 + (\omega_1^2 + \omega_2^2)s^2 + \gamma_2\omega_1^2 s + \omega_1^2\omega_2^2 - \epsilon^2 = 0, \quad (21)$$

where ω_1 is the frequency of the harmonic approximation to the reactive coordinate well frequency. The roots of this equation are the system eigenvalues. That Eq. (21) is a fourth degree polynomial indicates that there are four roots corresponding to the four degrees of freedom in the system $x_1, x_2, \dot{x}_1,$ and $\dot{x}_2$.

Figure 5(a) shows the general behavior of the system eigenvalues as a function of γ_2 for the anisotropic system of Fig. 2. For small γ_2 the roots consist of two complex conjugate pairs whose imaginary parts are much greater than their real parts. This implies that the system motion is highly oscillatory or underdamped. As γ_2 is increased to γ_{BI}, one complex conjugate pair moves onto the real line and bifurcates. One of the resulting real eigenvalues increases in magnitude with increasing γ_2 while the other decreases becoming small negative. The other complex conjugate pair remains complex for all γ_2 indicating that the corresponding modes are always underdamped. This is clearly seen in Fig. 4(a) where the imaginary part of each eigenvalue divided by its real part is plotted as a function of γ_2. As γ_2 is increased we find that for one complex conjugate pair the real part
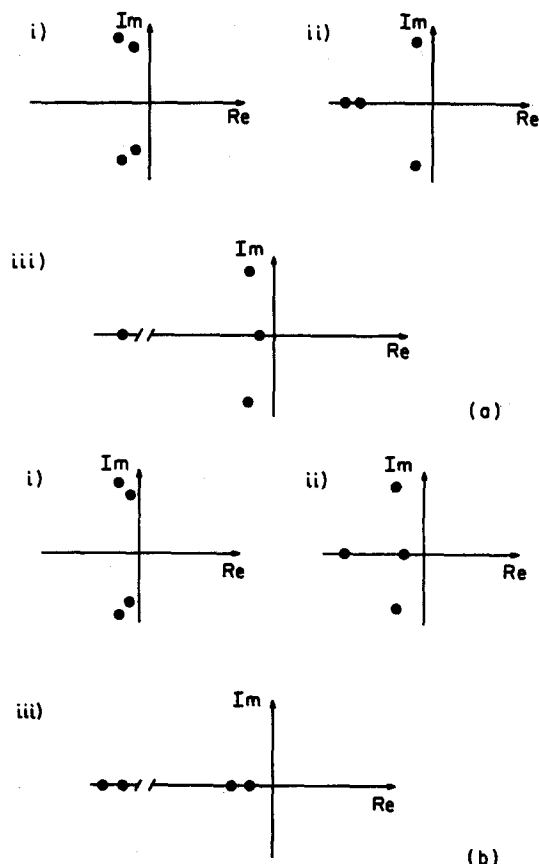

FIG. 5. Schematic diagram describing the qualitative behavior of the eigenvalues for (a) the anisotropic system of Fig. 2 and (b) the isotropic system of Fig. 3(b), for various values of the static friction (i) $\gamma_2 < \gamma_{BI}$, (ii) $\gamma_2 \approx \gamma_{BI}$, and (iii) $\gamma_2 > \gamma_{BI}$.

approaches in magnitude the imaginary part and then the imaginary part goes to zero at γ_{BI}, while the other pair decreases initially and then increases for $\gamma_2 > \gamma_{AE}$.

We may then interpret the behavior in Fig. 2 as follows. For $\gamma_2 < \gamma_{BI}$ the eigenvalues consist of two complex conjugate pairs indicating two-dimensional underdamped motion. Here we expect that for a strongly chaotic system, two-dimensional dynamics will apply and the rate will be best predicted by Eq. (8) multiplied by the proper factor $X \neq$ for the fraction of phase space contributing reactive trajectories.[1] For $\gamma > \gamma_{BI}$ the eigenvalues consist of one complex conjugate pair and one real pair. For couplings such that the major contribution to the reactive coordinate comes from the complex conjugate pair, the dynamics will correspond to one-dimensional energy diffusion of Eq. (6a). For $\gamma_2 > \gamma_{BI}$ we reach the adiabatic limit where Eq. (20) will apply. We would therefore expect the transition between one- and two-dimensional energy diffusion to occur near γ_{BI}. Examining Fig. 4(a) we find that γ_{BI} is closer to the transition region than γ_{AE}.

This transition is not sharp, occuring over a range of γ_2. We expect that for the eigenvalue pair which bifurcates, when the damping term in the complex conjugate pair approaches in magnitude the oscillatory term the mode will not execute a full oscillation without experiencing significant damping. This is the onset of overdamped behavior when the mode may be safely eliminated and treated with the bath. As

γ_2 is increased further we reach the adiabatic limit.

As another example of the eigenvalue method, we examine the dynamics of Eq. (9a) and (9b) for the case of isotropic friction $\gamma = \gamma_1 = \gamma_2$. The qualitative behavior is shown in Fig. 5(b). We find that at small γ the system eigenvalues consist of two complex conjugate pairs, whose imaginary parts greatly exceed their real counterparts. This indicates that the dynamics will correspond to two-dimensional energy diffusion. As γ is increased, one pair moves onto the real line at $\gamma_{\mathrm{BI}}^{<}$ leaving one complex conjugate pair and one-dimensional energy diffusion. For $\gamma > \gamma_{\mathrm{BI}}^{>}$ the system is characterized by two small and two large negative eigenvalues. This is the mark of a truly overdamped system, and spatial diffusion at the saddle will be rate limiting.[25] This reduced dimensionality leads to a reduction of the slope of the rate constant as the friction is increased. Therefore, as γ is increased we should first see two-dimensional energy diffusion followed by one-dimensional energy diffusion and a final transition to fully overdamped behavior where crossing of the saddle is rate limiting. The simulation data shown in Fig. 3 support this conclusion.

In summary, for an N-dimensional Markovian system we may linearize the equations of motion in the well resulting in $2N$ eigenvalues which characterize the system dynamics. For small damping the eigenvalues consist of N complex conjugate pairs with imaginary parts which greatly exceed their real counterparts. Here the dynamics should be described by N-dimensional energy diffusion. As the damping is increased some N_E complex conjugate pairs move towards the real line. *When their imaginary parts approach in magnitude their real counterparts the motion will become overdamped in character and the corresponding coordinates may then be eliminated from the reaction system.* Here the dynamics will be described by $N - N_E$ dimensional energy diffusion. As long as the reaction coordinate itself is not overdamped the system dynamics will remain underdamped in character with successively fewer degrees of freedom contributing to the rate as the damping on the nonreactive modes is increased.

VII. CONCLUSION

We have examined the dynamics of many-dimensional Markovian systems, both strongly anisotropic and isotropic, over a wide range of friction. We find that the system dynamics depends on the damping felt by each coordinate and that examination of the system eigenvalues is important in understanding the behavior as a function of the friction coefficient. In particular, we have compared the predictions of current theories for energy diffusion with simulation results for a two-dimensional Markovian system in the weak and intermediate coupling regimes. We find that one-dimensional theories, which eliminate nonreactive coordinates and treat the reactive coordinate with a renormalized friction and potential, have a limited range of validity.

For small enough frictions, the rate for energy transfer between the N_{ISO} coupled coordinates is faster than the rate for energy activation. All modes must be considered explicitly. The rate will be most accurately predicted by the N_{ISO} dimensional Markovian theory of Eq. (8) with the proper

prefactor for the measure of phase space contributing reactive trajectories. As the friction is increased on the nonreactive modes, these modes will eventually become overdamped so that their rate for energy transfer to the reactive mode is much less than the rate for energy activation. These modes, numbering N_E, may then be eliminated. The reaction system will consist of $N_{\mathrm{EFF}} = N_{\mathrm{ISO}} - N_E$ dimensions where the rate is in general predicted by the N_{EFF} dimensional non-Markovian theory. Of course, depending on the friction kernels it may be appropriate to use an N_{EFF} dimensional Markovian theory.[5] This results in a rate for energy diffusion which is much less than that predicted by Eq. (8) using $N_{\mathrm{EFF}} = N_{\mathrm{ISO}}$. The approximate value of the friction for which elimination is valid may be determined by considering the quantitative features of the system eigenvalues.

In applying these ideas, one must consider the details of the various assumptions made. In the process of energy diffusion, a particle will gain energy through small jumps imparted by the random force. For very low frictions, the trajectory will remain activated for a long time before being deactivated. During this time it will move within an energy shell near the barrier top. The energy diffusion theory of Eq. (8) assumes that the trajectory will cross the saddle many times before being deactivated so that its position will be randomized.[5] It will then be deactivated on either side of the TS with equal probability. This leads to the multiplicative factor of $\frac{1}{2}$ for a symmetric system.

For a particular physical system, the internal properties of the potential and the external properties of the random force will determine the validity of this assumption. For a given potential, there will be an average time (τ_{RAN}) for a trajectory to sample effectively all regions of the energy surface. This will be affected by the measure of irregular phase space in the isolated system which may contribute reactive trajectories,[1] and the friction which may increase the measure of irregular trajectories. For a given friction, there will be an average time (τ_{ACT}) for which a trajectory energy remains in the region of the barrier with the possibility of crossing the TS. The condition for the validity of Eq. (8) may then be expressed as $\tau_{\mathrm{ACT}} \gg \tau_{\mathrm{RAN}}$. When $\tau_{\mathrm{RAN}} \gg \tau_{\mathrm{ACT}}$ the activated trajectory will not have time to cover the full phase space and so there will be a reduced density of states contributing reactive trajectories and a reduced prefactor in Eq. (8).

A study of this effect has been made for the case of the BGK and strong collision models using a two-dimensional model potential.[1] Here, the particle is activated by a collision which thermalizes the momentum, or position and momentum, respectively. In each case, the majority of reacting trajectories are activated by a single collision and then move freely on an energy surface until being deactivated by the next collision. If the activated trajectory is in a region of phase space bounded by a KAM surface,[26] which prevents it from crossing the TS, it will never react.[27] Therefore, for small collision frequencies, the rate constant for energy activation will be reduced by a factor which accounts for the portion of regular, nonreactive phase space.

For a weak collision model such as Eq. (7), a trajectory is activated by the continuous action of an infinitesimal ran-

dom force which causes displacements in the position and momentum and therefore the energy. Unlike the BGK and strong collision models, the activated trajectory's dynamics are not solely determined by the irregularity, or *intrinsic stochasticity*, of a particular energy surface. Once activated, the trajectory is still subject to these weak collisions and therefore undergoes transitions between adjacent energy surfaces. This mechanism of diffusion between energy surfaces, due to the external random force coupled to the internal diffusion on each particular energy surface, determines the *extrinsic stochasticity* of the system. The details of external random jumps in phase and action for the standard mapping has been studied in some detail.[26] In the Appendix we present a summary of a few important mechanisms acting in extrinsic diffusion which may lead to quantitative differences between energy diffusion for the weak and strong collision models.

Experimental[28] results for the isomerization of cyclohexane have shown that as the pressure, or collision frequency, is increased there is a decrease in slope. Recently, the many-dimensional non-Markovian energy diffusion theory[6] has been used to interpret the experimental results.[29] It was decided, from consideration of the isolated system, that the dimension of the reaction system was most probably six. This led to the conclusion that the maximum in the rate occured in the gas phase, contrary to previous beliefs. Given our results, we question this conclusion. In particular, it is likely that while the low pressure behavior indicates a large number of dimensions contributing to the rate, at higher pressures a number of these dimensions may be eliminated leading to a decrease in the initial slope with increasing friction and a maximum rate predicted by a lesser dimensional theory. If the number of effective dimensions is reduced, from six at low pressures to three or less at high pressures, the maximum will occur in the liquid phase.[29] Recently Chandler *et al.* have carried out BGK simulations.[30] Their results corroborate our ideas.

APPENDIX: EXTERNAL NOISE AND ENERGY TRANSFER

For the purposes of this discussion we will confine ourselves to a bistable coordinate coupled to $N - 1$ oscillators. When the coordinates are uncoupled, the system is fully regular and there exist N constants of the motion for the system corresponding to the energies in each of the N independent coordinates. The phase space may be decomposed into KAM surfaces labeled crossing tori (CT) and trapping tori (TT).[27] In two dimensions the CT form a separatrix which confines the TT to either the reactant or product region (Fig. 1). As the coupling is increased, the KAM surfaces forming the separatrix will begin to break down leading to the formation of islands and increasing areas of irregular phase space. At higher coupling, the TT will become unstable. In highly nonlinear systems, for certain couplings and energy there may be a global transition to chaos where the full phase space is irregular. For other systems, such as Eqs. (18) and (19), there may be only a weak transition, i.e., for *any* value of the coupling there will still be preserved tori. In two dimensions, a KAM surface will form an uncrossable barrier. In three or more dimensions, all irregular regions of phase space are

connected by an Arnold web and diffusion inside this web.[26] Other "partial barriers" exist. These may be Cantori[31] or KAM tori which are partially destroyed known as "vague tori."[32] In each case there is motion along these tori as well as slow diffusion across them.

For weak collision models, the random force produces jumps in the momentum which causes transitions both *along* and *between* surfaces of constant energy. An activated trajectory may be thought to move in an energy shell whose width is determined by the short time fluctuations in energy which leave the trajectory activated. Below we discuss several mechanisms acting in weak collision models which may lead to faster diffusion in the irregular portions of phase space, as well as an increased area of phase space contributing reactive trajectories.

1. Resonance streaming

If the phase space is partially regular, containing large islands or KAM surfaces, a random force may lead to an increased rate of diffusion through the chaotic region.[26] An irregular trajectory moving near a KAM torus, in the form
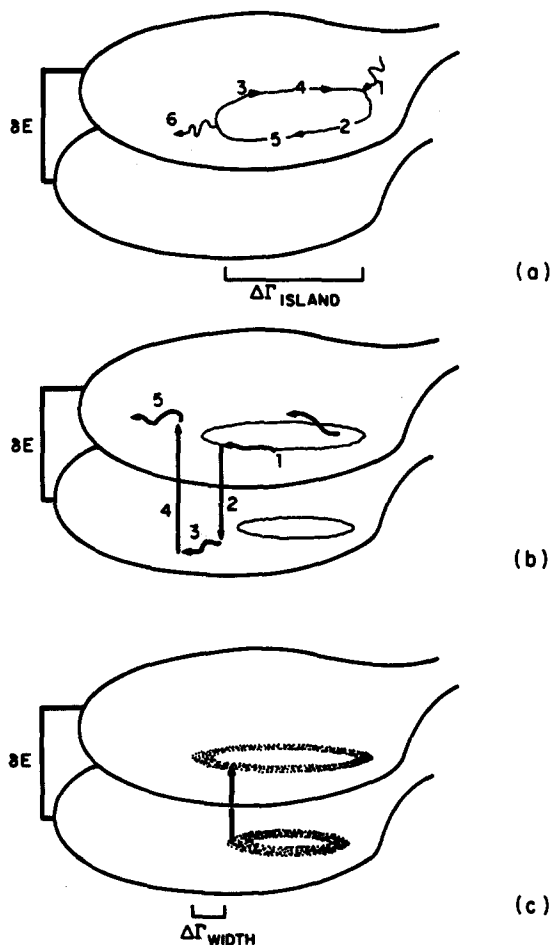

FIG. 6. Schematic diagram describing the transition between adjacent energy levels due to perturbations from the random force. (a) The solid line depicts the motion of a trajectory where the various fragments are labeled in the order of their occurrence. (b) The solid line depicts the motion of two trajectories where the various fragments are labeled in the order of their occurrence. (c) The arrow depicts a transition between two resonances on adjacent energy levels. The surrounding shaded region indicates the width of each resonance.

of an island, may be kicked onto the torus from an irregular region by the random force. The trajectory may then "stream" along the resonance surface for some time, its phase being randomized, before being kicked off into an irregular region [Fig. 6(a)]. If the torus is large, this may lead to a large jump in phase space and greatly enhanced diffusion. If the width of the island is $\Delta\Gamma_{island}$, and the time between transitions is τ, the diffusion due to resonance streaming will be approximately[26]

$$D_{RS} \approx \frac{\langle \Delta\Gamma_{island}^2 \rangle}{2\tau}. \tag{A1}$$

2. Surface crossing

A kick of the random force may simply move a trajectory off a KAM surface, if the perturbation is large enough that the motion becomes unstable. This will depend on the size of the stable region about the KAM surface and the size of the random fluctuations, which in turn depends on the temperature and friction.

A more complicated scenario for moving across a KAM surface is shown schematically in Fig. 6(b). The position of the KAM surface in phase space may change for changing energy. In the case of motion in a well, the area of phase space for each energy level will increase with increasing energy. Therefore, a trajectory moving *on* or *in* a KAM surface may be kicked to a lower energy surface *off* or *outside* of the corresponding KAM surface. There it may diffuse in the surrounding region before undergoing a transition up in energy. After this transition, the trajectory may be outside the original KAM surface. This mechanism may act to accelerate diffusion across Cantori[31] as well as allow transitions across a KAM torus which would be forbidden in conservative systems.

3. Resonance diffusion

This is similar to resonance streaming where the trajectory diffuses *within* a resonance width.[26] A trajectory diffusing in a well undergoes transitions in energy where the torus at higher energy is slightly displaced from the torus at lower energy [Fig. 6(c)]. If the difference in the torus position or size between energy levels is $\Delta\Gamma_{width}$, and the transition time is τ, the rate for diffusion is[26]

$$D_{RD} \approx \frac{\langle \Delta\Gamma_{width}^2 \rangle}{2\tau}. \tag{A2}$$

In practice, some or all of these mechanisms may act to accelerate diffusion. The role that each plays will depend on the particular potential, the degree of irregularity, the detailed island structure, the temperature, and the friction.

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