

Dynamics and Phase Space Structure for Reactions with Multiple Saddles

Johannes Reiff, Robin Bardakcioglu, Martin Tschöpe, Matthias Feldmaier, Jörg Main and Günter Wunner 1. Institut für Theoretische Physik, Universität Stuttgart, Germany

Introduction

Universität Stuttgart

Phase Space Structure: Lagrangian Descriptor (2)

- ▶ Dynamic potential $(\omega_{x,i} = \pi \forall i)$:
 - Complex, fractal-like behavior similar to [4]
 - Stable and unstable manifolds not uniquely identifiable



Rate Calculations (2)

Canonical Ensemble ($k_{\rm B}T = 2$)

- Three states: Reactant, intermediate and product
- Existence of global NHIM uncertain
 - \implies No definite point in time for a reaction
 - \implies Multiple definitions possible:
 - Crossing of first (left) NHIM (blue): Non-monotonic rate because of reflections at second barrier
 - Crossing of second (right) NHIM (orange)
 - NHIM crossing with lowest kinetic energy (green)



Phase space structure near saddle top in 1D, see e.g. [3]:

- \blacktriangleright Stable (\mathcal{W}_{s}) and unstable (\mathcal{W}_{u}) manifolds define four regions (forward/backward/no reaction)
- Intersection forms the Normally Hyperbolic Invariant Manifold (NHIM)
- Dividing Surface (DS) is attached to the NHIM



Model System

Two Gaussian barriers (M-Problem)

 $V(x,t) = \sum B_i \exp\{-a_i [x - x_{b,i}(t)]^2\}$

with time dependent positions

 $x_{\mathrm{b},i}(t) = x_{0,i} + \hat{x}_i \sin(\omega_{x,i}t + \varphi_{x,i})$

▶ Simulation units: $B_i = 1.75$, $a_i = 1$, $x_{0,1} = -1$, $x_{0,2} = 1$, $\hat{x}_i = 0.25$, $\omega_{x,i} = \pi$, $\varphi_{x,1} = 0$ and $\varphi_{x,2} = \pi$



Local Normally Hyperbolic Invariant Manifolds

- Use reactive regions to identify manifolds locally for each saddle (r: reactant, $x < x_{\text{NHIM}}$; p: product, $x > x_{\text{NHIM}}$)
- lterative algorithm finds NHIM for every t_0 , see [1] \implies Transition State Trajectory (cyan)



- At most 2 crossings with local NHIMs
- ► Few particles trapped within the observed time span
- Local recrossings because of reflections possible (left)





http://itp1.uni-stuttgart.de/

14th March 2018

johannes.reiff@itp1.uni-stuttgart.de