REACTION DYNAMICS IN AN ERGODIC SYSTEM: THE SIAMESE STADIUM BILLIARD *

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To study the roles of chaos in energy transfer and reaction dynamics in isolated molecules, we devise a simple classical dynamical system with measure preserving ergodic flow. Although the dynamical system is completely chaotic, it is found that dynamical correlations give rise to substantial deviations from RRKM theory.

1. Introduction

To understand how chemical rate laws and rate constants emerge from molecular dynamics we have studied the classical dynamics of simple hamiltonian systems consisting of between two and twelve degrees of freedom [1,2]. These systems were all capable of undergoing geometrical isomerization, and the transition from one isomer to another involved passage over potential barriers. Barrier crossing requires energy transfer between the reactive coordinate and the other molecular internal degrees of freedom. This process becomes random only if there is a transition from quasiperiodic motion (KAM regime) to chaotic motion involving reactive trajectories. Thus the reaction process must be studied in the light of modern developments in non-linear dynamics [3,4].

In our previous papers [1,2] we studied non-ergodic hamiltonian systems. In this paper we focus on reaction dynamics in an ergodic hamiltonian system; particularly with respect to the conditions required for RRKM behavior. First we devise a simple dynamical system with measure invariant ergodic flow that undergoes geometrical isomerization. Since this system is constructed from the stadium billiard [3], we call it the Siamese stadium billiard. The system is a K system – meaning that trajectories starting from neighboring points in phase space, no matter how close – separate exponentially in time [4]. This spreading in phase space occurs with a rate constant given by the maximal Lyapunov exponent λ or equivalently the [5,6] Kolmogorov entropy h. By studying time correlation functions, and particularly the reactive flux, it is possible to explore under what conditions unimolecular rate laws and rate constants exist, and moreover when RRKM theory is valid [1,2, 7]. In this paper we show that the reaction dynamics can be correlated with the Kolmogorov entropy (or equivalently the Lyapunov exponent). We show that deviations from RRKM behavior occur when the flow can recross the transition state in a time short compared to the mixing time τ_M, where τ_M is proportional to λ^{-1} (or equivalently to h^{-1}). This leads to results that at first sight appear to be paradoxical. For example, for energies very close to the barrier height, it might be expected that the system will get trapped in a well for times very long compared to the mixing time λ^{-1} so that by the time the particle recrosses the barrier it has equilibrated in the well. This would lead one to expect RRKM theory to be valid. Quite the contrary is observed, and it is easy to understand why this takes place.

In a subsequent paper [8] we study a generalization of the model for which the phase space decomposes into regular and irregular regions.

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2. Reaction dynamics in the Siamese stadium

The *Siamese stadium billiard* (SSB) consists of a point mass, $m = 1$, moving in a plane convex region with differentiable border (except for the hole) shown in fig. 1a.

The billiard moves freely inside the region, but suffers elastic collisions with the boundary. The particle can pass through the hole only if $m\dot{x}^2/2 > E_0$, otherwise it is elastically scattered from the hole. This leads to activated barrier crossing. For simplicity we study the dynamics for fixed $m = 1, E = 1, R = 1$. Since barrier crossing can take place only if $E > E_0$, it follows that $E_0 < 1$.

The *stadium billiard* (SB) defined in fig. 1b has played a prominent role in several recent studies [3]. While the circular billiard, $\gamma = 0$, is completely integrable, the stadium billiard, $\gamma > 0$, was proved by Bunimovich [9] to be a K flow (cf. fig. 1 for a definition of γ). Such systems are stochastic and ergodic. It is possible to map each trajectory of the Siamese stadium billiard (SSB) onto a particular trajectory of the stadium billiard (SB) by simply replacing $-x$ by $+x$ *whenever* $x < 0$ in the Siamese stadium. It follows that the Siamese stadium is also a K flow.

In a very lucid and exhaustive study of the stadium billiard (fig. 1b), Bennettin and Strelcyn [5] computed the maximum Lyapunov characteristic number, λ, for a series of stadium billiards with $0 < \gamma \leqslant 10$. These results are summarized in fig. 4 of ref. [3]. λ gives the rate at which trajectories starting at neighboring points in phase space, no matter how close, exponentially separate, and can thus be thought of as a mixing rate. Bennettin and Strelcyn [5] could find no variation of λ with the initial state. It follows from this that the Kolmogorov entropy h is identical to λ. At $\gamma = 0, \lambda = 0$ (as expected for a regular system). λ increases rapidly with γ, reaches a maximum at $\gamma \approx 1$ and then decreases very slowly with γ. Thus by varying the anisotropy, γ, it is possible to study systems as a function of mixing rate, λ (or mixing time $\tau_M \equiv \lambda^{-1}$). It is important to recognize that two stadiums with the same γ but different energy E, mass m and area A, have different Lyaponov exponents, but these scale as

$$\lambda(\gamma, m', A', E') = \lambda(\gamma, m, A, E)(E'Am/EA'm')^{1/2}, \tag{1}$$

where the area of a stadium is given by

$$A = A(l/2, r) = (4\gamma + \pi)R^2 . \tag{2}$$

Bennettin and Strelcyn's fig. 4 corresponds to a series of stadiums with $A = A(1, 1)$, $E = 1/2$ and $m = 1$.

Molecular dynamics in the Siamese stadium can be generated from a study of the stadium. If one samples trajectories from a microcanonical ensemble, then for every trajectory crossing the boundary from, say, left to right, there will be an equivalent trajectory passing from right to left. Therefore, dynamics in the Siamese stadium is equivalent to "tagging" trajectories in the ordinary stadium each time they hit and elastically reflect off the transition state (TS) region a. If we label the trajectory by $\sigma = -1$ or 1 depending on whether it would pass through the TS or not, then in addition to recording r and p we must also record σ. Needless to say, whether or not the trajectory passes through the hole depends on whether or not it satisfies $\dot{x}^2 > 2E_0$. Hence we need only consider dynamics in the ordinary stadium when determining averages over the microcanonical ensemble. It follows from the foregoing that the Lyaponov exponent λ for the Siamese stadium is identical to that of the stadium.

To study reaction dynamics in the SSB it is useful to determine the reactive flux [1,2]

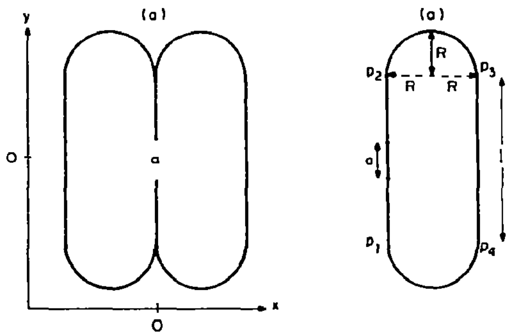

Fig. 1. (a) The Siamese stadium. (b) The stadium billiard consists of a unit point mass moving freely inside the boundary and elastically scattering off the walls. The boundary consists of two semicircles of radius R joined continuously at points P_1, P_2, P_2, P_3 and P_4 to parallel walls of length l, separated by a distance $2l$. The hole in the Siamese stadium is of length a. The parameters refered to in the text are $\kappa = a/l$, $\gamma = l/2R$, the energy barrier E_0, and the total energy E. In all studies $R = 1.0$ and $E = 1.0$.

$$k(t;E) \equiv (X_A X_B)^{-1} \langle \dot{x}(0)\delta(x(0))\,\theta(x(t))\rangle_E , \quad (3)$$

where $X_A = X_B = 1/2$ is the fraction of time spent in the wells A and B (cf fig. 1b), x is the reaction coordinate, $\dot{x}(0)\delta(x(0))$ is the incident flux through the TS, and $\theta(x(t))$ is the characteristic function that measures whether the trajectory is in the right well at time t. Its time dependence is recorded through the tagging process discussed previously. Eq (3) is evaluated using a microcanonical ensemble average at energy E. The delta function requires the system to be initially at the transition state $x = 0$. If $k(t, E)$ decays exponentially (at long time), then the decay rate τ_{Rxn}^{-1} is the kinetic rate constant (the sum of the forward and backward rate constants). The RRKM rate constant is found from the $t \to 0+$ limit of $k(t, E)$ [1,7]. This gives

$$\tau_{RRKM}^{-1} = (X_A X_B)^{-1} \langle \dot{x}\,\delta(x)\,\theta(\dot{x})\rangle_E . \quad (4)$$

It is thus convenient to define the normalized (dimensionless) reactive flux, $\hat{k}(t) \equiv k(t, E)\tau_{RRKM}$. Evaluation of this for the Siamese stadium billiard gives

$$\tau_{RRKM}^{-1} = (4a/A)\,[(E - E_0)/2]^{1/2}\,\theta(E - E_0). \quad (5)$$

Eq (3) is evaluated using the procedure outlined in appendix B of ref. [2]. The sampling procedure is used to choose initial states in the SB, and the tagged trajectories in the SB are used to determine $\hat{k}(t, E)$.

3. Results

Several systems were studied. Each system is defined by the parameters given in fig. 1a. The parameter $\kappa\,(\equiv a/l)$ defines the size of the TS, a, relative to the length, l, of the straight side of the stadium. The parameter $\gamma\,(\equiv l/2R)$ gives the length, l, to width, $2R$, ratio of the single stadium from which the Siamese stadium is composed. As indicated in fig. 1 the total energy E, the mass of the billiard m, and the radius r, are fixed at $E = 1$, $m = 1$, and $r = 1$ for all systems studied. The only other parameter considered is the barrier height, $E_0 < 1$, that determines whether or not the particle can pass through the hole.

In section 2 it was mentioned that the initial value of the reaction flux is the RKKM rate constant τ_{RRKM}^{-1}. The normalized reactive flux $\hat{k}(t)$ corresponding to $E_0 = 0.45$, $\kappa = 0.02$, $\gamma = 0.5$ is presented in fig. 2A1. Fig. 2A2 gives the logarithmic plot versus time. The flux $\hat{k}(t)$ decays exponentially in time with a decay constant τ_{Rxn}^{-1} which is found to be equal to τ_{RRKM}^{-1}, the RRKM rate constant. Since τ_{RRKM} gives an approximate measure of the time spent by a trajectory trapped in either the A or B stadium (cf. fig. 1a), and since λ^{-1} gives a measure of the mixing time or correlation time of the trajectories, the quantity $\lambda\tau_{RRKM}$ gives a measure of the number of independent mixing times spent by a trajectory while it is trapped in a well. If $\lambda\tau_{RRKM}$ is large, we expect that the system will have a chance to equipartition in a well before it has a chance to recross the hole. Using λ determined by Bennettin and Strelcyn [3] ($E = 2$, $m = 1$, $\gamma = 0.5$), properly transformed using eq. (1) to our system ($E = 1$, $m = 1$, $\gamma = 0.5$), corresponding to fig. 2A1, gives $\lambda\tau_{RRKM} = 97$. This is clearly a case where trajectories get trapped for periods long compared to the time required for equilibrating the system or equivalently equipartitioning the system. Because the overall flow is ergodic, the system can be described by a statistical theory of reaction dynamics such as RRKM theory.

It is of interest to see what happens when the system is changed to make $\lambda\tau_{RRKM}$ much smaller. This is easily accomplished by making the hole considerably larger. Fig. 2C1 gives the reactive flux $\hat{k}(t)$ for the system ($E_0 = 0.45$, $\kappa = 0.5$, $\gamma = 0.5$). This system is dynamically identical to the system presented in fig. 2A1, except that the relative width of the transition state, $\kappa = 0.5$, is 25 times larger. The flux, $\hat{k}(t)$, now has fine structure. It exhibits decay over two widely separated time scales. There is rapid decay in a time of order 1.4, a time corresponding to the time it takes a typical activated trajectory starting at the hole to cross the width of a stadium and return to the hole. If the trajectory is still activated, that is, still satisfies the energy condition of $\dot{x}^2 > 2E_0$, it will recross the TS and cease to contribute to the reactive flux until such time that it can cross the hole again. The rapid decay is due to those trajectories that rapidly recross the TS. The rise around $t \approx 10$ is due to those trajectories that leave the well and then on the next collision with the TS return. The long time decay, on the other hand, is due to those trajectories that emerge from the TS but are not sufficiently activated when they collide with the TS. Because it takes a time on the order of λ^{-1} to regain the energy to recross, these trajectories give rise to a slower decay. The long time decay seems to be exponential, but the relative fluc-

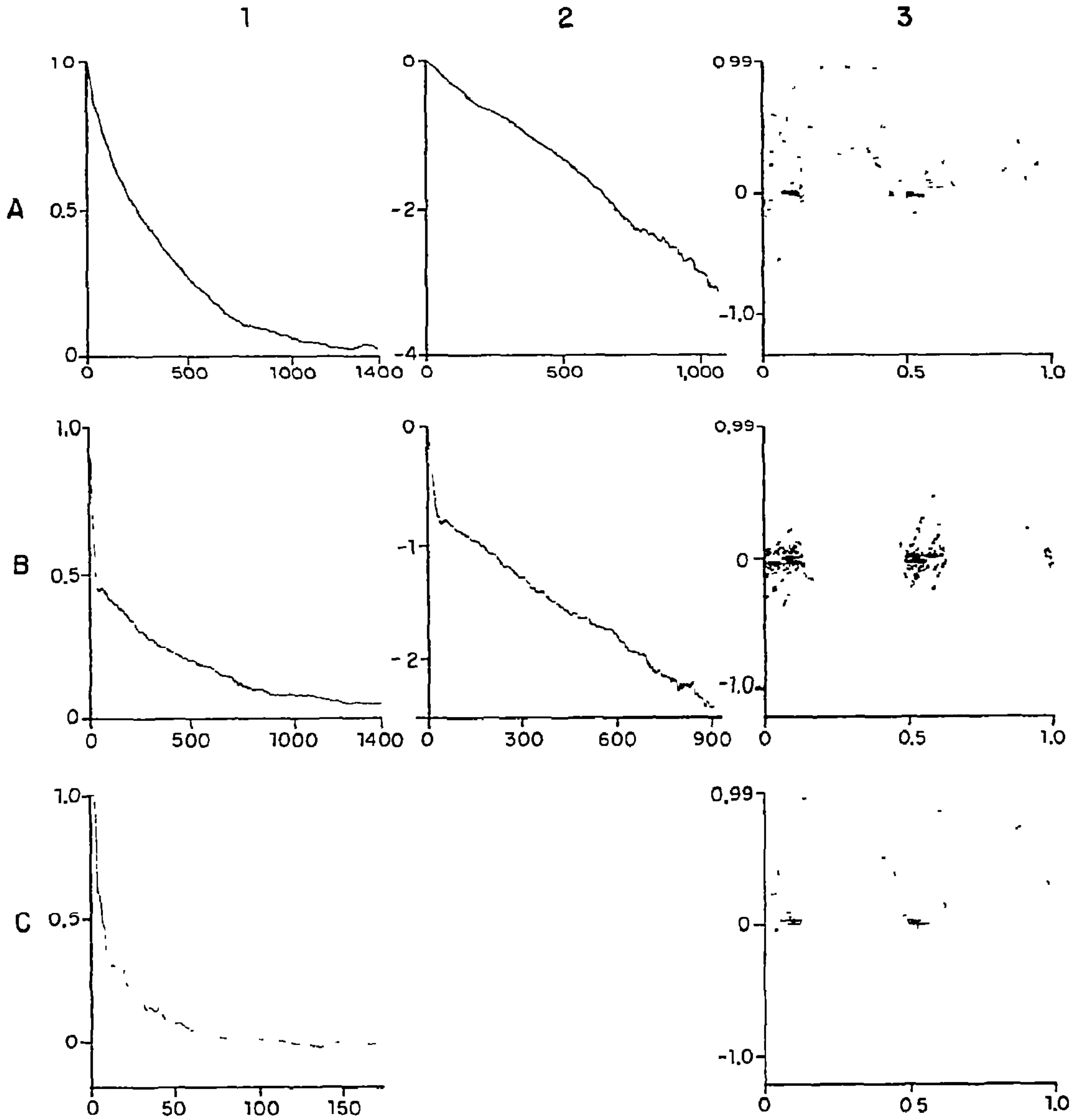

Fig. 2 Rows A, B and C correspond respectively to Siamese stadia with (E_0 = 0.45, κ = 0.1, γ = 0.5), (E_0 = 0.95, κ = 0.1, γ = 0.5) and E_0 = 0.45, κ = 1.0, γ = 0.5). Columns 1, 2 and 3 correspond respectively to the reactive flux, $k(t)$ [cf eq. (3)], the logarithm, $-\ln k(t)$, and the short-time global section determined by sampling the initial states from eq. (6) and following the motion for a short time. In A3 and B3, the trajectories were followed for 100 units, whereas in C3 they were followed for ≈ 15 units The ordinate and abscissa of the global section in column 3 are α and η respectively (see text preceeding eq (6))

tuations are so large that they do not permit an accurate determination of the rate constant. An approximate value is $\tau_{\mathrm{Rxn}}^{-1}/\tau_{\mathrm{RRKM}}^{-1} \approx 0.5$. This should be noted along with the fact that $\lambda\tau_{\mathrm{RRKM}} \approx 4$.

It is clear that even when a system is completely stochastic, RRKM theory is not always valid. This illustrates the requirement that the system must equipartition on a time scale fast compared to the time on which it recrosses the transition state. A K flow (which is a very strong property) does not necessarily satisfy this requirement.

It is worth mentioning at this point that there exists a measure preserving mapping of the stadium billiard that is analogous to the Poincaré surface of section used to locate regular and irregular motion in continuous systems [3]. A trajectory in the stadium can be characterized by the positions η at which the billiard collides with the boundary, and the angles θ (or better $\sin\theta$) made by the velocity vector with the inward normal through the boundary at the point of impact. The collision position is defined uniquely by determining the distance one must travel clockwise from some reference point (P1 in fig 1b) to the collision point. η is then defined as this distance divided by the length of the perimeter $|\Gamma|$ of the stadium. Any trajectory can then be mapped onto the cartesian space with $\alpha = \sin\theta$ as ordinate and $0 \leqslant \eta \leqslant 1$ as the abscissa This mapping was introduced by Bennettin and Strelcyn, who showed that the map is a global section. The stadium, being a K flow, gives rise to a random map with a uniform distribution of points

Fig 2, column 3 gives maps made by following the trajectories contributing to the reactive flux Each trajectory is followed for the time required for the flux to complete its fast decay The initial states are sampled from the normalized distribution

$$f(r,p) = \frac{\dot{x}\,\theta(\dot{x})\,\delta(x)\,\delta(E-H)}{\int \mathrm{d}\Gamma\,\dot{x}\,\theta(\dot{x})\,\delta(x)\,\delta(E-H)}\,. \tag{6}$$

Fig. 2A3 gives the short-time map of the trajectories used to compute fig. 2A1. The map looks perfectly uniform, except for trajectories corresponding to very small angles θ. The high density of points at small values of $\sin\theta$ correspond to trajectories that bounce back and forth many times before reaching the caps of the stadium where they get randomized. The effect of these trajectories gives rise to a very small short-time decay in the reactive flux (not observable in the fig.). The short-time map (fig. 2C3) corresponding to fig. 2C1 is very similar to fig. 2A3 since one is dealing with the same stadium.

The normalized reactive flux corresponding to $E_0 = 0.95$, $\kappa = 0.1$, and $\gamma = 0.5$ is shown in fig. 2B1. Fig. 2B2 gives the logarithm versus time. The long-time decay is seen to be exponential with rate constant $\tau_{\mathrm{Rxn}}^{-1}/\tau_{\mathrm{RRKM}}^{-1} = 0.49$. Interestingly $\lambda\tau_{\mathrm{RRKM}} = 65$ for the system, so that on the face of it we expect RRKM theory to be valid. Why then does RRKM theory fail to describe reaction dynamics in this system?

Fig. 2B1 exhibits several important features. At very short times we observe several small oscillations in $\hat{k}(t)$ These occur on time scale $t = 1.4$, and are due to trajectories of such small θ that they return to the hole in an activated state and can immediately recross several times The relative weight of these trajectories is given by the amplitude of the oscillations. This weight would grow if the hole size were made larger. A longer time decay, $t \approx 100$, is observed, and a very long time decay over a time of order 1000 is observed. The short-time map generated by following the initially sampled trajectories for a time $t \approx 100$ is shown in fig. 2B3. This map exhibits a very striking non-uniformity of points. What is this highly correlated short-time motion due to? Remember: over long periods of time the map should be uniform!

This behavior can be attributed to the fact that for high barriers, $E_0 = 0.95$, along the x direction, the initial set of trajectories has velocity vectors pointing largely along the x direction [the minimum value of $\dot{x}$ is $(2E_0)^{1/2}$]. This "cone" of trajectories widens as the barrier E_0 is decreased. Figs. 2B1–2B3 corresponds to a very high barrier, $E_0 = 0.95$, and therefore gives rise to a velocity distribution that is highly peaked in the forward direction (small $\sin\theta$). It is not difficult to show that a large fraction of these trajectories tend to get reflected back to the transition state with small $\sin\theta$ by the region of the semi-circle meeting with the two walls. In this case, because of the narrow velocity distribution, a sizeable fraction of the initial trajectories starting at the transition state continue to have small $\sin\theta$ for many collisions with the walls and return to the transition state with small $\sin\theta$, recrossing it before spreading out over the energy surface in phase space. The remaining trajectories that do not coherently recross get trapped in the well for long periods of time and escape through the hole at random times – hence the long-time exponential decay.

This mechanism explains the time decay of $\hat{k}(t)$ and the non-uniform feature of the short time map. The clustering in the map occurs for small values of $\sin\theta$, and reflects the sampling of initial states with velocities peaked in the forward direction, and the fact that small values of $\sin\theta$ are maintained by these trajectories over a long period of time. Since RRKM theory is expected to be valid only if equipartition can take place before recrossing, the relevant test is whether $\lambda\tau_c$ is large where τ_c is the time characterizing the fast decay. In the case corresponding to fig. 2C1, $\tau_c \approx 100$ and $\lambda\tau_c \approx 5$. Thus a large fraction of the trajectories recross the TS in a time short compared to λ^{-1}. This leads to the breakdown in RRKM theory. If the TS size is made small enough, the fraction that gets through is so severely reduced that RRKM is re-established. We note parenthetically that it should be possible to estimate the mixing time τ_M for an initial sampling from [6]

$$\tau_M \approx (-\ln\mu)/\lambda\,, \tag{7}$$

where this formula gives the time required for a point set of measure μ to cover phase space uniformly. For our purposes μ must be chosen as the relative measure of initial trajectories sampled by the distribution given in eq. (6). As the barrier height increases, μ decreases, and τ_M gets larger. Then the condition for RRKM behavior is that

$$\lambda\tau_{RRKM}/(-\ln\mu) \gg 1\,. \tag{8}$$

Fig. 3 summarizes our findings. The ordinate gives the ratio of τ_{Rxn}^{-1} to τ_{RRKM}^{-1}. Since in an ergodic system τ_{RRKM}^{-1} is an upper bound on τ_{Rxn}^{-1} the ordinate varies between 0 and 1. The abscissa is $\lambda\tau_{RRKM}$. Curve (A) corresponds to a series with $E_0 = 0.45$, $\gamma = 0.5$ as a function of relative TS size, κ. According to eq. (5) τ_{RRKM} increases as κ decreases. Since λ is fixed, increasing $\lambda\tau_{RRKM}$ corresponds to decreasing hole size, and it is seen that R ($\equiv\tau_{Rxn}^{-1}/\tau_{RRKM}^{-1}$) increases monotonically with $\lambda\tau_{RRKM}$ reaching unity – at which point RRKM theory is valid. All this means is that for small enough hole size equipartitioning takes place rapidly compared to recrossing of the hole. Curve (B) corresponds to a series with $\gamma = 0.5$, $\kappa = 0.1$, and E_0 varying between 0 and 0.95. From eq. (5)

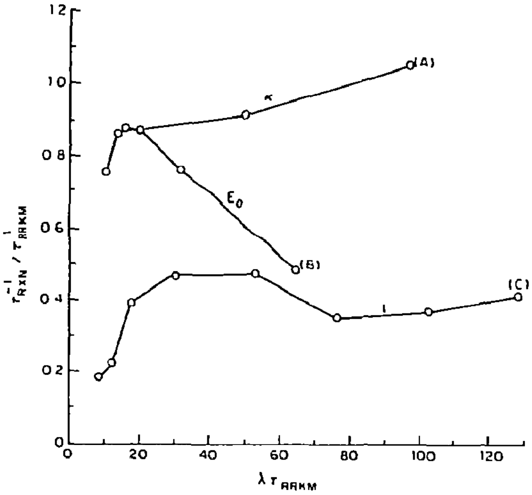

Fig. 3. A plot of the ratio R of the measured rate constant to the RRKM rate constant, versus the Lyapunov exponent times the RRKM lifetime in a well, $\lambda\tau_{RRKM}$. Curve (A) corresponds to a series of Siamese stadia ($E_0 = 0.45$, $\gamma = 0.5$) with variable κ. Curve (B) corresponds to a series of Siamese stadia with ($\kappa = 0.1$, $\gamma = 0.5$) with variable E_0 varying from 0 to 0.95. Curve (C) corresponds to a series of Siamese stadia with ($a = 0.2$, $E_0 = 0.95$) with variable γ (by varying γ at constant $R = 1.0$).

it can be seen the τ_{RRKM} increases as E_0 increases. Since κ is constant for the system, it follows that increasing $\lambda\tau_{RRKM}$ implies increasing E_0. Curve (B) shows that R decreases monotonically with $\lambda\tau_{RRKM}$. This is consistent with the foregoing discussion which shows that as E_0 increases, the trajectories contributing to $\hat{k}(t)$ are dominated by those with small $\sin\theta$, which can return from one collision with the "randomizing" cap of the stadium with again a small $\sin\theta$ and thereby cross. This happens in a time short compared to the equipartition time and leads to a non-statistical rate constant. If R is plotted versus $\lambda\tau_c$ or $\lambda\tau_m$, we expect a monotonic increase to $R = 1$. Curve (C) corresponds to a series at $E_0 = 0.95$, fixed hole size $a = 0.2$, but variable γ. Here τ_{RRKM} is fixed, but γ is varied (by varying γ at constant $R = 1$). From the work of Bennettin and Strelcyn [scaled by eq. (1)] we are able to determine the value of λ and thereby $\lambda\tau_{RRKM}$. For small values of γ (small l), λ is small. As γ is increased $\lambda\tau_{RRKM}$ increases and we observe that R grows, monotonically. Because $E_0 = 0.95$ we never observe pure RRKM behavior. This follows from our previous discussion. The overall behavior of the curve is consistent with the view that over and above this $E_0 = 0.95$ behavior, there is a dependence of the reaction dynamics and its associated rate constant on the time required for equipartitioning compared to the time between recrossings, which is controlled by γ.

Thus we conclude that even in purely stochastic measure preserving flows it is still possible to find interesting dynamical correlations that invalidate the assumptions on which RRKM theory is based. It has been shown that it is possible to correlate the dynamic contributions to the rate constant with the Lyapunov exponent. This correlation gives rise to the view that λ can be regarded as analogous to the "collision rate" in collision theories of reaction dynamics.

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