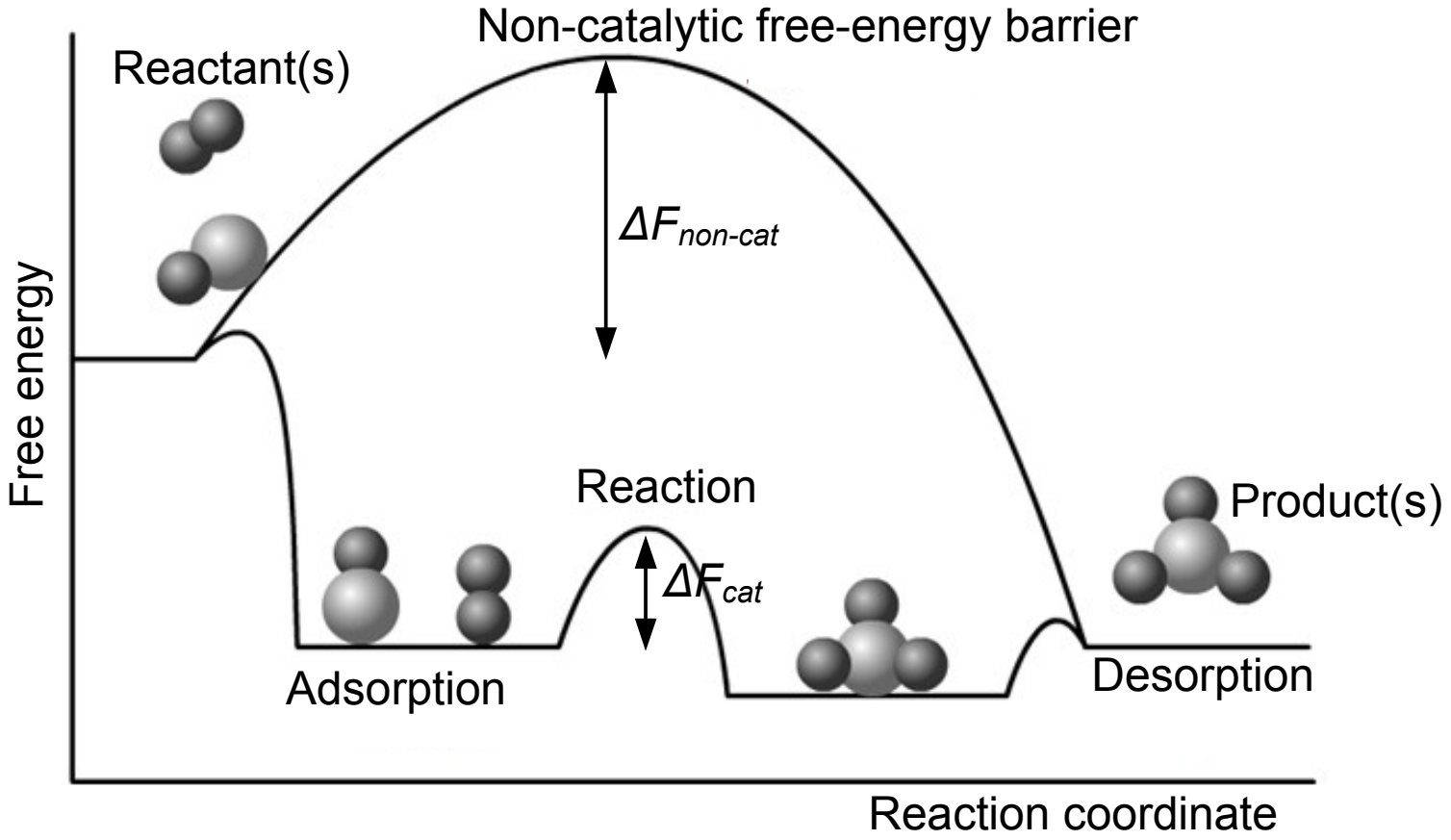
Search for Minimum Energy Paths: Nudged Elastic Band and Beyond

Luca M. Ghiringhelli

Density functional theory and beyond:
Computational materials science for real materials

Held at the Institute for Pure and Applied Mathematics (IPAM)
Los Angeles, USA, July 21 - August 1, 2014

Chemical energy conversion: catalysis



Issues:

- Reaction rate: proportional to *exp (- ΔF / kT)*
- Selectivity: eliminate or at least reduce the undesired products

To know more:

Further reading on rare events techniques:

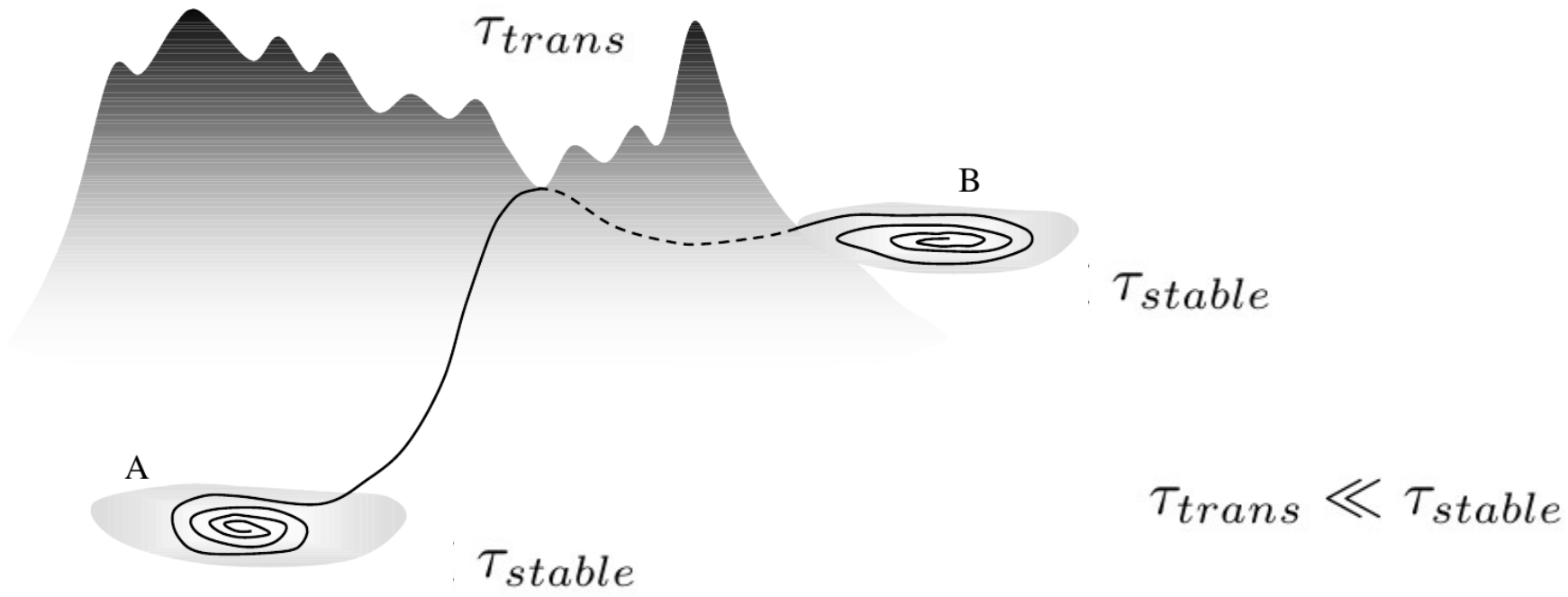
Efficient sampling of Rare Events Pathways
Daniele Moroni, PhD thesis.
http://www-theor.ch.cam.ac.uk/people/moroni/thesis.html

Transition-Path Theory and Path-Finding Algorithms for the Study of Rare Events
Weinan E and Eric Vanden-Eijnden
Annu. Rev. Phys. Chem. 2010. 61:391–420

Methods for Finding Saddle Points and Minimum Energy Paths
Graeme Henkelman, Gísli Jóhannesson, and Hannes Jónsson,
in Progress on Theoretical Chemistry and Physics, 269- 300, Ed. S. D. Swartz (Kluwer Academic, 2000)

Lectures related to this one in this school (Wed, July 30):
Peter Kratzer : kMC
Baron Peters : TPS

Study of rare events



• **the mechanism:** understanding the relevant features of the process, and the identification of a (set of) coordinates, called the reaction coordinate, that explains how the reaction proceeds.

• **the transition states:** what are the dividing passages, what is the relevant change that the system must undergo to switch state

• **the rate constants:** the transition probabilities per unit time. For the process A → B we call it k_{AB}. It can be considered as the frequency of the event, so that k_{AB}^{-1} is the lifetime of state A. Corresponding concepts hold for the reversed process and k_{AB}.

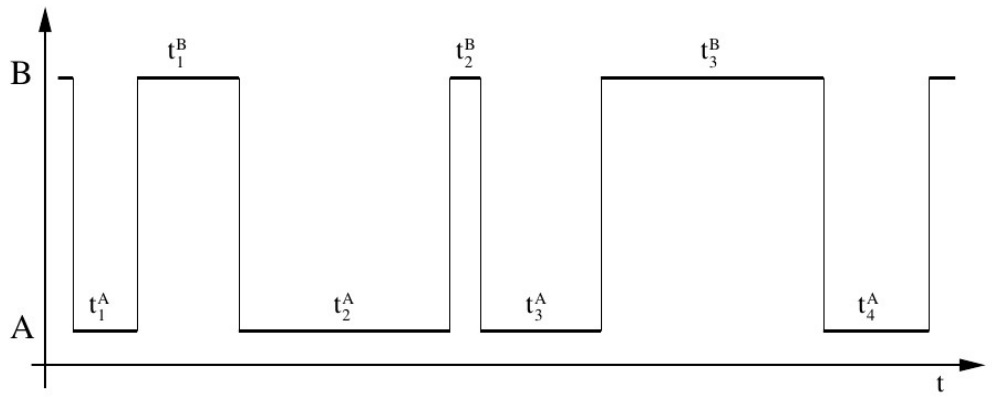
Road map

- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

Setting the stage: The random telegraph



Jump probability $$W(x|x') = \begin{cases} W_{AB} & \text{if } x = B, x' = A, \\ W_{BA} & \text{if } x = A, x' = B, \end{cases}$$

$$W(A|A) = 1 - W(B|A)$$
$$W(B|B) = 1 - W(A|B)$$

(Normalization)

Basic quantity of Markov processes:

$p(x,t|x',0)$ = Probability of being in x at time t provided that you were in x' at time 0

Setting the stage: The random telegraph

Master equation:

$$\frac{d}{dt}\,p(A,t|x',0) = -W_{AB}\,p(A,t|x',0) + W_{BA}\,p(B,t|x',0)$$
$$\frac{d}{dt}\,p(B,t|x',0) = W_{AB}\,p(A,t|x',0) - W_{BA}\,p(B,t|x',0)$$

Initial condition: $p(x,0|x',0) = \delta_{x,x'}$

Conserved quantity: $p(A,t|x',0) + p(B,t|x',0) = 1$

Solution:

$$p(A,t|x',0) = p_{st}(A) + e^{-(W_{AB}+W_{BA})t}\,[p(A,0|x',0) - p_{st}(A)]$$
$$p(B,t|x',0) = p_{st}(B) + e^{-(W_{AB}+W_{BA})t}\,[p(B,0|x',0) - p_{st}(B)]$$

Stationary probabilities:

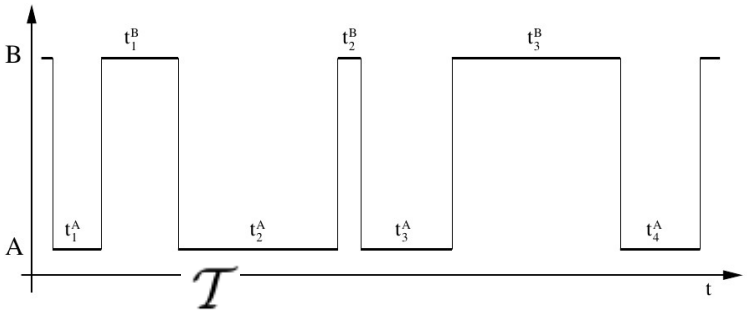
$$p_{st}(x) = p(x,+\infty|x',0)$$

$$p_{st}(A) = W_{BA}/(W_{AB}+W_{BA})$$
$$p_{st}(B) = W_{AB}/(W_{AB}+W_{BA})$$

Setting the stage: The random telegraph

Suppose, W is not known, but we want to measure it, through statistical sampling.

$$W(x|x') = \lim_{dt \to 0} p(x, dt|x', 0)/dt$$



Ensemble average or, via ergodicity, time average:

$$W_{AB} = \lim_{\mathcal{T} \to \infty} \frac{N_{A \to B}(\mathcal{T})}{t^A_{tot}(\mathcal{T})}$$

$N_{A \to B}(\mathcal{T})$: Number of A → B during

$\sum_i t_i^A$: Total time spent in A

W_{AB}: transition probability per unit time

The inverse of the matrix element has a simple meaning:

$$t_A^{mfp} = W_{AB}^{-1} = \lim_{\mathcal{T} \to \infty} \frac{1}{N_{A \to B}(\mathcal{T})} \sum_{i=1}^{N_{A \to B}(\mathcal{T})} t_i^A \equiv t_A^{mr}$$

t_A^{mfp}: mean first passage time

t_A^{mr}: mean residence time

Rate constant $\boxed{k_{AB} =} W_{AB} = (t_A^{mr})^{-1} = \boxed{(t_A^{mfp})^{-1}}$

Equality holds only if transition is instantaneous (not valid for “real” systems)

Road map

- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

Transition state theory: vocabulary

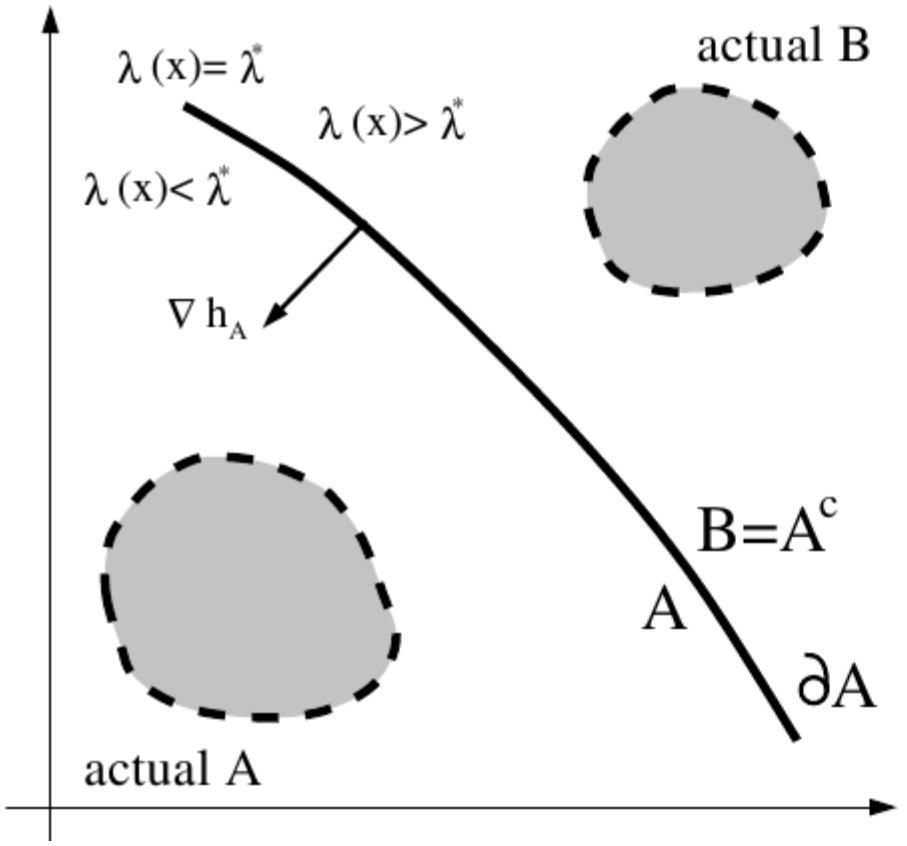
$$\int_\Omega \rho(r)dr = \langle h_\Omega(r)\rangle \qquad \langle h_A\rangle + \langle h_B\rangle \simeq 1$$

Not "=", due to existence of (small) buffer region

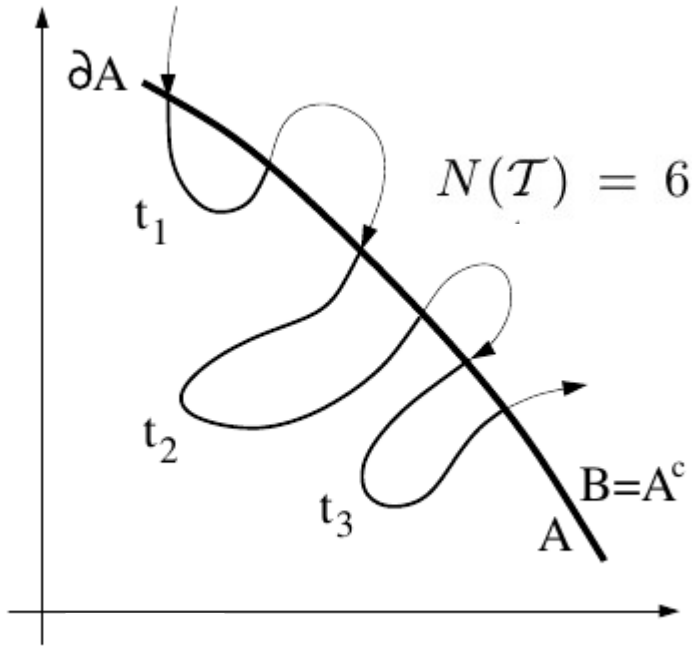
Eql. (Gibbs) distribution

TST: $B = A^c$

$$\langle h_A\rangle + \langle h_{B=A^c}\rangle = 1$$



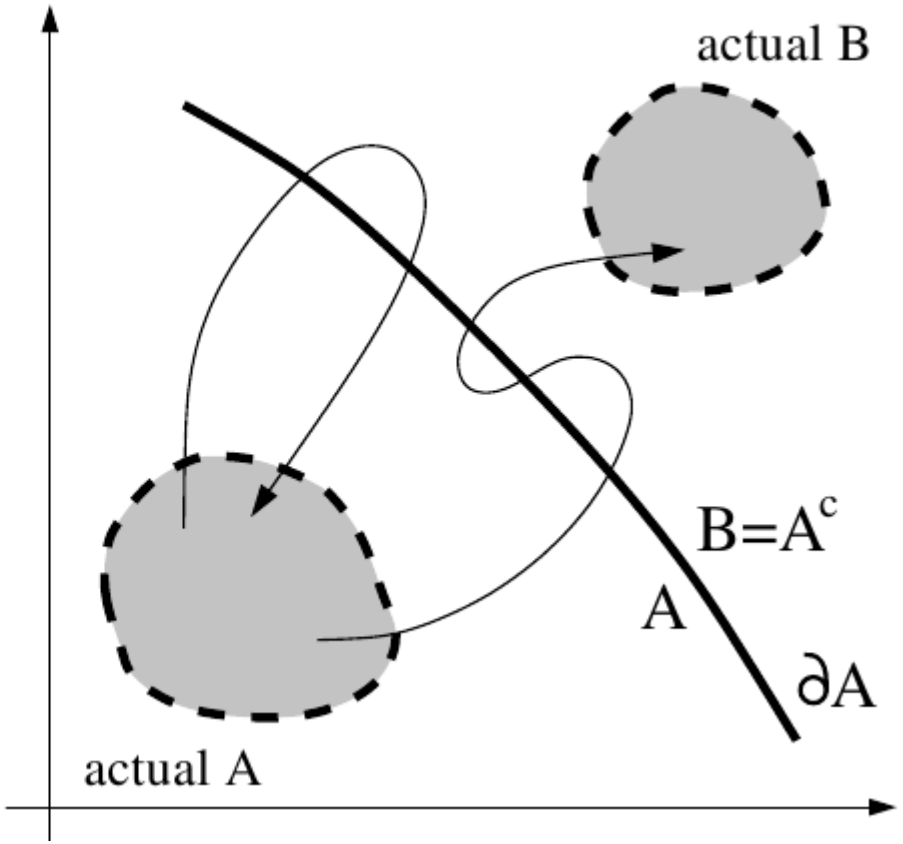
$$t_A^{mr} = \lim_{\mathcal{T}\to\infty} \frac{2}{N(\mathcal{T})} \int_0^{\mathcal{T}} h_A(r(t))dt$$



$N(\mathcal{T}) = 6$

$$t_A^{mr} = 2/6 \cdot \sum_i t_i = (t_1 + t_2 + t_3)/3$$

Transition state theory: vocabulary



Definition: $\nu^{TST} = \lim_{\mathcal{T}\to\infty} \frac{N(\mathcal{T})}{2\mathcal{T}}$

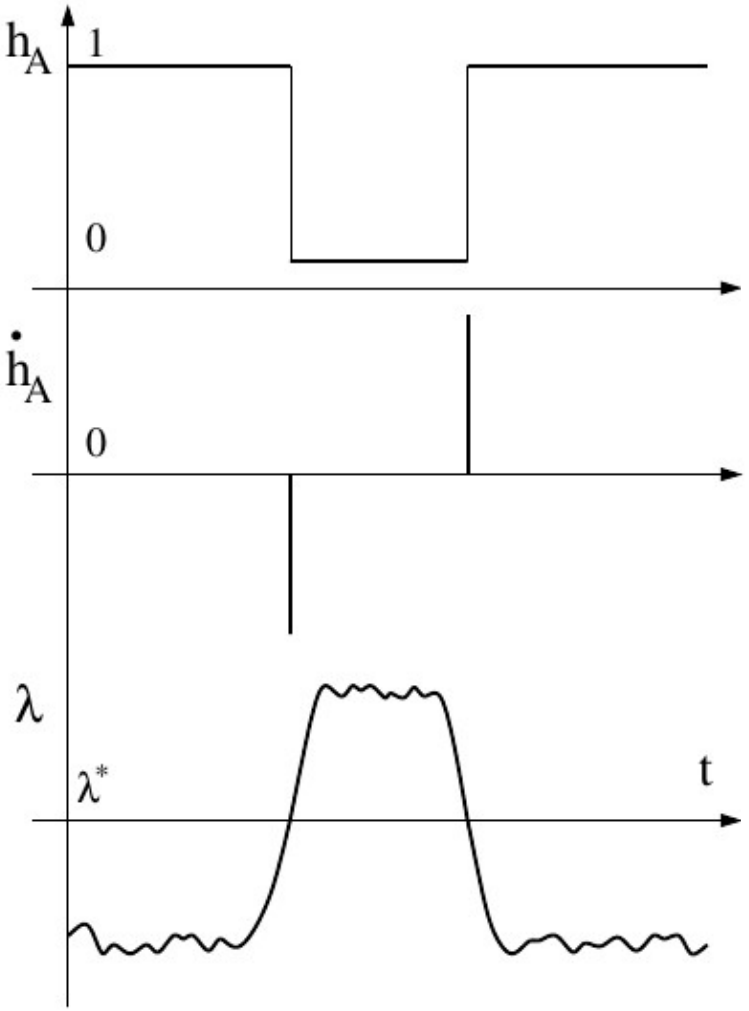
$$t_A^{mr} = \langle h_A \rangle / \nu^{TST}$$

$$t_{A^c}^{mr} = \langle h_{A^c} \rangle / \nu^{TST}$$

$$\langle h_A \rangle = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} h_A(r(t))dt = \int_A \rho(r)dr$$

$$k_{AB} = (t_A^{mr})^{-1} = \frac{\nu^{TST}}{\langle h_A \rangle} \qquad k_{BA} = (t_{A^c}^{mr})^{-1} = \frac{\nu^{TST}}{\langle h_{A^c} \rangle}$$

Transition state theory: vocabulary



$$\nu^{TST} = \lim_{\mathcal{T}\to\infty} \frac{1}{2\mathcal{T}} \int_0^{\mathcal{T}} |\dot{h}_A(r(t))| dt$$

$$= \lim_{\mathcal{T}\to\infty} \frac{1}{2\mathcal{T}} \int_0^{\mathcal{T}} |\nabla h_A(r) \cdot v(t)| dt$$

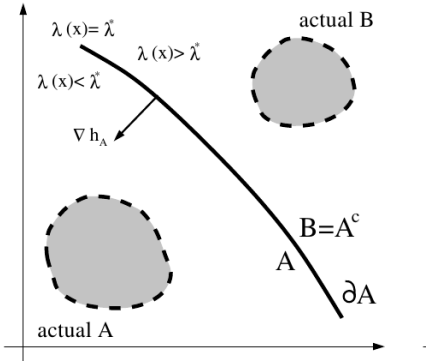
Velocities? Assume dynamic evolution, e.g., NVT-MD.
Invoking ergodicity:

$$= \frac{1}{2} \int_{\mathbb{R}^n \times \mathbb{R}^n} dr dv \rho(r,v) |\nabla h_A(r) \cdot v|$$

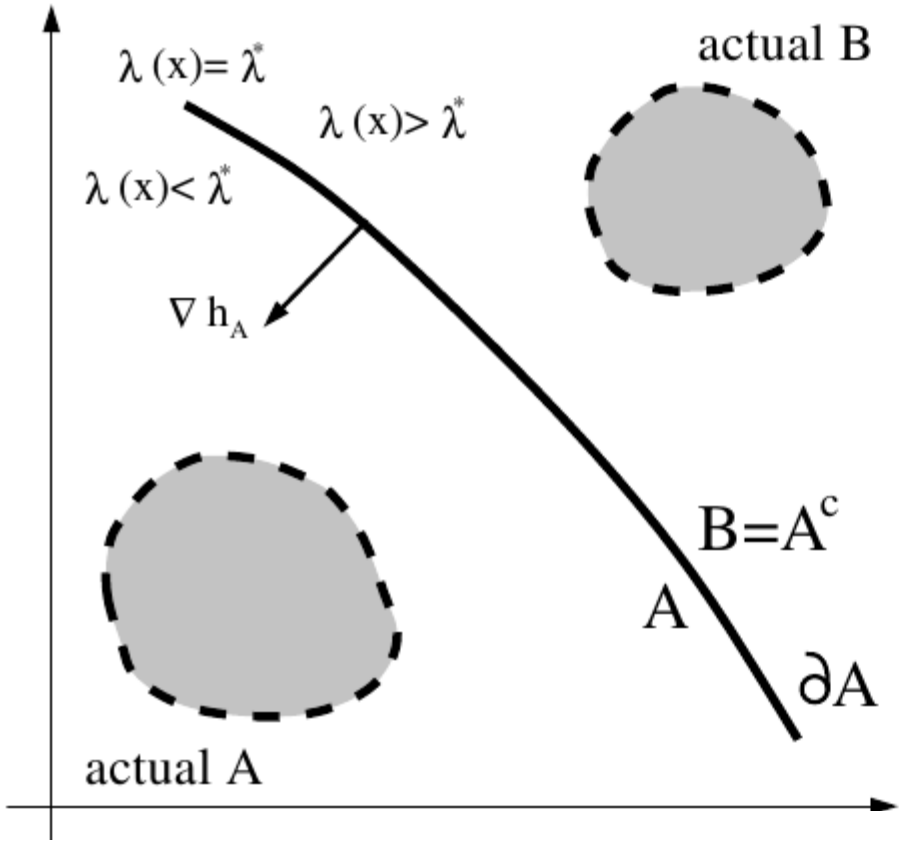
$$\lambda(r) : \mathbb{R}^n \to \mathbb{R}$$

$$A = \{r \in \mathbb{R}^n : \lambda(r) < \lambda^*\}$$

$$\partial A = \{r \in \mathbb{R}^n : \lambda(r) = \lambda^*\}$$



Transition state theory: vocabulary



$$\lambda(r) : \mathbb{R}^n \to \mathbb{R}$$

$$\begin{aligned} A &= \{r \in \mathbb{R}^n : \lambda(r) < \lambda^*\} \\ \partial A &= \{r \in \mathbb{R}^n : \lambda(r) = \lambda^*\} \end{aligned}$$

$$h_A(r) = \theta(-\lambda(r) + \lambda^*)$$

$$\nabla h_A(r) = -\delta(\lambda(r) - \lambda^*)\nabla\lambda$$

$$\begin{aligned} \nu^{TST} &= \frac{1}{2}\int_{\mathbb{R}^n \times \mathbb{R}^n} dr dv \rho(r,v)\delta(\lambda(r) - \lambda^*)|\nabla\lambda \cdot v| \\ &= \frac{1}{2}\int_{\mathbb{R}^n \times \mathbb{R}^n} dr dv \rho(r,v)\delta(\lambda(r) - \lambda^*)|\dot{\lambda}| \\ &\equiv \frac{1}{2}\langle\delta(\lambda(r) - \lambda^*)|\dot{\lambda}|\rangle \\ &= \langle\delta(\lambda(r) - \lambda^*)\dot{\lambda}\theta(\dot{\lambda})\rangle \end{aligned}$$

$$\rho(r,v) = \rho(r,-v)$$

Heaviside step function

Road map

- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

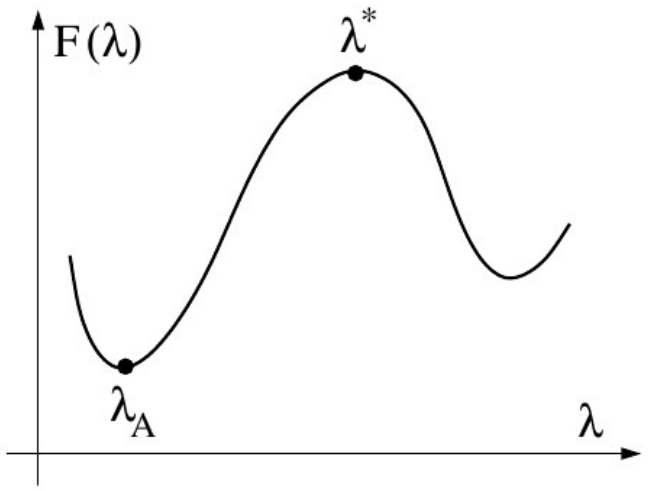
Transition state theory: rate constant

$$\left.\begin{aligned} \int_\Omega \rho(r)dr &= \langle h_\Omega(r)\rangle \\ \nu^{TST} &= \langle \delta(\lambda(r)-\lambda^*)\dot\lambda\theta(\dot\lambda)\rangle \\ k_{AB} &= (t_A^{mr})^{-1} = \frac{\nu^{TST}}{\langle h_A\rangle} \end{aligned}\right\} \quad k_{AB}^{TST} = \frac{\langle \delta(\lambda(r)-\lambda^*)\dot\lambda\theta(\dot\lambda)\rangle}{\langle \theta(\lambda^*-\lambda(r))\rangle}$$

We introduce a free-energy term:

$$e^{-\beta F(\lambda^*)} \equiv \langle \delta(\lambda(r)-\lambda^*)\rangle = \int_{\mathbb{R}^n} dr\rho(r)\delta(\lambda(r)-\lambda^*)$$

$$\begin{aligned} k_{AB}^{TST} &= \frac{\langle \delta(\lambda(r)-\lambda^*)\dot\lambda\theta(\dot\lambda)\rangle}{\langle \delta(\lambda(r)-\lambda^*)\rangle}\,\frac{\langle \delta(\lambda(r)-\lambda^*)\rangle}{\langle \theta(\lambda^*-\lambda(r)\rangle} \\ &= \langle \dot\lambda\theta(\dot\lambda)\rangle_{\lambda=\lambda^*}\,\frac{e^{-\beta F(\lambda^*)}}{\int_{-\infty}^{\lambda^*} e^{-\beta F(\lambda')}d\lambda'} \end{aligned}$$

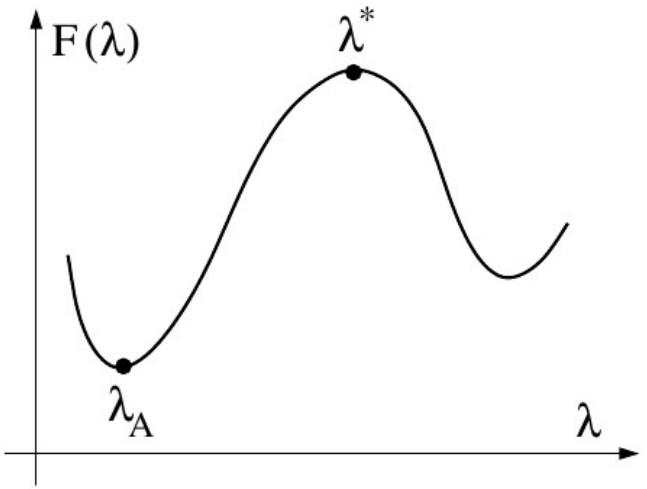


Transition state theory: rate constant

$$k_{AB}^{TST} = \langle \dot{\lambda}\theta(\dot{\lambda})\rangle_{\lambda=\lambda^*} \frac{e^{-\beta F(\lambda^*)}}{\int_{-\infty}^{\lambda^*} e^{-\beta F(\lambda')} d\lambda'}$$

For a double well: approximate the integral with Gaussian around the minimum λ_A

$$k_{AB}^{TST} \propto e^{-\beta(F(\lambda^*)-F(\lambda_A))} \equiv e^{-\beta \Delta F}$$



Dynamical problem (rate constant) turned into static (free-energy difference).

Note the pre-factor! $\langle \dot{\lambda}\theta(\dot{\lambda})\rangle_{\lambda=\lambda^*} = \frac{1}{2}\langle |\dot{\lambda}|\rangle_{\lambda=\lambda^*}$

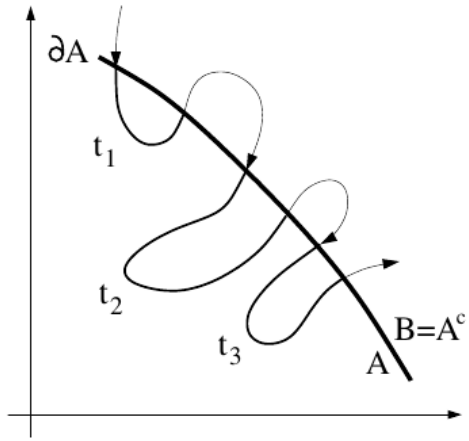
If $\lambda(r) = r_1$ (one of the Cartesian coordinates), then: $\dot{\lambda} = v_1$

Thus: $\sqrt{k_B T/2\pi m}$

Transition state theory: rate constant

$$k_{AB}^{TST} = \langle \dot{\lambda}\theta(\dot{\lambda}) \rangle_{\lambda=\lambda^*} \frac{e^{-\beta F(\lambda^*)}}{\int_{-\infty}^{\lambda^*} e^{-\beta F(\lambda')} d\lambda'}$$

$$k = \frac{\langle |v| \rangle}{2} \frac{Q^{\ddagger}}{Q_R}$$

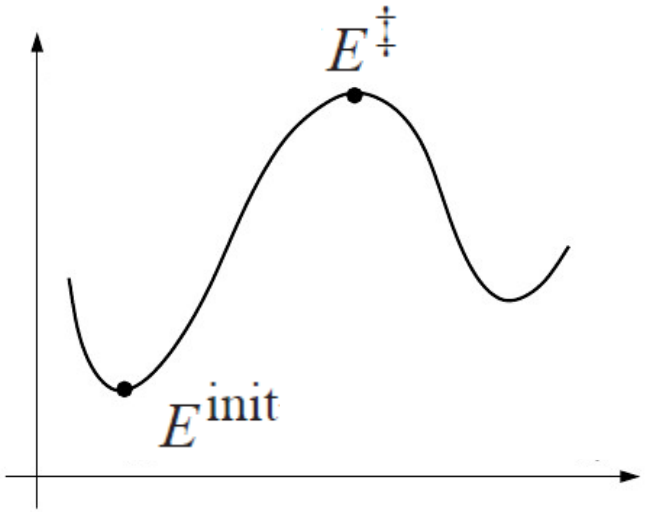


Note: the rate constant is **always** overestimated because the prefactor counts all crossings. This suggest the idea of moving the dividig surface until the number of counting crossings is *minimized*: **variational TST**

Harmonic Transition State Theory:

$$k^{\mathrm{hTST}} = \frac{\prod_i^{3N} \nu_i^{\mathrm{init}}}{\prod_i^{3N-1} \nu_i^{\ddagger}} e^{-(E^{\ddagger} - E^{\mathrm{init}})/k_B T}$$

Vineyard equation



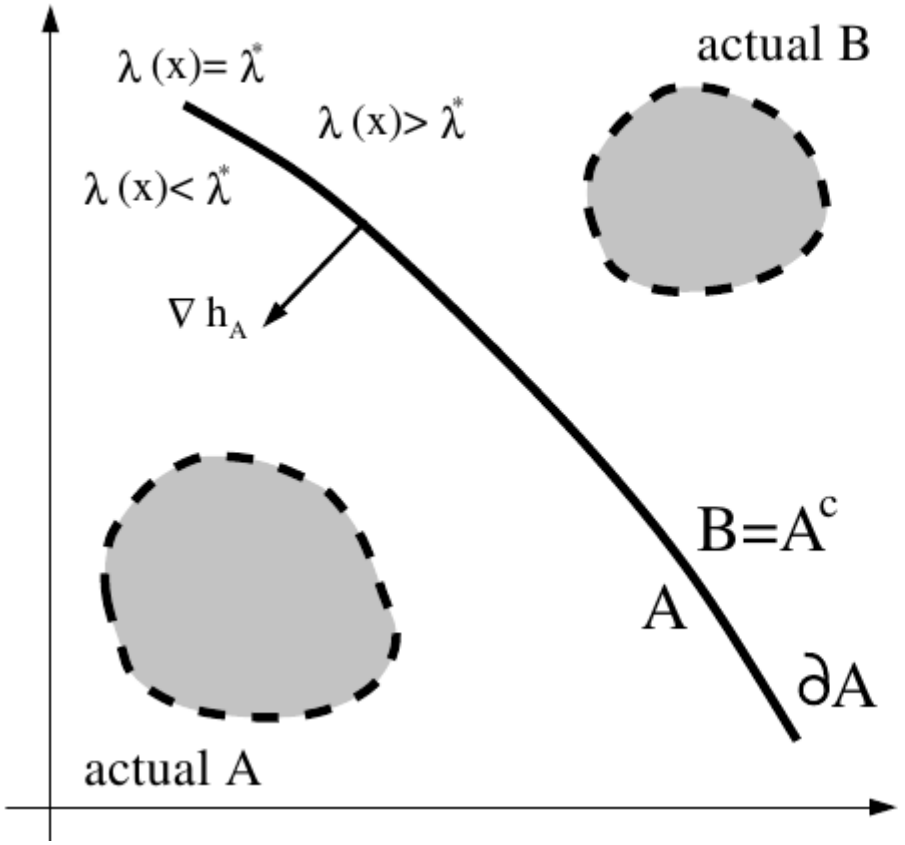
Road map

- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

Transition state theory: Bennet-Chandler approach



Correlation function

$$C(t) \equiv \frac{\langle h_A(0) h_B(t) \rangle}{\langle h_A \rangle}$$

For $\tau_{trans} \ll t \ll \tau_{stable}$:

$$C(t) \simeq (t_A^{mfp})^{-1} t = k_{AB}\, t$$

Key quantity (constant):
reactive flux

$$k(t) \equiv \dot{C}(t)$$

In TST:

$$h_A(r) = \theta(\lambda^* - \lambda(r))$$

$$h_B(r) = \theta(\lambda(r) - \lambda^*)$$

Translational invariance:

$$\langle h_A(0) h_B(t) \rangle = \langle h_A(-t) h_B(0) \rangle$$

$$\frac{d}{dt}\langle h_A(0) h_B(t) \rangle = \frac{d}{dt}\langle h_A(-t) h_B(0) \rangle = -\langle \dot{h}_A(-t) h_B(0) \rangle = -\langle \dot{h}_A(0) h_B(t) \rangle$$

Transition state theory: Bennet-Chandler approach

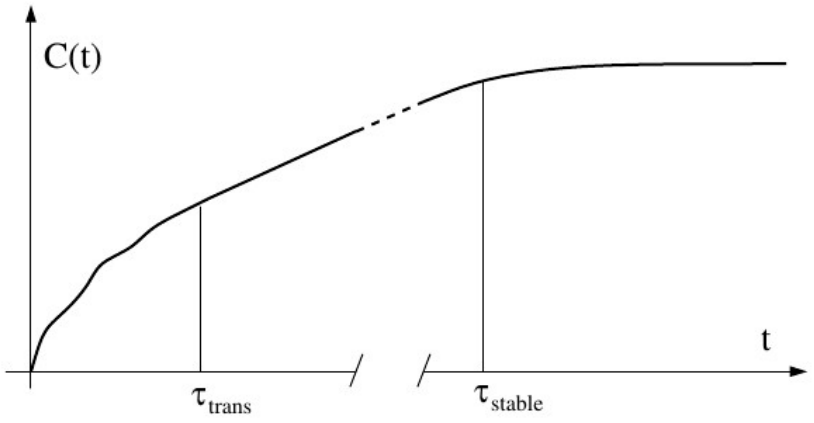
$$\frac{d}{dt}\langle h_A(0)h_B(t)\rangle = \frac{d}{dt}\langle h_A(-t)h_B(0)\rangle = -\langle \dot{h}_A(-t)h_B(0)\rangle = -\langle \dot{h}_A(0)h_B(t)\rangle$$

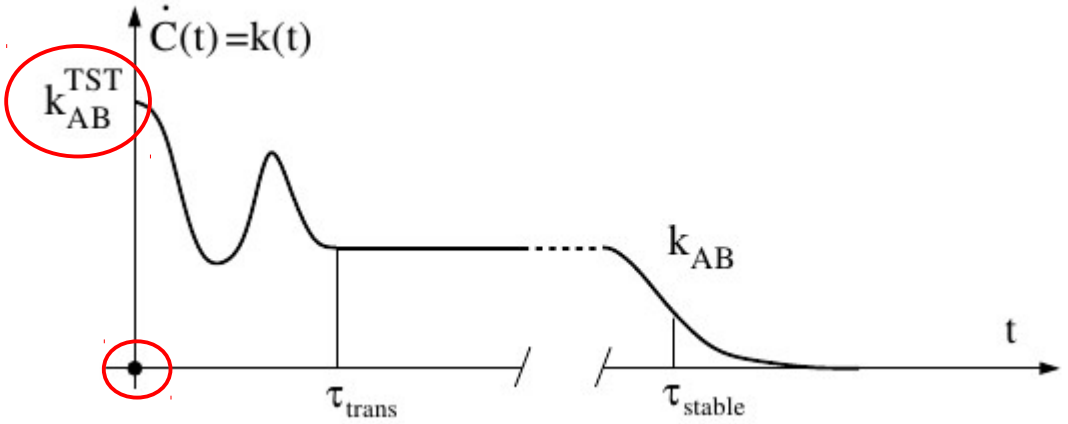
$$C(t) \equiv \frac{\langle h_A(0)h_B(t)\rangle}{\langle h_A\rangle}$$

$$h_A(r) = \theta(\lambda^* - \lambda(r))$$
$$h_B(r) = \theta(\lambda(r) - \lambda^*)$$

$$\dot{C}(t) = \frac{\langle \delta(\lambda^* - \lambda_0)\dot{\lambda}_0\theta(\lambda_t - \lambda^*)\rangle}{\langle \theta(\lambda^* - \lambda_0)\rangle}$$

$\lambda(r(t))$





Transition state theory: Bennet-Chandler approach

$$
\begin{aligned}
\dot{C}(t) &= \frac{\langle \delta(\lambda^* - \lambda_0)\dot{\lambda}_0 \theta(\lambda_t - \lambda^*)\rangle}{\langle \delta(\lambda^* - \lambda_0)\rangle} \frac{\langle \delta(\lambda^* - \lambda_0)\rangle}{\langle \theta(\lambda^* - \lambda_0)\rangle} \\
&= \langle \dot{\lambda}_0 \theta(\lambda_t - \lambda^*)\rangle_{\lambda_0=\lambda^*} \frac{e^{-\beta F(\lambda^*)}}{\langle \theta(\lambda^* - \lambda_0)\rangle} \\
&\equiv R(t) \frac{e^{-\beta F(\lambda^*)}}{\langle \theta(\lambda^* - \lambda_0)\rangle} = \frac{R(t)}{R(0^+)} R(0^+) \frac{e^{-\beta F(\lambda^*)}}{\langle \theta(\lambda^* - \lambda_0)\rangle} \\
&= \frac{\langle \dot{\lambda}_0 \theta(\lambda_t - \lambda^*)\rangle_{\lambda_0=\lambda^*}}{\langle \dot{\lambda}_0 \theta(\dot{\lambda}_0)\rangle_{\lambda_0=\lambda^*}} \langle \dot{\lambda}_0 \theta(\dot{\lambda}_0)\rangle_{\lambda_0=\lambda^*} \frac{e^{-\beta F(\lambda^*)}}{\langle \theta(\lambda^* - \lambda_0)\rangle} \\
&= k_{AB}^{TST} \frac{\langle \dot{\lambda}_0 \theta(\lambda_t - \lambda^*)\rangle_{\lambda_0=\lambda^*}}{\langle \dot{\lambda}_0 \theta(\dot{\lambda}_0)\rangle_{\lambda_0=\lambda^*}} \equiv k_{AB}^{TST} \kappa(t)
\end{aligned}
$$

Algorithm:

1) Choice of reaction coordinate $\lambda(r)$
   Actually crucial!
2) Free energy calculation $e^{-\beta F(\lambda^*)}$
   Via umbrella sampling, metadynamics, ...
3) Evaluation of the transmission coefficient $R(t)$

Road map

- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

Rate constant methods for different kinds of PES

- "Smooth" – Interested in saddle points connecting adjacent states – e.g. adatom hop on metallic surface

- "Rugged" – Smooth Potential Energy Surface – But interested in deep states separated by many minima – e.g. transformation of Lennard-Jones cluster from one structure to another

- "Rough" – Interested in deep states separated by many "minima" – Minima difficult to define or hard to count – e.g. autoionization of water

Rate constant methods for different kinds of PES

	Both initial and final state known: “Double-ended” search	Only initial state known: “Single-ended” search
Smooth	Nudged Elastic Band String method Growing string method	Hessian-based methods Dimer Activation-Relaxation technique
Rugged	Discrete Path Sampling	Accelerated Molecular On-the-fly KMC (aKMC)
Rough	Transition Path Sampling	Transition Interface Sampling Forward Flux Sampling

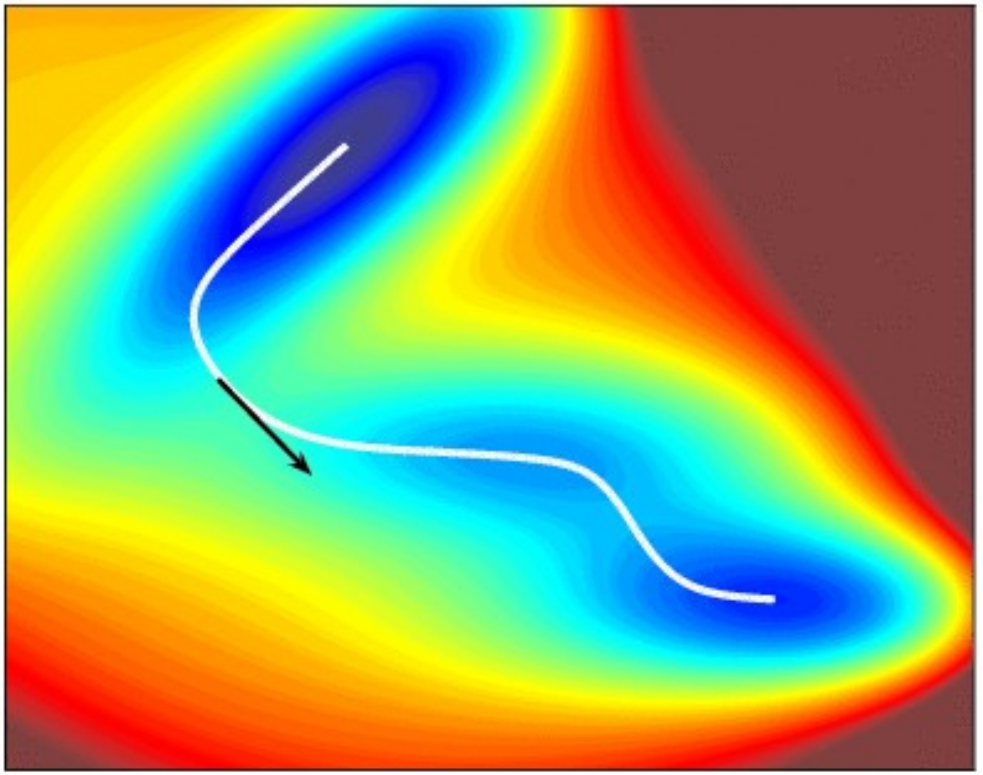
Road map

- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

Minimum Energy Path



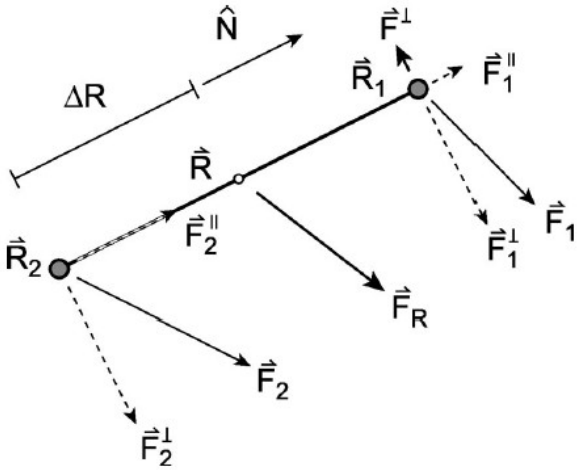
MEP:
- it connects two metastable states
- any point on the path in an energy minimum in all directions perpendicular to the path

$$[\nabla U]^{\perp} = 0$$

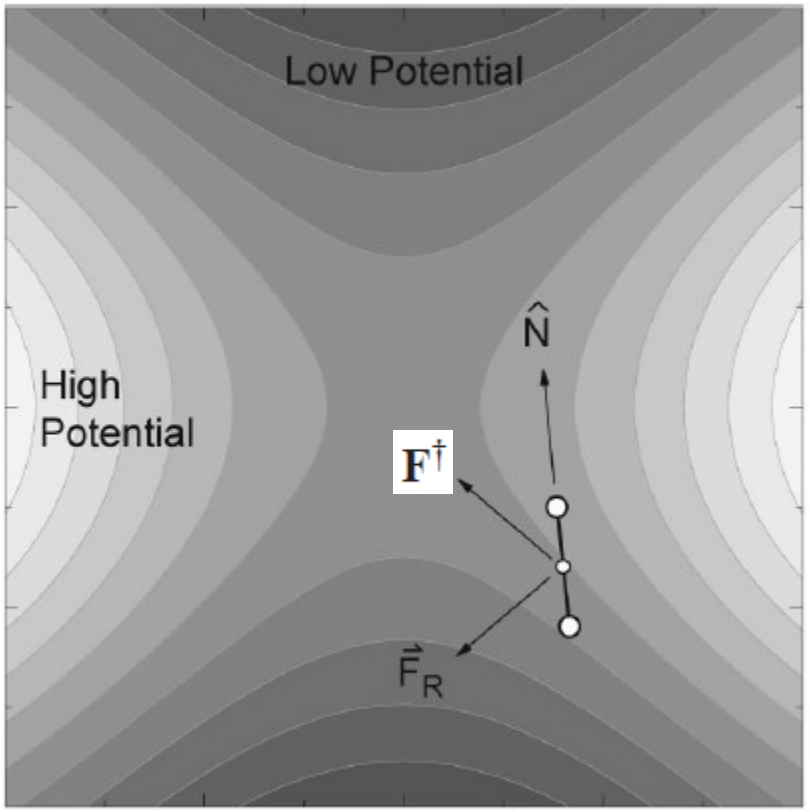
- The path passes through at least one first-order saddle point.

- It can be described as the union of steepest descent paths from the saddle point(s) to the minima

Single ended method: Dimer method



The dimer is rotated in order to find the lowest curvature mode of the potential energy at the point where the dimer is located.



Translation:

$$\mathbf{F}^{\dagger} = \mathbf{F}_R - 2\mathbf{F}^{\parallel}$$

G. Henkelman and H. Jónsson, J. Chem. Phys. 111, 7010 1999

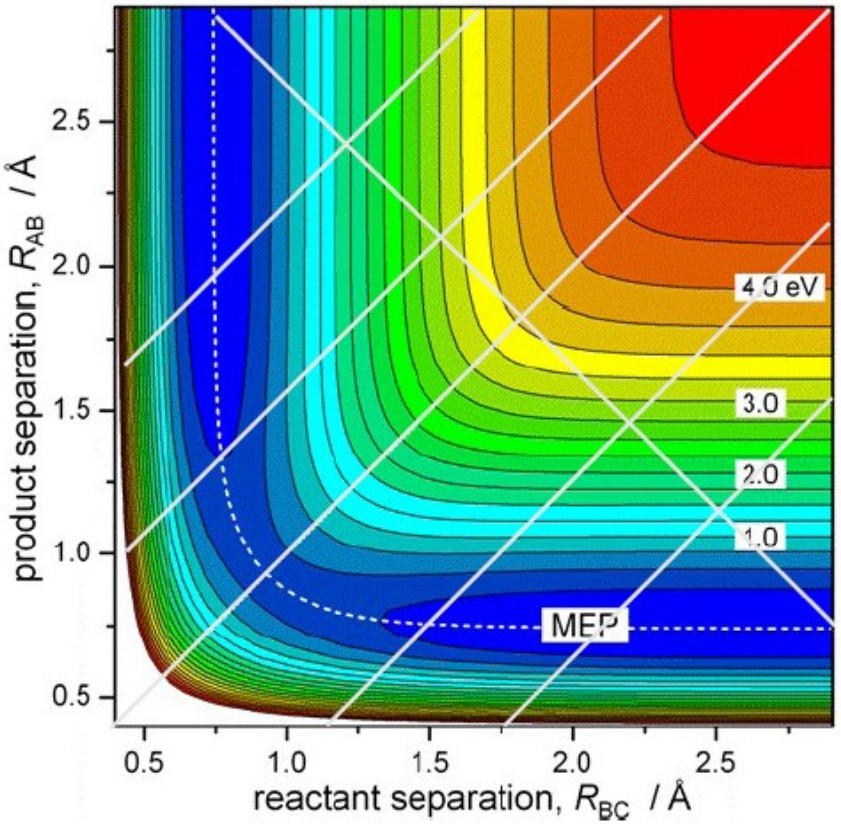
Road map

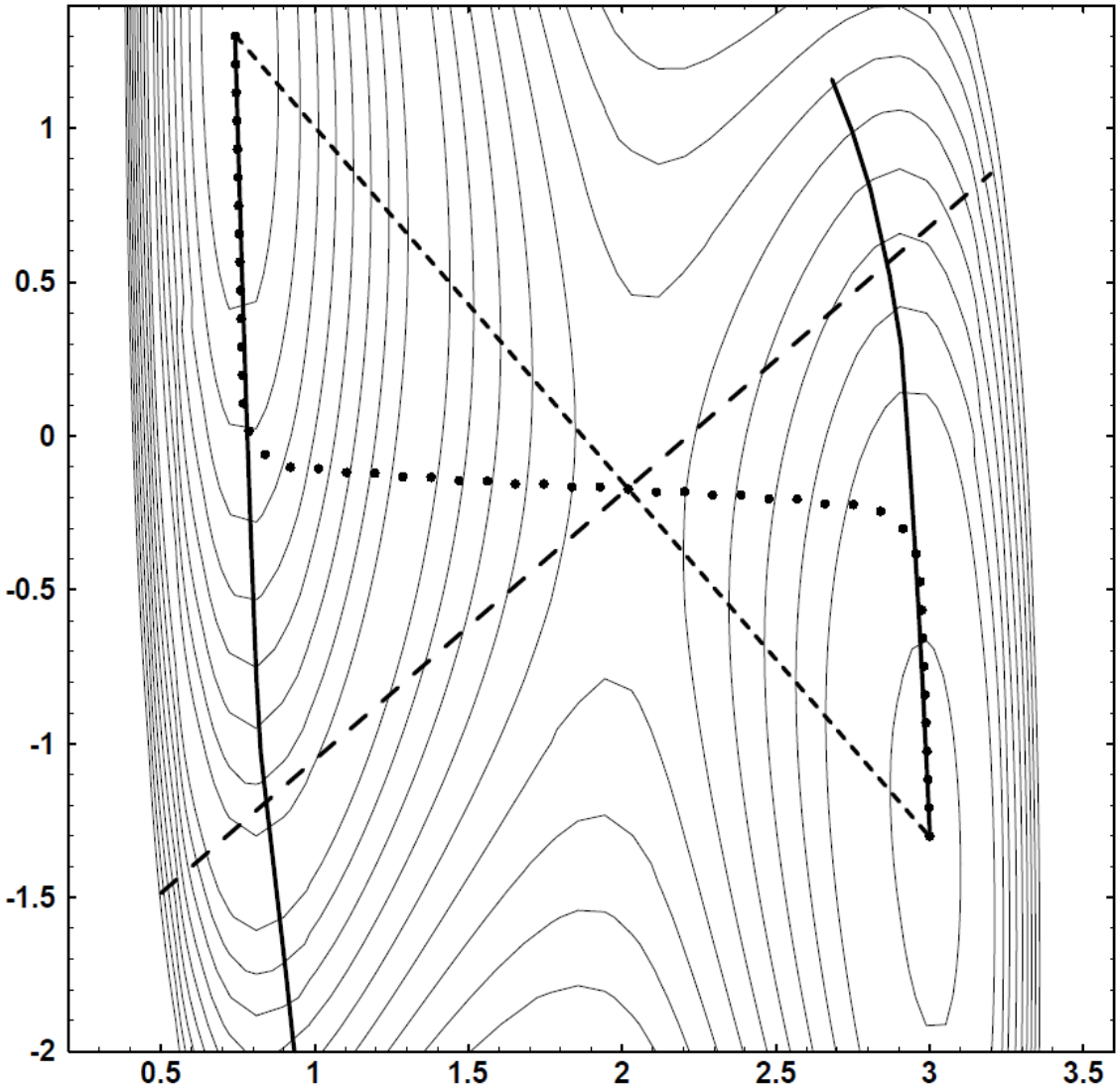
- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

Drag method





One degree of freedom, the drag coordinate, is chosen and is held fixed while all other D-1 degrees of freedom are relaxed, i.e. the energy of the system minimized in a D-1 dimensional hyperplane.

Road map

- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

Elastic Band

A string of images is defined: $[\mathbf{R}_0, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N]$

Initial state, (Reactant)

Final state (Product)

Idea: all images are optimized along all direction perpendicular to the string, while a series of string keep the image to collapse to either minimum.
The simplest implementation is:

$$S(\mathbf{R}_1, \ldots, \mathbf{R}_N) = \sum_{i=1}^{N-1} E(\mathbf{R}_i) + \sum_{i=1}^{N} \frac{k}{2}(\mathbf{R}_i - \mathbf{R}_{i-1})^2 \qquad (1)$$

It does not work because of:
- “corner cutting”: where object MEP is highly curved, springs tend to pull away from MEP
- “sliding down” : fewer images near the saddle point

Both problems are mended by force projections: this is the “nudging”

Nudged Elastic Band

$$\mathbf{F}_i = -\nabla E(\mathbf{R}_i)|_\perp + \mathbf{F}_i^s \cdot \hat{\tau}_i \, \hat{\tau}_i$$

$$\nabla E(\mathbf{R}_i)|_\perp = \nabla E(\mathbf{R}_i) - \nabla E(\mathbf{R}_i) \cdot \hat{\tau}_{||} \, \hat{\tau}_{||}$$

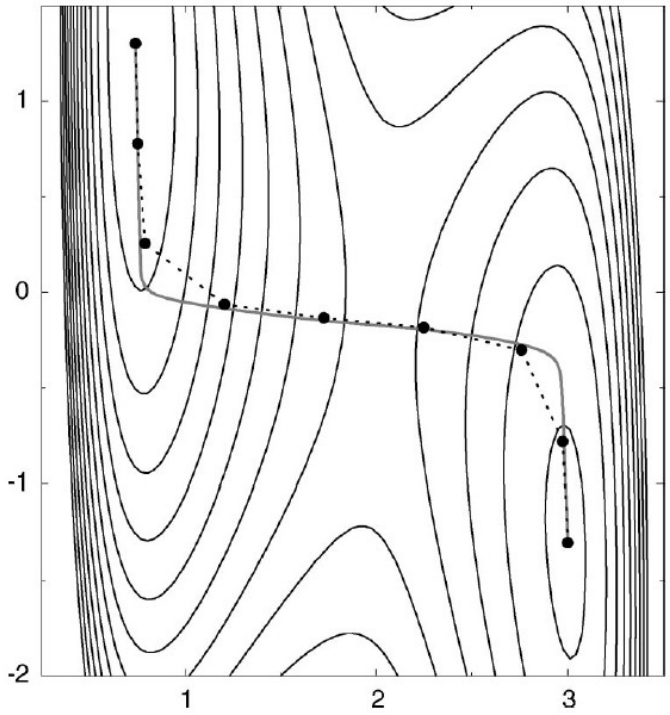
$$\mathbf{F}_i^s|_{||} = k\left(|\mathbf{R}_{i+1} - \mathbf{R}_i| - |\mathbf{R}_i - \mathbf{R}_{i-1}|\right)\hat{\tau}_i$$

Definition of tangent:

$$\hat{\tau}_i = \frac{\mathbf{R}_{i+1} - \mathbf{R}_{i-1}}{|\mathbf{R}_{i+1} - \mathbf{R}_{i-1}|}$$

Better definition of tangent:

$$\tau_i = \frac{\mathbf{R}_i - \mathbf{R}_{i-1}}{|\mathbf{R}_i - \mathbf{R}_{i-1}|} + \frac{\mathbf{R}_{i+1} - \mathbf{R}_i}{|\mathbf{R}_{i+1} - \mathbf{R}_i|}$$



- H. Jónsson, G. Mills, and K. W. Jacobsen, Classical and Quantum Dynamics in Condensed Phase Simulations, edited by B. J. Berne, G. Ciccotti, and D. F. Coker World Scientific, Singapore, 1998, pp. 385–404.
- G. Henkelman and H. Jónsson, J. Chem. Phys. 113, 9978 2000.
- G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. 113, 9901 2000

Climbing Image - Nudged Elastic Band

To improve location of the saddle point (after all the core of the business), after few iterations the highest energy image is singled out and a different evolution is applied:

$$\mathbf{F}_{i_{\max}} = -\nabla E(\mathbf{R}_{i_{\max}}) + 2\nabla E(\mathbf{R}_{i_{\max}})\big|_{\parallel}$$

$$= -\nabla E(\mathbf{R}_{i_{\max}}) + 2\nabla E(\mathbf{R}_{i_{\max}}) \cdot \hat{\boldsymbol{\tau}}_{i_{\max}} \hat{\boldsymbol{\tau}}_{i_{\max}}$$

There are other optimizers to converge efficiently to the saddle point once a good guess is found via NEB.

Note that, once the saddle point is known “exactly”, the MEP can be reconstructed to any level of accuracy by steepest descent to both minima

Road map

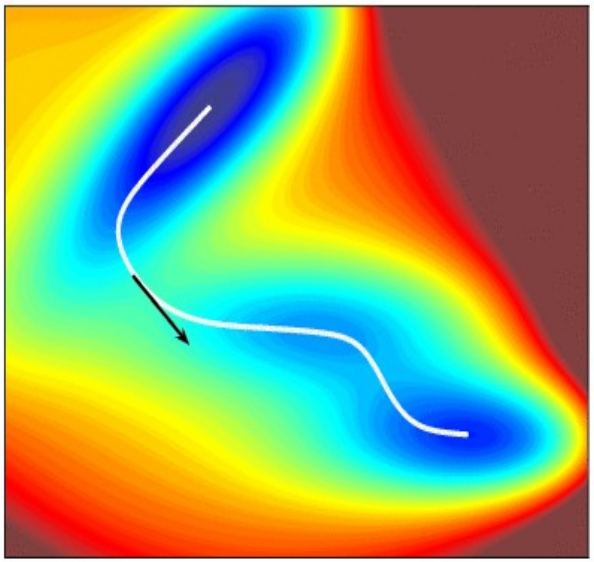
- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

String method

$$[\nabla U]^{\perp} = 0$$



Parameterization of the curve the evolves into the MEP

$$\gamma(t) = \{\varphi(\alpha, t) : \alpha \in [0,1]\} \qquad |\varphi'| = \text{constant}$$

(wrt α)

Choice: Equal-arc-length parameterization

$$\dot{\varphi} = -[\nabla U(\varphi)]^{\perp} + \lambda\hat{\tau} \qquad \hat{\tau} = \varphi'/|\varphi'|$$

Unit tangent vector along the string

Discretization $\{\varphi_i(t),\ i = 0, 1, \ldots, N\}$, where $\varphi_i(t) = \varphi(\alpha = i/N, t)$

1. Evolution of the string

$$\dot{\varphi}_i = -\nabla U(\varphi_i)$$

2. Reparameterization of the string

W. E, W. Ren, and E. Vanden–Eijnden, PRB 66, 052301 2002.
W. E, W. Ren, and E. Vanden–Eijnden, JCP 126, 164103 2007.

2a $\ell(0) = 0, \quad \ell(i/N) = \sum_{j=1}^{i} |\varphi_j - \varphi_{j-1}|, \quad i = 1, \ldots, N$

(arc-length function)

2b interpolate (e.g. cubic spline) to get: $\ell(\alpha_i) = \dfrac{i}{N}\ell(1)$

Road map

- Setting the stage: The random telegraph

- Transition state theory: the vocabulary
- TST: definition of the rate constant
- Bennet-Chandler TST: recrossing-free rate constant
- Classification of methods for evaluating rate constants

- The Minimum Energy Path
- Minimum energy path search (at zero kelvin) for rate constants:
-- the Nudged Elastic Band approach
-- the String Method
-- the Growing String Method

Growing String Method

The string is a path connecting reactant to product

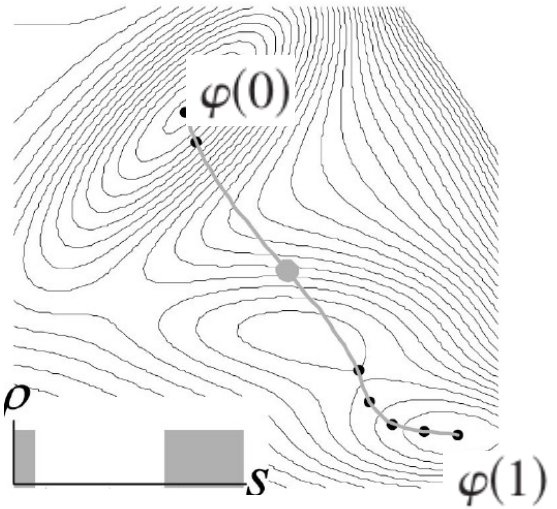
$\varphi(\sigma)$

σ is monotonic function of the arclength s

$\sigma(s)$

which is determined by the parameterization density

$\rho(s)$



Evolution step:

unit tangent vector

$$\mathbf{f}^{\perp}(\varphi(\sigma)) = -\nabla V(\varphi(\sigma)) + (\hat{\mathbf{t}}(\sigma)^{T}\nabla V(\varphi(\sigma)))\hat{\mathbf{t}}(\sigma)$$

MEP condition:

$$\mathbf{f}^{\perp}(\varphi_{\mathrm{MEP}}) = 0$$

implies minimization of the functional:

$$F[\varphi] = \int_0^1 d\sigma \mathbf{f}^{\perp}(\varphi(\sigma))^{T}\mathbf{f}^{\perp}(\varphi(\sigma))$$

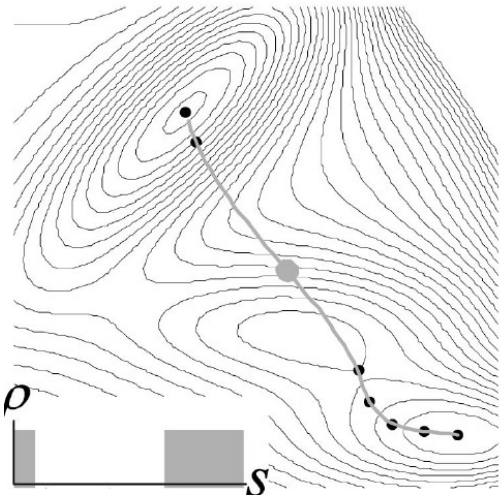
B. Peters, A. Heyden, A. T. Bell, and A. Chakraborty, J. Chem. Phys. 120, 7877 2004.

Growing String Method

$$F[\varphi] = \int_0^1 d\sigma \mathbf{f}^{\perp}(\varphi(\sigma))^T \mathbf{f}^{\perp}(\varphi(\sigma)) \quad \text{minimized}$$

Discretization:

$$F(\varphi(\sigma_0), \varphi(\sigma_1), \ldots, \varphi(\sigma_n)) = \sum_{k=0}^{n} |\mathbf{f}^{\perp}(\varphi(\sigma_k))|^2$$



Reparameterization step

$\sigma(s)$ uniform in $\sigma = 0, 1/n, 2/n, \ldots,$ and 1

$s(\sigma)$ $s(0) = 0$ $s(1) = 1$

parametrization density

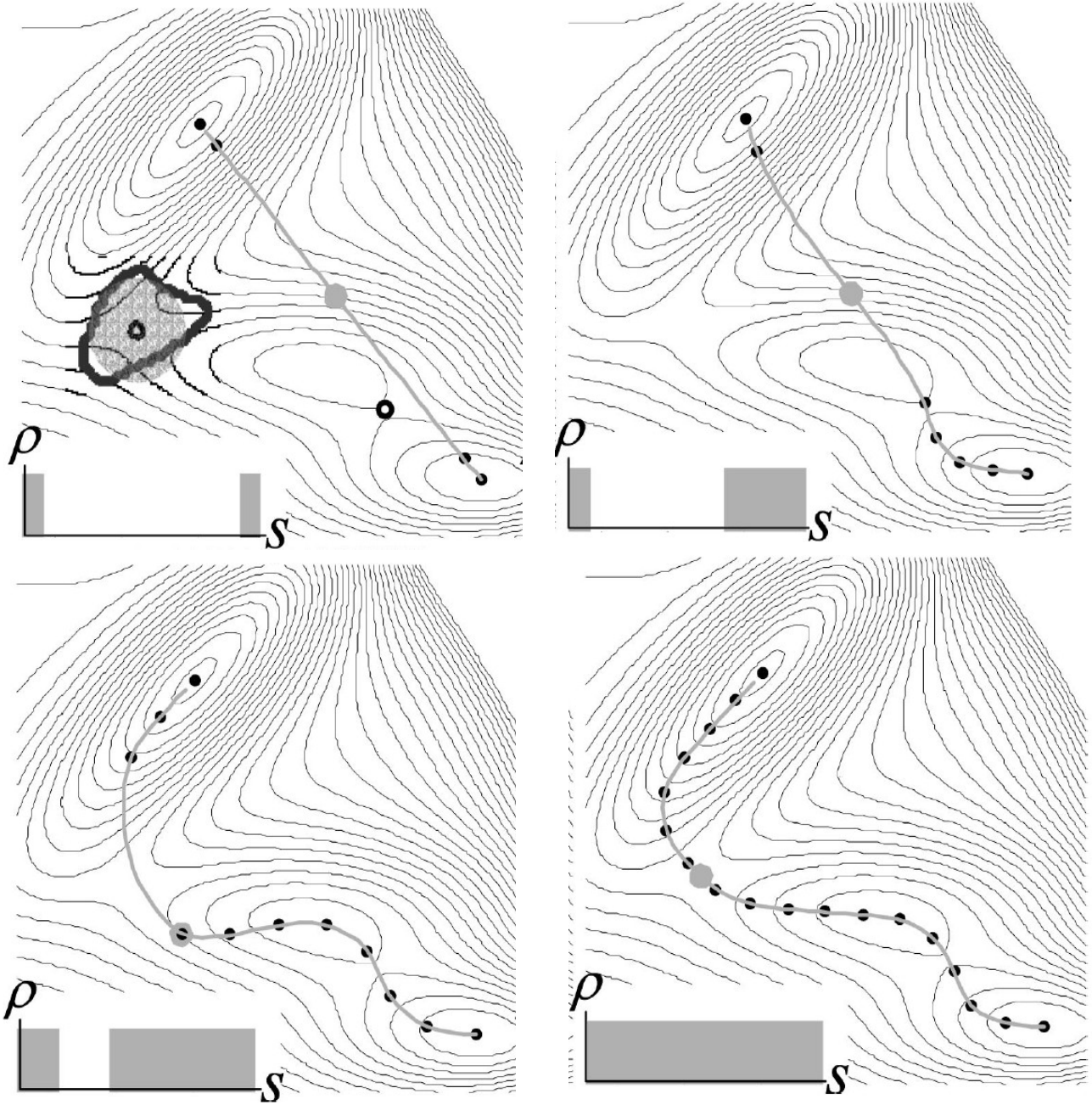
$$c = \int_0^1 \rho(s) ds$$

$$\sigma_k = k/n$$

$$\int_0^{s_k} \rho(s) ds = c\sigma_k$$

B. Peters, A. Heyden, A. T. Bell, and A. Chakraborty, J. Chem. Phys. 120, 7877 2004.

Growing String Method

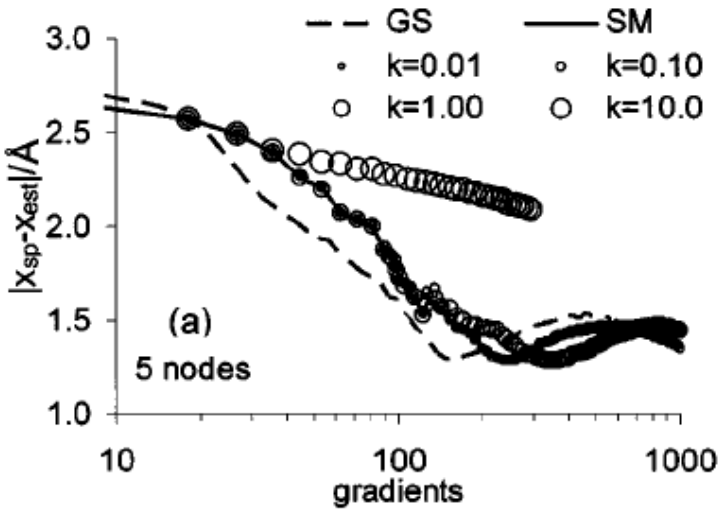


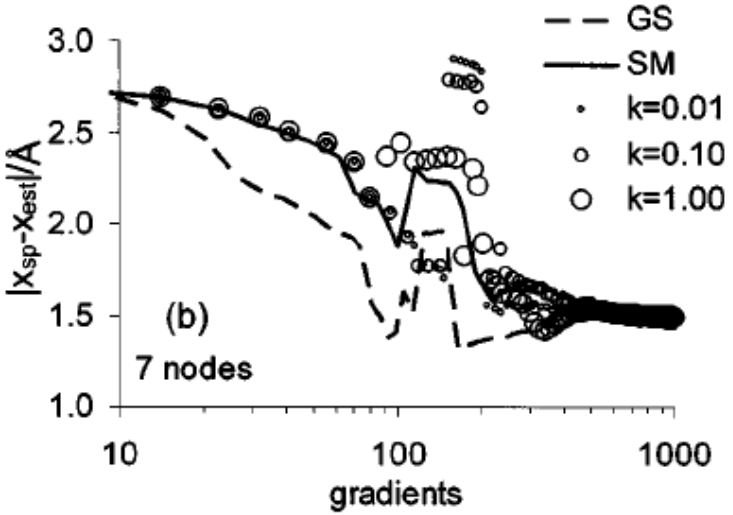
$$\rho_k(s) = \begin{cases} 1 & \text{if } s \in [0, a_1^{(k)}] \\ 0 & \text{if } s \in (a_1^{(k)}, a_2^{(k)}) \\ 1 & \text{if } s \in [a_2^{(k)}, 1], \end{cases}$$

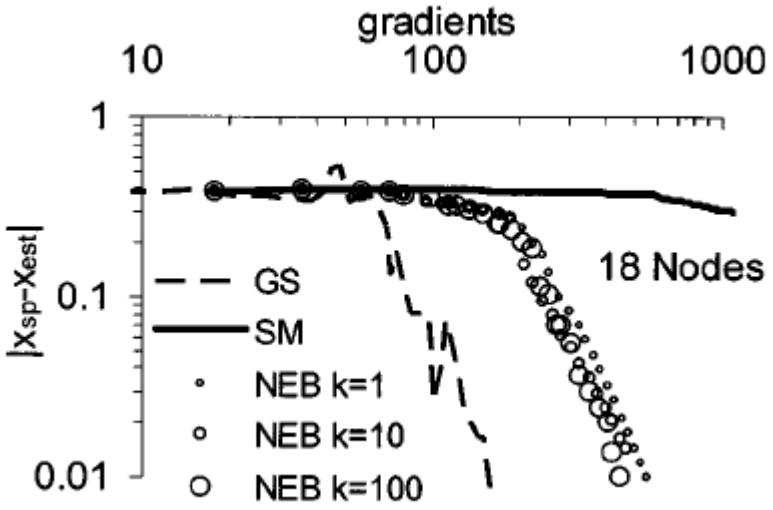
Parametrization density extended beyond a_1 and a_2 depending on the size of $|\mathbf{f}^{\perp}|$

Growing String Method

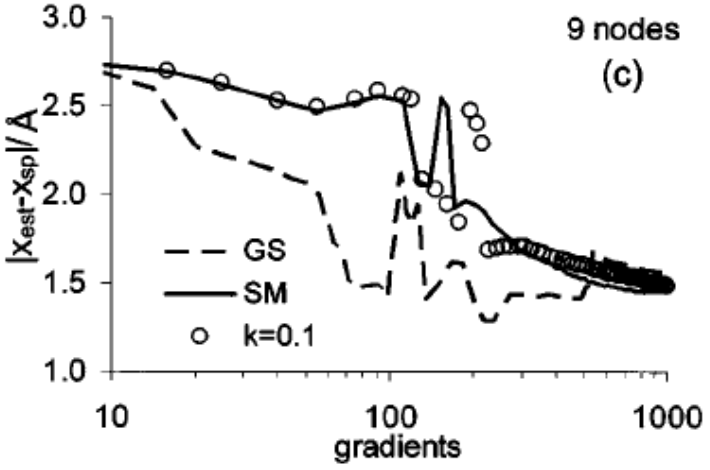
Alanine-dipeptide







Müller-Brown potential



Optimizers

- **Steepest Descent**

$$\mathbf{R}_{j+1} = \mathbf{R}_j + \alpha \mathbf{F}_j$$

Converges if α is less than $1/k_{\max}$, where $k_{\max}$ is the max curvature.

- **Conjugated gradients**

- **FIRE**, Fast Inertial Relaxation Engine (modified **quick-min**)

Quick-min projects "velocity" in the direction of the force and sets to zero "velocity" if antiparallel to the force. Then a Euler like step is taken:

$$\mathbf{R}_{j+1} = \mathbf{R}_j + \Delta t \mathbf{V}_j, \quad \mathbf{V}_{j+1} = \mathbf{V}_j + \Delta t \mathbf{F}_j$$

In addition, **FIRE**, makes the "Δt" adaptive and retains "velocity" component perpendicular to the force.

- **BFGS / L-BFGS / trusted-radius method / damped-BFGS**

- **Global** vs **local**. In global optimizer, all images are optimized at once

D. Sheppard, R. Terrell, and G. Henkelman, J. Chem. Phys. 128, 134106 2008.

Performance in short

- G. Henkelman, B. P. Uberuaga, and H. Jonsson, JCP 113, 9901 (2000)
- B. Peters, A. Heyden, A. T. Bell, and A. Chakraborty, JCP 120, 7877 (2004)
- P. Zimmerman, JCTC 9, 3043 (2013)
- Y. Yao and LMG (unpublished)

- Using internal rather than Cartesian coordinates is in general advisable

- Global optimizers outperform local optimizers

- The best optimizers are in the BFGS family

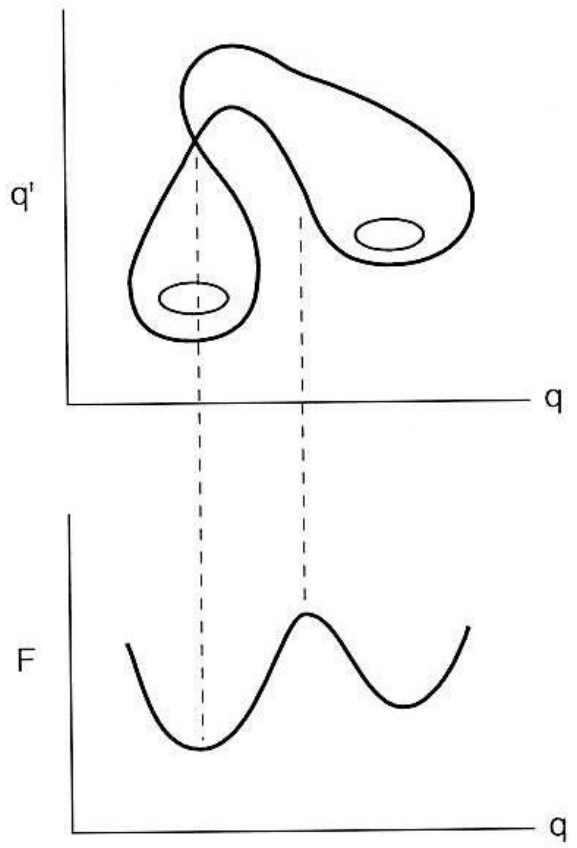
- Growing String Method normally outperforms NEB and SM

- **Growing String Method never fails convergence** (while for other methods it may heavily depend on good choice of initial set of images and other parameters for converging)

There is need of a well balanced test set!!!
(Beyond Müller-Brown and alanine-dipeptide)

Final remarks

- Beware of low dimensional “reaction coordinates”. The coordinate along the MEP is a natural reaction coordinate. Can it be related to anything intuitive? Can it be “interpreted”?



- For rugged and rough PES, the transition-path (MEP) concept is generalized (at finite T) into transition tube (actually, can be many tubes).

  The natural reaction coordinate is then the “commitor” function: to each point in the configurational space, one can assign the probability that a trajectory – assuming some dynamics - passing through it ends in the product set.

  The transition state becomes a transition ensemble (commitor level = 1/2)

  Daniele Moroni, PhD thesis. http://www-theor.ch.cam.ac.uk/people/moroni/thesis.html

- We have in implementation of chain-of-state methods (NEB, SM, GSM) with various optimizers, coupled to FHI-aims: aimsChain (look for the microtutorial).