STOCHASTIC AND DETERMINISTIC DISSOCIATION DYNAMICS OF A MORSE OSCILLATOR DRIVEN BY IMPULSIVE INTERACTIONS

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The classical dynamics of a Morse oscillator driven by impulsive external forces is studied. A periodic kick function gives rise to an instantaneous change of the oscillator's velocity whenever the equilibrium position is passed. The dynamics of the system is completely described by a two-dimensional map which is closely related to the well-known perturbed twist map. Depending on the strength of the kick and the frequency ratio of the external force and the oscillator the dynamics change from regular to chaotic. In particular the dissociation of the Morse oscillator is considered. It is shown that in the chaotic regime the decay approaches an exponential time dependence which can be understood from a simple bottleneck model for the dissociation. The model is applied to the vibrational predissociation of van der Waals complexes.

1. Introduction

Model studies play an important role in elucidating various aspects of "realistic" systems. In this work we use a model to study the vibrational predissociation of a triatomic molecule, or - more generally - the break-up of a vibrational bond coupled to its molecular surroundings. Dissociation dynamics of long lived states attracted a considerable amount of interest during the last few years. Here we give only some key references to important work on classical [1, 2, 3], quantum [3, 4, 5], and mixed classical–quantum [6, 7] dynamics of such processes. Within our model these complicated systems are simulated by one vibration which allows for dissociation and which is perturbed by a time-dependent force. Throughout this study we confine ourselves to classical mechanics and for simplicity we restrict the vibrational mode to a single degree of freedom. It will be shown, that even a simplistic model like this shows an extraordinarily complicated behaviour.

The essence of the present study is the reduction of the classical equations of motion to a discrete mapping equation, which allows very fast and accurate long-time computations without numerically solving differential equations (which may also be a source of numerical errors).

The study of iterated maps is a rapidly growing field of nonlinear mechanics and an excellent introduction can be found in two recent textbooks emphasizing physical [8] or mathematical [9] aspects.

In section 2 we discuss the basic features of our model. Applications to model systems are discussed in section 3. Section 4 simplifies the time evolution by means of an approximate rate equation. The paper concludes with a discussion of applications to vibrational predissociation in section 5.

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2. The discrete mapping equations

We consider a one-dimensional classical Morse oscillator. Its Hamiltonian is given by

\[ H(q, p) = \frac{p^2}{2m} + D(1 - \exp(-\alpha q))^2, \]  

(1)

where \( q, p \) denote the displacement from the equilibrium position \( q_0 = 0 \) and the conjugated momentum, respectively. The dissociation energy is given by \( D \). The interaction with the time-dependent force is assumed to be impulsive. The oscillator is perturbed by a kick whenever \( q \) passes through the equilibrium position \( q_0 = 0 \). The kick causes an instantaneous change of the momentum of the oscillator. The strength of the kick may depend on the time \( t \) when the momentum transfer occurs. The time development is most appropriately described by a discrete map. It generates time \( t_{n+1} \) and momentum \( p_{n+1} \) after the \( (n+1) \)th kick from time \( t_n \) and momentum \( p_n \) after the \( n \)th kick. It is convenient to use reduced quantities: the phase of the oscillation

\[ \Phi = t/T_0, \]  

(2a)

where \( T_0 \) is a characteristic time of the kick function \( f(\Phi) \), which is normalized according to \( \max |f(\Phi)| = 1 \). The reduced velocity is defined by

\[ u = p/\sqrt{2mD}, \]  

(2b)

i.e. \( |u| > 1 \) corresponds to energies above the dissociation limit. The mapping is \( (u_n, \Phi_n) \rightarrow (u_{n+1}, \Phi_{n+1}) \) is now easily established. At \( \Phi_n \) the oscillator's momentum is changed into \( (u_n + kf(\Phi_n)) \). The oscillator moves towards a turning point from where it is reflected. It arrives with momentum \( -(u_n + kf(\Phi_n)) \) at \( q_0 = 0 \). The first mapping equation reads

\[ u_{n+1} = -\left[u_n + kf(\Phi_n)\right], \]  

(3a)

where \( k \) measures the strength of the force and gives the maximum velocity change per kick. The phase \( \Phi \) is increased by the oscillation time of the oscillator for a half cycle, which depends on \( u_{n+1} \),

\[ \Phi_{n+1} = \Phi_n + \delta g(u_{n+1}). \]  

(3b)

The abbreviation

\[ \delta = T_M/2T_0 = \omega_0/2\omega_M \]  

(4)

is used, where \( T_M \) denotes the period of vibration of the Morse oscillator in the harmonic limit,

\[ T_M = \pi\sqrt{2m/D} / \alpha. \]  

(5)

The vibration time function \( g(u) \) is normalized according to \( g(0) = 1 \) and for the Morse oscillator (1) an analytical result is easily obtained,

\[ g(u) = \begin{cases} 
(1 - u^2)^{-1/2}(1 - 2/\pi \arcsin u), & |u| < 1, \\
\frac{2}{\pi} (u^2 - 1)^{-1/2} \ln \left[u + (u^2 - 1)^{1/2}\right], & u > 1.
\end{cases} \]  

(6a)

For further reference we note that

\[ g(u) \approx 1 - (2/\pi)u, \quad |u| \ll 1. \]  

(6b)

If \( u < -1 \) the oscillator will dissociate. Fig. 1 shows the vibrational time function \( g(u) \) as well as a schematic orbit of the system in phase space leading to dissociation after five kicks.

Relevant properties of the mapping are summarized as follows:

1) The mapping depends on two parameters \( k \) and \( \delta \). \( k \) measures the maximum velocity transfer per kick (i.e. if the initial velocity is zero the minimum number of kicks for dissociation is \( 1/k \)). In the following we assume \( k < 1 \). \( \delta \) is the ratio of the basic time scales: large \( \delta \) means high frequency of the kicks and small \( \delta \) means fast vibration of the oscillator. For \( \delta = 0 \) the vibrational motion is fixed \( (\Phi_n = \Phi_0) \) and all points move from \( u_0 \) to \( u_i = -(u_0 + kf(\Phi_0)) \) and back to \( u_0 \) (for \( u_i > -1 \)). In the other extreme \( \delta \rightarrow \infty \) we expect intuitively an almost random phase of the oscillator at the moment of the next kick. A study of the
transition to this random or stochastic behaviour will be a main topic of the next section.

2) In the \((u, \Phi)\)-plane the mapping is area preserving. The Jacobian \(\partial(u_{n+1}, \Phi_{n+1})/\partial(u_n, \Phi_n)\) takes the value \(-1\). The orientation of a phase space element is inverted in each step as a consequence of the change of the sign of the velocity in each step. It is basically this inversion phenomenon by which the mapping is different from other mappings discussed in the literature [8].

3) The mapping is one-to-one, the inverted map is given by

\[
\Phi_n = \Phi_{n+1} - \delta g(u_{n+1}),
\]

\[
u_n = -u_{n+1} - kf(\Phi_n).
\]

4) In the following only periodic kick functions \(f(\Phi)\) are discussed. Then the mapping is related to the perturbed twist map [8, 10, 11]. This becomes evident if we iterate eq. (3) once,

\[
u_{n+2} = u_n + k(f(\Phi_n) - f(\Phi^*)),
\]

\[
\Phi_{n+2} = \Phi_n + \delta [g(-u_{n+2} - kf(\Phi^*)) + g(u_{n+2})],
\]

with

\[
\Phi^* = \Phi_n + \delta g(-u_n - kf(\Phi_n)).
\]

The iterated map is area preserving with a Jacobian equal to \(+1\). The perturbation parameter is \(k\), since for \(k = 0\) eqs. (3a''), (3b'') reduce to the well-known twist map.

The mapping generates fixed points, which are important for the global dynamics of the system. A fixed point of \(m\)th order is defined by

\[
u_m = u_0,
\]

\[
\Phi_m = \Phi_0 \quad (\text{mod} \ 1).
\]

Here fixed points of first and second order are considered. From eqs. (3) it is easily deduced that the fixed points of first order are given by

\[
\delta g(u_0) = M,
\]

\[
u_0 = \frac{1}{2} kf(\Phi_0).
\]

Eq. (8a) can be solved for an infinite number of \(u(M), M = 1, 2, \ldots\) accumulating at \(u = -1\). Eq. (8b) implies, however,

\[
|\nu_0| \leq k/2,
\]

which opens only small windows for the existence of a finite number of first order fixed points, depending on \(k\) and \(\delta\). For small values of \(k/2\), which is typical for the situations studied in section 3, \(|u|\) is also small and eqs. (6b), (8a), and (9) give approximately

\[1 + k/\pi \geq M/\delta \geq 1 - k/\pi ,
\]

or—treating \(k\) as a fixed parameter at the moment—first order fixed points exist only for \(\delta\) values in the interval

\[M/(1 + k/\pi) \leq \delta \leq M/(1 - k/\pi),
\]

centered at integer values of \(\delta = M = 1, 2, \ldots\), with width \(2kM/\pi\). A schematic picture of the first order fixed points (an orbit of period one) is
Fig. 2. Schematic orbits in phase space of the Morse oscillator starting in a fixed point of \( M \)th order. (a) \( M = 1 \); (b) \( M = 2 \).

shown in fig. 2. The stability of fixed points will be discussed below. It will be found that all first order fixed points correspond to unstable periodic orbits. Stable fixed points describe stable nondissociating orbits and give rise to the existence of a set of neighbouring trajectories which will also never dissociate. This set is of nonvanishing measure and governs the overall dissociation dynamics of the system. Of special importance are the lowest order stable orbits, in the present case orbits of period two: \((u_0, \Phi_0) \rightarrow (u_1, \Phi_1) \rightarrow (u_0, \Phi_0)\), i.e. successive excitation and deexcitation processes (see fig. 2). These second order fixed points will be studied in more detail. Second order fixed points are determined by

\[
\begin{align*}
\Phi_2 &= \Phi_0 + \delta g(u_0) + \delta g(u_1) = \Phi_0 \quad \text{(mod 1).} \\
\end{align*}
\]

Eq. (12) implies

\[
\begin{align*}
f(\Phi_0) &= f(\Phi_1) \\
\end{align*}
\]

and

\[
\begin{align*}
\delta g(u_1) + \delta g(-u_1 - kf(\Phi_1)) &= N, \\
\end{align*}
\]

where \( N \) is an integer. We have to distinguish between two types of fixed points. First we consider the case

\[
\Phi_1 = \Phi_0 \quad \text{(mod 1),}
\]

which satisfies eq. (13a) for arbitrary \( \Phi_0 \). Since eq. (3b) requires

\[
\delta g(u_1) = M',
\]

with integer \( M' \), we find from eq. (13b)

\[
\delta g(u_0) = M.
\]

All pairs \((u_0, u_1)\) with \(|u_0 + u_1| < k\) form the second order fixed points provided \( f \) is continuous in \((0, 1)\). The phase \( \Phi_0 \) is determined from

\[
u_1 + u_0 = -kf(\Phi_0).
\]

In fig. 3b solutions of eq. (13b') are shown for various orders \( M \). For a given \( k \) we have to distinguish between two kinds of \( \delta \). If eq. (13b') has a solution \( u_0 \) with \((1 - k) \leq u < 1\) there are infinitely many fixed points of this type otherwise they are limited to a finite number. This is a universal property of eq. (3a) for arbitrary \( f \) and \( g \) provided \( g \) is monotonically decreasing with increasing \( u \) and diverges at \( u = -1 \). For \( k \ll 1 \) we may approximate \( g(u) \) in the vicinity of \( u = 1 \) by

\[
\frac{2}{\pi} - 2\pi(u - 1)/3.
\]

Then we find immediately the \( \delta \)-interval belonging to an infinite number of fixed points

\[
\frac{1}{2} \pi N/(1 + k/3) \leq \delta \leq \frac{1}{2} \pi N, \quad N = 1, 2, 3, \ldots.
\]

Moreover it is straightforward to show that all these fixed points are linearly unstable and of ordinary hyperbolic type [8]. They accumulate at \( u = -1 \) and may form a repulsive barrier which hinders dissociation.

If the kick function is a one-to-one function over one period there are no further fixed points of second order. Additional points arise if \( f \) is not one-to-one. The solution of eq. (12) and eq. (13) can then be considerably simplified if the force function \( f(\Phi) \) has at least a symmetry. Let us assume

\[
f\left(\frac{1}{4} + \Phi\right) = f\left(\frac{1}{4} - \Phi\right)
\]
which will be satisfied for \( f(\Phi) = \sin 2\pi \Phi \) chosen in the numerical example in the following section. In this case the solutions of eq. (13) are related by

\[
\Phi_0 + \Phi_1 = \frac{1}{2} \pmod{1}. \tag{15'}
\]

Eq. (12b) gives

\[
\Phi_1 = \frac{1}{4} + \frac{1}{2} \delta g(u_1) \pmod{1} \tag{16}
\]

and eq. (13b) reduces to a single variable equation

\[
\delta g(u_1) + \delta g(-u_1 - kf(\frac{1}{4} + \frac{1}{2} \delta g(u_1))) = N, \tag{17}
\]

which must be solved for the fixed point \( u_1 \). \( \Phi_1 \) is determined by (16). Note that these fixed points occur in pairs. Fig. 3a displays the location of second order fixed points as function of \( \delta \). Independent of \( \delta \) there are infinitely many fixed points accumulating at \( u = -1 \). In contrast to the fixed points of the first kind discussed before there are now areas of stable and unstable behaviour. In a similar way higher order fixed points can be found, because the mapping (3) with symmetry (15) may be factored into a product of two involutions [8].

5) Next the linearized mapping is considered. It allows one to determine whether the mapping is stable or not. Small perturbations \( (\Delta u, \Delta \Phi) \) obey the linearized mapping at a phase point \((u_n, \Phi_n)\),

\[
\begin{pmatrix}
\Delta u_{n+1} \\
\Delta \Phi_{n+1}
\end{pmatrix} = A(u_n, \Phi_n) \begin{pmatrix}
\Delta u_n \\
\Delta \Phi_n
\end{pmatrix},
\]

where \( A \) is the (2 by 2) Jacobian matrix at the phase point \((u_n, \Phi_n)\). The eigenvalues \( \lambda \) of \( A \) are
given by

\[ \lambda_i = \frac{1}{2} \text{TrA} \pm \left[ \frac{1}{4} (\text{TrA})^2 - |A| \right]^{1/2}, \quad (19) \]

with

\[ \text{TrA} = -k \delta g'(u_n) f'(\Phi_n), \quad (20) \]

where the prime denotes the derivative. Since \( |A| = -1 \) the eigenvalues are real everywhere satisfying

\[ \lambda_1 \lambda_2 = -1. \quad (21) \]

The motion is linearly unstable [8]. With respect to fixed points this result has the following interesting consequence. Consider a \( k \)th order fixed point family \((u_0, \Phi_0) \rightarrow (u_1, \Phi_1) \rightarrow \cdots \rightarrow (u_k, \Phi_k) = (u_0, \Phi_0)\). The linearized mapping at the fixed point can then be written as

\[ \begin{pmatrix} \Delta u_k \\ \Delta \Phi_k \end{pmatrix} = B \begin{pmatrix} \Delta u_0 \\ \Delta \Phi_0 \end{pmatrix}, \quad (22) \]

with

\[ B = A(u_{k-1}, \Phi_{k-1})A(u_{k-2}, \Phi_{k-2}) \cdots A(u_0, \Phi_0), \quad (23) \]

and

\[ |B| = (-1)^k. \quad (23') \]

Consequently, all fixed points of odd order are unstable. A similar statement for the fixed points of even order cannot be deduced.

### 3. The kicked Morse oscillator

Let us now consider the dissociation of the kicked Morse oscillator. A simple harmonic kick function

\[ f(\Phi) = \sin 2\pi \Phi \quad (24) \]

is applied. The temporal evolution depends on the initial condition \((u_0, \Phi_0)\) and on the parameters \( k \) and \( \delta \). \( k \) is the maximum velocity change per kick and \( \delta \) is the frequency ratio of the kick function and the Morse oscillator in the harmonic limit. It is instructive to consider this harmonic limit first. Then we have \( g(u) = 1 \) and the system becomes linear. Eqs. (3) can be solved analytically to give

\[ u_n = (-1)^n \left[ u_0 + k \sum_{j=0}^{n-1} (-1)^j \sin 2\pi(\Phi_0 + j\delta) \right], \quad \Phi_n = \Phi_0 + n\delta. \quad (25) \]

Half-integer values of \( \delta \) lead to resonant excitation. Then the oscillator is dissociated after \( 1/k \) kicks if \( u < -1 \) is considered to induce dissociation. Integer values of \( \delta \) do not contribute to dissociation except for \( u > (1 - k) \). Other rational \( \delta \) may dissociate depending on \( k \) and the number of kicks while irrational ones will always lead to decay provided the number of kicks is large enough. We will see that the nonlinearity of the Morse oscillator changes the picture completely. A dominating feature of the kicked Morse oscillator is its instability. Linear stability analysis shows [8] that a small displacement \((\Delta u, \Delta \Phi)\) increases per step by the instability factor

\[ \lambda = \max(|\lambda_1|, |\lambda_2|), \]

where the \( \lambda \)'s are the eigenvalues of the Jacobian matrix. For \( |u| \ll 1 \) we estimate

\[ \lambda \approx k\delta + \left(1 + (k\delta)^2\right)^{1/2}. \]

For increasing \( |u| \), \( \lambda \) increases on the average. The number of steps \( N \) after which instabilities become important can be estimated from

\[ \epsilon\lambda^N > 1, \]

where \( \epsilon \) is the accuracy of the computer used. In our experience this local criterion gives a very pessimistic estimate of the global instability. For a
In the following we discuss the dissociation mechanism of the kicked Morse oscillator. Firstly dissociation from the bottom of the oscillator $u_0 = 0$ has been investigated. Results are given in fig. 4 as function of $\delta$ for $k = 0.1$ for $N = 500$ kicks. We can clearly distinguish between two regions: For $\delta > 3$ dissociation is always possible. For smaller $\delta$ it is unlikely that the oscillator dissociates except for two small windows close to $\delta = \frac{1}{2}$ and $\delta = 2$. The first situation allows for resonant excitation with mostly monotonically increasing $|u|$. The anharmonicity causes the small shift to smaller $\delta$'s. The resonance at $\delta = 2$ cannot be explained similarly. It is caused by a complicated interplay of successive anharmonic shifts for $\Phi$.

A fairly complete overview of the dissociation phenomena is given in fig. 5. The time $T$ needed for dissociation is plotted as function of the initial condition $(u_0, \Phi_0)$. If the decay happens with the $l$th kick $T$ is given by $T = \Phi_l - \Phi_0$. A maximum of $N = 500$ kicks is applied. For small values of $\delta$ dissociation occurs only for energies just below threshold. Near the resonance $\delta = \frac{1}{2}$ clearly structured areas exist from which dissociation is forbidden. Areas which cannot be dissociated correspond to adiabatic islands [8, 9]. Trajectories starting in these areas are limited to a particular island and/or transitions between islands. For larger $\delta$ (however smaller than $\delta < 1.75$) the adiabatic islands increase and form a large area of initial conditions which do not allow for dissociation. The adiabatic islands are bounded by an adiabatic invariant curve which may form a band extending to all phase angles. In the vicinity of $\delta = 1$ the phase increases approximately by unity per kick. The increase in $u$ in one step is deleted in the following kick. In this way a stop band [8] is reached. It can be overcome for larger $\delta$ at $\delta = 2$. Again for $2.2 \leq \delta \leq 3$ a domain of destructive interference between successive phases $\Phi$ is experienced. However this time only small $|u|$ are effected since the correlation of phase decreases. For $\delta > 3$ the islands vanish and the motion appears to be chaotic. Indications for chaos are the fact that the dissociation time depends sensitively on the initial condition. Moreover we are with $\lambda = 1.38$ deep in the region of the numerically relevant instability.

In fig. 6 the numerical instability is demonstrated for $k = 0.3$ and $\delta = 7$. The trajectory starts at the fixed point of first order $u = 0, \Phi = 0.5$. Numerical errors obscure the fixed point property. The error grows exponentially at a rate which can be estimated from the linear stability

![Fig. 4. Dissociation probability as function of $\delta$ for $u = 0$ and $k = 0.1$. Maximum number of steps $N = 500$.]
Fig. 5. Logarithmic plot for the time of dissociation $T$ as function of the initial conditions $u_0$ and $\Phi_0$. $k = 0.1$, $N = 500$. The largest bars correspond to initial conditions not leading to dissociation.
Fig. 5. continued.
Fig. 5. continued.
The probability for dissociation $P$ as function of the initial $u$ is presented in fig. 7. It shows the expected result that in general dissociation is more probable the higher the initial energy of the oscillator is. However near the $\delta = \frac{1}{2}$ resonance the dissociation of $u_0 = 0$ is strongly enhanced leading to a nonmonotonic dependence of $P$ on $u_0$. This particular behaviour is caused by low lying adiabatic islands clearly visible in fig. 2. Next we study the long time average dissociation probability for fixed initial velocity $u_0$ and randomly distributed phase $\Phi$. We have to distinguish three cases: (1) The line $u_0 = \text{const.}$ is separated from the dissociation limit by an adiabatic invariant curve. We have zero dissociation probability in this case (see fig. 5a). (2) The $u_0 = \text{const.}$ line is cut by an adiabatic invariant curve separating dissociative and nondissociative regions. In this situation a fraction of all trajectories remains nondissociated. Fig. 8 shows as an example the case $u_0 = 0$ for $\delta = 0.46$ (compare fig. 5c). The dissociation probability reaches an asymptotic limit of 0.66 if the number of iterations is increased. (3) In the glob-
ally stochastic regime $\delta > 3$ the dissociation probability converges towards unity.

The dissociation rate (number of dissociating trajectories per unit time) in the stochastic region is shown in fig. 9 for $u_0 = 0$, $k = 0.1$, and two values of $\delta$ ($\delta = 7$ and $\delta = 14$). Both plots have been computed from a sample of 8000 trajectories with a random distribution of the initial phase.

We observe in both cases an exponential decay

$$n(\Phi - \Phi_0) \sim \exp\left(-\frac{\Phi - \Phi_0}{\tau}\right).$$

The numerical value of the time constant, however, depends sensitively on the accuracy of the calculations. Table I shows that $\tau$ can change as much as a factor of 1.3 if the number of significant digits varies. Exponential decay is observed for all $\delta \geq 3$. There are, however, small deviations from the exponential behaviour if the number of relevant digits is smaller than seven. The dependence on $k$ has been explored in a few cases. Increasing $k$ leads to decreasing adiabatic islands. All resonance effects discussed above are less pronounced. For $k = 0.3$ for instance dissociation is possible for all $\delta > 0.1$.

4. An approximate rate equation

In this section we propose a rate equation treatment of the dissociation process. This approach replaces the discrete mapping eqs. (3) of the phase space onto itself by a set of differential equations in time. For such a description to be valid it is necessary that the phases $\Phi$ between steps are uncorrelated and random. In the chaotic limit both conditions are fulfilled. Meaningful results can only be expected for large times corresponding to a large number of kicks. Substituting the discrete number $n$ by the continuous varying time implies that the short time behaviour cannot be accounted for.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\tau/\delta$ (7)</th>
<th>$\tau/\delta$ (14)</th>
</tr>
</thead>
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<tr>
<td>7</td>
<td>348</td>
<td>384</td>
</tr>
<tr>
<td>9</td>
<td>325</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>—</td>
<td>384</td>
</tr>
<tr>
<td>12</td>
<td>263</td>
<td>393</td>
</tr>
</tbody>
</table>

$^a$) Number of significant digits.

$^b$) $\delta = 7$.

$^c$) $\delta = 14$. 
The $u$-axis is discretized by introducing levels $1, \ldots, N$. The probability that the interval $u_i - \varepsilon \leq u \leq u_i + \varepsilon$ is populated is denoted by $P_i$. The mean velocity in level $i$ is given by

$$u_i = -1 + 2i/N, \quad i = 1, 2, \ldots, N \quad (27)$$

and the level width is then

$$\varepsilon = 1/N. \quad (28)$$

The temporal evolution of the $P_i$'s is determined from the rate equations

$$\frac{dP_i}{dt} = \sum_{j=1}^{N} W_{ij}P_j - \sum_{j=1}^{N} W_{ji}P_i - W_{di}P_i, \quad (29)$$

where $W_{ij}$ is the probability per unit of time for a transition from level $i$ to level $j$. The time $t$ is measured in units of $T_0$. The first and second term in eq. (29) generate population and depopulation among the levels. The third term is a loss term responsible for dissociation.

A crucial step is the somewhat arbitrary choice of the transition probabilities $W_{ij}$. They should be designed to model the mapping eq. (3) as close as possible. Here we used the following prescription. The $W_{ij}$ consist of two factors

$$W_{ij} = w_1(\Delta u)w_2(u_j). \quad (30)$$

The first factor $w_1$ is the probability for the transferred velocity in a kick $\Delta u = |u_i + u_j|$. It depends solely on the kick function $f$. For a sinusoidal $f$ one easily obtains

$$w_1(\Delta u) \sim \left[1 - (\Delta u/k)^2\right]^{-1/2}. \quad (31)$$

The second term $w_2$ takes into account that the time $\delta g(u)$ elapses until the velocity $u_j$ is reached. Usually one adopts [14]

$$w_2(u_j) = \left[\delta g(u_j)\right]^{-1}. \quad (32)$$

this choice implies that the mean life time in level $i$ with respect to decay into level $j$ is $\delta g(u_j)$. We found it more appropriate to require that the decay into level $j$ takes place with equal probability before and after the time $\delta g(u_j)$ is elapsed. One finds a slight modification of eq. (32);

$$w_2(u_j) = \ln 2\left[\delta g(u_j)\right]^{-1}. \quad (33)$$

The loss rate constants are only different from zero for levels $(1-k) \leq u$, 

$$W_{di} = \kappa \int_{(1-u_i)}^{k} w_1(\Delta u) \, d(\Delta u). \quad (34)$$

Here the $w_2$-factor is to be omitted since in our definition the dissociation is completed at the time of the kick that produces $u < -1$. Therefore the loss processes have to be much faster than climbing up the levels $i$. It implies

$$W_{di} \gg W_{ji}. \quad$$

The condition above is fulfilled by sufficiently large values for $\kappa$. Proper choices of $\kappa$ are characterised by a $\kappa$-independent dissociation behaviour. The temporal evolution depends then only $W_{ji}$ and from eq. (29) it is obvious that the time scales with $\delta$. Results have been obtained from a numerical integration of the rate equations. The number of levels was taken to be $N = 81$. Test calculations with $N = 91$ and $N = 121$ lead to the same results. Initially the ground state levels $-k/2 \leq u \leq k/2$ are populated. The dynamics of the dissociation is monitored by the decrease of the total population

$$P(t) = \sum_{i=1}^{N} P_i(t). \quad (35)$$

The long-time behaviour of $P(t)$ is exponential to a very high degree of accuracy for $k = 0.1$ and $k = 0.3$ (see fig. 9a). At short times $t/\delta < 25$ one observes deviations from the exponential dependence due to incubation effects.
In fig. 10a results for the decay time have been plotted. For $k = 0.3$ there is good agreement with the outcome of the mapping eq. (3). For $\delta > 5$ the decay time approaches the results from the rate equations. The degree of convergence is rather small, the scatter is outside the statistical error bars for the decay time. We have also entered the decay time for the randomized mapping defined by

$$u_{n+1} = -u_n - kf(\Phi_n),$$  \hspace{1cm} (36a)  $$\Phi_{n+1} = \Phi_n + g(u_{n+1}) + r,$$  \hspace{1cm} (36b)

where $r$ is a random variable uniformly distributed in $(-\frac{1}{2}, \frac{1}{2})$. The random term destroys all phase correlations. Mapping (36a, 36b) is expected to describe the kicked oscillator in the limit of complete chaos. It is then obvious that the decay time scales with $\delta$ for arbitrary $\delta$. As expected the agreement with the time constants for the rate equation is here in general even better. The smaller value of $k$ ($k = 0.1$) shows also similar decay times for the rate equations and the randomized mapping. The deterministic mapping eqs. (3) generate much larger reduced decay times, which depend still on $\delta$. With increasing $\delta$, however, the time constant seems to converge to an asymptotic value coinciding with the results from the randomized mapping and the rate treatment. These findings demonstrate that the apparent chaos in fig. 5 has still deterministic components. We conjecture that the density of fixed points of second order near $u = -1$ are mainly responsible for these effects. In the present case the determinism hinders the dissociation. The chaotic components take care that the decay is still exponential.

The exponential time dependence of $P$ and the short incubation time suggest a simple bottleneck model for the dissociation dynamics. The bottleneck is located near $u = -1$, where the transition probabilities per unit time become infinitely small. To achieve dissociation, the system has to occupy levels in $(-1, -1 + k)$ at least once. In the model the process consists of two steps: During the short incubation time the ground state levels are depleted and only levels with $u \approx -1$ are populated. These levels are depopulated through the bottleneck with a small rate constant $\tau^{-1}$. The dynamics can be described by a single rate equation

$$\frac{dP}{dt} = -(1/\tau)P,$$ \hspace{1cm} (37)

or

$$P(t) = \exp\left(-t/\tau\right).$$ \hspace{1cm} (37')

Thus the bottle neck model explains very simply the exponential time dependence. The rate constant can be estimated from

$$\tau^{-1} = \frac{1}{2} \int_{-1}^{-1+k} \ln 2[\delta g(u)]^{-1} du,$$ \hspace{1cm} (38)
where $\tau^{-1}$ is just an average over the reciprocal time the system spends in the bottleneck. The factor $\frac{1}{2}$ accounts for the fact that only phases $0 \leq \Phi < \frac{1}{2}$ favour dissociation. For $k \ll 1$ (still valid for $k = 0.3$) one finds

$$\frac{\tau}{\delta} \sim 6.121 k^{-3/2} \times [1 + 0.337\sqrt{k} + 0.121k^2 + \cdots]^{-1}. \quad (39)$$

Results from eq. (39) have been compared with those of the randomized mapping. The agreement is surprisingly good in regard to the simplicity of the bottleneck model (see fig. 10b).

5. Application to vibrational predissociation

Consider, for example, a triatomic molecule consisting of a strongly bound diatomic subsystem to which an atom is weakly attached by van der Waals forces. If the energy of the molecule is larger than the dissociation energy of the van der Waals bond the molecule is unstable and will dissociate sooner or later. Necessary for the process to occur is a coupling between the vibration of the diatomic and the van der Waals oscillator. If the coupling is weak it may last many periods till the weak bond is broken. It is in general not easy to follow the details exactly using quantum or classical mechanics. Numerical calculations either quantal or classical tend to become inaccurate for long integration times. Since the mapping technique is designed to describe motion easily for long times it seems to be worthwhile to adopt eq. (3) to model the predissociation of van der Waals complexes. All rotational effects are neglected. The kick function represents the coupling with the strong diatomic oscillator. It is assumed that its energy exceeds the dissociation energy by far. Thus the small energy loss due to transfer to the weak oscillator can be safely neglected. The latter is described by the Morse oscillator. The most severe assumption (and possible source of criticism) concerns the coupling. It is only non-vanish-

<table>
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<th>$D_e$ (1/cm)</th>
<th>$\tau_c$ (Ångström)</th>
</tr>
</thead>
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<tr>
<td>128</td>
<td>4911</td>
<td>3.016</td>
</tr>
<tr>
<td>18</td>
<td>139</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table II

Molecular properties of $I_2$–He and $I_2$ (after [2])

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<th>$\tau_c$</th>
</tr>
</thead>
<tbody>
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<td>128</td>
<td>4911</td>
<td>3.016</td>
</tr>
<tr>
<td>18</td>
<td>139</td>
<td>4.0</td>
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</tbody>
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Table III

$\tau/\delta$ as function of $u$ and $k$. $\delta = 3.55$

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Acknowledgements

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References