Fragmentation kinetics of a Morse oscillator chain under tension

Joseph N. Stember, Gregory S. Ezra *

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, NY 14853, United States

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Abstract

The bond dissociation kinetics of tethered atomic (Morse potential) chains under tensile stress is studied. Both RRKM (fully anharmonic, Monte Carlo) and RRK (harmonic approximation) theory are applied to predict bond dissociation rate constants as a function of energy and tensile force. For chains with \( N \geq 3 \) atoms a hybrid statistical theory is used involving a harmonic approximation for motion in the transition state for bond dissociation. For chains with \( N = 2–5 \) atoms, while the RRK approximation significantly overestimates the dissociation rate constant, the fully anharmonic RRKM rate is quite close to simulation results. For the \( N = 2 \) chain, a novel approach to the extraction of decay rate constants based on the classical spectral theorem is implemented. Good agreement between the RRKM and dynamical rate constants is obtained for \( N = 2 \) despite the fact that the reactant phase space contains a significant fraction of relatively short-lived trajectories.

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1. Introduction

A fundamental understanding of the intramolecular dynamics and kinetics of fragmentation (bond dissociation) of atomic chains subject to a tensile force is needed to provide a solid foundation for theories of material failure under stress [1,2], polymer rupture [3–7], adhesion [8], friction [9], mechanochemistry [10–12] and biological applications of dynamical force microscopy [13–17]. In chain scission models for polymer fiber failure, the primary failure events are breaking of covalent bonds within individual chains [1,2,18,19]. Although trajectory studies on model polyethylene chains suggest that complete intramolecular vibrational energy redistribution (IVR) can occur on a picosecond timescale [20,21], extensive theoretical work has shown that the rate of bond breakage in single polymer chains under constant stress/strain can be up to several orders of magnitude slower than calculated on the basis of statistical approaches such as transition state theory [22–30]. Of course, studies of energy transfer and equipartition in single chains of coupled anharmonic oscillators have a long history, beginning with the seminal work of Fermi et al. [31,32]. (For some recent work on dynamics of atomic chains see [33–38].)

In the present paper we study numerically the kinetics of bond breaking in single atomic chains under stress. The dissociation of a 1D chain subject to constant tensile force is a problem in unimolecular kinetics. A fundamental issue in unimolecular kinetics concerns the applicability of statistical approaches such as RRKM [39–43] or transition state theory [44]. Previous theoretical work has suggested that dissociation of atomic chains under stress is not amenable to simple statistical approaches [22–30]. Early trajectory simulations on the dynamics of Morse chains [22–25] showed that correlated motions of ~5–10 chain atoms are necessary for bond breaking to occur. Moreover, simple bond stretching or force criteria for bond rupture were found to fail, in that apparently broken bonds were observed to reform (bond healing). A significant fraction
of dissociative events occurred via a two-stage process: an initial, relatively persistent local bond stretching, followed by rapid breaking of the stretched bond [24]. Simulations of the fragmentation of 1D Lennard–Jones (LJ) chains at constant strain with inclusion of a frictional damping term and a stochastic force modelling interaction with a heat bath show that, while fragmentation rate constants fit an Arrhenius form with activation energy consistent with a static picture at constant strain [45], the magnitude of the preexponential factor was at least three orders of magnitude smaller than expected on the basis of naive dynamical considerations [27] (see, however, Ref. [46]). Healing of incipient breaks is highly efficient. Comparison of polymer rupture with single-bond dissociation dynamics for the same damping/fluctuating force via Kramers theory [47] shows that stochastic forces are not responsible for the bond healing. Bolton, Nordholm and Schranz (BNS) have studied the dissociation of 1D Morse chains (N = 2–20) under stress [28], following earlier work on the classical dynamics of unstressed chains [48–50]. Nonexponential decay, failure of RRKM theory, and extensive transition state recrossing effects were found. Interestingly, the presence of lateral interchain coupling increased recrossing effects. Standard harmonic classical TST has been applied to the dissociation of a 1D Morse chain [29,30], with the transition state for dissociation of a given bond located at the maximum of the effective potential (see below). The harmonic canonical TST rate constant did not agree with molecular dynamics calculations, but effects of anharmonicity [43,28] on the predictions of TST were not systematically investigated. Molecular dynamics studies on thermal degradation in polyethylene [51] indicate that the dependence of bond scission rate on average thermal excitation energy can be fit with RRK theory [52], suggesting that bending and torsional modes might play an important role in establishing statistical behavior. (Refs. [53–56] are representative studies of the role of torsional and bending degrees of freedom in intramolecular dynamics.)

Dissociative trajectories in 1D LJ chains do not exhibit the sensitive dependence on initial conditions expected for chaotic systems [26]; this suggests a significant degree of regularity at the transition state (saddle point) for single bond dissociation. Such regularity is analogous to that found for isomerization reactions in clusters (see, for example, [57,58] and references cited therein).

In the present work classical trajectory simulations are used to investigate the fragmentation kinetics and phase space structure of short tethered atomic chains under constant tensile stress. Morse parameters in the simulations can be chosen, for example, to model the effective CH2-CH2 bond potential in polyethylene [51]. We focus on non-statistical aspects of the dissociation dynamics and the role of anharmonicity.

In Section 2 we introduce the model Hamiltonian to be studied, which consists of a tethered chain of identical atoms interacting via pairwise Morse potentials subject to constant tensile stress. Section 3 discusses application of statistical theories such as RRKM and RRK (harmonic approximation to RRKM) to our model. We describe the numerical procedures used to implement a fully anharmonic version of RRKM theory using Monte Carlo integration to determine reactant and transition state phase space volumes as a function of energy. (See also recent work by Zhao and Du [59].) Section 4 outlines the procedures used to extract dissociation rate constants from classical trajectory simulations of chain fragmentation. In Section 5 we discuss in some detail the phase space structure for the N = 2 case, as visualized through use of Poincaré surfaces of section [60]. For the N = 2 chain, there are two distinct transition states corresponding to dissociation of the two different bonds, and we examine intersections of the stable and unstable manifolds of the two transition states in order to give a phase space picture of short-time (direct) dynamics in terms of reactive cylinders [61–65]. Section 6 compares the values of trajectory dissociation rate constants with those obtained using statistical approaches for the N = 2 chain. In Section 7 we explore the possibility of making a more stringent comparison between dynamical and statistical rate constants by introducing corrections to the RRKM expression based on the classical spectral theorem [66–73]. Section 8 presents a comparison of statistical and dynamics rate constants obtained for chains with N = 3–5 atoms, while Section 9 concludes.

2. Model potential and Hamiltonian

2.1. Potential energy surface

We consider first a one-dimensional Morse oscillator plus potential linear in bond coordinate, describing a particle tethered to a wall (infinite mass) and acted on by a constant tensile force f. The potential for this system takes the form

$$V(r, f) = V_{M}(r) - f(r - r_{eq}^{0})$$  \hspace{1cm} (1a)

$$= D_{0}[1 - \exp\{-\beta(r - r_{eq}^{0})\}]^{2} - f(r - r_{eq}^{0}).$$  \hspace{1cm} (1b)

Unless otherwise specified, we shall measure length in units of r_{eq}, the zero-force Morse oscillator equilibrium bond distance, and energies in units of D_{0}, the unperturbed Morse dissociation energy.

For the Br2 molecule, for example, r_{eq} = 2.28 Å, D_{0} = 45.89 kcal/mol and \beta = 4.432/r_{eq}^{0} [28]. For the typical tensile stress value of 25 kcal mol^{-1} Å^{-1} studied by Bolton et al., f = 1.24D_{0}/r_{eq}^{0} [28]. For the CC bond in model polyethylene (pe), r_{eq}^{0} = 1.529 Å, D_{0} = 83 kcal/mol and \beta = 2.94/r_{eq}^{0} [74,75,51,76]. At the representative tensile stress value of 1 GPa [2], f = 0.053D_{0}/r_{eq}^{0}. We have studied Morse chains with \beta values in the range 1–3. All the calculations reported here are carried out for the tensile stress value f = 0.02.

The potential (1a) is plotted versus r in Fig. 1 for various f values and \beta = 1. For f \leq f_{crit} = \frac{1}{2}, potential (1a) has two
stationary points, one at the potential minimum \( r = r_{\text{eq}} \) and one at the saddle point, \( r = r^1 \): In general, the critical values of the potential are given by

\[
\begin{align*}
    r_{\text{eq}} &= \frac{1}{\beta} \ln \left[ \frac{\beta - \sqrt{\beta(2f + \beta)}}{f} \right] + r_{\text{eq}}^0, \\
    r^1 &= \frac{1}{\beta} \ln \left[ \frac{\beta + \sqrt{\beta(2f + \beta)}}{f} \right] + r_{\text{eq}}^0.
\end{align*}
\]

As \( f \) increases, \( r^1 \) decreases while \( r_{\text{eq}} \) increases slightly. The depth of the potential well decreases from the zero-force value \( D_0 \) until \( f \) reaches the critical value \( f_{\text{crit}} \), at which point the well disappears completely. For \( \beta = 1 \) and \( f = 0.02 \), we have \( r_{\text{eq}} = 1.010 \) and \( r^1 = 5.595 \).

Now consider a linear chain of \( N \) atoms. For this system with \( N \geq 2 \) degrees of freedom, the conversion from internal (bond) coordinates \( r \) to external (lab-fixed) coordinates \( x \) is given by (see Fig. 2)

\[
x_k = \frac{1}{\beta} \ln \left[ \frac{\beta - \sqrt{\beta(2f + \beta)}}{f} \right] + r_{\text{eq}}^0, \quad k = 1, \ldots, N.
\]

We assume that the potential between atoms is pairwise Morse (nearest neighbors only) and that the tensile force acts only on the outermost atom, giving a potential function for the chain

\[
V(x, f) = V_M(x_1) + V_M(x_2) + \cdots + V_M(x_N) - f(x_N - N r_{\text{eq}}^0) = \sum_{i=1}^{N} [V_M(r_i) - f(r_i - r_{\text{eq}}^0)].
\]

The force is distributed through the chain so that the potential in each bond coordinate \( r_k \) has the same functional dependence on bond length as the one-particle potential (1a). Hence the equilibrium bond length between any adjacent pair of atoms at the global minimum in the \( N \geq 2 \) chain is just the equilibrium bond length for the one-dimensional case. A similar equivalence holds for the critical bond length. For example, the equilibrium and saddle configurations corresponding to breaking bond 1 are

\[
x_k = kr_{\text{eq}}, \quad k = 1, \ldots, N,
\]

\[
x_{k,\text{saddle}} = r^1 + (k - 1)r_{\text{eq}}, \quad k = 1, \ldots, N.
\]

For a single tethered atom, Fig. 1 shows the existence of a well-defined configuration space transition state for bond breaking located at the top of the effective potential energy barrier. For a chain of atoms under stress, there is an analogous critical configuration associated with the dissociation of each bond. Detailed static analyses of polymer chains subject to tensile force (both constant strain and constant stress) have been given [45,77]. Although the static analysis leads to a clear view of the nature of certain important cuts through the multibody potential (for example, one bond stretched with all other bonds having equal displacements from equilibrium), it provides limited insight into fracture dynamics.

Contours of the \( N = 2 \) potential energy surface (PES), Eq. (4a), as a function of the single-particle coordinates \( x_1 \) and \( x_2 \) are plotted in Fig. 3a. There is a global minimum corresponding to the bound chain and two saddle points associated with the two possible bond dissociation pathways. Along the minimum energy pathway for breaking of bond 1, both \( x_1 \) and \( x_2 \) coordinates increase, while the path for breaking of bond 2 is approximately a vertical line, \( x_1 \sim \text{const} \). Bound motions at the respective transition states are approximately perpendicular to the minimum energy paths (see below).

The potential energy barrier to dissociation, i.e., the activation energy \( E_a = E_f^* \), is defined to be

\[
E_f^* = V(r^1, f) - V(r_{\text{eq}}, f).
\]

For any particular value of the force \( f \), all energies are measured from the \( f \)-dependent minimum energy \( V(x_{\text{eq}}(f)) \). For \( \beta = 1 \) and \( f = 0.02 \) we have \( E_a = 0.8881 \).

2.2. Hamiltonian

In single particle coordinates, the \( N \)-atom chain Hamiltonian is simply

\[
H(x, f) = \sum_{i=1}^{N} \frac{1}{2m_i} p_i^2 + V(x, f),
\]

Fig. 1. Potential \( V(r, f) \) for a tethered Morse particle under tensile stress, Eq. (1a). The unit of length is \( r_{\text{eq}}^0 \), the zero-force Morse oscillator equilibrium bond distance, and the unit of energy \( D_0 \), the unperturbed Morse dissociation energy. Force parameter \( f: f = 0 \) (black), \( f = 0.04 \) (green), \( f = 0.06 \) (blue), \( f = 0.08 \) (purple), \( f = 0.1 \) (light blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Definition of single-particle coordinates \( \{x_i\} \) for a tethered chain of \( N = 4 \) atoms under tensile stress.
where $p_j$ is the momentum of particle $i$. We shall take all particles to have the same mass $m_j = m$. Fixing the unit of mass specifies a unit of time; with $D_0 = r_{eq}^0 = m = 1$, the period of the harmonic oscillation at the bottom of the Morse potential well with $\beta = 1$ is $\tau_{\text{HO}} = 2\pi/\sqrt{2}$. Although the overall magnitudes of dissociation rate constants depend on the value of the particle mass $m$, the ratios of rate constants computed from two different methods (e.g., trajectory and RRK) do not (see Section 6.1).

In terms of bond coordinates, the $N$-atom chain Hamiltonian is

$$H(r, f) = \frac{1}{2} \sum_{k=1}^N p_{r_i}^2 + \sum_{k=1}^N \sum_{j=k+1}^N \left( p_{r_i} r_{f_{ij}}^2 - \sum_{k=1}^N \sum_{j=k+1}^N p_{r_j} r_{f_{ij}} \right) + (V_{\text{M}}(r_i) - f(r_i - r_{eq}^i)).$$

(8)

In terms of single-particle coordinates the kinetic energy is therefore separable while the potential energy is nonseparable, whereas in bond coordinates the potential energy separates while the kinetic energy has coupling terms $-p_{r_i} r_{f_{ij}}$.

3. RRKM and RRK dissociation rate constants

3.1. RRKM theory

The RRKM expression for the $E$ and $f$-dependent molecular fragmentation rate constant associated with breaking of bond $j$ is [39–43]

$$k_{\text{RRKM}}(E, f) = \frac{\mathcal{N}^j(E - E^j_f)}{\rho(E)},$$

(9)

where $\mathcal{N}^j(E - E^j_f)$ is the classical sum of states (phase space volume) at the transition state for breaking of bond $j$, $E^j_f$ is the force-dependent dissociation energy, and $\rho(E)$ is the classical density of states for the reactant region of phase space,

$$\rho(E) = \frac{d\mathcal{N}^j(E)}{dE},$$

(10)

with $\mathcal{N}^j(E)$ the classical sum of states (phase space volume) at total energy $E$.

For an $N$-mode system, $\rho$ has dimensions $(qp)^{N-1}/J = (Js)^N/J = (Js)^{N-1}/s$. The classical transition state sum of states $\mathcal{N}^j$ is the phase space volume for an $(N - 1)$-degree-of-freedom system at the critical configuration, and has dimensions $(qp)^{N-1} = (Js)^{N-1}$. The ratio of the two, which is the classical unimolecular rate dissociation rate constant as defined in (9), then has units of inverse time, $(Js)^{N-1}/(Js)^{N-1} = s^{-1}$, as it should. The unit of time used in our calculations, $\tau_0$, is discussed in Section 4.1.

The quantum density of states $\rho_Q$ is obtained in the semiclassical limit by dividing $\rho$ by the volume of a phase space “cell”. For an $N$ mode system, $\rho_Q = \rho/\hbar^N$. Similarly, the quantum transition state sum of states is $\mathcal{N}_Q^j = \mathcal{N}_Q^j/h^N$. We therefore have

$$k_{\text{RRKM}} = \frac{\mathcal{N}_Q^j}{\rho_Q} = \frac{h^{N-1}\mathcal{N}_Q^j}{\hbar^N},$$

(11a)

$$= \frac{1}{\hbar} \frac{\mathcal{N}_Q^j}{\rho_Q},$$

(11b)

so that the usual expression for $k_{\text{RRKM}}$, Eq. (11b), explicitly contains Planck’s constant $\hbar$ [39–43]. The absence of Planck’s constant in the formula (9) expressed in terms of purely classical quantities is nevertheless appropriate and entirely correct.

Broadly speaking, in order for the RRKM rate constant expression to be valid it is necessary that $k_{\text{rxn}} \ll k_{\text{IVR}}$, i.e., the rate of intramolecular energy transfer should be greater...
than the reaction rate. Many studies have been carried out on the validity of RRKM theory (9) and the connection between deviations from statisticality and intramolecular dynamics (for example, the existence of bottle-necks to intramolecular energy flow) [66,78–83]. Our focus here is on the validity of expression (9) for the particular case of atomic chains under tensile stress [28–30].

We shall consider energies low enough so that the dissociation of two or more bonds is not energetically possible. If the overall statistical rate constant for chain fragmentation via single bond dissociation is

\[ k_{\text{RRKM}}^{\text{NR}} = \sum_{j=1}^{N} k_j^{\text{RRKM}} \]  

(12)

where the total number of decay channels is equal to the number of bonds in the chain, then \( N(t) \), the number of bound molecules at time \( t \), exhibits exponential decay,

\[ N(t) = N(0) e^{-k_{\text{RRKM}} t} \]  

(13)

In general we define the overall dissociation rate constant, when it exists, by

\[ k = -\frac{1}{N(t)} \dot{N}(t) \]  

(14a)

\[ = \sum_{j=1}^{N} k_j \]  

(14b)

\[ = + \frac{1}{N(t)} \sum_{j=1}^{N} \dot{n}_j(t), \]  

(14c)

where \( n_j(t) \) is the number of molecules that have dissociated via channel \( j \) at time \( t \). In a regime where the system exhibits exponential decay, the rate constant for dissociation via channel \( j \) is given in terms of the branching ratio \( b_j \) as

\[ k_j = \frac{n_j(t)}{\sum_{n=1}^{\text{crit}} n_n(t)} k \equiv b_j k. \]  

(15)

3.2. RRK theory: a harmonic approximation to RRKM theory

RRK theory is the harmonic limit of RRKM theory [52]. We approximate the potential function \( V(x) \) by a second order expansion about the potential minimum and saddle points. At these critical points, linear terms vanish, and we have

\[ V^{\text{crit}}(x) = V(x^{\text{crit}}) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \Delta x_i \Delta x_j \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right) \bigg|_{x=x^{\text{crit}}} + \cdots \]  

(16)

There are \( N \) real normal mode (angular) frequencies for the reactant, \( \{\omega_i\}_{i=1}^{N} \), and \( N-1 \) real frequencies, \( \{\tilde{\omega}_i\}_{i=1}^{N-1} \), for the transition state, together with a single imaginary frequency associated with unstable motion off the saddle. For an \( r \)-dimensional harmonic oscillator, frequencies \( \{\omega_i\}_{i=1}^{N} \), the phase space volume \( \mathcal{N}(E) \) at energy \( E \) is

\[ \mathcal{N}(E) = \frac{(2\pi)^r}{r!} \frac{E^r}{\prod_{i=1}^{N} \omega_i}, \]  

(17)

so that the harmonic (RRK) approximation to the RRKM rate constant (9) for dissociation via transition state \( \alpha \) is

\[ k_j^{\text{RRkm}}(E; \alpha) = \frac{1}{2 \pi} \int_{-\infty}^{\infty} \prod_{i=1}^{N} (\omega_i) \left( \frac{E - E_{\text{f},\alpha}}{E} \right)^{N-1} \right), \]  

(18)

where \( E_{\text{f},\alpha} \) is the critical energy for dissociation of bond \( \alpha \) under external force \( f \). It should be noted that in our present model with all atoms identical, \( E_{\text{f},\alpha} = E_f \) is the same for all transition states because \( \beta \) and \( \rho_{\text{eq}} \) are the same for each term in potential (4a).

3.3. Computation of RRKM rate constant

3.3.1. Reactant phase space volume

To compute \( k_j^{\text{RRkm}}(E) \) we must determine the reactant phase space volume \( \mathcal{N}(E) \), from which the reactant density of states can be obtained via Eq. (10). \( \mathcal{N}(E) \) is the volume of the region of phase space consisting of all points with energy less than or equal to \( E \):

\[ \mathcal{N}(E) = \int d\xi_1 dp_1 d\xi_2 dp_2 \cdots d\xi_N dp_N \Theta(E - H(x, p)) \]  

(19)

where \( \Theta \) is the Heaviside step function. This integral has no analytical solution for our system (cf. [84]), necessitating use of either a harmonic approximation to the potential or numerical (Monte Carlo) integration. As the validity of the harmonic approximation versus the role of anharmonicity in the reactant density of states is an important question when assessing the validity of RRKM theory for treating stressed polymer chains [28,29], for comparison with the harmonic approximation we shall evaluate the fully anharmonic reactant density of states and transition state sum of states essentially exactly using a numerical Monte Carlo approach.

To evaluate the phase space volume numerically, we consider a region (“hypercube”) in phase space \( M_0 \) with volume \( V_0 \) large enough to contain all reactant phase points with energy \( E \leq E_{\text{MC}} \). To compute \( \mathcal{N}(E) \), the phase space volume as a function of energy, we determine the volumes \( V_x \) of subsets \( M_x \subset M_0 \) containing phase points with \( E \leq E_x \leq E_{\text{MC}} \). If \( n_x \) phase points \( \{x_i, p_i\}_{i=1}^{n_x} \subset M_0 \) are chosen randomly, and \( n_x \) of these points lie within \( M_x \), then, for large enough \( n_x \), the volume \( V_x \) is

\[ V_x \approx \frac{n_x}{n_x} V_0. \]  

(20)

From the set of pairs \( \{E_x, V_x\}_{x=1}^{n_{\text{max}}} \), we can fit the phase space volume \( \mathcal{N}(E) \) to a polynomial in \( E \),

\[ \mathcal{N}(E) \approx E^n (c_0 + c_1 E + \cdots), \]  

(21)

that is, harmonic oscillator phase space volume plus anharmonic corrections. The associated reactant density of states is then obtained by differentiating the fitted \( \mathcal{N}(E) \) with respect to \( E \). Details of the sampling procedure are further discussed in Appendix A.
For $N = 2$, the configurational projection of $M_0$ is the union of the rectangular region and adjacent triangular region shown in Fig. 4. It should be noted that the sampling procedure used for $N = 3–5$, which employs a simpler phase space hypercube, gives approximately the same density of states for $N = 2$ as that obtained using the more elaborate shape shown in Fig. 4.

Harmonic and anharmonic reactant densities of states are shown for $N = 2–5$ in Fig. 5.

As mentioned above, we consider energies low enough such that multiple bond breakages (3-body dissociation when $N = 2$) do not occur. For $f = 0.02$, $\beta = 1$, this means that the maximum energy we consider is $E_{\text{max}}^{MC} = 1.5281$ (with respect to the $f$-dependent minimum energy).

### 3.3.2. Transition state sum of states

For determination of the phase space sum of states for the transition state associated with channel 1, it is convenient to transform to Jacobi coordinates

$$X = \frac{1}{2}(x_1 + x_2) = r_1 + \frac{1}{2}r_2$$

$$\zeta = x_2 - x_1$$

$$P = p_1 + p_2$$

$$\Pi = \frac{1}{2}(p_2 - p_1)$$

using the generating function [85,60]

$$F_2(x_1, x_2; \Pi, P) = \Pi(x_2 - x_1) + \frac{1}{2}P(x_1 + x_2).$$

The Hamiltonian in the transformed coordinates is then

$$H(X, P, \zeta, \Pi) = \frac{P^2}{4} + \Pi^2 + V(\zeta, X; f).$$

The PES in Jacobi coordinates (Fig. 3b) indicates that the configuration space transition state 1 can approximately be defined by $X^1 = \frac{1}{2}(x_1 + x_2) = \frac{1}{2}(r_1 + (r_1 + r_{eq})) = r_1 + \frac{1}{2}r_{eq}$ ($=6.10$ for $f = 0.02$ and $\beta = 1$), which is just the harmonic approximation nonreactive normal mode. In single particle

![Fig. 4. Configuration space projection (light blue) of the phase space region used for sampling of coordinates in the Monte Carlo determination of reactant phase space volume $\mathcal{M}(E)$. Contours of the potential energy and the location of saddles (saddle 1 (red) and saddle 2 (blue)) are also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 5. Harmonic approximation (red) and fully anharmonic Monte Carlo (blue) reactant density of states versus energy for (a) $N = 2$, (b) $N = 3$, (c) $N = 4$ and (d) $N = 5$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image2)
coordinates, the configuration space projection of transition state 1 lies along the line $x_2 = -x_1 + 2r^1 + r_{eq}$.

The 2D “hypercube” $M^*_0$ used to sample transition state 1 is defined by conditions

$$X = r^1 + \frac{1}{2} r_{eq}$$

$$\zeta \in [0, r^1]$$

$$P = 0$$

$$\Pi \in \left[ -\sqrt{E_{\text{MC}} - E_f^0}, \sqrt{E_{\text{MC}} - E_f^0} \right]$$

Thus the $N = 2$ transition state 1 hypercube has volume $V_{0,1}^1 = 2r^1 \sqrt{E_{\text{MC}} - E_f^0}$. The transition state 2 sampling hypercube is defined as

$$x_1 \in [0, 3.303]$$

$$x_2 = r_{eq} + r^1$$

$$p_1 \in \left[ -\sqrt{2 \left( E_{\text{MC}} - E_f^0 \right)}, \sqrt{2 \left( E_{\text{MC}} - E_f^0 \right)} \right]$$

$$p_2 = 0,$$

and has volume $V_{0,2}^1 = 6.606 \sqrt{2(E_{\text{MC}} - E_f^0)}$. Again, the $x_1$ range endpoint of 3.303 marks the position of the barrier to 3-body dissociation products from transition state 2 for $f = 0.02$ and $\beta = 1$.

For both the reactant and transition state Monte Carlo calculations, we use $n_{\text{max}} = 100$, with $n_{\text{rand}} = 10^7$. Transition state sums of states are fitted to functions of the form

$$\mathcal{N}(E - E_f^j) = (E - E_f^j)^{V-1} |\zeta_0 + \zeta_1 (E - E_f^j) + \cdots |.$$

4.2. Sampling phase points on the energy shell

To compare the predictions of RRK and RRKM theory at constant energy $E$ with trajectory results, it is necessary to sample trajectory initial conditions $z = (x, p)$ distributed with suitable measure on the energy shell $H(z) = E$. The sampling procedure used is discussed in more detail in Appendix B.

4.3. Extraction of rate coefficient $k(E)$

Given a microcanonical ensemble of $N(0)$ initial conditions $\{z_i(0)\}_{i=0}^{N(0)}$, and defining $N(t) \leq N(0)$ as the number of trajectories that have not reacted by time $t$, we can compute an effective rate constant $k(E,f)$ if we assume that the system exhibits exponential decay with time-independent rate constant. The associated lifetime distribution is

$$N(t) = N(0) \exp[-k(E,f) t].$$

For each energy we run $N(0) = 50,000$ trajectories and record the times at which dissociation of each trajectory occurs (if it ever does for that trajectory). For $f = 0.02$ and $\beta = 1$ the condition for dissociation of bond $j$ is taken to be

$$r_j > r^1 + 2r_{eq}^0, \quad j \in [1, \ldots , N].$$

The resulting data are histogrammed. Transient behavior (the first $350$ time steps for $\beta = 1$ and $f = 0.02$) is ignored and an exponential fit to the histogram at longer times gives approximate $k(E,f)$ values.

It should be noted that the bond dissociation criterion (30) is intended to ensure that recrossing effects are excluded from the numerical determination of the long-time (asymptotic) decay rate, which is the quantity to be compared with statistical theories.

Values of the decay rate constants obtained via trajectory simulation are compared with the predictions of statistical theory below. We also compare these dynamical decay rates with those obtained via an analysis based on the classical spectral theorem [66–73].

5. Phase space structure and dynamics for $N = 2$

Before turning to a detailed comparison of RRKM and trajectory dissociation rate constants, we examine the phase space structure for the $N = 2$ chain. For the tethered chain with $N = 2$ atoms, we can use the standard Poincaré surface of section (SOS) construction [60] to examine the system phase space at constant energy $E$.

5.1. Surfaces of section

5.1.1. SOS along a dissociative coordinate: PODS and turnstiles

At constant energy $E$, we can define a SOS by the condition (given in terms of Jacobi coordinates)

$$\Pi = 0, \quad \dot{\Pi} > 0.$$ (31)
We will refer to this SOS as SOS$_1$. Fig. 6 shows SOS$_1$ for $f = 0.02$, $\beta = 1$ at energies $E = E_f^* - 0.4$, $E_f^*$, $E_f^* + 0.01$ and $E_f^* + 0.1$.

The overall shape of the separatrix [60] defining the reactant phase space region [79] is clearly visible in Fig. 6b. The critical configuration for dissociation via transition state 1 is located on SOS$_1$ at $P = 0$, $X = 6.10$. At energies above the activation barrier, the periodic orbit dividing surface (PODS [88–90]; see below) appears as an unstable fixed point on SOS$_1$ (Fig. 6c and d); the PODS and its associated stable/unstable manifolds are computed below. The points spilling out towards $X \to \infty$ are reactive trajectories that dissociate via breaking of bond 1.

For $E > E_f^*$ we also see “lobe” or “turnstile” structures near the boundaries of the reactive complex region. The turnstiles mediate transport between phase space regions, and detailed analysis of turnstile dynamics can be used to understand rates of intramolecular energy flow and unimolecular dissociation [91,79,92]. Regions of lower trajectory density in SOS$_1$ are associated with trajectories that dissociate through channel 2, and so do not return to the SOS (see below).

Also evident in the interior of the complex region is an area of bounded, regular behavior, which appears as a transverse slice through a set of invariant tori [60]. Classical trajectories with initial conditions on invariant tori do not
dissociate. The fact that a significant proportion of the tethered chain phase space volume is occupied by bound trajectories means that, to obtain a more accurate prediction of the dissociation rate constant using statistical assumptions, it is necessary to correct RRKM theory by removing bound phase space regions from consideration [93–95,79,96].

SOS$_1$ is symmetric about the line $P = 0$; this time-reversal symmetry can be exploited to determine relevant periodic orbits [97,98]. (An analogous SOS suitable for channel 2, SOS$_2$, is defined by the conditions $p_1 = 0$, $p_2 > 0$. Whereas SOS$_1$ is symmetric about the line $P = 0$, SOS$_2$ is symmetric about the line $p_2 = 0$.)

In the $(X,P)$ plane of SOS$_1$, the unstable fixed point on the line $P = 0$ is the intersection of the PODS [88–90] associated with the transition state for bond 1 cleavage with the SOS. This hyperbolic fixed point and its associated stable/unstable manifolds (plus the analogous structures for reaction 2) are phase space structures that determine the dissociation dynamics of the $N = 2$ tethered chain.

Consider determination of the PODS for channel 1. To locate the PODS, we sample a line of initial conditions on SOS$_1$ along the symmetry line $P = 0$. The SOS conditions on $II$ and $P$ imply that points on the symmetry line have $p_1 = p_2 = 0$, so that these trajectories start on the classical zero-velocity manifold $V(x) = E$. Any trajectory that returns to the symmetry line in a single iteration of the Poincaré map is a periodic orbit [97,98]. The location of the PODS on the symmetry line can therefore be determined using a Newton–Raphson procedure [99].

Fig. 7 shows configuration space projections of PODS associated with both transition states at several energies. The shapes of the PODS conform approximately to the harmonic prediction of a slanted line segment for transition state 1 and an approximately horizontal line segment for transition state 2. Close inspection of the PODS reveals that they are in fact curved, an anharmonic dynamical effect.

Numerical approximations to the stable/unstable manifolds $W^{u/s}$ of the PODS are obtained by propagating phase points close to the periodic orbit on the respective linearized manifolds (computed as outlined in Appendix C) forwards/backwards in time [60]. To visualize $W^{u/s}$, we select 1000 initial conditions along short segments of the linearized manifolds $E\mathrm{^{10l/s}}$ close to the PODS and propagate all these phase points either forward or backwards in time. The resulting manifolds for $E^+_1 + 0.1$ are shown in Fig. 8. Taken together, these two manifolds define a bound complex region. One possible definition of a direct trajectory is one that does not enter or exit the bound separatrix region via a turnstile [79].

5.1.2. SOS in reactant region ($r_1 = r_2$): reactive cylinders

An informative view of the dynamics is provided by the SOS defined by crossings of the hypersurface $\Sigma_k \equiv \{x | r_1 = r_2, r_2 > r_1\}$. To formulate the crossing condition in terms of a single variable, we consider a canonical transformation to coordinates

$$X = \frac{1}{2}(x_1 + x_2)$$

$$\Delta r = r_2 - r_1 = x_2 - 2x_1$$

with generating function [60,85]

$$F = \frac{1}{2}(x_1 + x_2)p + (x_2 - 2x_1)p_{x2},$$

from which we deduce the relation between conjugate momenta

$$P = \frac{2}{3}(p_1 + 2p_2)$$

$$p_{x2} = \frac{1}{3}(p_2 - p_1).$$

Fig. 7. PODS shown together with potential energy contours for $f = 0.02$. Saddle points 1 and 2 are marked as black dots, PODS$_1$ and PODS$_2$ are shown at energies $E = E^+_1 + 0.1$ (red), $E^+_1 + 0.2$ (green), $E^+_1 + 0.3$ (blue), $E^+_1 + 0.4$ (yellow), $E^+_1 + 0.5$ (purple) and $E_{\max}$ (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. SOS (green) at $E = E^+_1 + 0.1$ defined by $II = 0, \dot{II} > 0$; The stable manifold $W^s$ (blue) and unstable manifold $W^u$ (red) of the PODS are also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
(Note that the momentum $P$ conjugate to $X$ in the $\{X, \Delta r\}$ coordinate system differs from the momentum $P$ in the $\{X, \xi\}$ coordinate system.) From the non-diagonal kinetic energy

$$T = \frac{P^2}{4} - \frac{Pp_{\Delta r}}{2} + \frac{5p_{\Delta r}^2}{2},$$

we have

$$p_{\Delta r} = \frac{1}{10}P \pm \frac{1}{10}\sqrt{40T - 9P^2}.$$

We select the positive branch of solutions for $p_{\Delta r}$, which is equivalent to imposing the surface crossing condition $p_{\Delta r} > \frac{1}{10}P$ or

$$p_2 > 2p_1,$$

which is just the condition $p_2 - p_1 > p_1$ i.e. $r_2 > r_1$. Thus, an equivalent definition of our surface is $\Sigma_+ \equiv \{z|\Delta r = 0, p_{\Delta r} = \frac{1}{10}P + \frac{1}{10}\sqrt{40T - 9P^2}\}$. We examine the fate of trajectories initiated on a grid of initial conditions with

$$r_1(0) = r_2(0) = x_1(0) = \frac{1}{2}x_2(0) \in [0, 3.5]$$

$$P(0) \in [-2.6, 2.6],$$

where $r(0)$ and $P(0)$ values are evenly-spaced. Initial momenta $\{p_1(0), p_2(0)\}$ are obtained from

$$p_1 = \frac{P}{2} - 2p_{\Delta r},$$

$$p_2 = \frac{P}{2} + p_{\Delta r},$$

where the $p_{\Delta r}(0)$ values are chosen to be on the positive branch of (36) so as to place the initial conditions on $\Sigma_+$. The resulting initial grid is shown in Fig. 9a, and the SOS generated from this initial condition set is in Fig. 9b.

A plot of the grid of initial conditions on $\Sigma_+$ under one iteration of the return map is shown in Fig. 9c. One noteworthy feature of Fig. 9b is the presence of “holes”, regions within the SOS structure that are either devoid of or sparsely filled by iterates.

To elucidate the dynamical significance of these holes, we initiate trajectories on transition states 1 and 2 (that is, distributed along the corresponding PODS), propagate them forward in time, and examine their intersection with $\Sigma_+$. The successive intersections of these trajectories with the SOS are shown in Fig. 10. Let $\Sigma_{+}^{u_1} \subset \Sigma_+$ be the region corresponding to the $m$th intersection of $\Sigma_+$ by the set of trajectories initiated on transition state $j$. (The superscript $u$ indicates that the region $\Sigma_{+}^{u}$ is bounded by the intersection of the unstable manifold of the PODS with $\Sigma_+$.) Fig. 10a shows that $\Sigma_{+}^{u_1}$ and $\Sigma_{+}^{u_2}$ are the two holes toward the bottom of the SOS structure that contain no phase points; that is, regions $\Sigma_{+}^{u_1}$ and $\Sigma_{+}^{u_2}$ are composed of phase points with no pre-image on $\Sigma_+$. The regions $\Sigma_{+}^{u_2}$ and $\Sigma_{+}^{u_2}$, first visible in Fig. 10b, are cross sections of cylindrical structures in phase space, so-called reactive cylinders [61–63]. Upon further iterations, shown in Fig. 10c–e, the cylinder cross sections stretch out, twist and generally spread themselves through the reactive region. We infer that the set of reactive phase points on $\Sigma_+$ is the closure of $\bigcup_{j=1}^{2} \bigcup_{m=1}^{\infty} \Sigma_{+}^{u_j}$.

Of equal importance to the sets $\Sigma_{+}^{u_j}$, $j = 1, 2$, which react through transition states 1 and 2, respectively, in negative time, is the set of trajectories $\Sigma_{+}^{s_j}$, which react in forward time. We define $\Sigma_{+}^{s_j}$ to be the set of trajectories that react through transition state $j$ after undergoing $m - 1$ further intersections with $\Sigma_+$. (The superscript $s$ indicates that these trajectories are associated with the stable manifold of the corresponding PODS; they are calculated by propagating backwards in time from the relevant transition state.) In particular, we consider the regions $\Sigma_{+}^{s_j}$, $j = 1, 2$, which consist of phase points that react immediately in forward time, where immediate means without an intervening intersection of the SOS.

Fig. 11a displays $\Sigma_{+}^{s_1} \cup \Sigma_{+}^{s_2}$ along with the grid of initial conditions on $\Sigma_+$ that intersect $\Sigma_+$ for some positive time value. That $\Sigma_{+}^{s_1} \cup \Sigma_{+}^{s_2}$ fills the “holes” in the SOS, which consist of phase points that never return to the surface in positive time, and so react immediately.

It is informative to observe intersections between the forward and backward direct reactive tubes, $\Sigma_{+}^{s_1} \cap \Sigma_{+}^{s_1}$ and $\Sigma_{+}^{s_2} \cap \Sigma_{+}^{s_2}$ (One could just as well inspect the intersections $\Sigma_{+}^{s_1} \cap \Sigma_{+}^{s_2}$ and $\Sigma_{+}^{s_1} \cap \Sigma_{+}^{s_2}$, which appear in ure Fig. 11b and are simply the time-evolved iterations of $\Sigma_{+}^{s_1} \cap \Sigma_{+}^{s_1}$ and $\Sigma_{+}^{s_2} \cap \Sigma_{+}^{s_2}$, respectively for one mapping of $\Sigma_+$.) To illustrate the information afforded by these overlaps, the area $\mathcal{A}(\Sigma_{+}^{s_1} \cap \Sigma_{+}^{s_1})$ reflects the phase space volume of trajectories that enter the reactant region through transition state 1 and exit through transition state 1 after $2 + 1 - 1 = 2$ intersections with the SOS $\Sigma_+$. Hence, $\mathcal{A}(\Sigma_{+}^{s_1} \cap \Sigma_{+}^{s_1})$ should correlate with the fraction $P_{\Sigma_+}(E - E_{int})$ of transition state 1 belonging to direct trajectories, where direct trajectories could be defined as those having only two intersections with $\Sigma_+$, noting that since $\Sigma_{+}^{s_1} \cap \Sigma_{+}^{s_1}$ and $\Sigma_{+}^{s_2} \cap \Sigma_{+}^{s_2}$ are zero for most energies except those near $E_{max}$, where a thin strip of non-zero overlap $\Sigma_{+}^{s_2} \cap \Sigma_{+}^{s_2}$ begins to emerge, as is evident in Fig. 11d–f. Thus, there are virtually no trajectories that enter through transition state $m$ and exit through transition state $n, m \neq n$, without crossing SOS $\Sigma_+$ at least three times.

6. Statistical theories compared with dynamical rate constants

6.1. Ratios of rate constants are independent of choice of mass unit

We shall compare absolute values of dissociation rate constants obtained from classical trajectory simulations with those calculated using RRKM-type theories. Recall that our unit of time is defined in terms of the choice of
mass unit, \( \tau_0 \sim \sqrt{m} \). Although absolute values of dissociation rate constants depend upon the value of \( m \) used, ratios of rates do not. Thus, from Eq. (18) for the RRK rate constant, and recalling the mass dependence of harmonic oscillator frequencies, we see that

\[
k_{RRK}^R (E) \sim \frac{(1/\sqrt{m})^N}{(1/\sqrt{m})^{N+1}} \sim \frac{1}{\sqrt{m}}.
\]

The RRKM rate constant is given by the ratio (9). Both the reactant phase space volume and the density of states \( \rho(E) \) scale in general as \((\sqrt{m})^N\), where \( N \) is the number of degrees of freedom, while \( \mathcal{N}(E-E_f) \) scales as \((\sqrt{m})^{N-1}\). The anharmonic RRKM rate constant therefore scales in the same way with mass as the RRK rate constant, as \( 1/\sqrt{m} \). Finally, to determine the mass dependence of simulation results \( k_{sim} \), we note that increasing \( m \) means that particles are effectively moving more slowly by a factor of \( 1/\sqrt{m} \); we therefore have \( k_{sim} \sim 1/\sqrt{m} \).

Rate constants \( k_{RRK}^R \), \( k_{RRKM}^R \), and \( k_{sim} \) therefore all have the same mass dependence and the ratio of any two of these \( k \) values is mass-independent.

6.2. Comparison of RRK with RRKM and simulation rate constants

RRK, RRKM and simulation rate constants for the total dissociation rate for \( N = 2, f = 0.02, \beta = 1 \) are shown.
Fig. 10. The \( n \)th crossing of \( r_1 = r_2, r_2 > r_1 \) for trajectories initiated on transition states 1 (red) and 2 (blue), \( E = E_f + 0.1 \). (a) \( n = 1 \); (b) \( n = 2 \); (c) \( n = 3 \); (d) \( n = 4 \); (e) \( n = 10 \). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
as functions of energy in Fig. 13a. While the harmonic RRK approximation significantly overestimates the RRKM rate constant (cf. Refs. [27–29]), the RRKM value is only slightly larger than the simulation results, with the disparity growing larger at higher energies. This level of agreement is perhaps surprising, given the non-negligible fraction of regular phase space occupied by invariant tori, as noted above. We comment further on this point below.

6.3. Relative rate calculations

As the phenomenon of reactive selectivity is of central interest in chemistry, it is important to examine the relative rates of competing reactions. For \( N = 2 \), the two competing reactions are the cleavage of bonds 1 and 2, respectively. We therefore study the ratio of rate constants \( k_2/k_1 \). We consider the statistical predictions for the branching ratio \( k_2/k_1 \) and compare with simulation results.

6.3.1. RRK and RRKM calculations, \( N = 2 \)

From expression (9) for \( k^{RRKM}(E,\gamma) \), the ratio of RRKM rate constants for reactions 1 and 2 is simply

\[
\left( \frac{k_2}{k_1} \right)_{RRKM} = \frac{\mathcal{N}_2(E - E_j^*)}{\mathcal{N}_1(E - E_j^*)},
\]

as the reactant density of states at energy \( E \) cancels out. The ratio in the harmonic approximation is then

\[
\left( \frac{k_2}{k_1} \right)_{RRK} = \frac{\omega_j^1}{\omega_j^2},
\]

where \( \omega_j^i \) is the harmonic frequency of the nonreactive normal mode taken about the \( j \)th saddle point.

6.3.2. Trajectory results

If \( k_{sim} \) is the total rate constant for dissociation as determined from trajectory simulation, the rate constants for channels 1 and 2, \( k_{1,sim} \) and \( k_{2,sim} \) respectively, are given in terms of the respective branching ratios multiplied by the overall rate constant:

\[
\left( \frac{k_j}{k_{sim}} \right) = \frac{n_j}{n_1 + n_2}, \quad j = 1, 2
\]

where \( n_1, n_2 \) are the number of trajectories that have reacted through channels 1, 2 respectively at some relatively long time (we use 2000 time steps) with all nonstatistical, transient trajectories omitted. The rate ratio is then

\[
\left( \frac{k_2}{k_1} \right)_{sim} = \frac{n_2}{n_1}
\]

6.3.3. Periodic orbit dividing surface actions

If the transition state of (locally) minimal flux at energy \( E \) is the phase space region \( \mathcal{A} \), then for the \( N = 2 \) case it follows from the variational principle of classical mechanics [100] that the boundary \( \partial \mathcal{A} \) of the region \( \mathcal{A} \) is a periodic classical trajectory defining the periodic orbit dividing surface (PODS) [88,89]. The associated flux is then the action of the PODS

\[
\mathcal{N}_{PODS}^{-1}(E - E_j^*) = \int_{\partial \mathcal{A}} dp \wedge dq = \int_{\partial \mathcal{A}} p dq
\]

defined as a line integral over one cycle of the PODS. Because the PODS is a dynamically determined object and \( \mathcal{N}_{PODS}^{-1}(E - E_j^*) \) reflects the full anharmonic dynamics in the vicinity of the saddle point, this method for calculating the sum of states \( \mathcal{N}^{-1}(E - E_j^*) \) provides a check on the accu-
Fig. 12. Red points are initial conditions for trajectories having at least one intersection with the SOS $r_1 = r_2, r_2 > r_1$. Green points are the iterates under the Poincaré map $E = E_0 + \Delta E$. (a) $\Delta E = 0.1$; (b) $\Delta E = 0.2$; (c) $\Delta E = 0.3$; (d) $\Delta E = 0.4$; (e) $\Delta E = 0.5$; (f) $\Delta E = 0.6$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
racy of the corresponding harmonic and Monte Carlo calculations. We evaluate the PODS sum of states at energy $E$ as
\[
Z_{PODS} \left( \sum \limits_{p_1}^\infty \sum \limits_{q_1}^\infty dt + \sum \limits_{p_2}^\infty \sum \limits_{q_2}^\infty dt \right) = Z_{PODS} \left( \sum \limits_{p_1}^\infty \sum \limits_{p_2}^\infty 2 \right) |_{H=E} dt,
\]
using PODS initial conditions obtained as described above.

Fig. 14 shows $N_j(E/C_0)$, $N_j(E/C_3)$, $j = 1, 2$, versus energy $E$ for the harmonic approximation, Monte Carlo integration and the PODS action method just described. We see that the anharmonic Monte Carlo areas agree essentially exactly with the PODS actions (the true dynamical local fluxes). It is also evident that the harmonic approximation to the transition sum of states is reasonably accurate, especially at lower energies.

Fig. 15 shows the RRK and PODS branching ratios $k_j/k_1$ versus energy compared with simulation results. The value of the RRK branching ratio ($\sqrt{2}$) is essentially determined by the ratio of the reduced masses for breaking bonds 1 and 2, and is independent of energy (cf. Ref. [28]). To the extent that motion along the PODS (the dynamically defined configuration space transition states) corresponds to separable motion along the bond coordinates, the RRKM/PODS branching ratios will be identical with the harmonic value. Only the ratio obtained from simulations exhibits any significant energy dependence; further analysis of its dynamical origins will require a more detailed investigation of “lobe dynamics” [92] via the surface of section shown in Fig. 9.

7. Correcting RRKM theory

7.1. General considerations

While Fig. 6a–d show that a nonnegligible portion of the reactant phase space is occupied by regular, bound trajectories, RRKM rate constants for bond dissociation calculated using an anharmonic density of states are in fairly close agreement with trajectory values, at least for $N = 2$ (see Fig. 13a–d). Given that the reactant phase space is certainly not globally chaotic, and given the probable existence of barriers to IVR in the vicinity of the regular regions of phase space (cantori [91,79]), it is possible that the good agreement between RRKM and trajectory rate constants is to some degree fortuitous.

In order to explore this point further, and to make a proper comparison between the “statistical” rate constant and the dynamical result, we need to ensure that the influence of bound and direct trajectories on the RRKM-type calculation is taken into account. A noteworthy discussion of this problem has been given by Berblinger and Schlier in the context of the dissociation of the H$_3^+$ molecule [96].
and simulation results can be presumably be attributed to dynamical effects such as slow IVR (existence of significant phase space bottlenecks) in the reactive portion of phase space.

The analysis of Berblinger and Schlier can be summarized in the following formula for the corrected RRKM dissociation rate constant \[ k_{\text{corrected}}^\text{RRKM} = k_{\text{corrected}}^\text{RRKM} \cdot \frac{(1 - \phi_{\text{direct}})}{(1 - \phi_{\text{bound}} - \phi_{\text{direct}})}, \] (47)

where \( \phi_{\text{bound}} \) is the fraction of the reactant phase space region occupied by bound (unreactive) trajectories, \( \phi_{\text{direct}} \) is the fraction of phase space occupied by direct ("nonstatistical") trajectories, \( \phi_{\text{direct}}^\text{stat} \) is the fraction of the phase space at the transition state occupied by direct trajectories, and \( \kappa \) is a factor that corrects for recrossing of reactive trajectories at the transition state (the transmission coefficient).

Rather than attempt to implement a corrected statistical rate theory in the form given by Berblinger and Schlier, we now discuss a related approach for the \( N = 2 \) chain based on the classical spectral theorem [66–73].

### 7.2. Computation of statistical and dynamical rate constants via the classical spectral theorem

In classical unimolecular rate theory it has been known at least since the work of Thiele [66] that the appropriate invariant measure on the energy shell for reactive trajectories is given by the volume element (see also refs [67–73])

\[
d\sigma = dq^1 \wedge dp^1 \wedge dt,
\] (48)

where \((q^1,p^1)\) are canonical coordinates on the transition state (we consider the \( N = 2 \) case for simplicity), and \( t \) is the time along a trajectory initiated on the transition state passing into the interior of the reactant region. The total density of non-bound trajectories on the energy shell \( H = E \) in the reactant region is therefore obtained by integrating the volume element \( d\sigma \) over the transition state(s) and over the gap time for each trajectory; this is the content of the classical spectral theorem [66–73]. Thus, trajectories initiated on transition states \( j = 1, 2 \) are run backwards in time until they either pass out of the reactant region or a suitably large cutoff time has elapsed. (Note that only a set of measure zero of these trajectories initiated at the transition state will remain trapped in the reactant region forever.) The time interval between entry into and exit from the reactant region is the gap time \([101, 66]\). Details of the sampling procedure and computation of gap times are given in Appendix D.

For \( N = 2 \), the total density of non-bound trajectories on the energy shell for \( H = E \) is then

\[
\rho_{\text{nonbound}}(E) = \mathcal{N}_1^1(E - E^1_f)(t)_1 + \mathcal{N}_2^1(E - E^1_f)(t)_2,
\] (49)

where \( \mathcal{N}_j^1(E - E^1_f) \) is the sum of states for transition state \( j \) and \((t)_i\) is the average gap time for trajectories that leave the reactant region via transition state \( i \) (in forward time).
having entered through either channel. Eq. (49) may be interpreted as an expression for the combined volume of two (bifurcated) reactive cylinders [61–63] with cross-sectional areas $A_j(A - E_j^f)$ and lengths $(t)_j, i = 1, 2$.

The density of states defined in Eq. (49) excludes bound regions of phase space, as bound trajectories by definition do not pass through the transition state; direct trajectories, however defined, are still included.

By initiating trajectories on transition state $j$, we can determine $N_j(t)$, the number (or fraction) of unbound species left at time $t$ that will ultimately decay through channel $j$. It is straightforward to show that, whereas products in channel $j$ appear at rate characterized by the constant $k_j$, the subpopulation of reactive species that dissociate through channel $j$ undergoes the same exponential depletion $\exp(-k_j t)$ as the overall reactant concentration.

For those reactant species destined to dissociate through channel $j$, a suitably normalized distribution of gap times is (assuming an exponential distribution [66])

$$f_j(t; E) = \frac{\exp(-k(E)t)}{\int_{t_c}^{\infty} \exp[-k(E)t']dt'},$$

where $t_c > 0$ is a cutoff time beyond which all transient, nonexponential behavior has died out. The average gap time for reaction through channel $j$ is then given by

$$\langle t_j(E; t_c) \rangle = \int_{t_c}^{\infty} t f_j(t'; E)dt' = \frac{1}{k(E)} + t_c,$$

and depends on the cutoff time $t_c$. The values of $k(E)$ obtained with this method are denoted by $k^\text{PODS}_j(E)$, where the notation indicates that the intercept $1/k$ is in practice obtained by fitting the observed linear behavior of $\langle t_j \rangle$ at large cutoff times $t_c \to \infty$ and extrapolating back to find the intercept. A representative plot of $\langle t \rangle(E)$ versus $t_c$ (Fig. 16) shows transient, nonexponential behavior for shorter $t_c$ values and linear behavior — corresponding to exponential decay — for larger $t_c$ values.

Also of interest is the quantity $k_0(E)$, the statistical dissociation rate constant corrected for the presence of bound regions of reactant phase space (and obtained via the spectral theorem with $t_c = 0$). By definition of the average gap time, $\rho_j(t)$, the portion of the reactant density of states destined for dissociation through channel $j$, is given by

$$\rho_j(E) = A_j(A - E_j^f)/(t)_j,$$

where $(t)_j$ is obtained with $t_c = 0$, so that all “direct” trajectories are included in the average. The rate constant $k_0(E)$ is obtained from

$$k_0(E) = \frac{\sum_{j=1}^{N} A_j(A - E_j^f)}{\sum_{j=1}^{N} \rho_j(E)}.$$

7.3. Comparison of statistical and dynamical dissociation rates for $N = 2$

Total dissociation rate constants for $N = 2, f = 0.02$ and $\beta = 1$ obtained using various methods are shown in Fig. 17. We can see that there is a significant (roughly threefold) disparity between the RRK and the RRKM predictions, representing a qualitative failure of the harmonic approximation. This is not unexpected, as the harmonic approximation is especially inadequate for the reactant region (see Fig. 5a–d). At fixed energy per mode, $E = E/N$, the disparity between harmonic and anharmonic statistical rate theory increases with the number of atoms $N$ (see below).

If we consider the reactant density of states for $N = 2$, it should apparently always be the case that

$$\rho_1(E) + \rho_2(E) \leq \rho(E),$$

as the RHS of (54) includes bound as well as non-bound phase points, so that we expect the inequality

$$k_0(E) \geq k_{\text{RRKM}}(E)$$

to hold. As we can see in Fig. 17, inequality (55) holds only up to a certain energy, $E - E_j^f \approx 0.4$, above which the rate

![Fig. 16. Plot of average gap time $\langle t \rangle(t_c)$ as a function of cutoff time $t_c$ for trajectories initiated on PODS$_1$, $E = E_j^f + 0.4$. Note linear behavior consistent with exponential decay as $t_c \to \infty$.](image)

![Fig. 17. Rate constants $k_{\text{RRK}}(E - E_j^f)$ (red), $k_{\text{RRKM}}(E - E_j^f)$ (blue), $k_{\text{calc}}(E - E_j^f)$ (green circles), $k_0(E - E_j^f)$ (black circles) and $k_{\text{PODS}}(E - E_j^f)$ (purple) versus energy above threshold, $E - E_j^f$, for $N = 2, f = 0.02$ and $\beta = 1$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)
constant $k_0(E)$ actually becomes smaller than the RRKM rate constant. We resolve this apparent paradox by noting that $\rho(E)$ is calculated using the fixed configuration space sampling region shown in Fig. 4, while the densities $\rho^{(i)}$ are obtained via the spectral theorem using the PODS. As the PODS move progressively outwards from their respective saddle points with increasing energy, the increase of the associated densities of states with energy is sufficient to outweigh the effects of the presence of bound regions, resulting in a violation of the inequality (55).

The anharmonic RRKM results are close to total dissociation rate constants determined via simulation. However, the RRKM results begin to disagree with the simulation rates with increasing energy, the disparity eventually reaching a factor of roughly three. This is perhaps not surprising, given the lack of global chaos seen in the SOS for $N=2$. At the very highest energies, it becomes difficult to fit the lifetime distributions to a pure exponential decay; nevertheless, the fits obtained for $k_{\text{sim}}$ and $k_0$ agree at these energies.

Dissociation rate constants obtained using the classical spectral theorem essentially match those obtained by simulation. Of course the spectral theorem approach, which is based upon the distribution of gap times, must reflect the same dynamical information as a standard trajectory simulation. It is nevertheless gratifying to see that the two approaches agree so well. It seems likely that the spectral theorem approach will prove useful in the multimode case ($N \geq 3$ dof) in combination with the normal form based analysis of the transition state of Uzer et al.[102,103].

8. $N \geq 3$ atom chains

A significant jump in dynamical complexity occurs in going from $N=2$ to $N \geq 3$-atom chains. For $N \geq 2$, the dynamics and phase space structure cannot easily be visualized via a SOS [60,104]. Further, the transition states for chain fragmentation are themselves ($N-1 \geq 2$)-degree of freedom dynamical systems, making visualization and accurate anharmonic sampling difficult using the approaches described above for $N=2$ atom chains.

Accurate determination of transition states in $N$-atom chains under tensile stress is a problem that seems well-suited to the application of recent advances in normal form expansion techniques recently developed by Uzer et al.[102,103,105]. In the present work, however, we restrict ourselves to the computation of a “hybrid” harmonic–anharmonic rate constant for our statistical predictions of chain fragmentation rates.

As Fig. 14 shows, for $N=2$ at least the harmonic transition state sum of states is a close approximation to the anharmonic result at energies close to the dissociation threshold $E'$. We therefore combine a harmonic oscillator approximation for the transition state sum of states with a full numerical determination of the reactant density of states to give our RRKM expression for $N \geq 3$-atom chains:

$$k_{\text{RRKM/}HO}(E) = \frac{\lambda \gamma}{\rho_{\text{anh}}(E)}.$$  \hspace{1cm} (56)

Total bond dissociation rate constants obtained using RRK, RRKM and simulation with $f=0.02$ and $\beta=1$ are plotted as a function of energy $E$ for $N=2–5$ in Fig. 13. To further examine the validity of the harmonic and statistical approximations to the dynamical rate constant, we plot the ratios of harmonic (RRK) to anharmonic (hybrid RRKM) and anharmonic to simulation results as a function of energy per degree of freedom, $E/N$, in Figs. 18 and 19, respectively.

The ratios of RRK to hybrid RRKM rate constants are simply the ratios of harmonic and anharmonic reactant densities of states. Fig. 18 shows that, while the discrepancy between the RRK and RRKM rate constants grows with the number of atoms $N$ at fixed energy per mode, $\varepsilon = E/N$, at constant total energy $E$ the ratio of RRK and RRKM rate constants approaches unity (harmonic limit) as $N$ increases. For example, for total energy $E=1$ the ratios are 3.24 ($N=2$), 2.46 ($N=3$), 2.12 ($N=4$) and 1.89 ($N=5$). RRKM total dissociation rate constants com-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig18.pdf}
\caption{Ratio $k_{\text{RRK}}(E)/k_{\text{RRKM}}(E)$ as a function of energy per mode, $E/N$, for $N=2$ (red), $N=3$ (green), $N=4$ (blue) and $N=5$ (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig19.pdf}
\caption{Ratio $k_{\text{RRKM}}(E)/k_{\text{sim}}(E)$ as a function of energy per mode, $E/N$, for $N=2$ (red), $N=3$ (green), $N=4$ (blue) and $N=5$ (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)}
\end{figure}
obtained using trajectory simulations for chains of statistical predictions with dynamical dissociation rate phase space volumes as a function of energy. Comparison Carlo integration to determine reactant and transition state version of RRKM theory is implemented using Monte function of energy and tensile force. A fully anharmonic have been applied to predict bond-dissociation rates as a Statistic theories of unimolecular dissociation rate con-

tensile stress. Our focus has been the nonstatistical aspects

of the kinetics of tethered atomic (Morse potential) chains under increasing trend with increasing $E/N$. RRKM to simulation rate constant shows an overall agreement between the RRKM and dynamical rate constants is obtained despite the fact that the reactant phase space contains a significant fraction of relatively short-lived trajectories (as judged by the number of intersections with the SOS). For the $N=2$ chain, we also implement a novel approach to the extraction of decay rate constants based on the classical spectral theorem. This approach corrects for the presence of invariant bound (nonreactive) regions of reactant phase space, and yields total dissociation rates in close agreement with dynamical simulation. 

Our statistical predictions for chains with $N \geq 3$ atoms are obtained using a hybrid statistical theory involving a harmonic approximation for motion in the transition state for bond dissociation. Further exploration of the dynamics in the vicinity of the transition state in multimode chains along the lines of the recent work by Uzer and Jaffe [102,103,105] would clearly be worthwhile, as would an investigation of the applicability of the spectral theorem approach.

Appendix A. Determining the reactant phase space volume $N(E)$

For $N=2$, the configurational projection of $M_0$ is the union of the rectangular region and adjacent triangular region shown in Fig. 4. The shape of this region ensures that phase points in the vicinity of transition states 1 and 2 are sampled appropriately while avoiding “leakage” of sampled points into nearby exit channels.

For example, for $f=0.02$ and $\beta=1$ the line $x_1=3.303$ is taken to define a suitable boundary between sampling regions in the vicinity of transition states 1 and 2 (see Fig. 4). The line $x_2 = -x_1 + 2r^1 + r_{eq}$ defining transition state 1 intersects this line at (3.303, 8.898). The phase space sampling for the rectangular region is then

$$x_1 \in [0, 3.303] \quad (A.1a)$$

$$x_2 \in [0, r_{eq} + r^1] \quad (A.1b)$$

$$p_j \in [-\sqrt{2E_{\text{max}}}, \sqrt{2E_{\text{max}}}], \quad j = 1, 2, \quad (A.1c)$$

while that for the triangular region is

$$x_2 \in [0, 8.898] \quad (A.2a)$$

$$x_1 \in [3.303, -x_2 + 2r^1 + r_{eq}] \quad (A.2b)$$

$$p_j \in [-\sqrt{2E_{\text{max}}}, \sqrt{2E_{\text{max}}}], \quad j = 1, 2. \quad (A.2c)$$

The phase space region $M_0$ therefore has volume

$$N(E)$$

put with an anharmonic reactant density of states are within a factor of 2 of the simulation result. The ratio of RRKM to simulation rate constant shows an overall increasing trend with increasing $E/N$.

Finally, Fig. 20 shows the ratios ($k_{\text{sim}}/k_{\text{RRKM}}$) and ($k_{\text{RRKM}}/k_{\text{sim}}$) as a function of $E/N$, $N=2–5$, for tethered chains with potential parameters corresponding to model polyethylene [74,75,51,76] and tensile force $f=0.02$.

9. Summary and conclusions

In this work we have studied the bond dissociation kinetics of tethered atomic (Morse potential) chains under tensile stress. Our focus has been the nonstatistical aspects of the dissociation kinetics and the role of anharmonicity. Statistical theories of unimolecular dissociation rate constants, both RRKM and RRK (harmonic approximation) have been applied to predict bond-dissociation rates as a function of energy and tensile force. A fully anharmonic version of RRKM theory is implemented using Monte Carlo integration to determine reactant and transition state phase space volumes as a function of energy. Comparison of statistical predictions with dynamical dissociation rate constants obtained using trajectory simulations for chains with $N=2–5$ atoms shows that, while the RRK approximation significantly overestimates the dissociation rate, the fully anharmonic RRKM theory is quite accurate. The effects of anharmonicity are at least partly able to rationalize discrepancies between trajectory results and classical transition state theory noted previously [29].

For the two-atom chain, $N=2$, we also carry out a detailed examination of phase space structure using Poincaré surfaces of section. We note that good agreement between the RRKM and dynamical rate constants is obtained despite the fact that the reactant phase space contains a significant fraction of relatively short-lived trajectories (as judged by the number of intersections with the SOS). For the $N=2$ chain, we also implement a novel approach to the extraction of decay rate constants based on the classical spectral theorem. This approach corrects for the presence of invariant bound (nonreactive) regions of reactant phase space, and yields total dissociation rates in close agreement with dynamical simulation.

Our statistical predictions for chains with $N \geq 3$ atoms are obtained using a hybrid statistical theory involving a harmonic approximation for motion in the transition state for bond dissociation. Further exploration of the dynamics in the vicinity of the transition state in multimode chains along the lines of the recent work by Uzer and Jaffe [102,103,105] would clearly be worthwhile, as would an investigation of the applicability of the spectral theorem approach.
\[ V_0 = \left( 2 \sqrt{2E_{\text{max}}} \right)^2 \left\{ 3.303(r_{eq} + r^2) + \frac{1}{2} \left[ 8.898(2r^2 + r_{eq} - 3.303) \right] \right\} . \]  
\hfill (A.3)

For \( N = 2 \) the phase space volume \( \mathcal{N}(E) \) is fitted to the form
\[ \mathcal{N}(E) \approx E^{2c} (c_0 + c_1 E + \ldots) , \]  
\hfill (A.4)

For \( N \geq 3 \), \( \text{dim}(M_0) = 2N \) and the region \( M_0 \) is defined by the following ranges of phase space coordinates:
\[ x_j \in [x_{j-1}, x_{j-1} + r^2], \quad j = 1, \ldots, N \]  
\hfill (A.5a)

\[ p_j \in [-\sqrt{2E_{\text{max}}}, \sqrt{2E_{\text{max}}}], \quad j = 1, \ldots, N . \]  
\hfill (A.5b)

with \( x_0 = 0 \). Hence for the reactant region of phase space, \( V_0 = (2r^2 \sqrt{2E_{\text{max}}} \)^N , and the function \( \mathcal{N}(E) \) is fitted to the form
\[ \mathcal{N}(E) \approx E^N (c_0 + c_1 E + \ldots) , \]  
\hfill (A.6)

that is, harmonic oscillator phase space volume plus anharmonic corrections.

**Appendix B. Sampling phase points on the energy shell**

For \( N \) degrees of freedom, the phase space volume element is
\[ d\mathbf{z} = dx_1 dp_1 \cdots dx_N dp_N . \]  
\hfill (B.1)

Introducing polar coordinates in momentum space, this becomes
\[ d\mathbf{z} = dx_1 \cdots dx_N p^{N-1} dp d\omega . \]  
\hfill (B.2)

where \( d\omega \) is the associated angular volume element. For \( N = 2 \), \( d\omega = d\phi \), with \( 0 \leq \phi \leq 2\pi \), while for \( N = 3 \), \( d\omega = \sin \theta d\theta d\phi \), with \( 0 \leq \theta \leq \pi \) and \( 0 \leq \phi \leq 2\pi \). To specify phase points on the energy shell, we change variable from \( p \) to \( E \), using
\[ \frac{\partial H}{\partial p} = \frac{\partial T}{\partial p} = p . \]  
\hfill (B.3)

(setting all masses \( m = 1 \)) to obtain
\[ d\mathbf{z} = dx_1 \ldots dx_N p^{N-2} dE d\omega . \]  
\hfill (B.4)

On the energy shell, the \((2N - 1)\)-dimensional element of hypersurface area \( d\sigma = d\mathbf{z}|_{H=E} \) is therefore
\[ d\sigma = dx_1 \cdots dx_N p^{N-2} d\omega . \]  
\hfill (B.5)

The task is then to sample points distributed according to the distribution function implied by (B.5) (see also [106,28]).

**B.1. \( N = 2 \) degrees of freedom**

The situation for \( N = 2 \) dof is very straightforward. The volume element is
\[ d\sigma_{N=2} = dx_1 dx_2 d\phi . \]  
\hfill (B.6)

To sample phase points, we simply choose points uniformly in some region \( \mathcal{R} \) of configuration space, \( \mathbf{x} = (x_1, x_2) \in \mathcal{R} \). If \( V(\mathbf{x}) \leq E \), we determine the value of the momentum magnitude \( p \) required to satisfy \( H = E \). Momentum components are then defined according to \( \mathbf{p} = (p \sin \phi, p \cos \phi) \), with angle \( \phi \) chosen at random in the interval \( 0 \leq \phi \leq 2\pi \).

**B.2. \( N \geq 3 \) degrees of freedom**

The volume element in this case is
\[ d\sigma = dx_1 dx_2 dx_3 p d\omega . \]  
\hfill (B.7)

It is therefore necessary to weight momentum values according to \( p \) rather than the natural 3D weighting \( p^2 \).

To accomplish this we use a rejection method [99].

Points are sampled uniformly at random inside a region \( \mathcal{R} \) of \( \mathbf{x} = (x_1, x_2, x_3) \) space. For any given energy \( E \), there is a maximum possible momentum magnitude \( P \), which will be determined by the value of the kinetic energy at the potential minimum. For any sampled point \( \mathbf{x} \), provided \( V(\mathbf{x}) \leq E \), we determine the associated scaled momentum magnitude,
\[ \eta = \frac{p}{P}, \quad 0 \leq \eta \leq 1 . \]  
\hfill (B.8)

Now choose a random number \( \rho \) between 0 and 1.

(1) If \( \eta < \rho \), we reject the point.

(2) If \( \eta > \rho \), we accept the point. Gaussian variates in 3D are then used to compute a random orientation for the momentum vector in 3D. If \( \mathbf{n} \) is a randomly chosen vector on the 2-sphere, the chosen phase point is
\[ \mathbf{z} = (\mathbf{x}, \mathbf{p} = \eta \mathbf{Pn}) \].

Analogous rejection procedures are used for sampling the energy shell for \( N > 3 \).

Let \( N_{\text{traj}} \) be the number of sampled points satisfying \( V(\mathbf{x}) \leq E \); this is the total number of points sampled on the energy shell, some of which will be rejected as above. Let the number of accepted points \( \{z_k\} \) be \( N_{\text{accept}} \). The average value of any property \( F(\mathbf{z}) \) is then
\[ \langle F \rangle = \frac{\sum_k F(z_k)}{N_{\text{accept}}} \]  
\hfill (B.9)

where the sum is over accepted points.

**Appendix C. Stable and unstable manifolds of the PODS**

The first step in computing the full nonlinear stable and unstable manifolds \( \mathcal{W}^{s/u} \) of the PODS is determination of the linearized manifolds, \( E' \) and \( E'' \), respectively [107]. The monodromy matrix \( \mathbf{M} \) corresponding to one trip around the unstable periodic orbit PODS\(_i\) provides a linearized approximation to the iterated dynamics of a phase point on the SOS displaced from the PODS by \( \Delta \mathbf{x} = (\Delta X, \Delta P) \).
Appendix D. Computing average gap times

To determine \( \mathbf{M} \) we propagate the displaced phase points \( \Delta \mathbf{z}_{\Delta X} = (\Delta X, 0) \) and \( \Delta \mathbf{z}_{\Delta P} = (0, \Delta P) \) for one iteration of the SOS mapping. If \( \Delta \mathbf{z}_{\Delta X} \) and \( \Delta \mathbf{z}_{\Delta P} \) evolve to \( \Delta \mathbf{z}' \) and \( \Delta \mathbf{z}'' \) respectively under the mapping, then \( \Delta X \mathbf{M}_{XX} + \Delta X \mathbf{M}_{XP} \mathbf{P}' = \Delta X' \mathbf{P}' \) and \( \Delta P \mathbf{M}_{XP} + \Delta P \mathbf{M}_{PP} = \Delta P' \mathbf{P}' \). The matrix \( \mathbf{M} \) thus obtained can then be diagonalized to obtain eigenvalues and eigenvectors.

For example, for \( E = E_f + 0.1 \), eigenvalues are \( \lambda_1 = 0.715 \), \( \lambda_2 = 1.399 \) with corresponding stable and unstable eigenvectors \( \mathbf{z}_o = (x_o, p_o) = (-0.9808, 0.1948) \) and \( \mathbf{z}_u = (x_u, p_u) = (-0.9808, -0.1948) \), respectively. The determinant of \( \mathbf{M} \) is 1.00006, verifying symplecticity (area conservation) of the linearized dynamics [60] to within reasonable numerical accuracy.

Points on the (nonlinear) manifolds \( \Psi^{\mu \nu} \) are obtained by propagating phase points close to the periodic orbit on the respective linearized manifolds forwards/backwards in time. To visualize \( \Psi^{\mu \nu} \), we select 1000 initial conditions along short segments of \( \hat{E}_{\mu \nu} \) close to the PODS and propagate all these phase points either forward or backwards in time. The resulting manifolds for \( E_f + 0.1 \) are shown in Fig. 8. The bound complex region can be defined to be the phase space volume enclosed by these two manifolds between the PODS and their first intersection [79].

### References
