Does the transition state encode the rate of a driven reaction?

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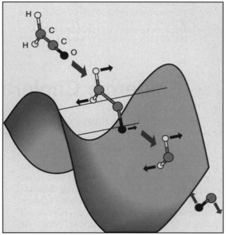
Transition State Theory

Crossing an energy barrier:
Crucial reaction dynamics in small Transition State region

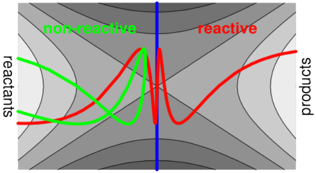


(Marcus: Science **256** (1992) 1523)

Provides:

- simple zero time rate formula
- simple picture of the reaction mechanism

Reaction rate is counted in a dividing surface that should be free from recrossings.

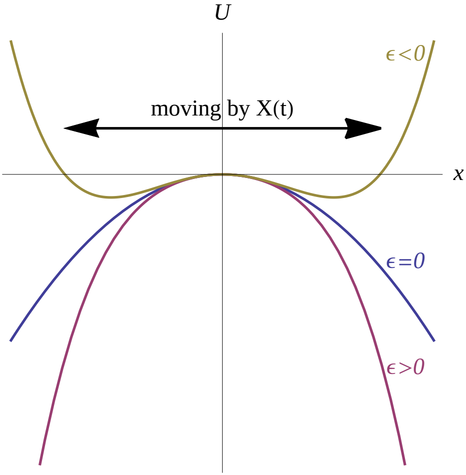


Dual purpose:

- Define reactant and product regions
- Identify reactive trajectories

The model: A driven barrier

$$\dot{x} = v$$
$$\dot{v} = -U'(x - X(t)) - \gamma v$$



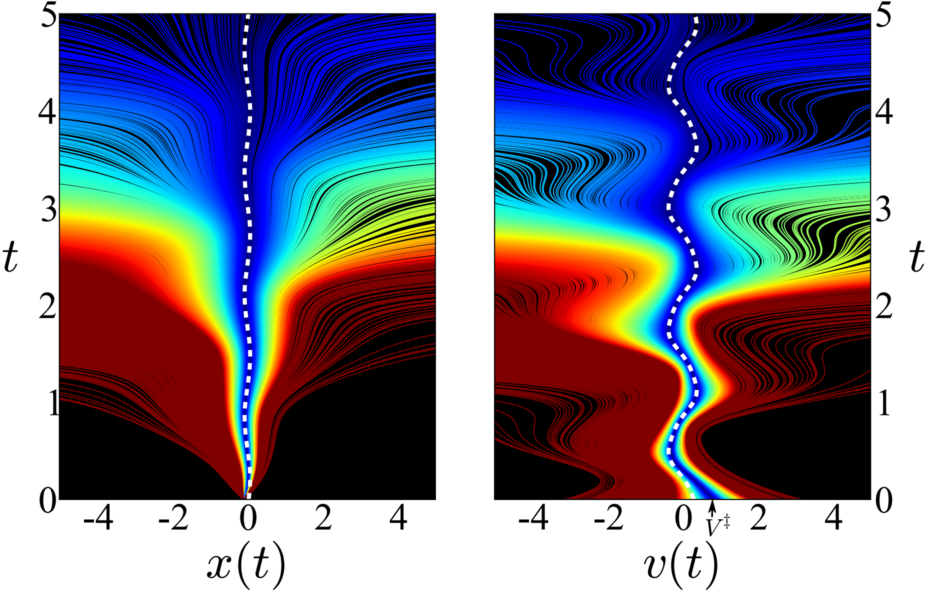
Barrier potential

$$U(x) = -\tfrac{1}{2}\omega_{\mathrm{b}}^2 x^2 - \tfrac{1}{4}\epsilon x^4$$

Periodic driving

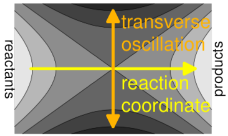
$$X(t) = a\sin(\Omega t + \varphi)$$

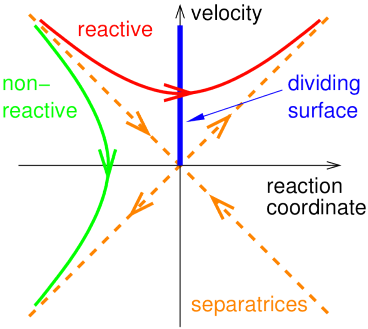
An ensemble of trajectories

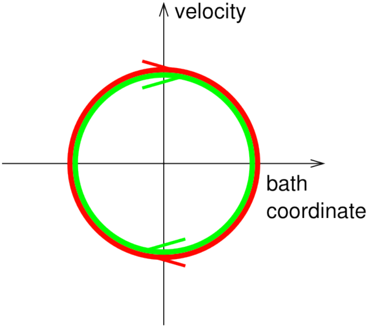


A fixed barrier seen in phase space

Harmonic approximation:
The reaction coordinate and transverse degrees of freedom decouple.







These geometric structures persist in coupled systems: Invariant manifolds

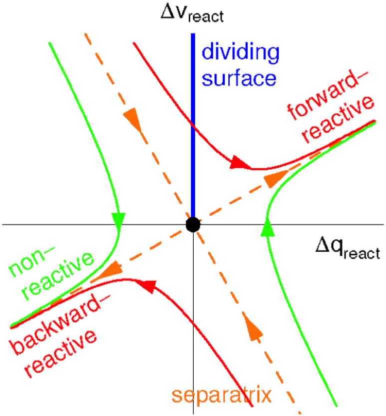
Centre of the construction: dynamical fixed point

A moving barrier seen in phase space

Choose unstable periodic orbit $x^{\ddagger}(t)$
as moving saddle point
(Transition State trajectory)

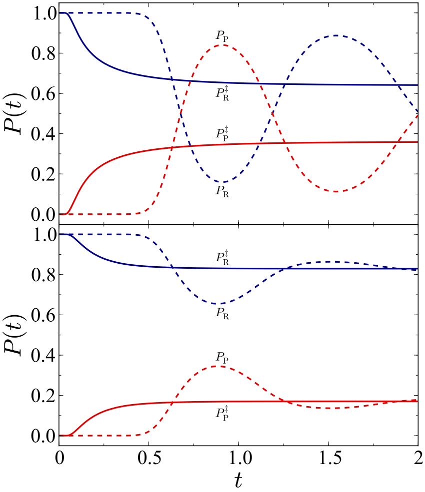
Relative coordinate $\Delta x = x - x^{\ddagger}(t)$
has autonomous dynamics
on a harmonic barrier

Stable / unstable manifolds
are trapped by the PO.



Invariant manifolds are moving through phase space.

Reactant and product populations



$\epsilon = 0$

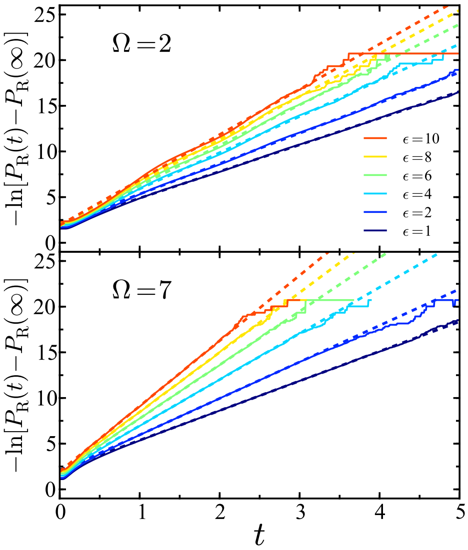
$\epsilon = 5$

Define product region by

- fixed dividing surface, or
- moving dividing surface

Moving surface is recrossing free.

Definition of reaction rates



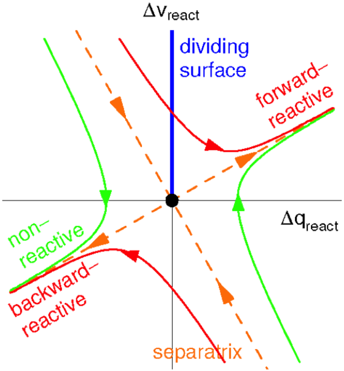
Moving surface allows to define a reaction rate.

Long-time dynamics

Determined by trajectories
near the stable manifold,
mostly near TS trajectory.

Linear dynamics near the TS trajectory:
Time-periodic coordinate system

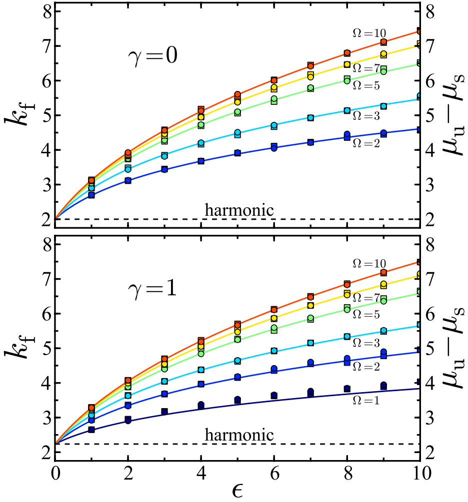
$$\alpha_s(t) = \alpha_s(0)\, e^{\mu_s t}$$
$$\alpha_u(t) = \alpha_u(0)\, e^{\mu_u t}$$



Determine when a given trajectory will cross the DS.

Reactive flux per period decays as $e^{(\mu_u - \mu_s)T}$.
Exponential decay rate $\mu_u - \mu_s$.

Reaction rates



Numerical simulation (symbols), Floquet exponents (curves)

Conclusions

- Structures of reaction dynamics are visible in phase space.
- A time-dependent dividing surface is recrossing free, advantageous for rate calculations.
- Decay rates can be computed from the Floquet exponents of the TS trajectory
  — at least sometimes.

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