REACTION DYNAMICS IN A NON-ERGODIC SYSTEM: THE SIAMESE STADIUM BILLIARD *

Nelson DE LEON** and B J. BERNE
Department of Chemistry, Columbia University, New York, New York 10027, USA

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A simple classical dynamical system with measure preserving non-ergodic flow is devised in order to better understand reaction dynamics in isolated molecules This model gives rise to rate constants for activated barrier crossing that are larger than the RRKM rate constants for the system. This behavior is discussed in the light of recent theoretical work which generalizes the statistical theory of reaction rates to chaotic but non-ergodic dynamical systems

1. Introduction

Statistical theories of reaction dynamics, such as RRKM theory and transition state theory, have played an important role in the modern understanding of chemical dynamics [1–3]. A necessary but not sufficient condition for these theories is that the dynamical system be ergodic. In a companion paper [4] we have shown that even in ergodic systems, there are conditions in which dynamical correlations give rise to large deviations from RRKM theory. In a previous publication we showed that even when a system is non-ergodic, it is possible to derive a statistical theory of reaction rates [5,6] In non-ergodic systems phase space is decomposable into regular and irregular regions. Motion in the regular region is quasiperiodic, with trajectories confined to invariant manifolds of lower dimensionality than the energy hypersurface in phase space [7]. Motion in the irregular region is chaotic. If it is assumed that the motion in the irregular region randomizes on a time scale short compared to reaction, then it is possible to show that the kinetic rate constant for barrier crossing is given by [5,6]

$$\tau_{\mathrm{NLRRKM}}^{-1} = (X_A X_B)^{-1} \frac{\int d\Gamma\, B(\Gamma)\, \dot{x}\, \theta(\dot{x})\, \delta(x)\, \delta(E - H(\Gamma))}{\int d\Gamma\, B(\Gamma)\, \delta(E - H(\Gamma))}, \quad (1)$$

where Γ indicates a point in phase space, x is the reaction coordinate, $x = 0$ is the transition state, and $H(\Gamma)$ is the hamiltonian, and where

$$B(\Gamma) = 0 \quad \Gamma \in \mathrm{reg}, \qquad = 1 \quad \Gamma \in \mathrm{irreg}, \quad (2)$$

is a characteristic function indicating when Γ is in the irregular region of phase space. Eq (1) should be contrasted with the RRKM rate constant [3] which assumes the space to be ergodic

$$\tau_{\mathrm{RRKM}}^{-1} = (X_A X_B)^{-1} \frac{\int d\Gamma\, \dot{x}\theta(\dot{x})\, \delta(x(0))\, \delta(E - H(\Gamma))}{\int d\Gamma\, \delta(E - H(\Gamma))}. \quad (3)$$

In the event that all crossing trajectories are chaotic so that B can be taken as unity in the numerator of eq. (1), the only difference between eq. (3) and eq. (1) is the denominator. Since the denominator of eq. (3) counts fewer states than that of eq. (2), it follows that in this case

$$\tau_{\mathrm{NLRRKM}}^{-1} > \tau_{\mathrm{RRKM}}^{-1}. \quad (4)$$

This inequality arises from the fact that in the non-ergodic system, the regular region of phase space is

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** Present address Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA.

occupied by invariant tori. The irregular trajectories are excluded from the regions occupied by these tori and this gives rise to an "excluded volume effect".

In our previous study [5,6] of a continuous hamiltonian flow we could not detect any case in which the actual reaction rate τ_{Rxn}^{-1} was larger than $\tau_{\mathrm{RRKM}}^{-1}$ as predicted by eq. (3). The failure of statistical theory was attributed to correlations in the irregular motion, and particularly to motion on vague tori [8].

To better understand this problem we here devise a very simple reactive system which consists of two stadium billiards [9] connected at an edge. Motion through the transition state (TS) requires activation. This dynamical model is similar to a model studied in a companion paper [4]. In that paper the system is a K system, that is, an ergodic system. Here we explore a generalization which gives non-ergodic flow. We show that under certain conditions, this model definitely gives rise to rate constants larger than RRKM rate constants, a result consistent with eq. (1). We also find that under certain conditions, correlations in the irregular trajectories give rise to deviations from eq. (1) which reduce the rate constant

2. The generalized Siamese stadium

The model consists of a billiard [9] of mass $m = 1$ moving freely in the interior of the boundary given in fig. 1a, and suffering elastic collisions with the wall. P_1P_2 and P_3P_4 are parallel straight lines and P_2P_3 and P_4P_1 are arcs of circles of radius $r = 1$. In the limit $S \to 0$ the stadium becomes a rectangle which is a completely regular system. On the other hand when $S = 1$, the system is an ordinary stadium which is completely ergodic. Motion through the hole is activated; that is, only when

$$\tfrac{1}{2}m\dot{x}^2 > E_0 \tag{5}$$

can the particle pass through the hole.

As pointed out in a previous publication [4], motion in the Siamese stadium (fig. 1a) can be generated by following motion in the single stadium (fig. 1b) by tagging the trajectory with $\sigma = -1$ when it hits the transition state (TS) a, and can cross [that is, simultaneously satisfies eq. (5)]. Otherwise, the trajectory is tagged $\sigma = +1$. With these trajectories it is possible to determine the reactive flux,

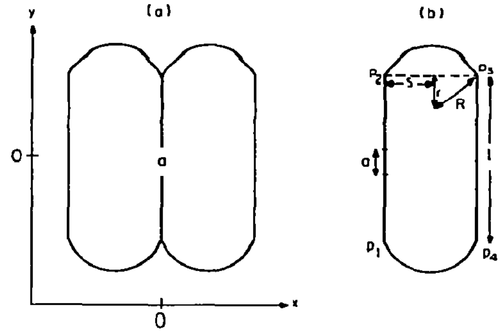

Fig 1 (a) The Siamese stadium. (b) The generalized stadium. billiard consists of a unit point mass moving freely inside the boundary and elastically scattering off the walls. The boundary consists of arcs of a circle of radius R, joined discontinuously at points P_1, P_2, P_3, and P_4 to parallel walls of length $l = 1.0$, separated by a distance $2S$ The hole in the Siamese stadium is of length a The parameters used in the text are $\kappa = a/l$, $\xi = 2S/l$, the energy barrier E_0, the total energy E. Systems with $\xi = 2.0, 1.8, 1.6, 1.0, 0.05$ with fixed $\kappa = 0.1$, $E_0 = 0.95$ and $E = 1.0$ are studied in this paper

$$k(t) = (X_A X_B)^{-1} \times \frac{\int d\Gamma\, \dot{x}(0)\,\delta(x(0))\;\theta(x(t))\,\delta(E - H(\Gamma))}{\int d\Gamma\, \delta(E - H(\Gamma))}, \tag{6}$$

where $X_A = X_B$ is the fraction of time spent by trajectories in wells A and B. $k(t)$ is a quantity whose initial value gives the RRKM rate constant, eq. (3), and whose long-time exponential decay, $e^{-t/\tau_{\mathrm{Rxn}}}$ gives the exact rate constant τ_{Rxn}^{-1}. The reactive flux is computed by sampling initial states from the distribution

$$f(\Gamma) = \frac{\dot{x}\,\theta(\dot{x})\,\delta(x)\,\delta(E - H)}{\int d\Gamma\,\dot{x}\,\theta(\dot{x})\,\delta(x)\,\delta(E - H)} \tag{7}$$

and then computing eq. (6).

To better understand the dynamics of the Siamese stadium it is useful to employ the global section introduced by Bennettin and Strelcyn [9]. Each collision of the billiard with the boundary is defined by the parameters

$$0 \leqslant \eta = \Psi/|\Gamma| \leqslant 1\,, \quad -1 \leqslant \alpha = \sin\theta \leqslant 1\,, \tag{8}$$

where Ψ is the distance measured clockwise from the point P_1 (cf. fig. 1b) to the point of collision, and $|\Gamma|$ is the circumference of the stadium. The collision angle θ is the angle made by the velocity (just prior to collision) with the inward normal to the boundary at the point of collision. Thus each collision is defined by the coordinate (η, α) and can be represented by a point in a bounded two-dimensional cartesian space. A trajectory gives a point set in this space. Quasiperiodic trajectories give rise to closed curves (or "tori") whereas irregular trajectories give rise to a random set of points that must lie in the region not occupied by tori. This global section is the analogue of the Poincaré surface of section in continuous systems. One way of studying reaction dynamics is to determine the global short-time section resulting from sampling initial points from the distribution given in eq. (7). This is the method used in ref. [1], and adopted here to demonstrate the dynamical contribution to the reaction dynamics.

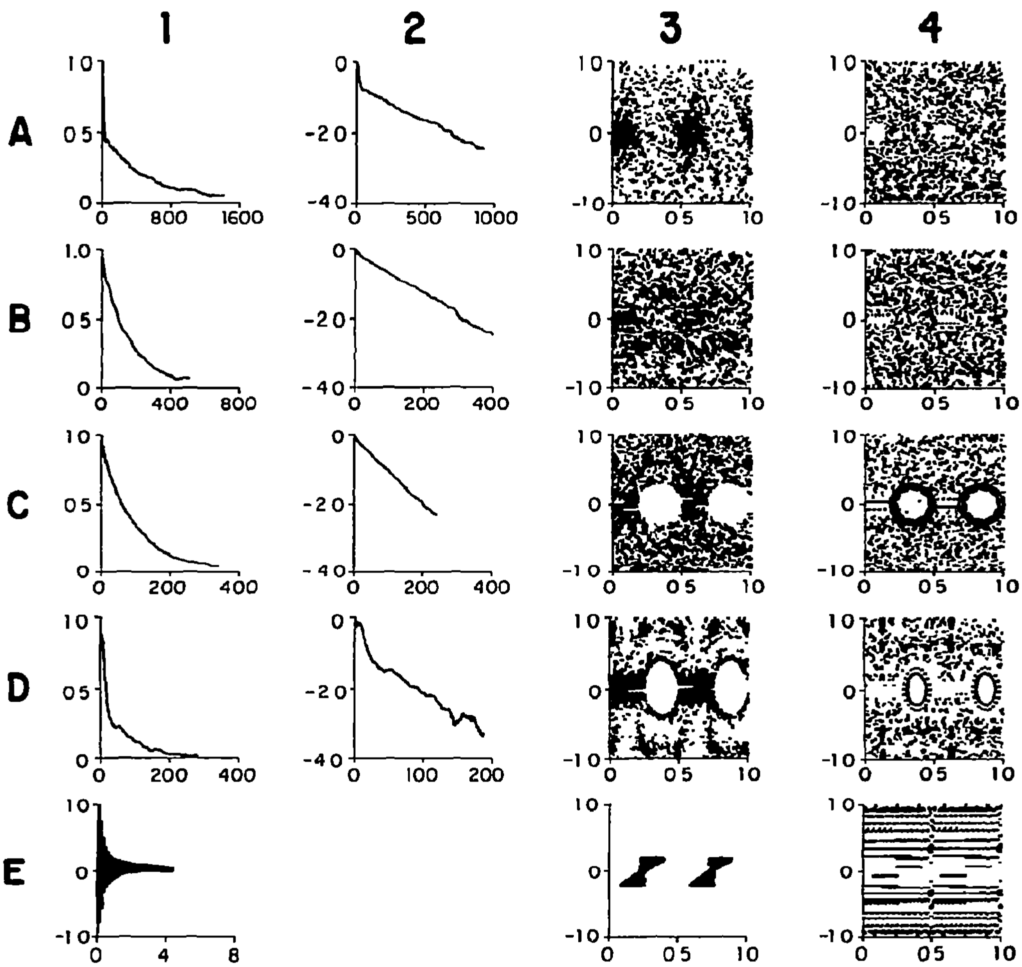

Fig. 2. Rows A–E correspond respectively to stadia with ξ = 2.0, 1.8, 1.6, 1.0 and 0.05. Columns 1–4 correspond respectively to the reactive flux $k(t)$ (cf. eq. (6)), $-\ln k(t)$, the short-time global section generated by sampling initial states from eq. (7), and the full global section as defined in the text. The ordinates and abscissas of the global section in columns 3 and 4 are α and η respectively [cf. eq. (8)].

3. Results

To better understand reaction dynamics in nonergodic systems, we study a series of Siamese stadiums all having energy $E = 1$, barrier height $E_0 = 0.95$, length $l = 1.0$, radius $R = 1$, relative hole size $\kappa = a/l = 0.1$, and mass $m = 1$, but different widths $\zeta = 2S$ ranging from 2.0 to 0.05. When $\zeta = 2.0$ the system is the fully ergodic stadium studied by Bennettin and Strelcyn. When $\zeta = 0.05$ the system looks very much like a long thin rectangle and is highly regular.

Representative results of this study are presented in fig. 2. The rows are labeled A–E and the columns are labeled 1–4. Rows A–E respectively give the results for increasingly regular systems with $\zeta = 2.0$, 1.8, 1.6, 1.0 and 0.05. Column 1 gives the normalized flux, $\hat{k}(t)$, that is, $k(t)\tau_{RRKM}$ where τ_{RRKM}^{-1} is the RRKM rate constant [cf. eq. (3)] which has the explicit form

$$\tau_{RRKM}^{-1} = 4[(E - E_0)/2]^{1/2}(l\kappa/\pi A)\theta(E - E_0) , \quad (9)$$

where A is the area of the stadium in fig. 1b. Column 2 gives a logarithmic plot of the normalized flux from which the rate constant τ_{Rxn}^{-1} is determined (cf. table 1). Column 3 gives the global section (short time) and column 4 gives the global section (long time) found by sampling initial points from eq. (7).

System A in fig. 2 is fully stochastic, as can be seen from the global section in fig. 2A4. In all systems studied here, the barrier height is very large ($E_0 = 0.95$). The states sampled from eq. (7) consequently have a velocity distribution peaked in the forward (x) direction, and these have small initial collision angles. These propagate to the caps, and in the full stadium (system A), where the cap joins the straight wall continuously, they propagate back with small collision angles – hence the dense set of points in the short-time section, fig. 2A3. As was pointed out in a previous publication [5], this correlated motion leads to recrossing of the transition state at $t \approx 100$ (as seen in fig. 2A1) and gives rise to a large deviation ($\tau_{Rxn}^{-1}/\tau_{RRKM}^{-1} = 0.5$) from RRKM theory even in an ergodic system.

System B in fig. 2B is also fully ergodic as can be seen from its global section, fig. 2B4, but now the circular caps do not join the straight walls continuously. Thus although the trajectories are still sampled with small collision angles, these propagate to the caps and upon first colliding with caps have large collision angles. The net effect is that the short-time correlation is largely wiped out, as can be seen in the short-time section in fig. 2B3, and in the reactive flux in figs. 2B1 and 2B2. The normalized reactive flux is a single exponential decay with $\tau_{Rxn}^{-1} = \tau_{RRKM}^{-1}$ (cf. table 1).

System C in fig. 2C has a global section, fig. 2C4, that exhibits closed curves (tori). Trajectories giving rise to these closed curves are quasiperiodic. Irregular (or stochastic) trajectories also exist and give rise to the "random" points in the global section. The short-time section in fig. 2C3 consists only of the random points, thus indicating that all the crossing trajectories are random. These trajectories cannot visit regions of phase space occupied by tori, hence the open regions in fig. 2C3.

System C looks like a system in which the crossing trajectories are ergodic in the irregular region of phase space. Given the foregoing, a statistical theory [cf. eq. (1) and the appendix of ref. [3]] should be applicable [with the added condition that B can be taken as unity

Table 1

System	$\zeta (= 2S)$	$\tau_{Rxn}^{-1}/\tau_{RRKM}^{-1}$	$\tau_{RRKM}^{-1} (\times 10^2)$ [a]
A	2.0	0.49	0.39
B	1.8	0.98	0.62
C	1.6	1.2	0.81
D	1.0	0.81	1.7
E	0.05	–	40.2

[a] Where the absolute unit of time is $2^{1/2}$ s

in the numerator of eq. (1) because all the crossing trajectories are irregular]. This leads us to predict that the reactive flux [cf. eq. (6)] will be a single exponential decay with decay constant τ_{Rxn}^{-1} given by eq. (1) (with $B = 1$ in the numerator). Figs. 2C1 and 2C2 give excellent agreement with this prediction, and moreover, $\tau_{\mathrm{Rxn}}^{-1}/\tau_{\mathrm{RRKM}}^{-1} = 1.2$; that is, τ_{Rxn}^{-1} is greater than the RRKM rate constant as expected. Unfortunately we have not yet been able to make an ab initio calculation of eq. (1); however, it is clear that this can be done based on methods outlined in a recent note [10].

System D, in fig. 2D, is much more regular than system C, as can be seen by comparing the global sections in figs. 2D4 and 2C4. The short-time section, fig. 2D3, shows that the crossing trajectories appear to be random, but not uniformly distributed in the irregular regions of phase space. Thus we do not expect that the statistical theory of eq. (1) will be valid, and indeed it is not. The reactive flux given in figs. 2D1 and 2D2 is highly non-exponential, indicates short-time correlations similar to those in fig. 2A, and gives rise to $\tau_{\mathrm{Rxn}}^{-1}/\tau_{\mathrm{RRKM}}^{-1} < 1$ (cf. table 1). This correlation cannot be attributed to the same mechanism invoked in fig. 2A because the caps join the walls discontinuously. Is this correlation, which leads to rapid recrossing, due to vague tori [2,3]? We simply do not know! This requires further study.

System E in fig. 2E is a highly regular system ($\zeta = 0.05$), as shown by the global section, fig. 2E4, and the short-time section, fig. 2E3. The reactive flux consists of a superposition of periodic and quasiperiodic crossing trajectories with different periods, and thus exhibits an oscillatory decay due to dephasing. Reaction rate constants do not exist at all.

4. Summary

Several points are illustrated by the study of the Siamese stadium:

(a) When the system is ergodic, dynamical correlations can give rise to deviations from RRKM theory leading to $\tau_{\mathrm{Rxn}}^{-1}/\tau_{\mathrm{RRKM}}^{-1} < 1$ (cf. fig. 2A).

(b) When the system is ergodic, and there are no dynamical correlations, RRKM theory is valid (cf. fig. 2B).

(c) When the system is non-ergodic, and the irregular trajectories uniformly fill the irregular region of phase space, a statistical theory of reactions [cf. eq. (1)] is valid and leads to $\tau_{\mathrm{Rxn}}^{-1}/\tau_{\mathrm{RRKM}}^{-1} > 1$ (cf. fig. 2C).

(d) Dynamical correlations in the irregular trajectories (perhaps due to vague tori) [8] give rise to strong deviations from the statistical theory [eq. (1)] and lead to $\tau_{\mathrm{Rxn}}^{-1}/\tau_{\mathrm{NLRRKM}}^{-1} < 1$. It can accidently happen that $\tau_{\mathrm{Rxn}}^{-1} = \tau_{\mathrm{RRKM}}^{-1}$; but that does not signify the validity of RRKM theory (cf. fig. 2D).

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