Chemical dynamics and rare events in soft matter physics

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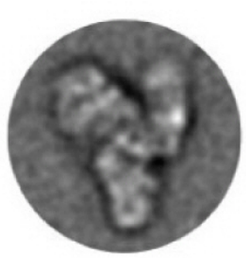
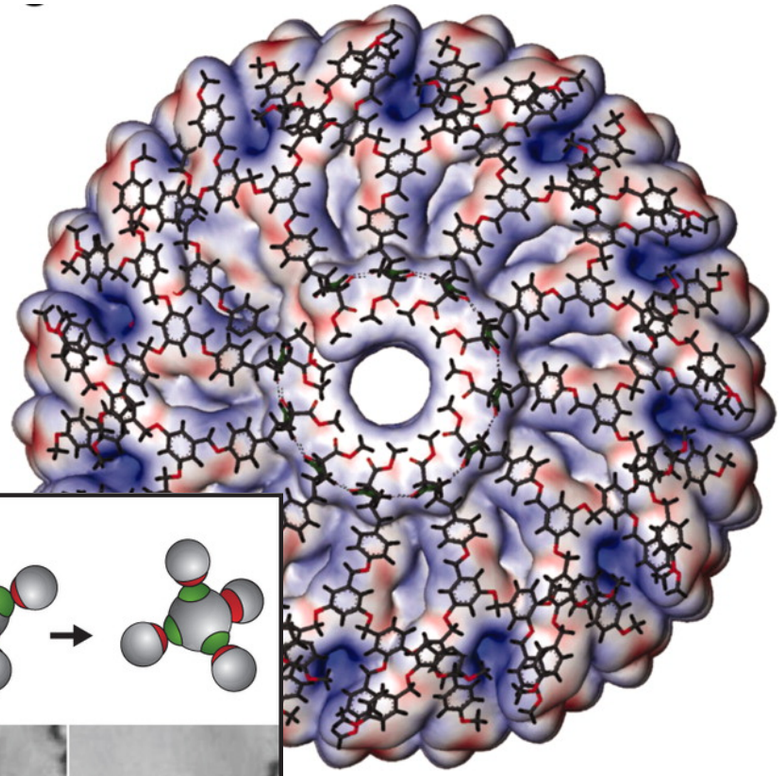
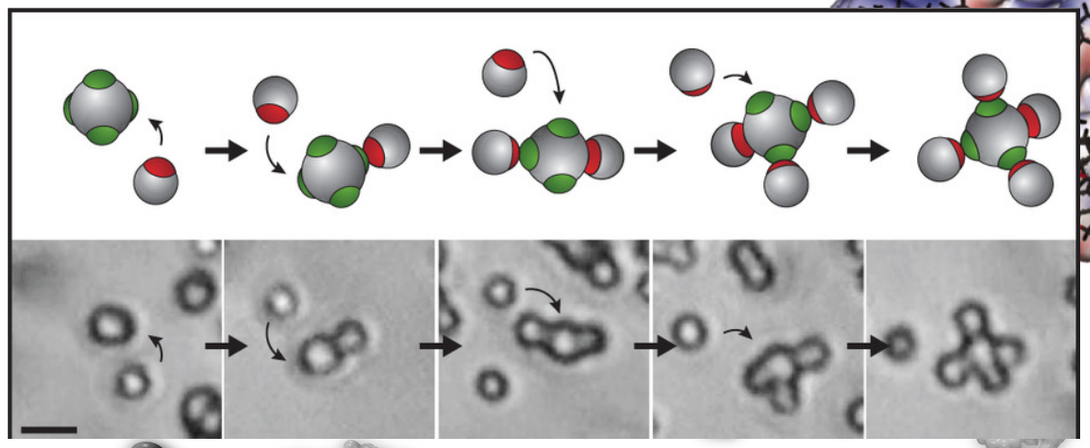
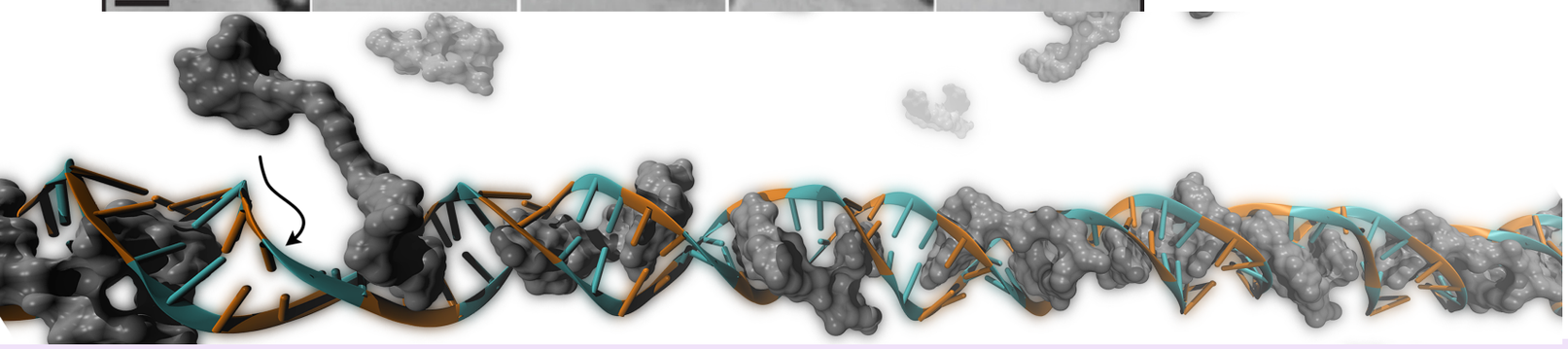
Big picture

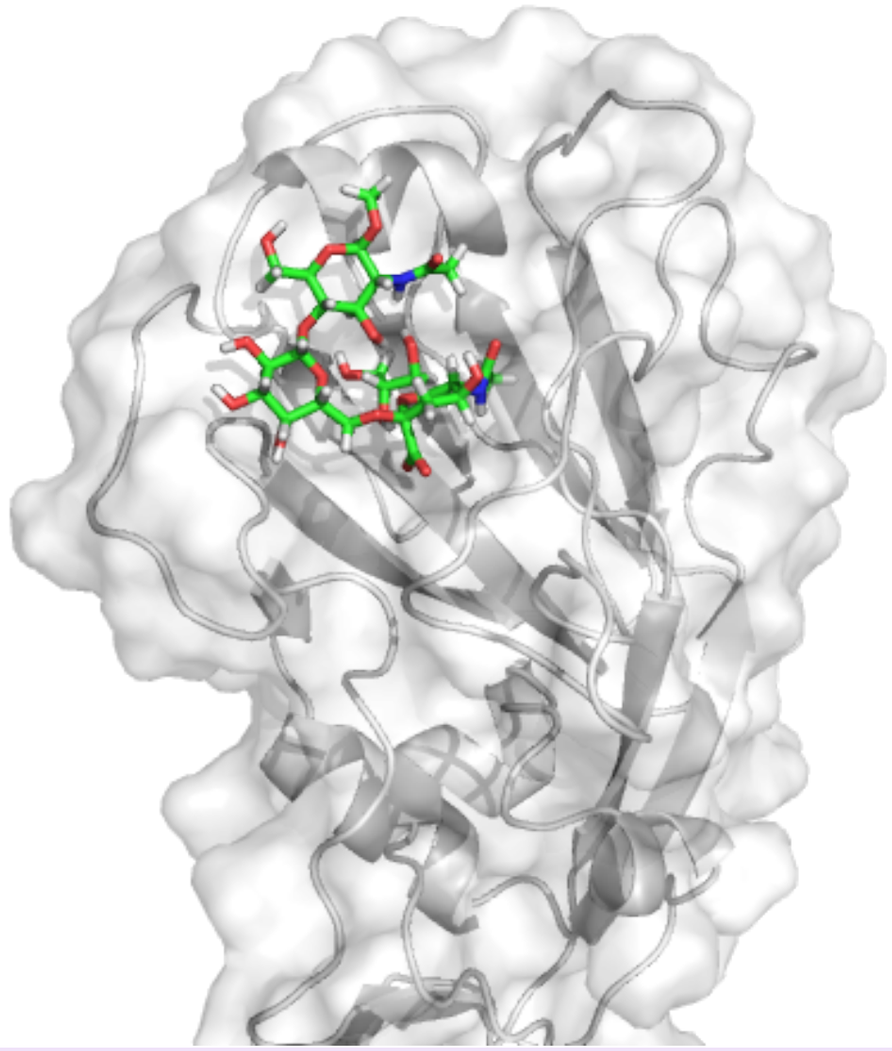
- systems of interest in biology, materials, catalysis…











Outline

- motivation
- from *ab initio* to energy landscapes
- friction
- chemical dynamics and the transition state theory
- molecular simulations and the relaxation path sampling
- future directions

Molecules and reactions

- description of system in physics - position x and velocity v

$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} = \mathbf{f}(\mathbf{x}, \mathbf{v}, t) \qquad \frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = \mathbf{g}(\mathbf{x}, \mathbf{v}, t)$$

- molecules - clusters of atoms bound by strong bonds
- system described by identity of species and concentration

$$\frac{\mathrm{d}\mathbf{c}}{\mathrm{d}t} = \mathbf{h}(\mathbf{c}, t)$$

- solving rate equations -> chemical kinetics

The first principles

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." (Paul Dirac)

$$\Psi(x_1^e, x_2^e, ..., x_{3M\times n}^e, x_1^n, x_2^n, ..., x_{3N\times n}^n)$$

$$\psi(x_1^e, x_2^e, ..., x_{3M}^e, x_1^n, x_2^n, ..., x_{3N}^n)$$

$$\psi(x_1^e, x_2^e, ..., x_{3M}^e; x_1^n, x_2^n, ..., x_{3N}^n)$$

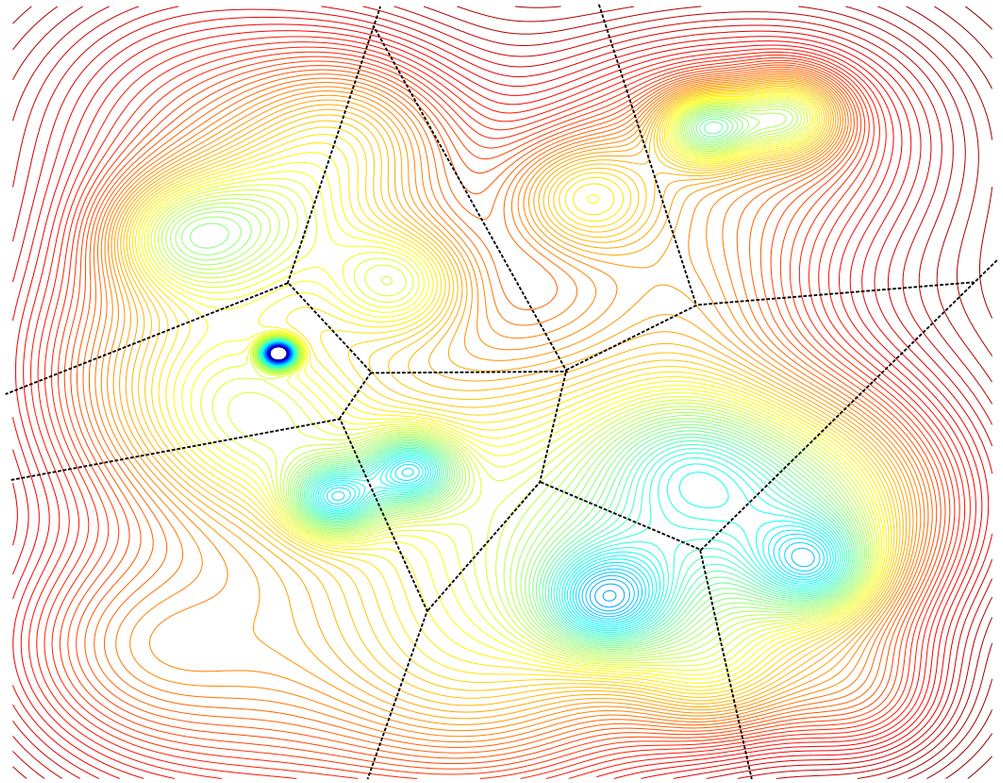
- separation of molecules
- separation of motion - nuclei static compared to electrons

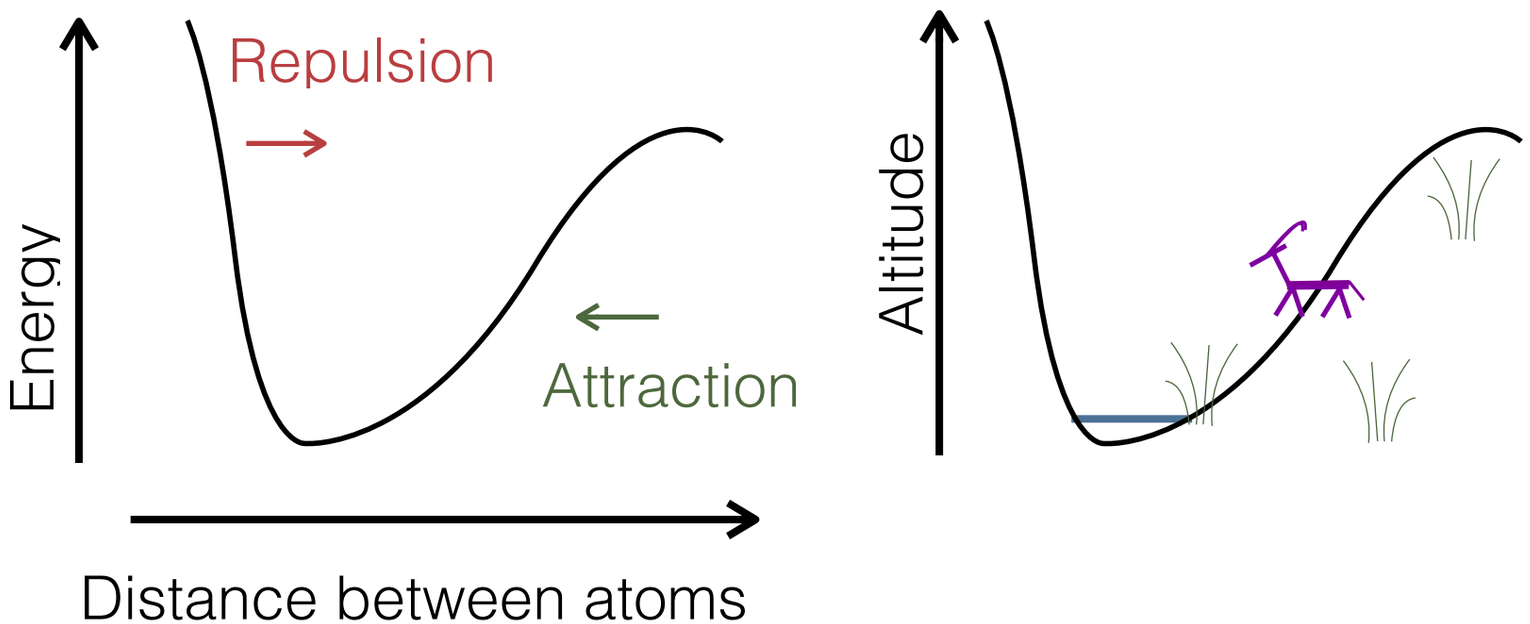
Energy landscapes

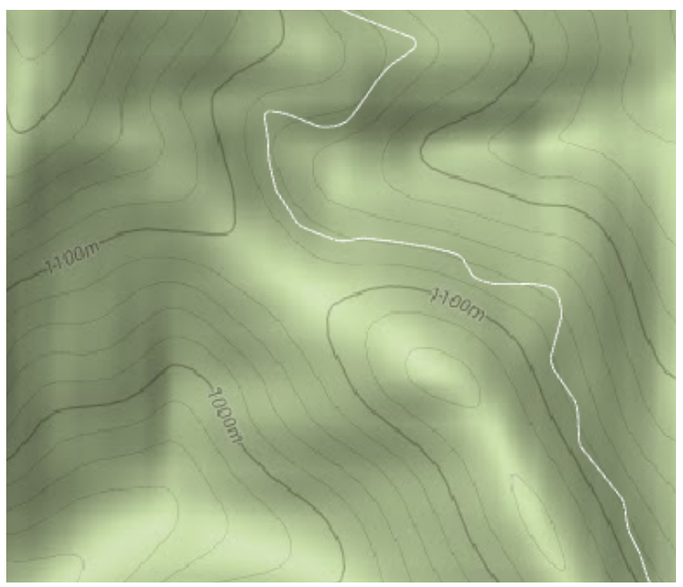
$$V(x_1^n, x_2^n, ..., x_{3N}^n)$$

- all properties defined by the potential energy function

- in 2D resembles mountain landscape







Energy, temperature and entropy

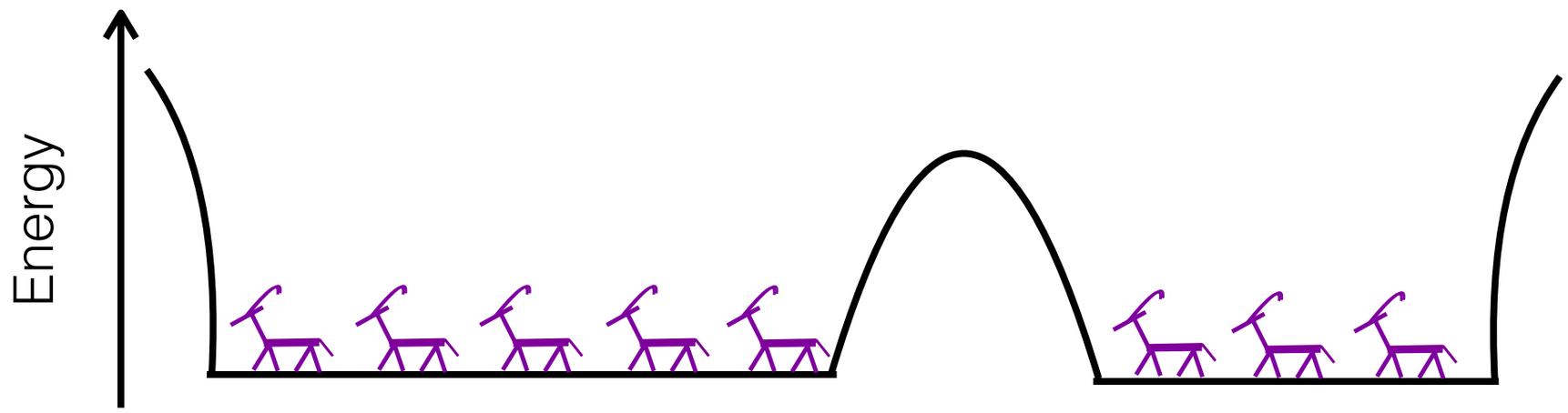
- probability of each configuration given by its potential energy

$$P(\mathbf{x}) \propto e^{-\frac{V(\mathbf{x})}{k_B T}}$$

- grouping configurations into observable states results in information loss -> entropy

H H H	H H T	H T H
H T T	T H H	T H T
T T H	T T T	

- grouping of coin tossing, volume

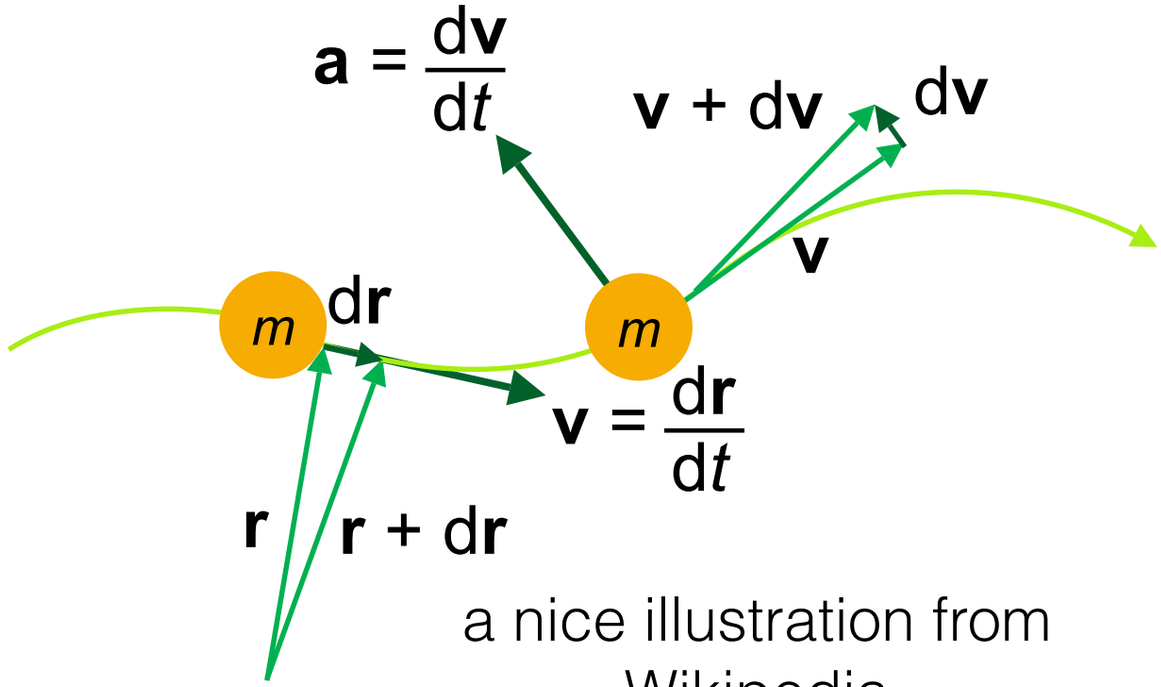


Dynamics on energy landscapes

- no relativity for nuclei
- classical dynamics of nuclei
- Newton's equation of motion

(in 1 dimension)

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = -\frac{\mathrm{d}V}{\mathrm{d}x}$$

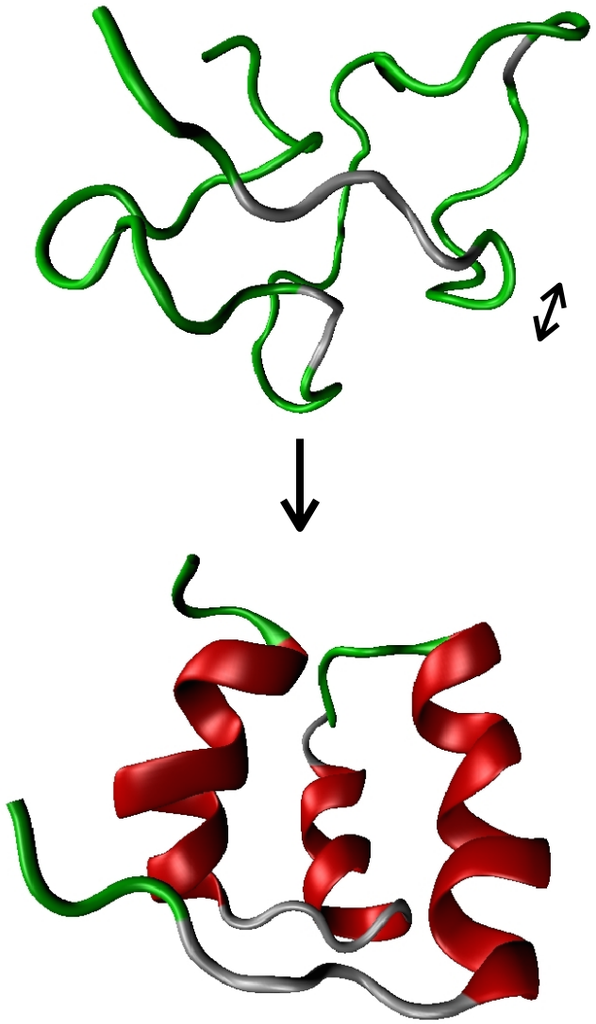


a nice illustration from Wikipedia

- Can be discretised and numerically propagated from an initial structure = molecular dynamics

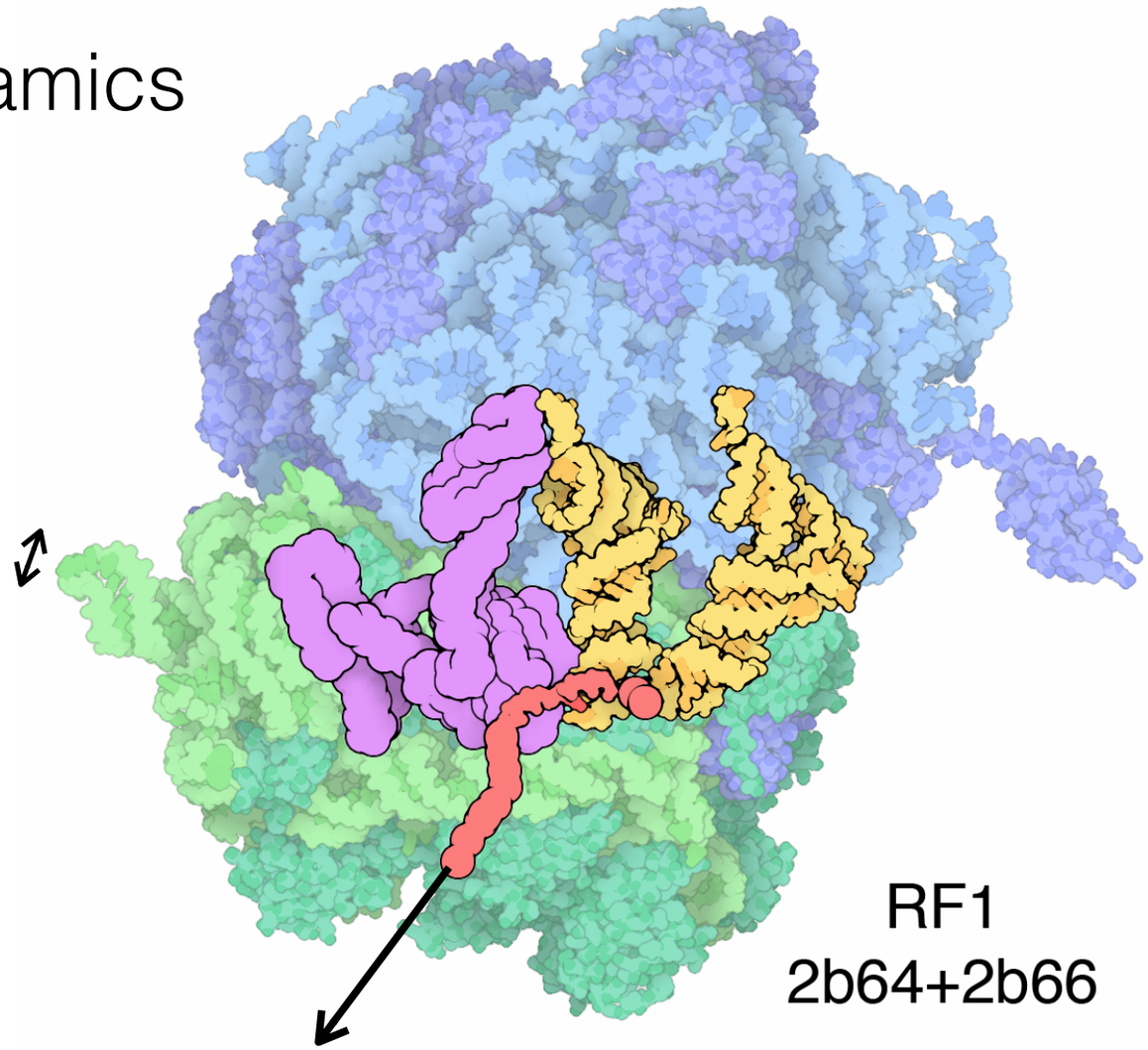
Rare events in nature

- ratio of the largest and lowest relevant timescales >> 1
- challenge for molecular dynamics



molecular vibration
(~1 fs)

folding
(~1 ms)



RF1
2b64+2b66

elongation of
protein chain (~40 ms)

Density of particles

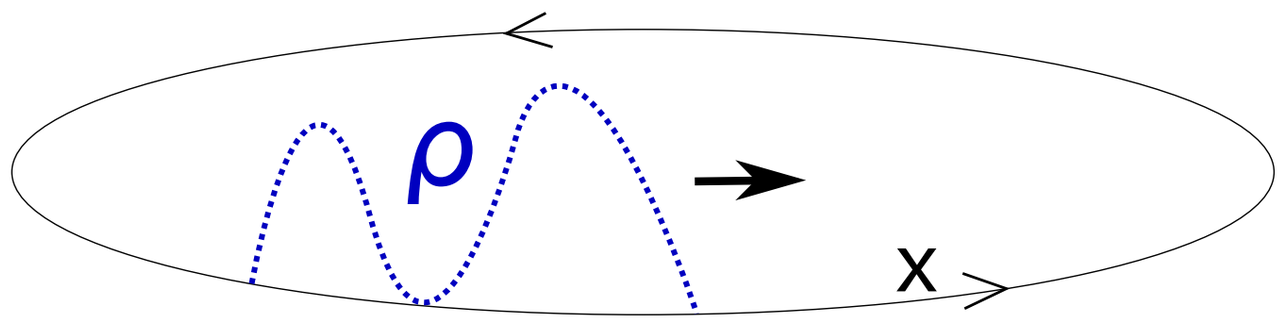
- in a beaker, we have an ensemble of (10^{23}) molecules following the same rules

- in the limit of infinitely many particles we can write density

- Newton equation -> Liouville's equation for the density

(in 1D, zero potential)

$$\frac{\partial \rho(x,t)}{\partial t} = -v \frac{\partial \rho(x,t)}{\partial x}$$



adding forces:

$$\frac{\partial \rho(x,v,t)}{\partial t} = \frac{1}{m} \frac{\partial V(x)}{\partial x} \frac{\partial \rho(x,v,t)}{\partial v} - v \frac{\partial \rho(x,v,t)}{\partial x}$$

Adding friction

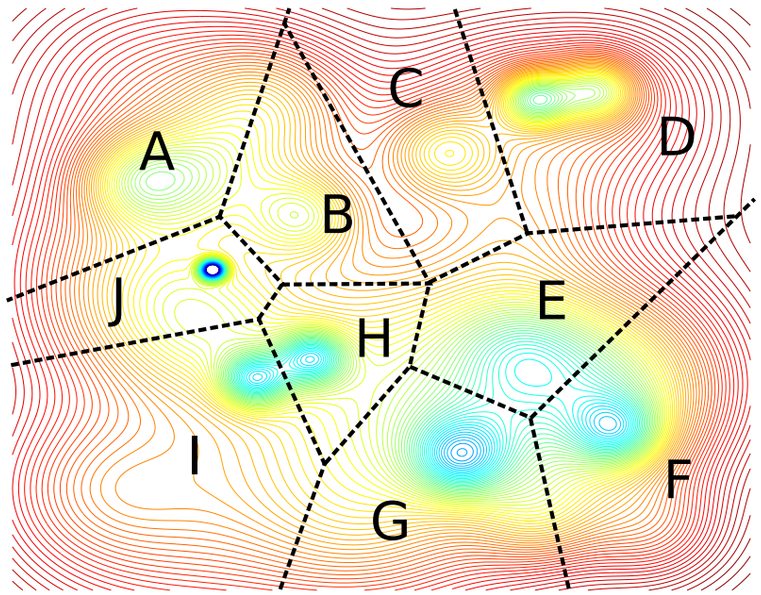
- motion on a rough landscape
- what is not included in our model causes random bumps

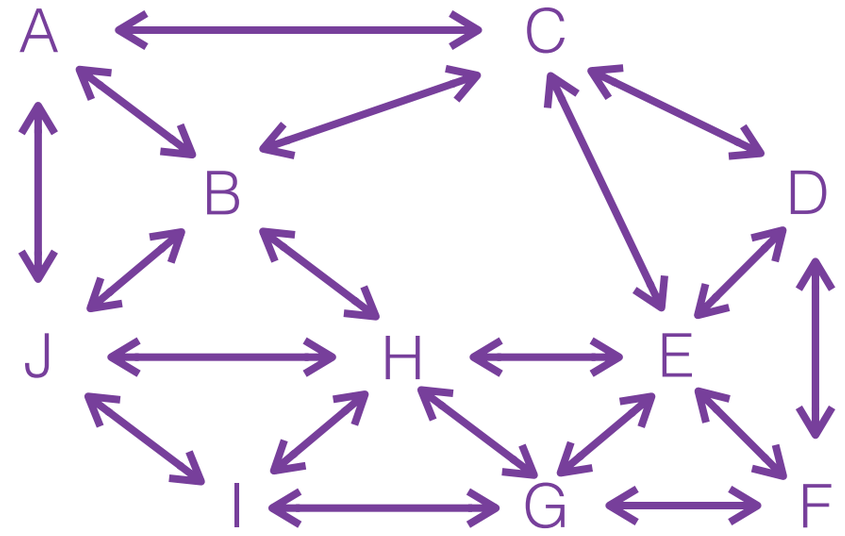
$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = -\frac{\mathrm{d}V}{\mathrm{d}x} - \gamma v + \sqrt{2k_BT}\gamma^{1/2}\eta(t),$$

Generally: $$\frac{\partial\rho(\mathbf{x},\mathbf{v},t)}{\partial t} = \mathcal{F}\left[\rho(\mathbf{x},\mathbf{v},t)\right]$$

	no friction	some friction	large friction
SODE	Newton	Langevin	Brownian motion
PDE	Liouville	Fokker-Planck	Smoluchowski

Partitioning the space in cells

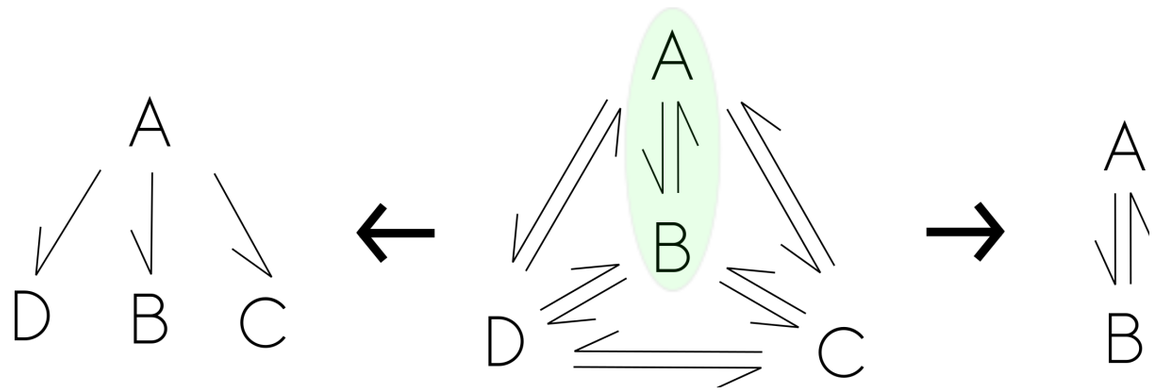




- rate matrix R is calculated from simulations

$$\frac{\mathrm{d}\mathbf{c}}{\mathrm{d}t} = \mathbf{R}\ \mathbf{c}$$

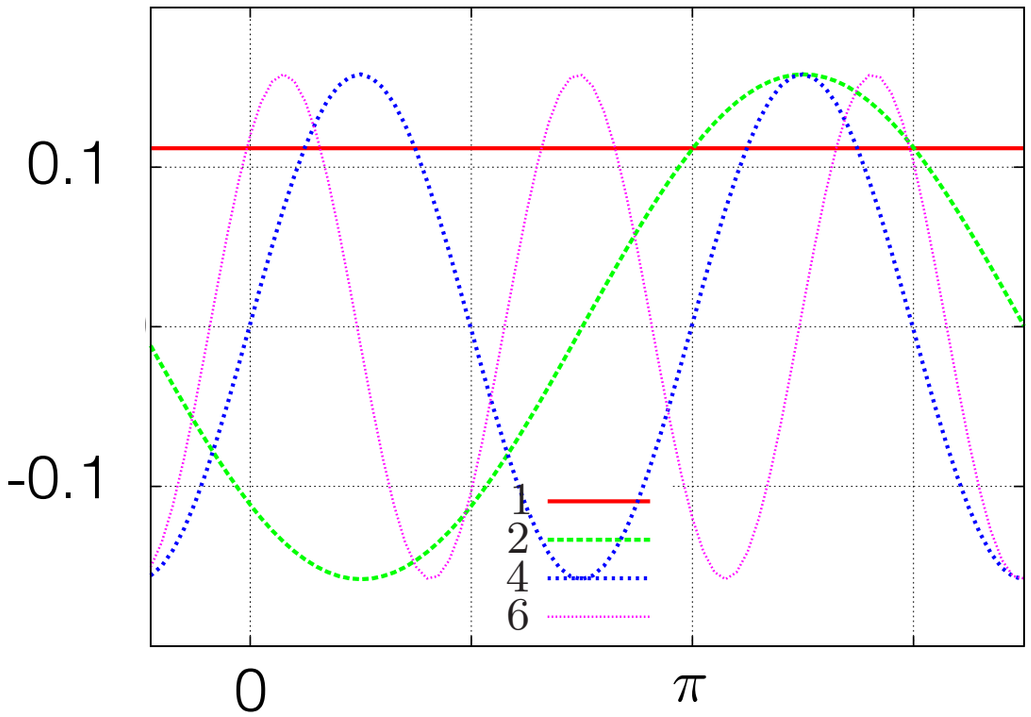
- extraction of a smaller system = isolation of cells



General solution to the FPE

$$\frac{\partial \rho(\mathbf{x}, \mathbf{v}, t)}{\partial t} = \mathcal{F}\left[\rho(\mathbf{x}, \mathbf{v}, t)\right]$$

- eigenfunctions of the operator can be found only for some systems



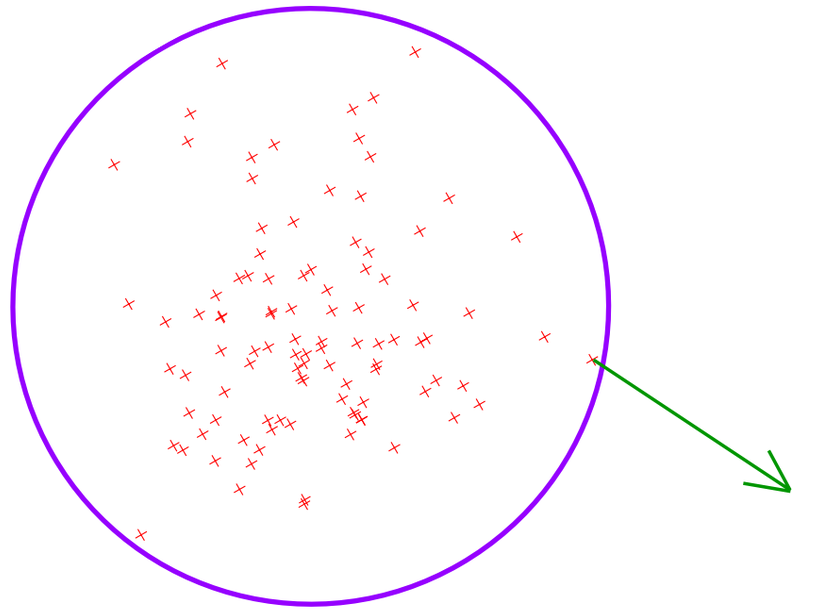
Eigenfunctions of operator $\mathcal{F}$ describing diffusion on a circle with zero potential everywhere.

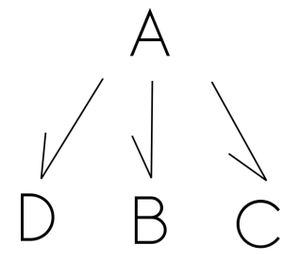
Red line (the first eigenfunction) corresponds to the equilibrium distribution

- we are only interested in $c_i(t) = \int_{B_i} \mathrm{d}\mathbf{x} \int_{-\infty}^{\infty} \mathrm{d}\mathbf{v}\ \rho(\mathbf{x}, \mathbf{v}, t)$

The transition state theory

$$\frac{\mathrm{d}}{\mathrm{d}t}[A] = k_{AB}[A]$$

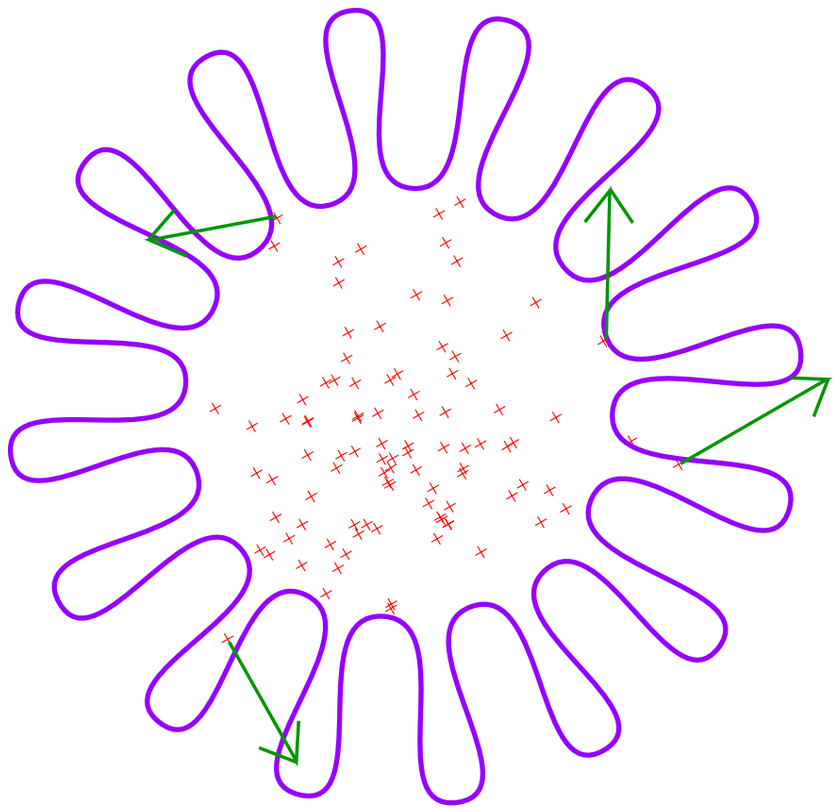




$$k_{\mathrm{AB}}^{\mathrm{TST}} = \frac{\text{eq.flux}}{\text{eq.population}}$$

$$k_{\mathrm{a}}^{\dagger}(T) = \frac{kT}{h}\frac{Z^{\dagger}}{Z_{\mathrm{a}}}\mathrm{e}^{-\Delta V/kT}$$

$$k_{\mathrm{a}}^{\dagger}(E) = \frac{\bar{\nu}_{\mathrm{a}}^{\kappa}}{\bar{\nu}^{\dagger(\kappa-1)}}\left(\frac{E-V^{\dagger}}{E-V_{\mathrm{a}}}\right)^{\kappa-1}$$



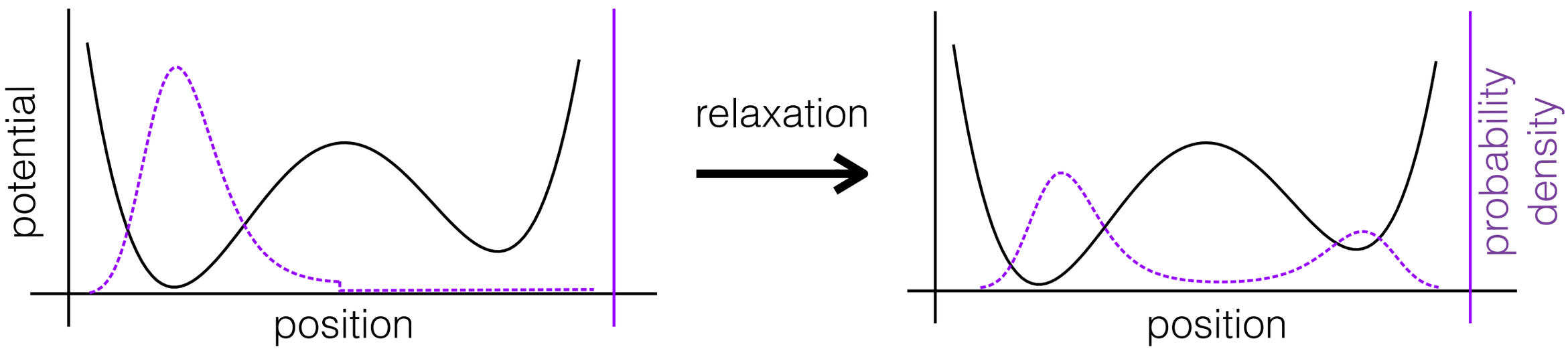
Rate constants from trajectories

- (if we have to simulate trajectories) CAN WE DO BETTER?

- for system of 2 states, rate constant from mean exit times (formula proven for 1D):

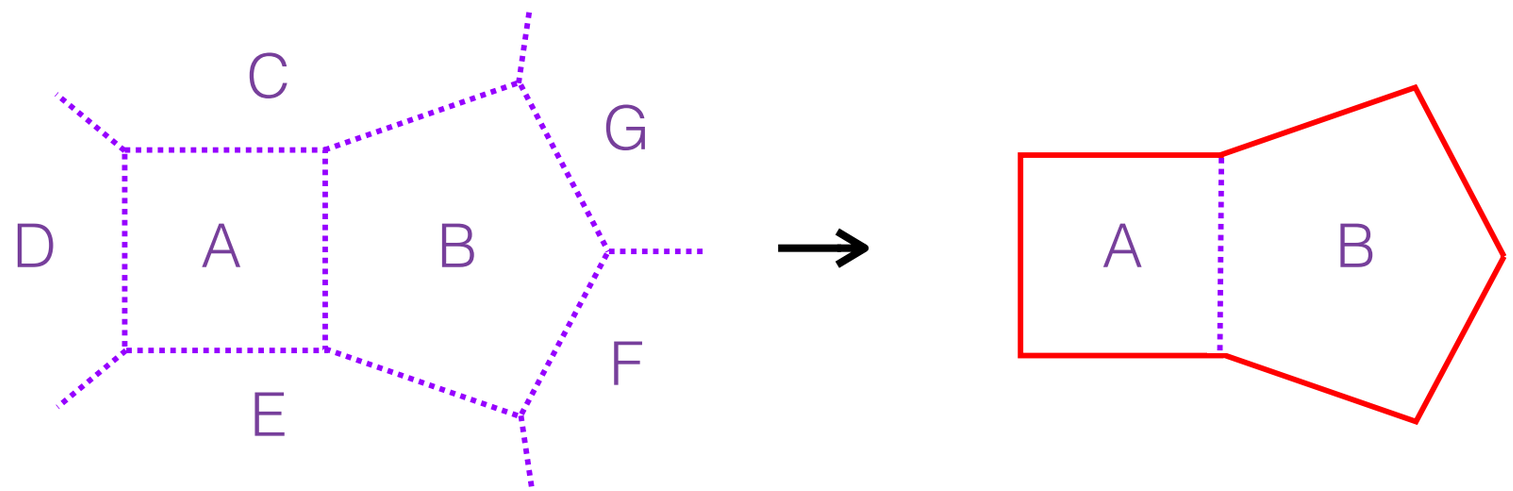
$$k_{\mathrm{AB}}^{\mathrm{ex}} = \frac{p_{\mathrm{B}}^{\mathrm{eq}}}{p_{\mathrm{A}}^{\mathrm{eq}}\tau_{\mathrm{B}}^{\mathrm{ex}} + p_{\mathrm{B}}^{\mathrm{eq}}\tau_{\mathrm{A}}^{\mathrm{ex}}}$$

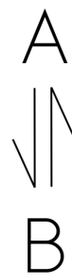
- relaxation involves both exit and penetration - best approach



Our approach

- boundary conditions for the isolation

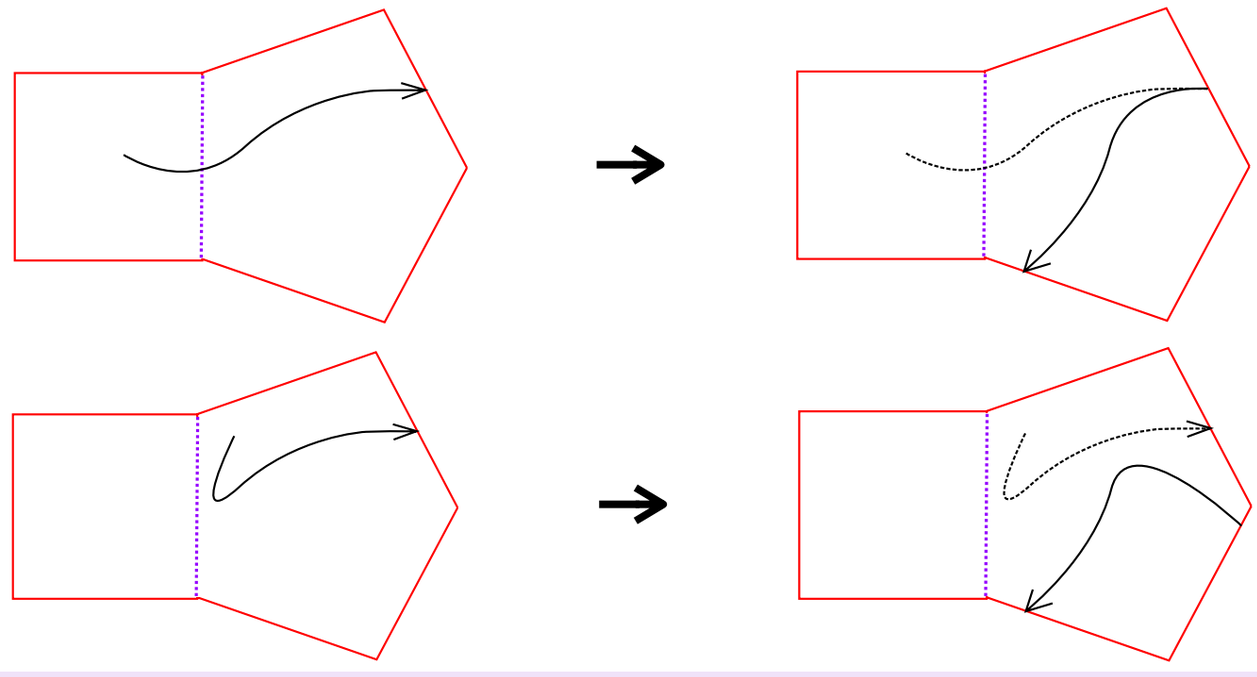




$$\frac{\partial \rho(\mathbf{x}, \mathbf{v}, t)}{\partial t} = \mathcal{F}\left[\rho(\mathbf{x}, \mathbf{v}, t)\right]$$

$$\rho(\mathbf{x}, \mathbf{v}, t) = \rho(\mathbf{x}, -\mathbf{v}, t)$$

$$\rho(\mathbf{x}, \mathbf{v}, t) = \rho_{\mathrm{eq}}(\mathbf{x}, \mathbf{v}) \frac{f_{\mathrm{out}}(t)}{f_{\mathrm{eq}}}$$



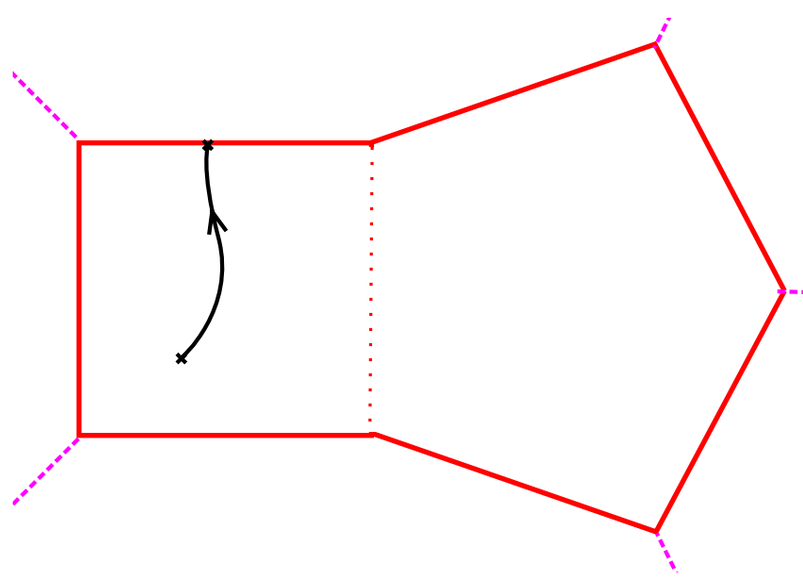
More formal exit

- looking at relaxation from cell B_i to cell B_j

- $f^e_{i,k}(t)$- probability density that a trajectory initiated at equilibrium in B_i exits this cell toward B_k at time t

exit probability $$p^e_{i,k} = \int_0^\infty f^e_{i,k}(t)\ \mathrm{d}t$$

mean exit time $$\tau^e_{i,k} = \frac{1}{p^e_{i,k}} \int_0^\infty f^e_{i,k}(t)\ t\ \mathrm{d}t$$



for each neighbour B_k of B_i

More formal supply

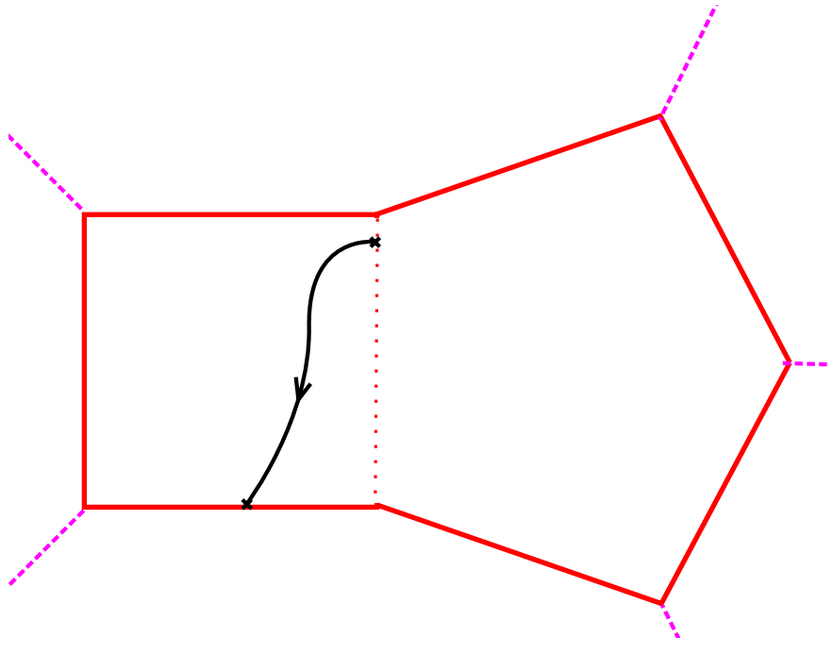
- $f^e_{i,k}(t)$- probability density that an equilibrium trajectory entering B_i from B_j at time s exits this cell toward B_k at time $s+t$

conditional exit probability

$$p^i_{j,k} = \int_0^\infty L^i_{j,k}(t)\ \mathrm{d}t$$

mean trajectory time

$$\tau^i_{j,k} = \frac{1}{p^i_{j,k}} \int_0^\infty L^i_{j,k}(t)\ t\ \mathrm{d}t$$



for each pair of neighbours of B_i

Combining exit times and the TST

- TST rate constant

$$k_{i,j}^{\mathrm{TST}} = \frac{p_{i,j}^{e}}{\sum_{k\sim i} p_{j,k}^{i} \tau_{j,k}^{i}}$$

- Exit time rate constant

$$k_{i,j}^{\mathrm{ex}} = \frac{c_{j}^{e}}{c_{j}^{i}\tau_{i,j}^{e} + c_{i}^{e}\tau_{j,i}^{e}}$$

- Relaxation rate constant

$$k_{i,j} = \frac{(p_{j}^{*,e})^{2}}{\tau_{j,i}^{*} - \tau_{i,j}^{*}}$$

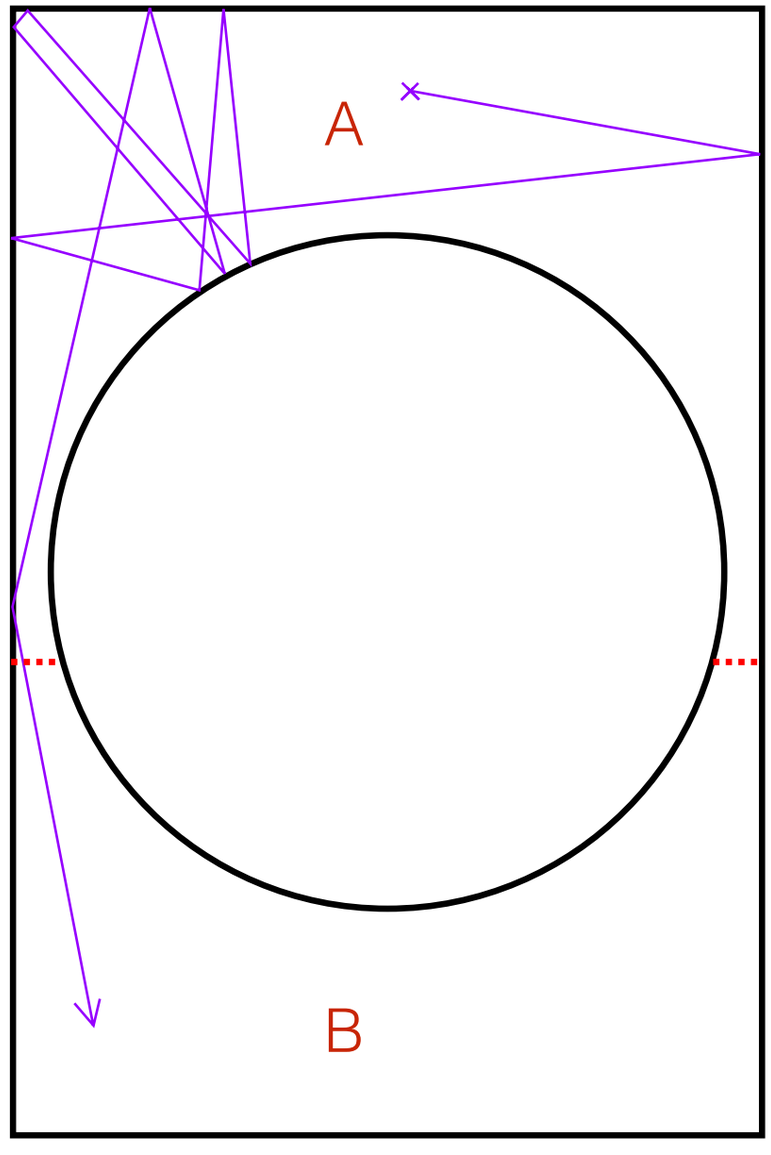
where all 3 terms in the equation are obtained by solving certain sets of linear equations

Illustration on Sinai billiards

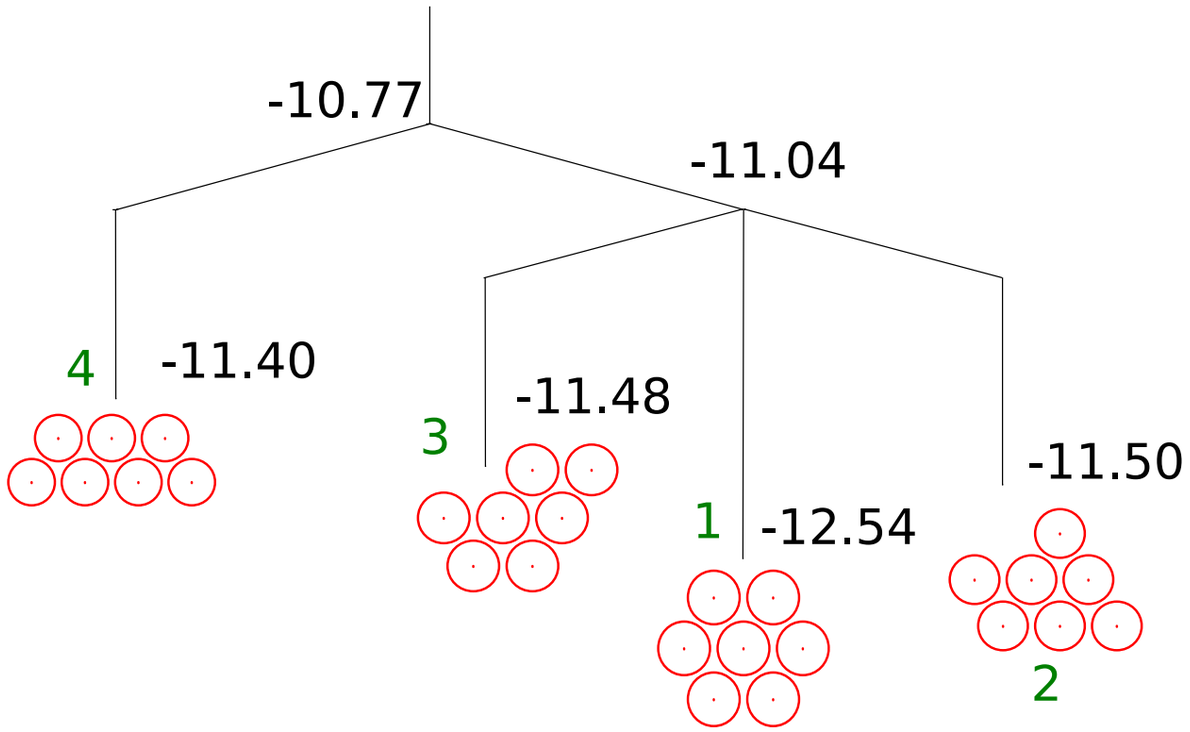
- non-interacting particles with equal velocities elastically reflect from walls of the billiard and the circle inside

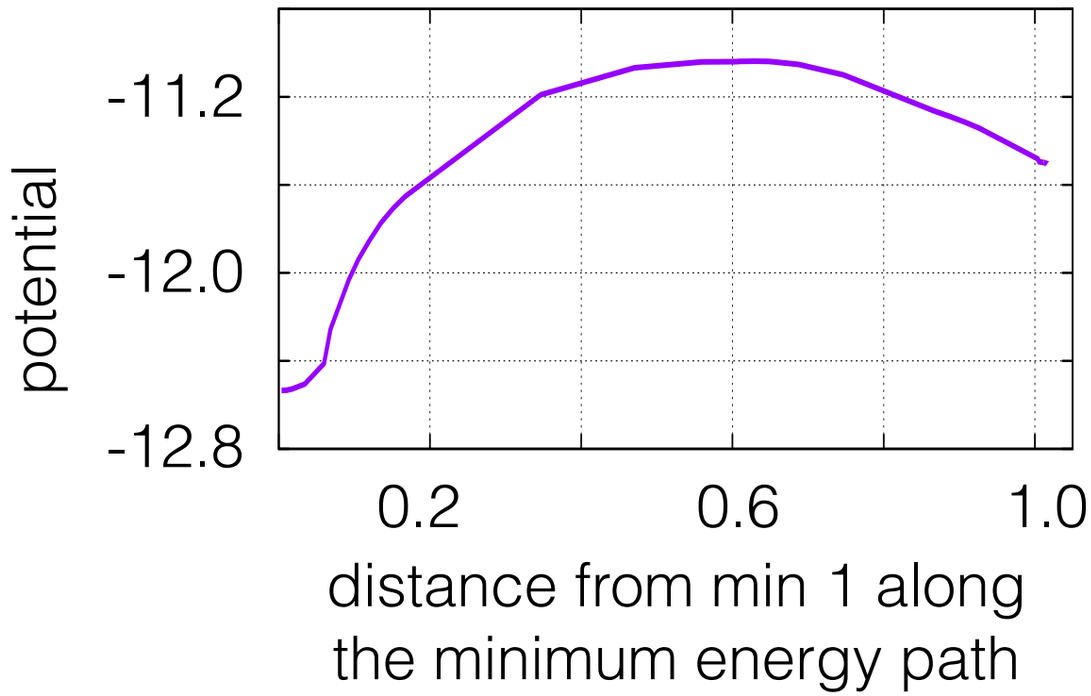
- circle forms a bottleneck - transition through the dividing surface is a rare event

- small change in definition of the dividing surface should not cause large change in the rate constants



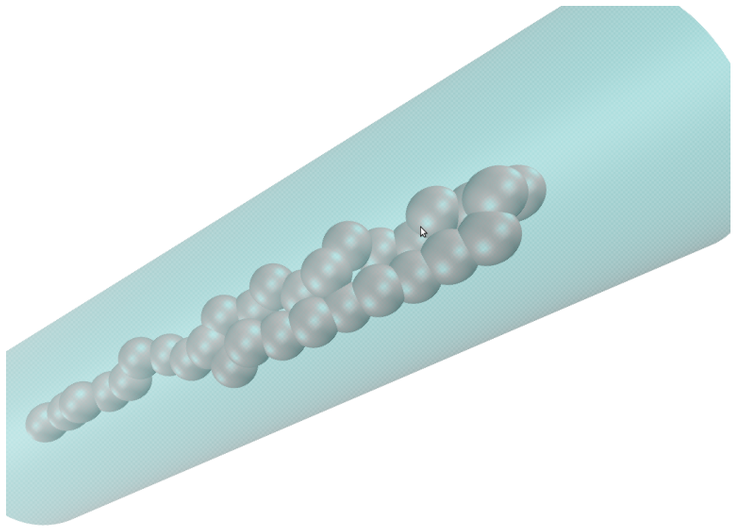
Toy system:
Cluster of Lennard-Jones disks



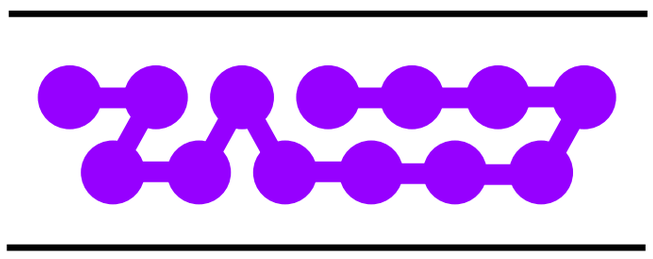


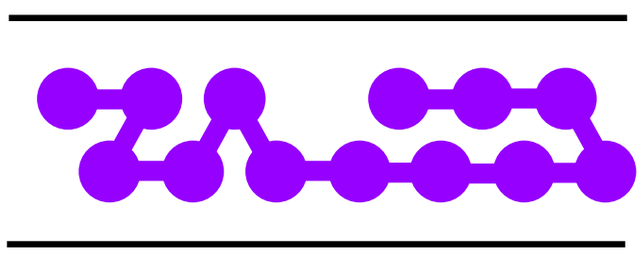
- search for rotation-permutation isomers
- 10-50 cells placed along the collective coordinate - root mean square distance from minimum 2

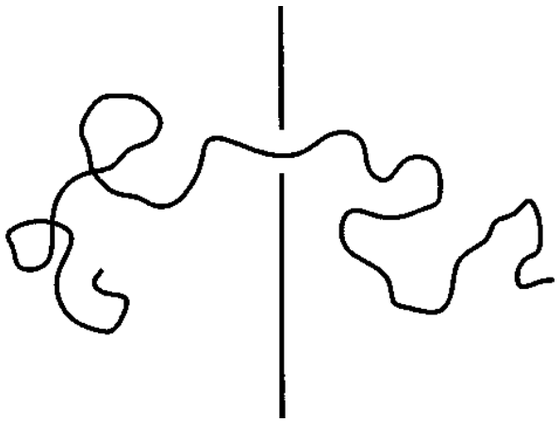
Towards biology



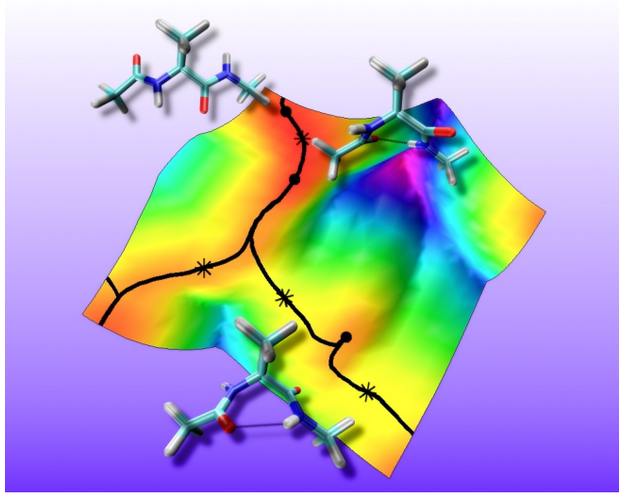
polymer reversal



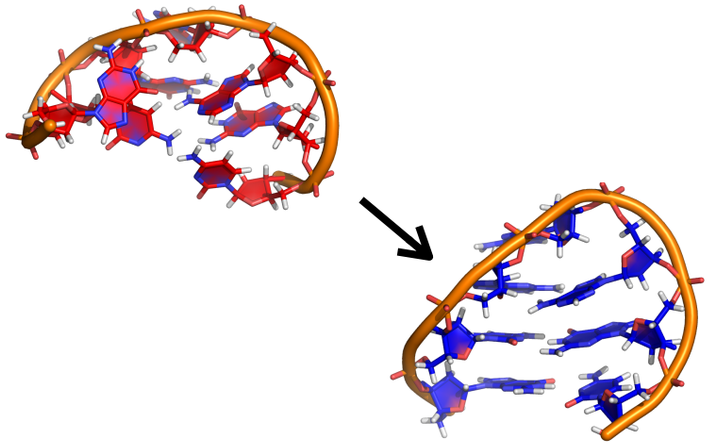




polymer translocation

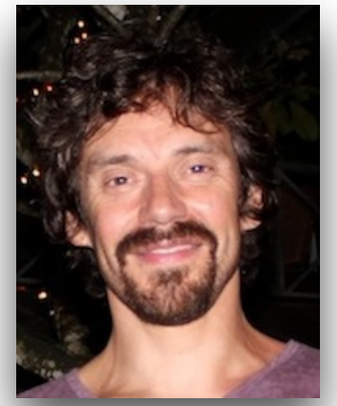


peptide dynamics



biomolecular folding

Acknowledgements



Nadace
Zdeňka Bakaly