Reaction Pathways of Metastable Markov Chains - LJ clusters Reorganization

Eric Vanden-Eijnden
Courant Institute

- Spectral approach to metastability - sets, currents, pathways;
- Transition path theory or how to focus on a specific `reactive' event;
- Application to Lennard-Jones clusters reorganization (with Masha Cameron).

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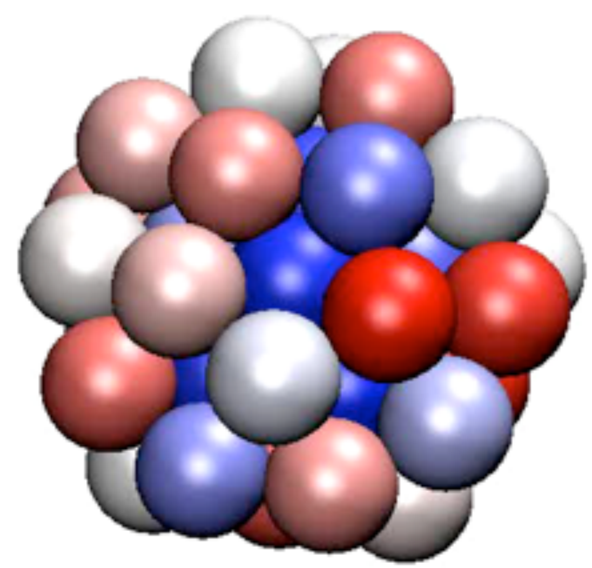
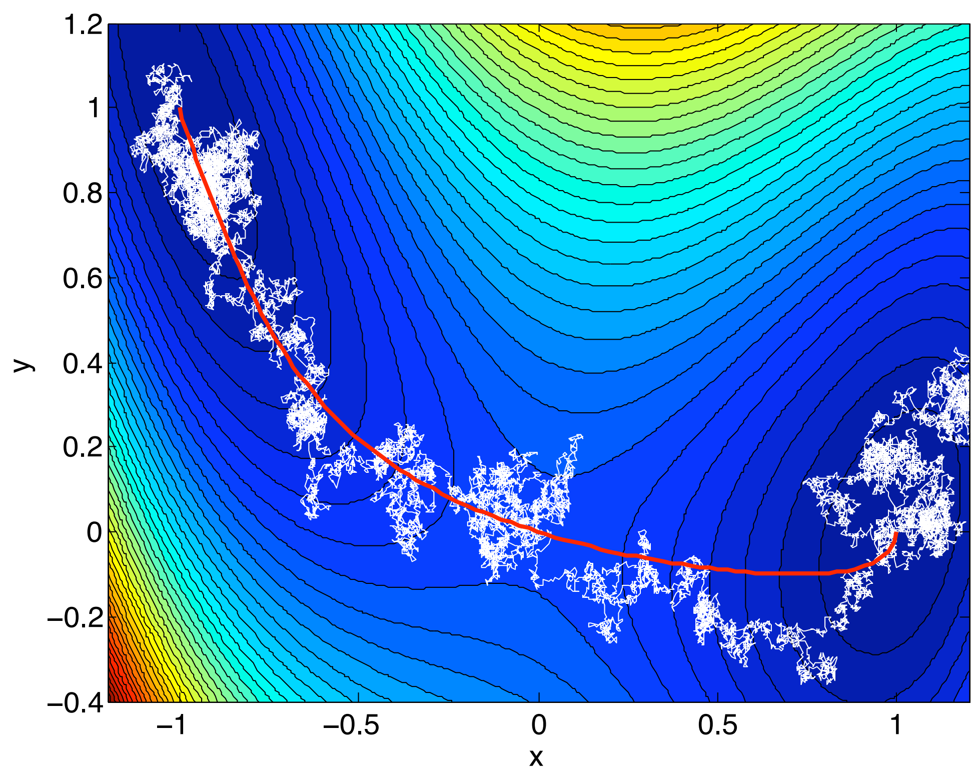
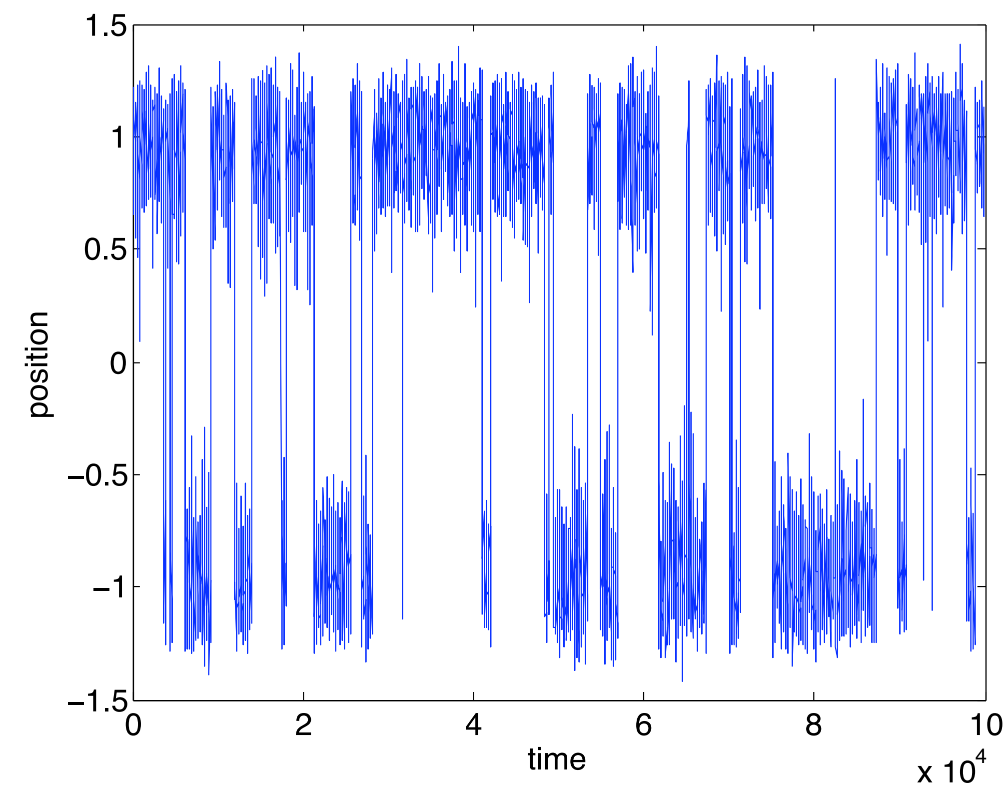


Spectral approach to metastability

- Metastability associated with presence of one or more groups of small eigenvalues of the generator, corresponding to slow relaxation processes in the system.

- Eigenvectors/eigenfunctions associated with these small eigenvalues indicate what the metastable sets are and what the mechanism of transition (reaction) between them is.





Spectral approach to metastability

- Overdamped Langevin equation: $$dX = -\nabla V(X)dt + \sqrt{2\varepsilon}\, dW \quad (X \in \Omega \subseteq \mathbb{R}^n)$$
- Generator: $$L = \nabla V \cdot \nabla - \varepsilon\Delta$$
- Eigenvalue/eigenfunction: $$L\phi = \lambda\phi$$

$$0 = \lambda_0 < \lambda_1 \leq \lambda_2 \leq \cdots$$

- Spectral representation of transition probability distribution:

$$p_t^x(dy) = \sum_{k=0}^{\infty} e^{-\lambda_k t}\phi_k(x)\phi_k(y)C^{-1}e^{-V(y)/\varepsilon}dy,$$

$$C = \int_\Omega e^{-V(y)/\varepsilon}dy,$$

Spectral approach to metastability

- Suppose there exists a group of K small eigenvalues:

$$0 = \lambda_0 < \lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_{K-1} \ll \lambda_K \leq \cdots$$

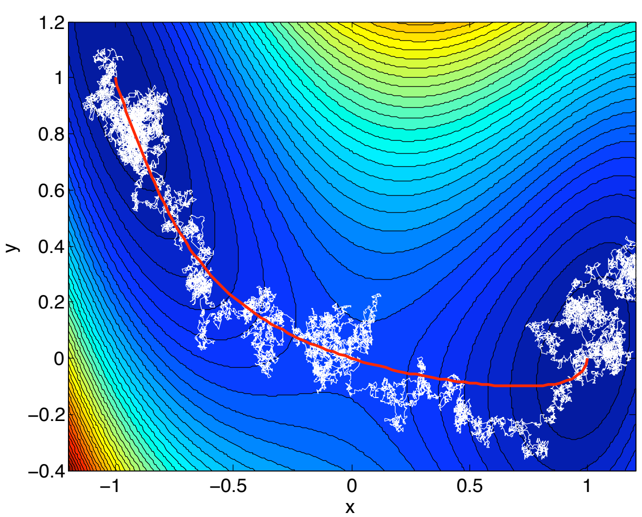
- *Indicative of metastability.* More precisely, on timescales such that

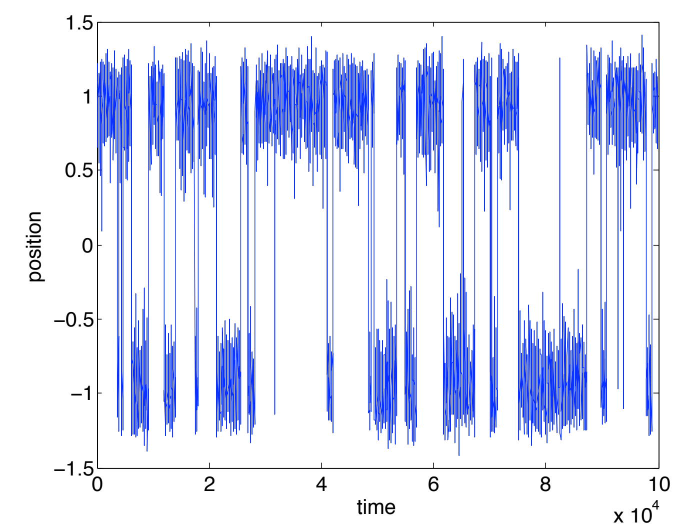
$$\lambda_{K-1} t \sim 1, \qquad \lambda_K t \gg 1$$

the processes described by the eigenvectors of index K or higher will have decayed and the remaining part of the dynamics will be described by the slow first K eigenvectors

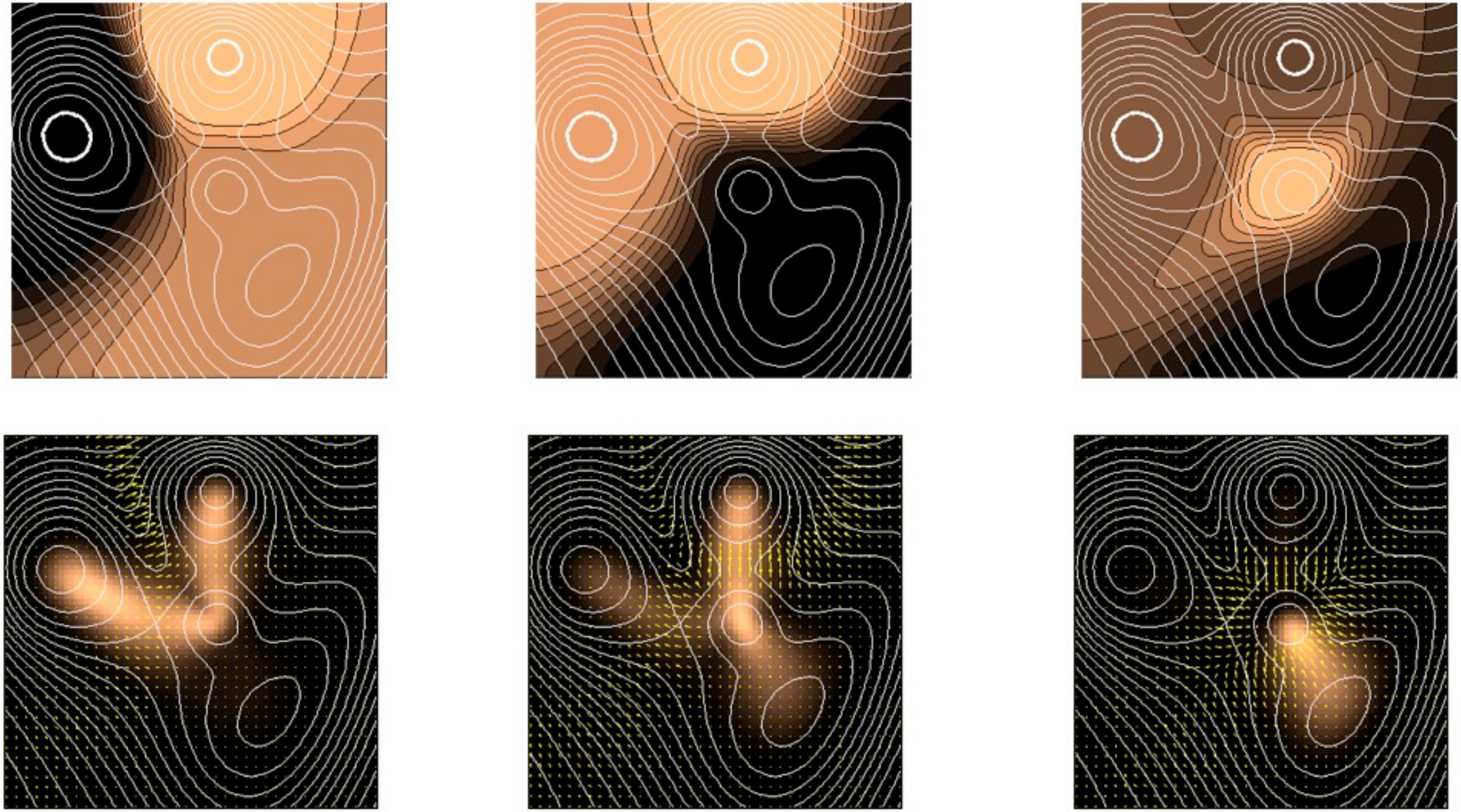
Note that the transition probability relaxes slowly if there is metastability, but the process itself is fast - rare events are infrequent but when they occur they typically do so fast!

$$p_t^x(dy) = \sum_{k=0}^{\infty} e^{-\lambda_k t} \phi_k(x) \phi_k(y) C^{-1} e^{-V(y)/\varepsilon} dy,$$





Example on 2D potential with 4 wells



Simulations by Masha Cameron

Spectral approach to metastability

- Forward Kolmogorov equation as a conservation law:

$$\partial_t \rho_t^x = -\mathrm{div}\, j_t^x, \qquad j_t^x = -\nabla V \rho_t^x - \varepsilon \nabla \rho_t^x \qquad\qquad p_t^x(dy) = \rho_t^x(y)dy$$

- Spectral decomposition of currents:

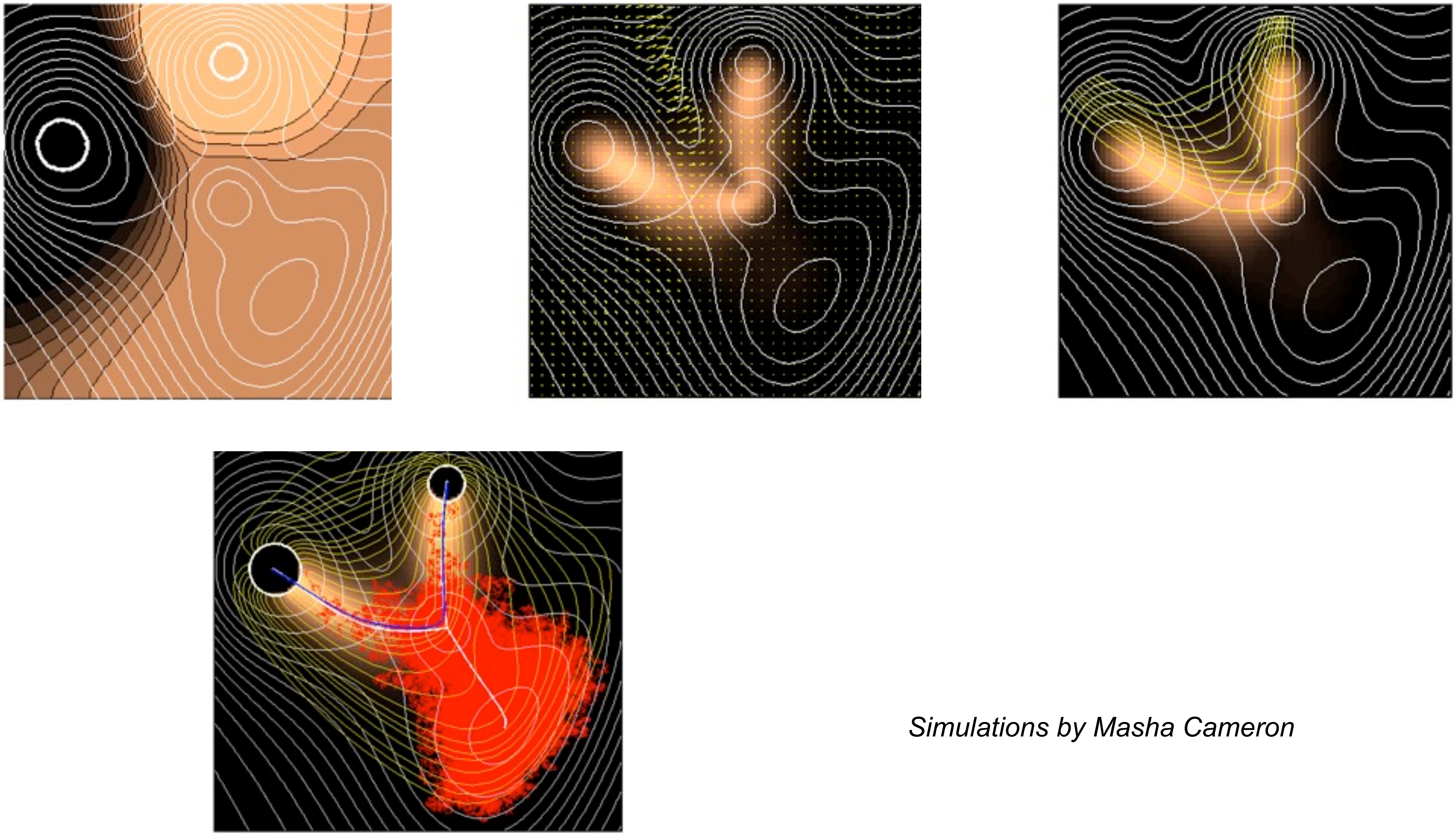
$$j_t^x(y) = \sum_{k=0}^{\infty} e^{-\lambda_k t} \phi_k(x) j_k(y), \qquad j_k(y) = C^{-1} e^{-V(y)/\varepsilon} \nabla \phi_k(y)$$

Analysis of 1-form in Witten complex

Flowlines of current indicative of mechanisms by which slow relaxation occurs

$$\frac{dx}{d\tau} = j_k(x)$$

Slowest modes in 2D potential with 4 wells



Simulations by Masha Cameron

Transition Path Theory

- How to make spectral approach practical as a *computational tool*?

In applications, one is typically in high dimensional systems whose spectrum is enormously complicated and cannot be calculated explicitly (even numerically).

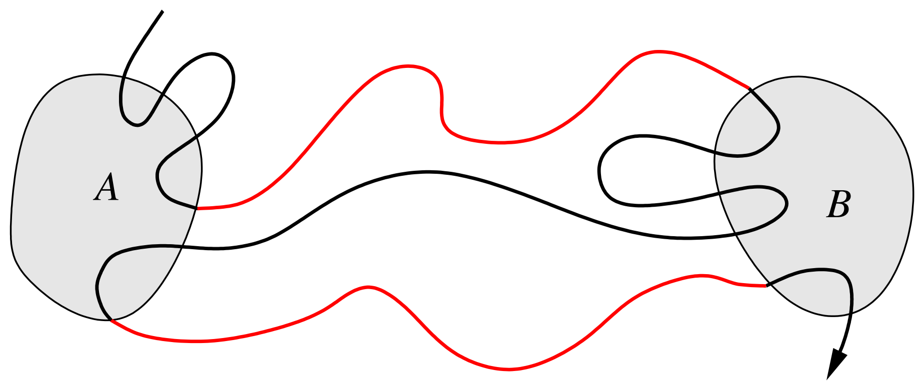
- Global viewpoint of metastability also problematic - the longest timescales may not be the relevant ones (i.e. they could be associated with presence of deadends or dynamical traps), there may be many of them (subgroups into groups), etc..

- Can we focus on a single `reaction’ rather than having to analyze them all thru calculation of the spectrum? (Indeed in a given system there may be specific reactions of interest and we don’t know a priori to which part of the spectrum they are associated)

- Can this all be done even if there is no metastability (i.e. no small parameter)?

Transition Path Theory

- Main idea: focus on `reactive' trajectories associated with a given transition (reaction)



- Probability distribution of reactive trajectories

$$\mu_R(dy) = C^{-1} e^{-V(y)/\varepsilon} q(y)(1 - q(y))dy$$

- Probability current of reactive trajectories

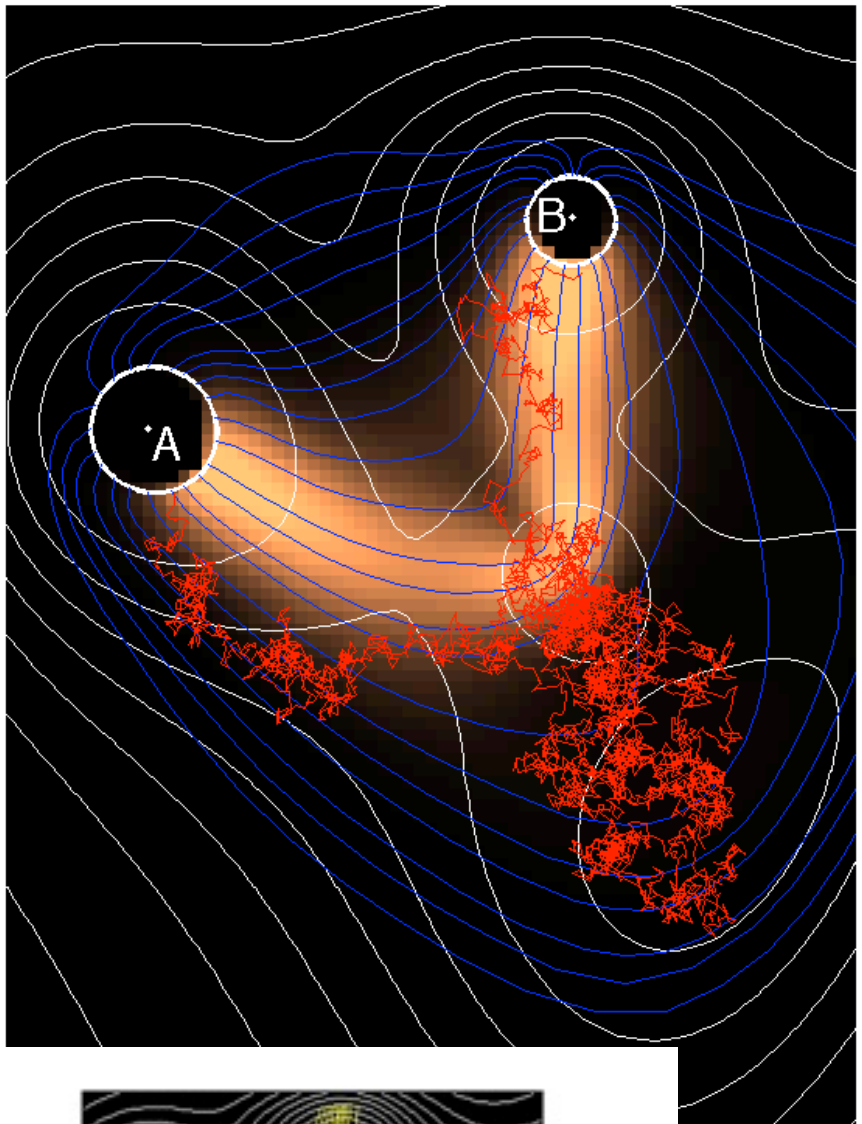
$$j_R(y) = C^{-1} e^{-V(y)/\varepsilon} \nabla q(y)$$

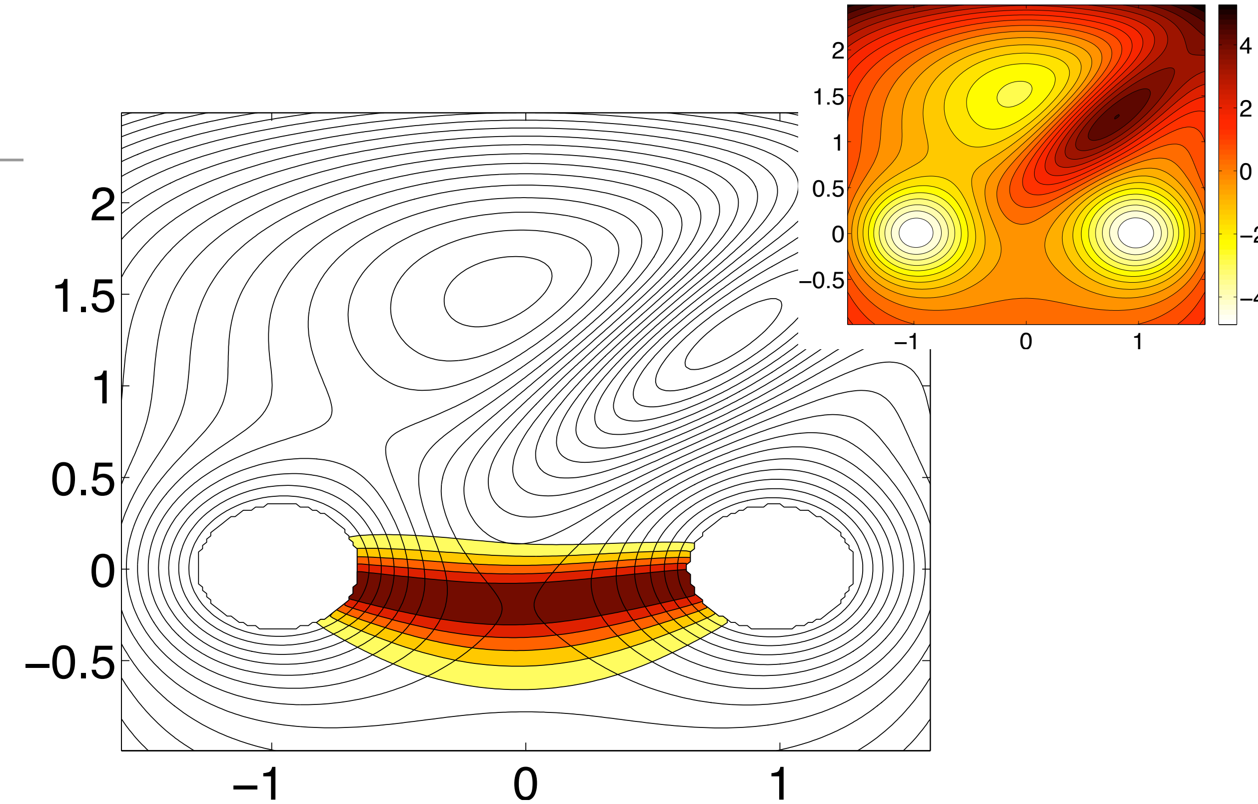
- Committor function (capacitor):

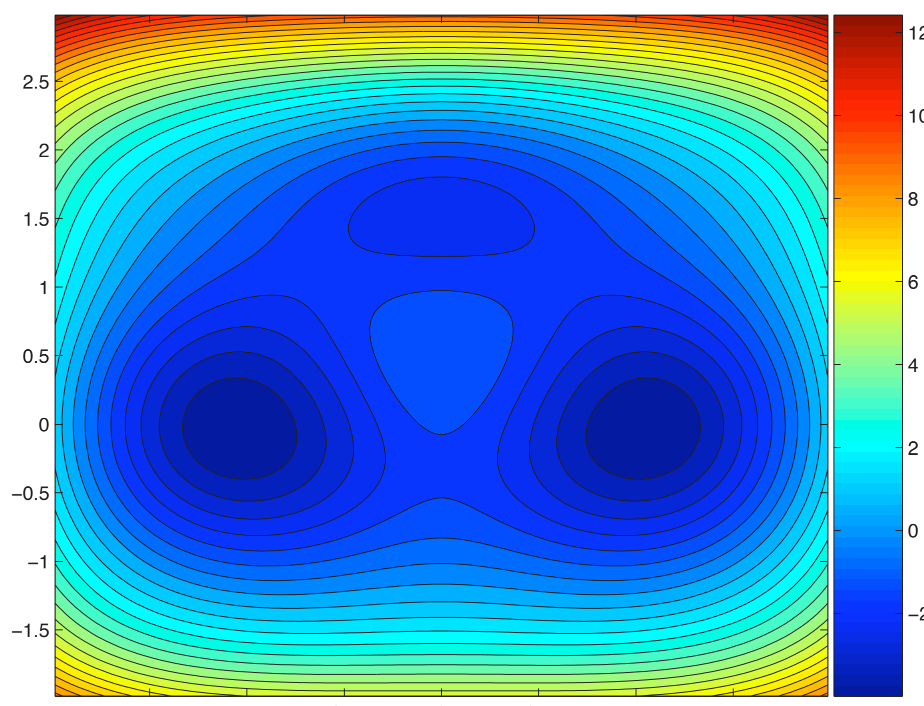
$$q(y) = \mathbb{E}^y(\tau_B < \tau_A)$$

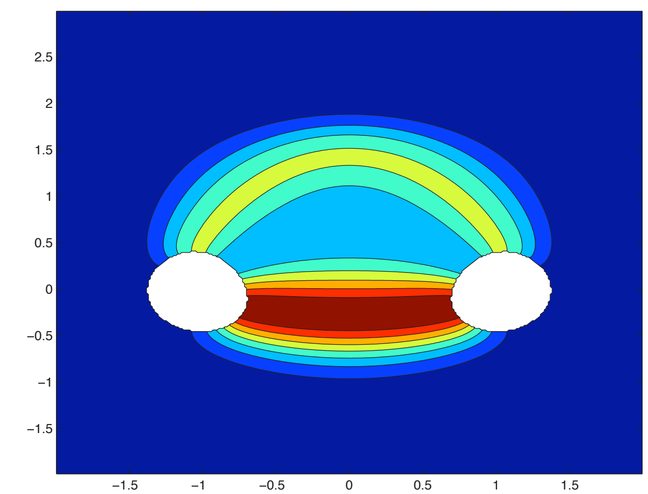
Related to Bovier's potential theoretic approach, but exact (no small parameter)!
Can be generalized to non-reversible processes.

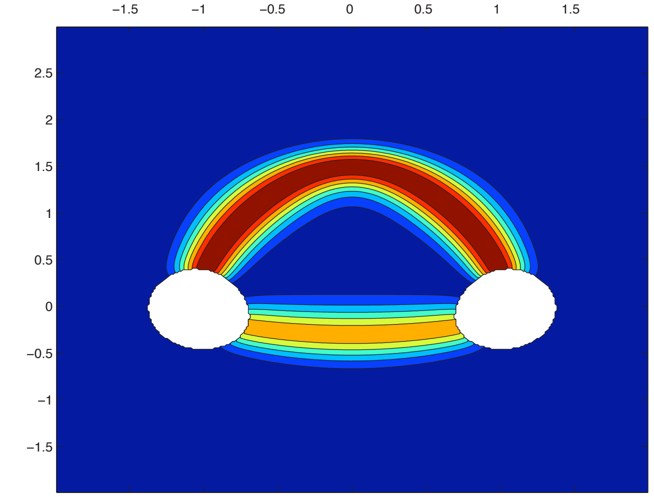
Some low D examples











Transition Path Theory for MJP

- Generator = transition rate matrix $L_{i,j}$ $i, j \in S = \{1, 2, \ldots, N\}$

- Microscopic reversibility (detailed balance)

$$\mu_i L_{i,j} = \mu_j L_{j,i}$$

- Probability distribution of reactive trajectories

$$\mu_i^R = \mu_i q_i (1 - q_i)$$

- Probability current of reactive trajectories

Generator of loop erased reactive paths

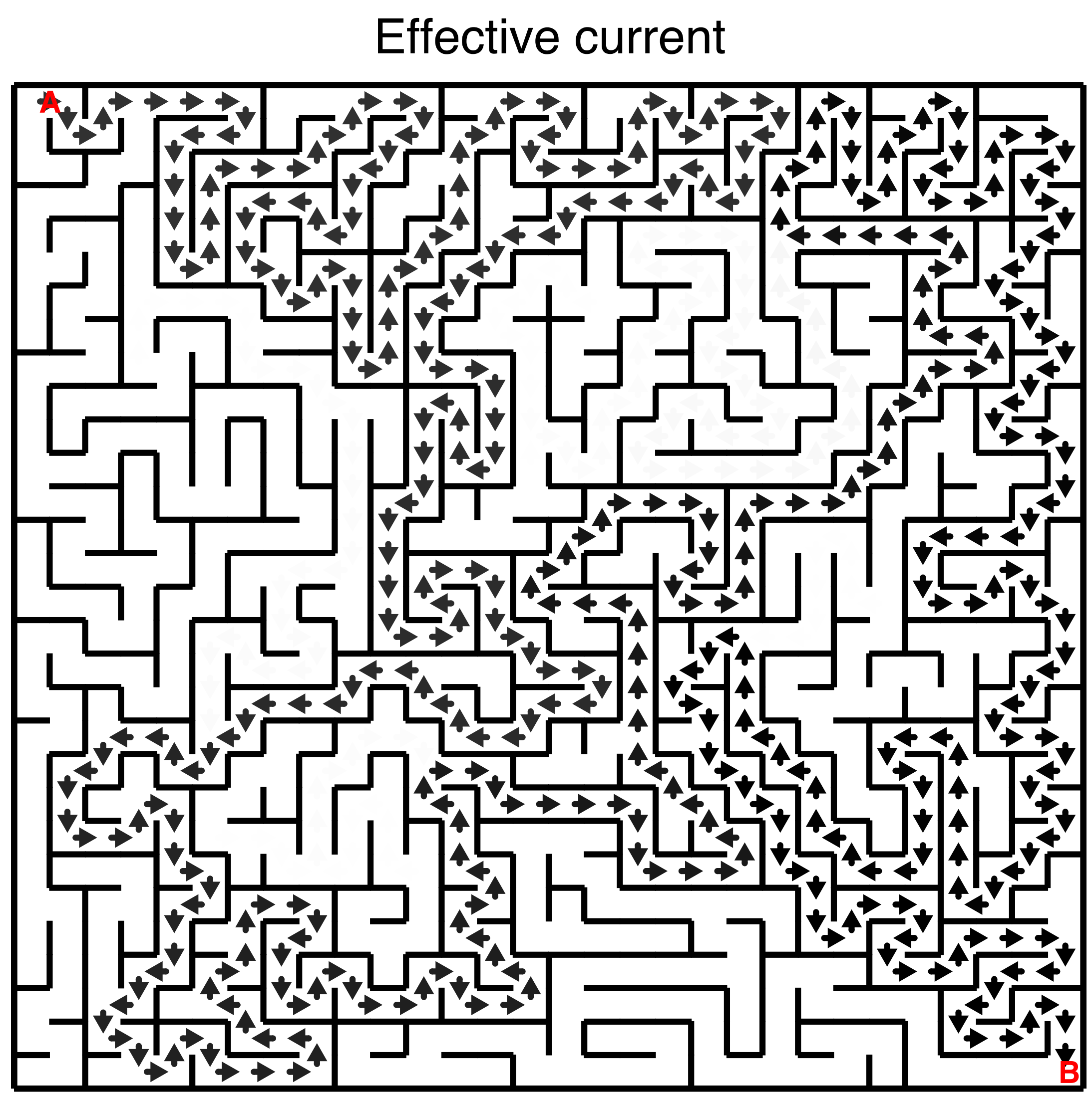
$$f_{i,j}^R = \mu_i L_{i,j} (q_j - q_i)_+ \qquad L_{i,j}^R = L_{i,j} (q_j - q_i)_+$$

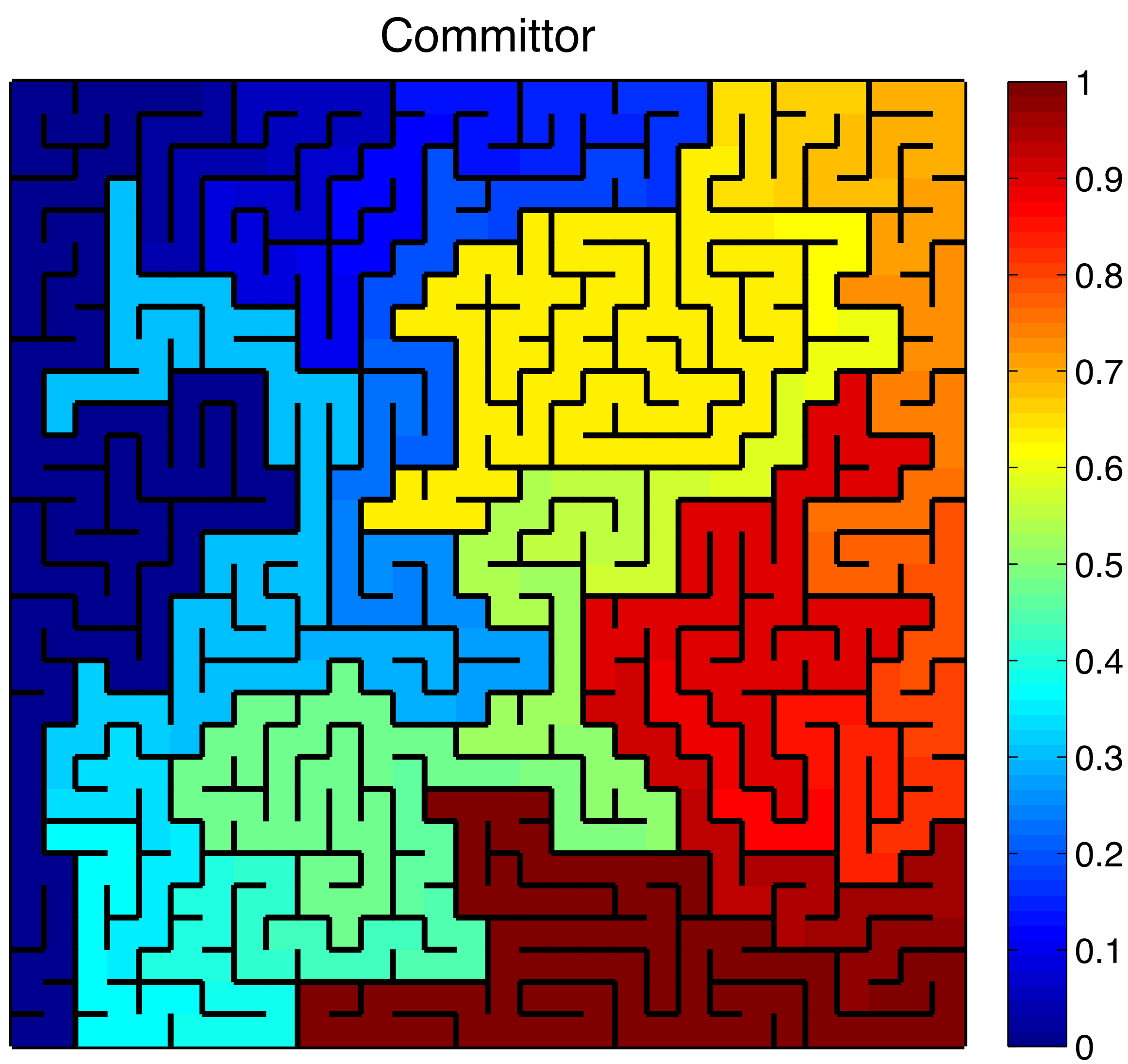
- Committor function:

$$q_i = \mathbb{E}^i (\tau_B < \tau_A)$$

Can again be generalized to non-reversible processes.

Transition Path Theory for MJP





Example of a maze (not metastable!)

Reorganization of LJ cluster after self-assembly

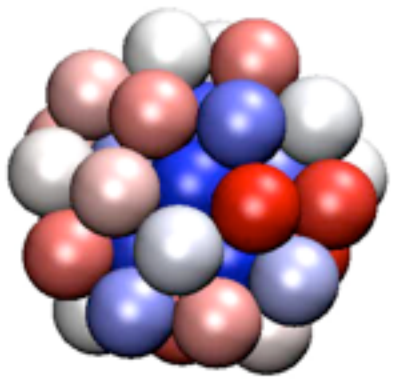
with Masha Cameron

- Double funnel landscape - ground state is not accessible directly by self-assembly and requires dynamical reorganization;
- Can be described by a MJP using the network calculated by Wales;
    - ~1e4 local minima of potential;
    - ~1e4 saddle points between these minima;
    - Network of orbits (minimum energy paths);
    - Transition matrix ;

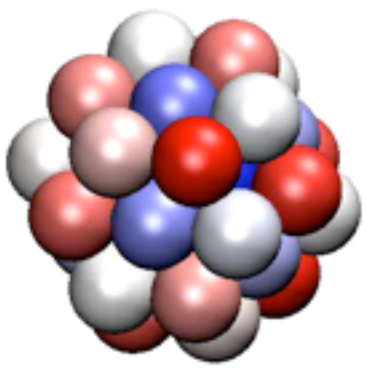
$$L_{i,j} = \nu e^{-\Delta V_{i,j}/\varepsilon}$$

- Spectral analysis difficult (large network, many small eigenvalues).
- Can be analyzed by TPT.
- LDT only applicable at extremely low temperatures. At small temperature, systems remains strongly metastable, but pathway and rate of transition are different than those predicted by LDT (entropic effects).

icosahedron

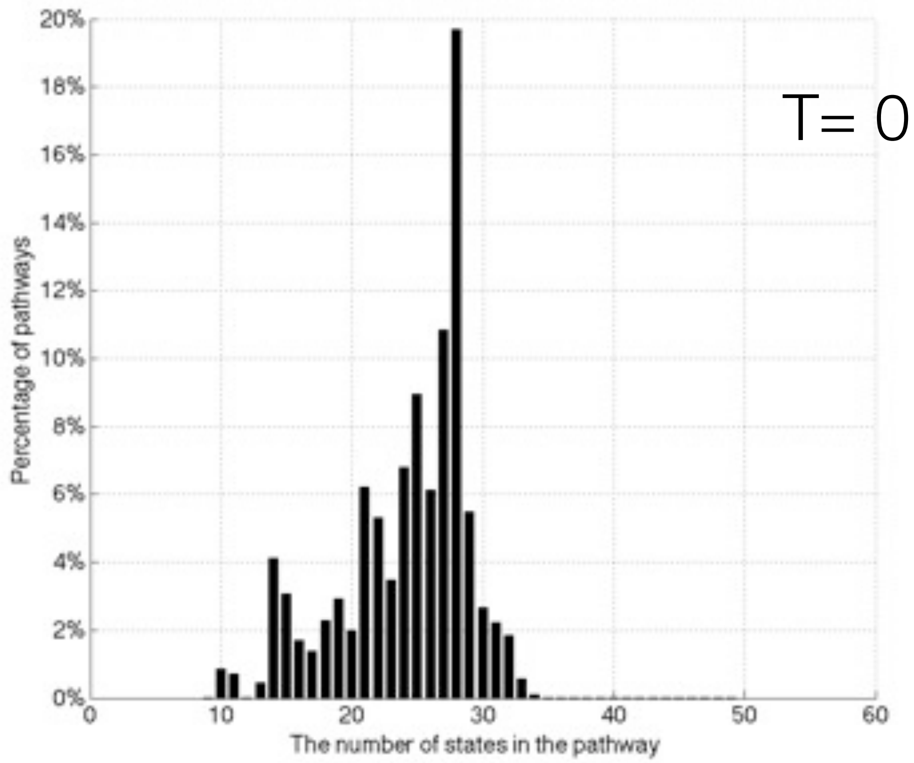


octahedron

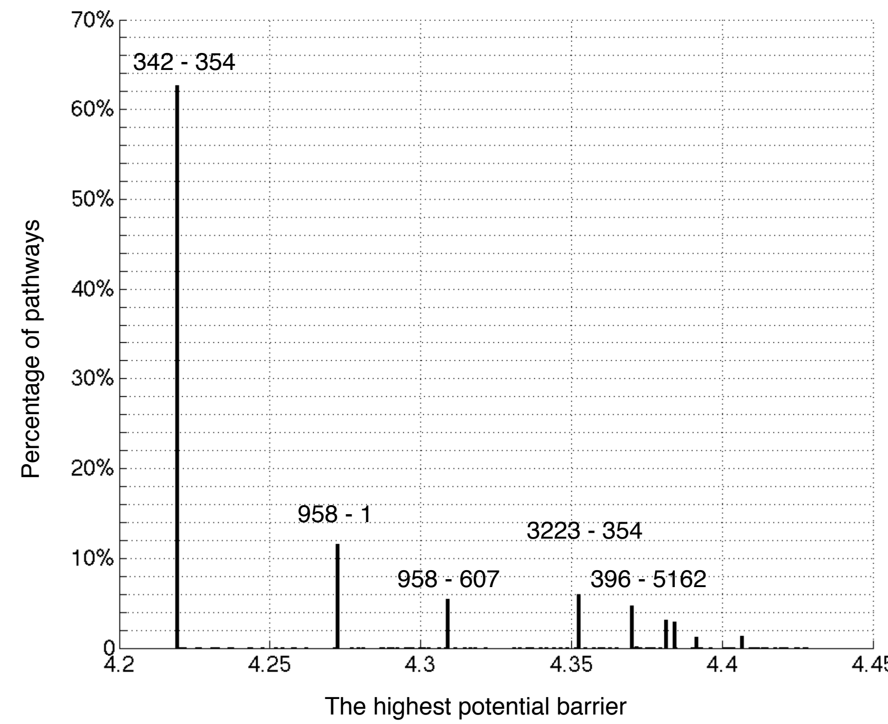


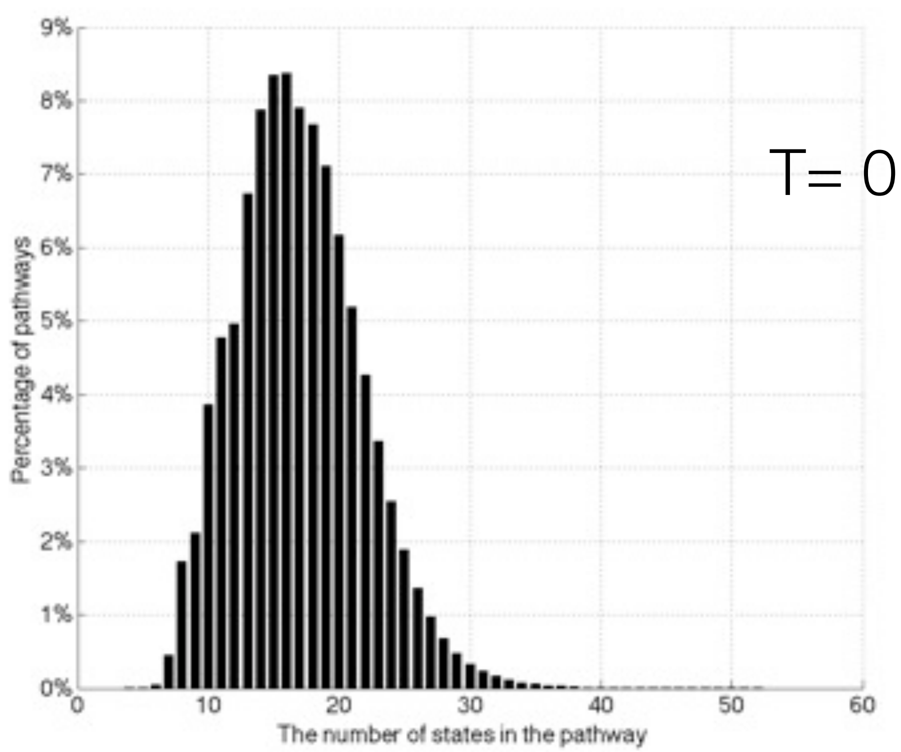
Reorganization of LJ cluster after self-assembly

with Masha Cameron

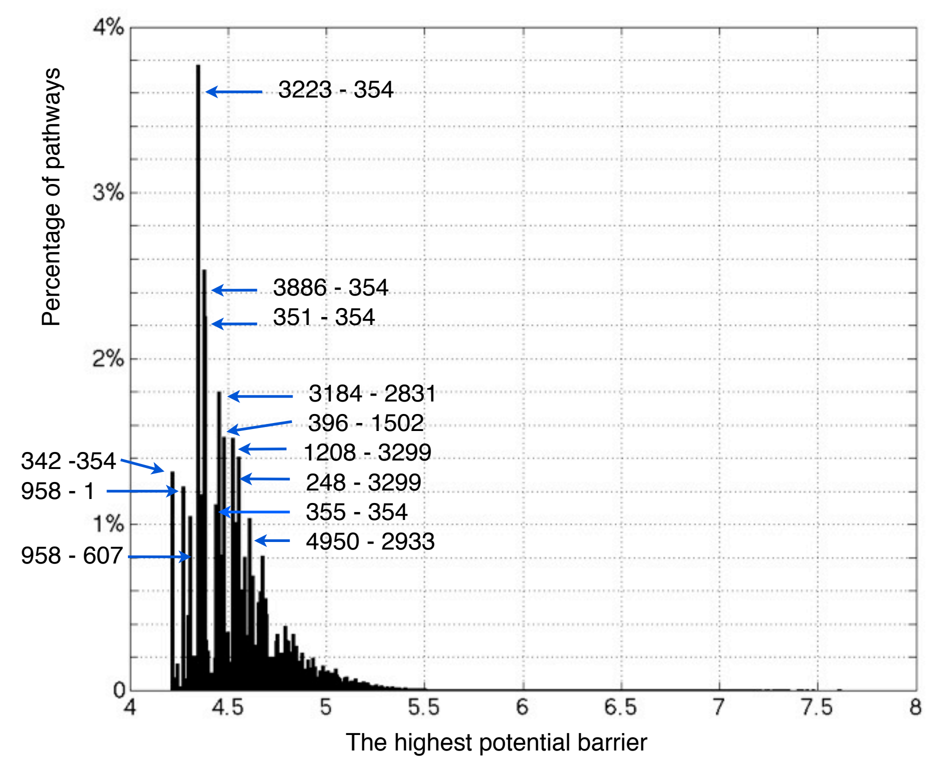


T= 0.05



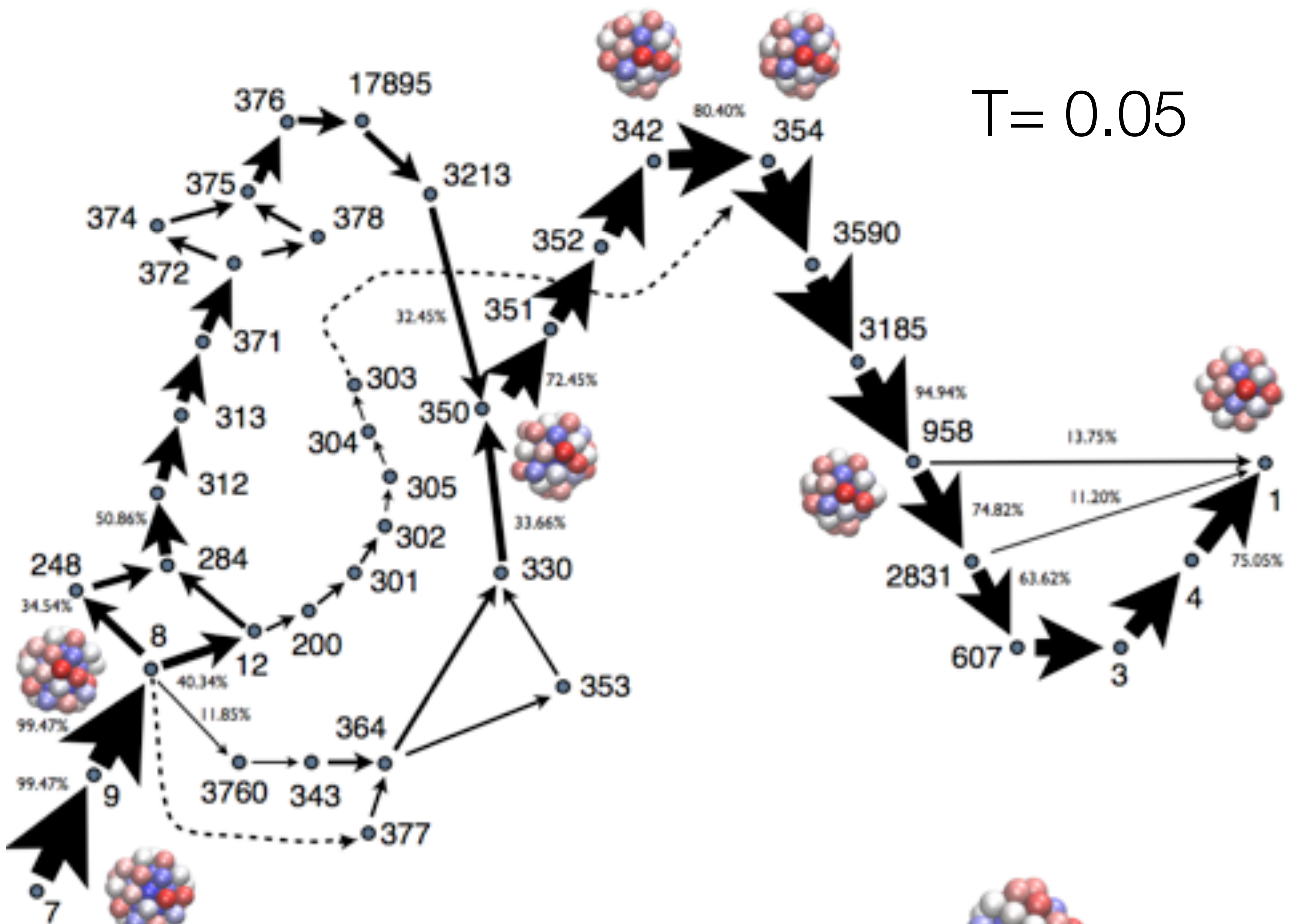


T= 0.15



Reorganization of LJ cluster after self-assembly

with Masha Cameron

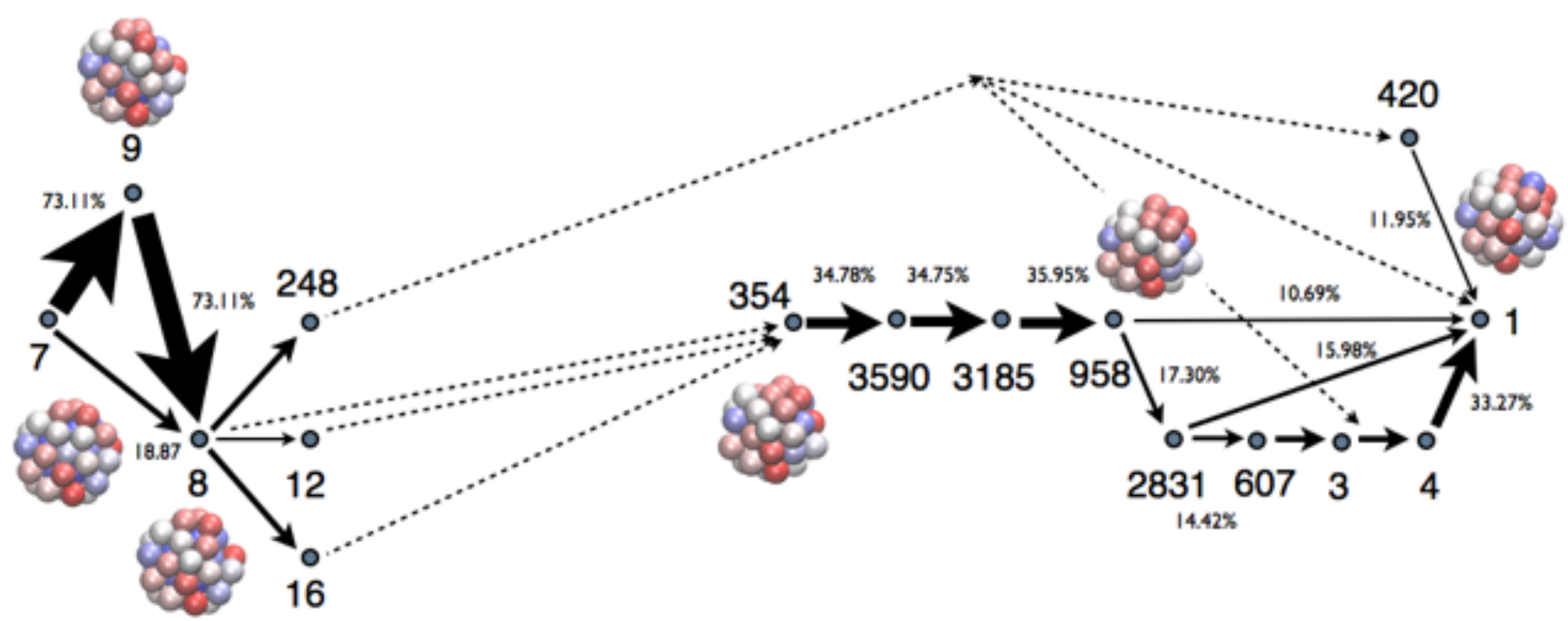


T= 0.05

Number of transition pathways increase with T

They become shorter and go thru higher barriers

T= 0.15



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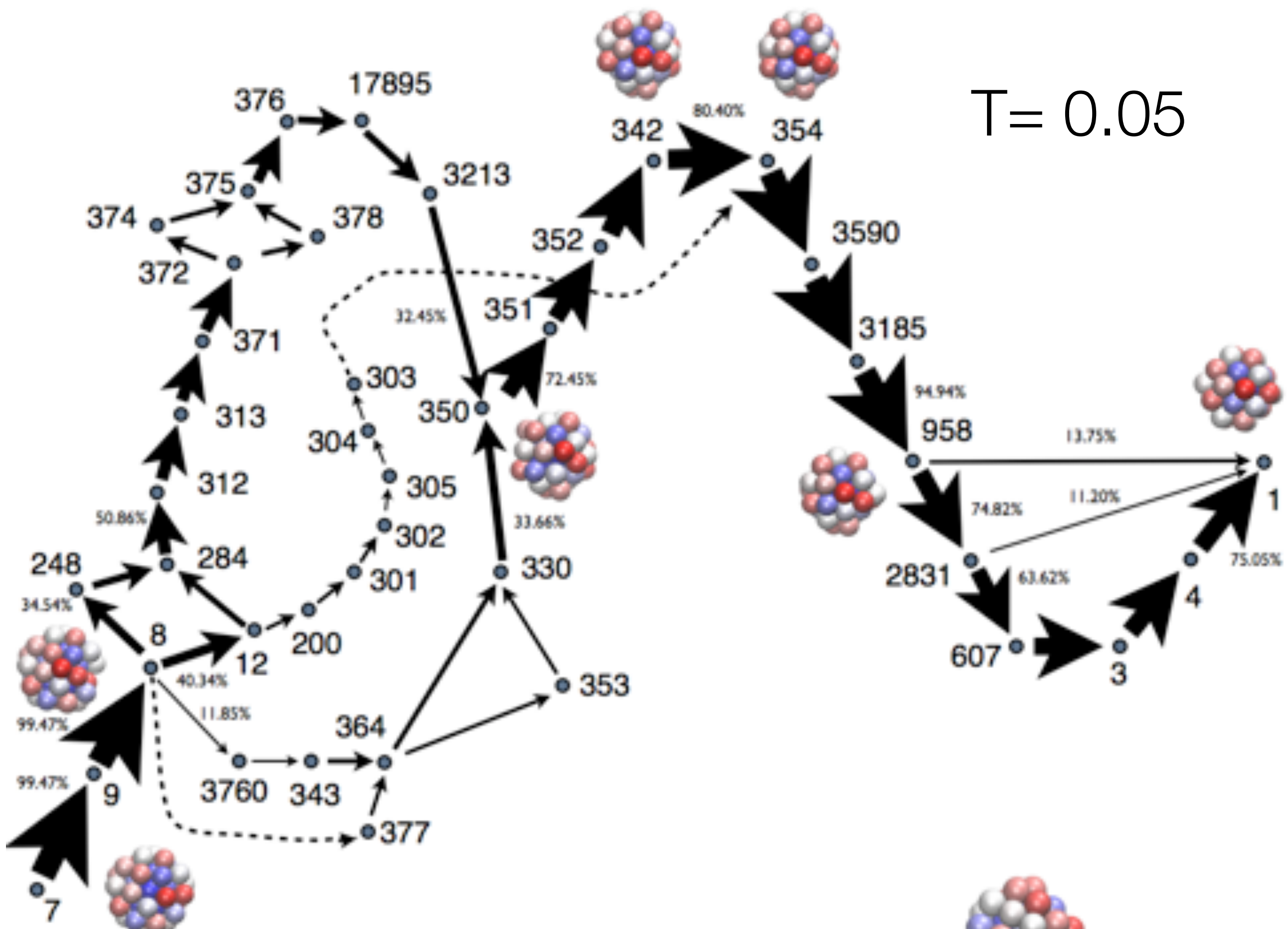

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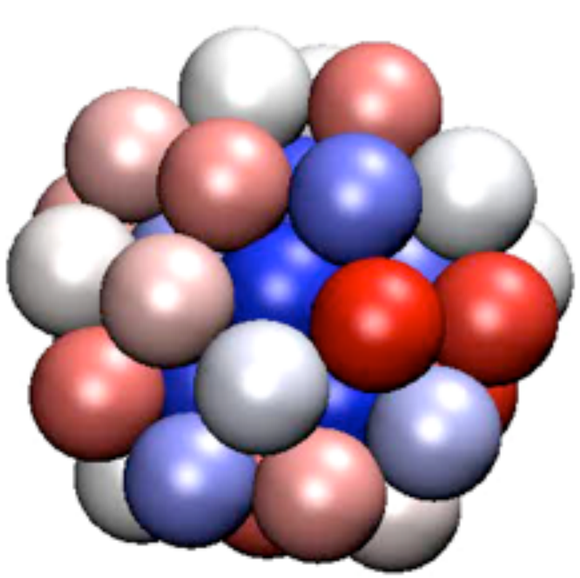

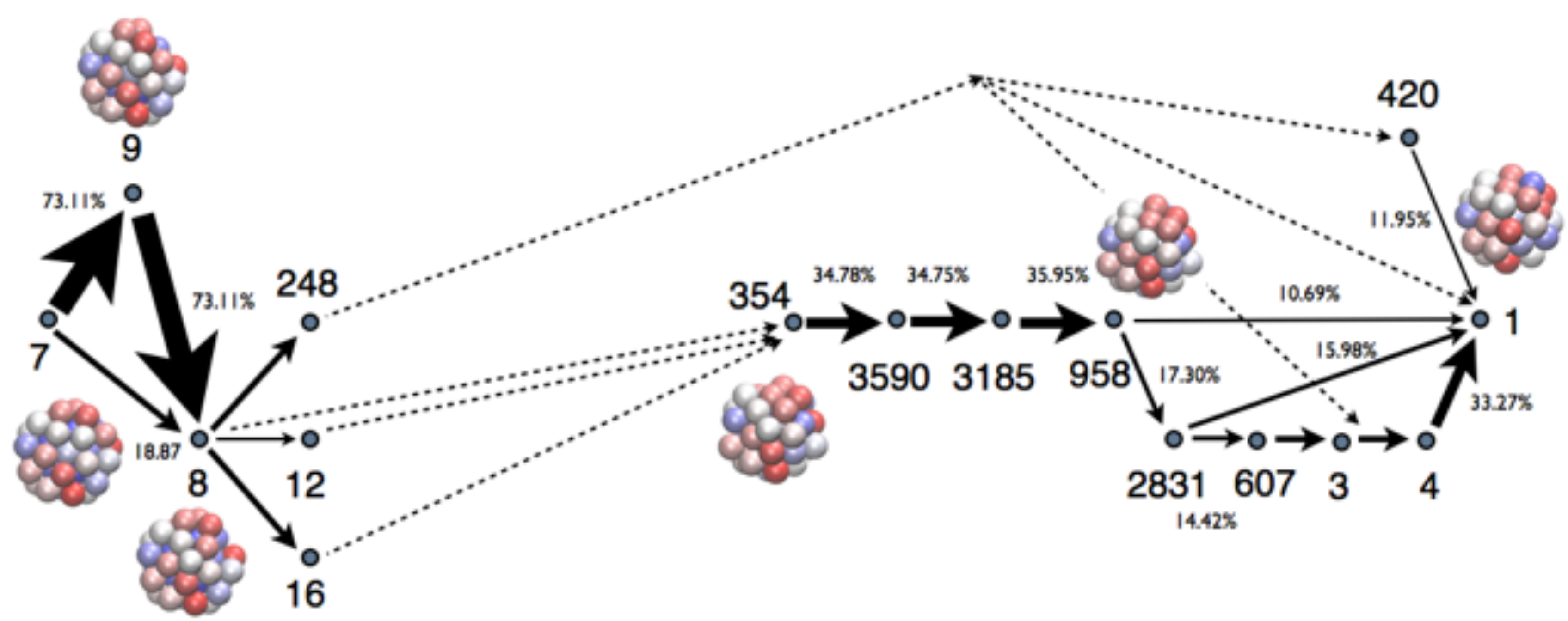

Reorganization of LJ cluster after self-assembly

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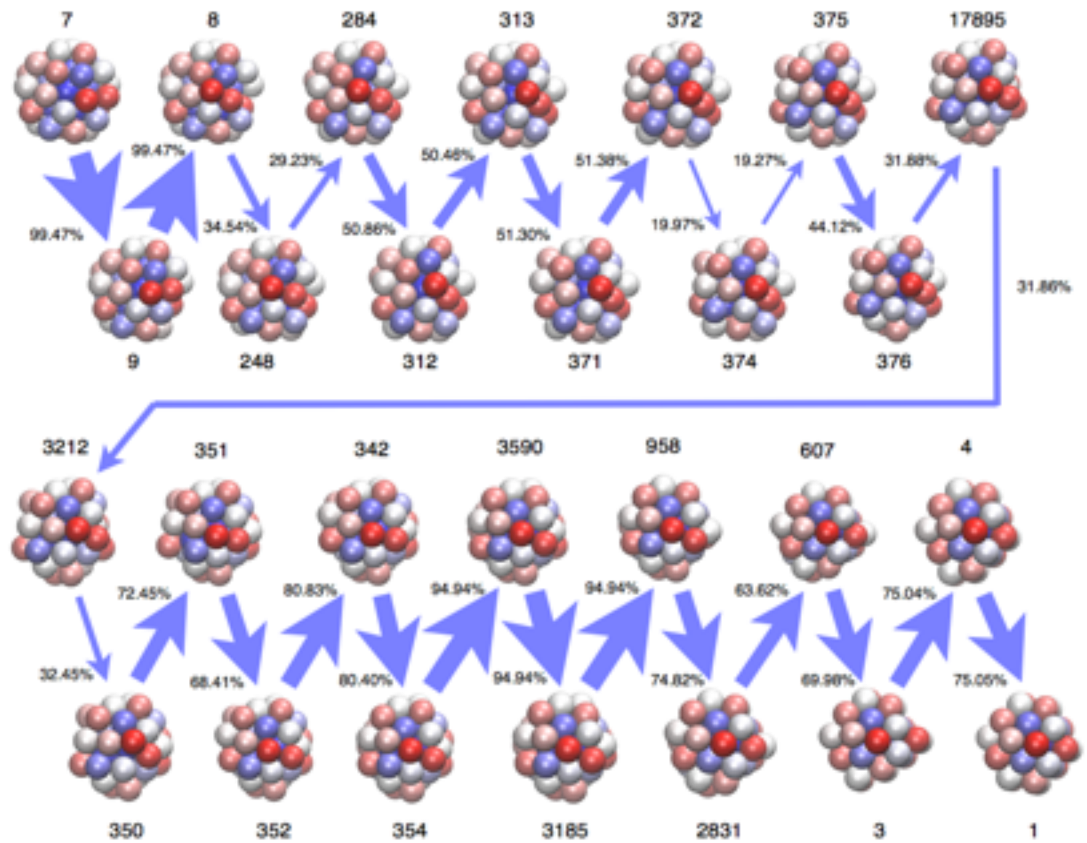

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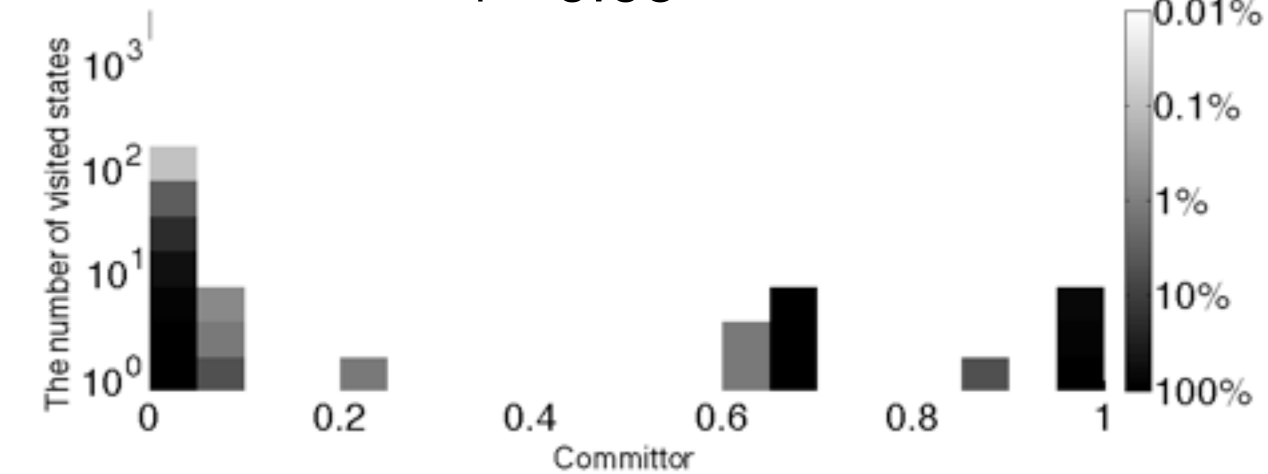

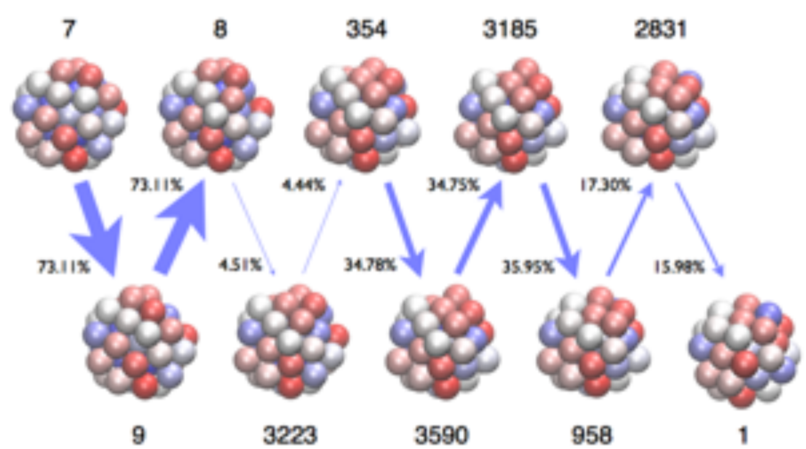

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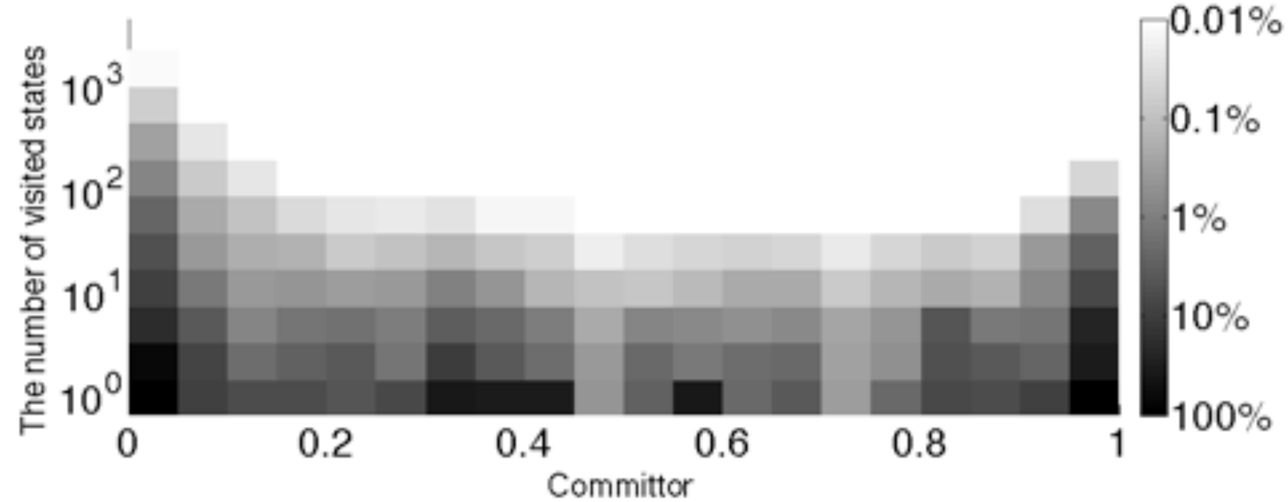
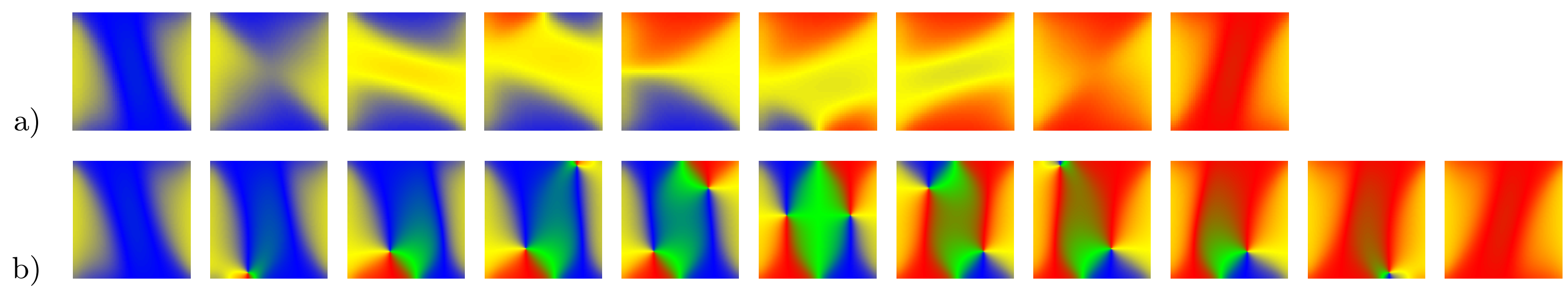


Conclusions

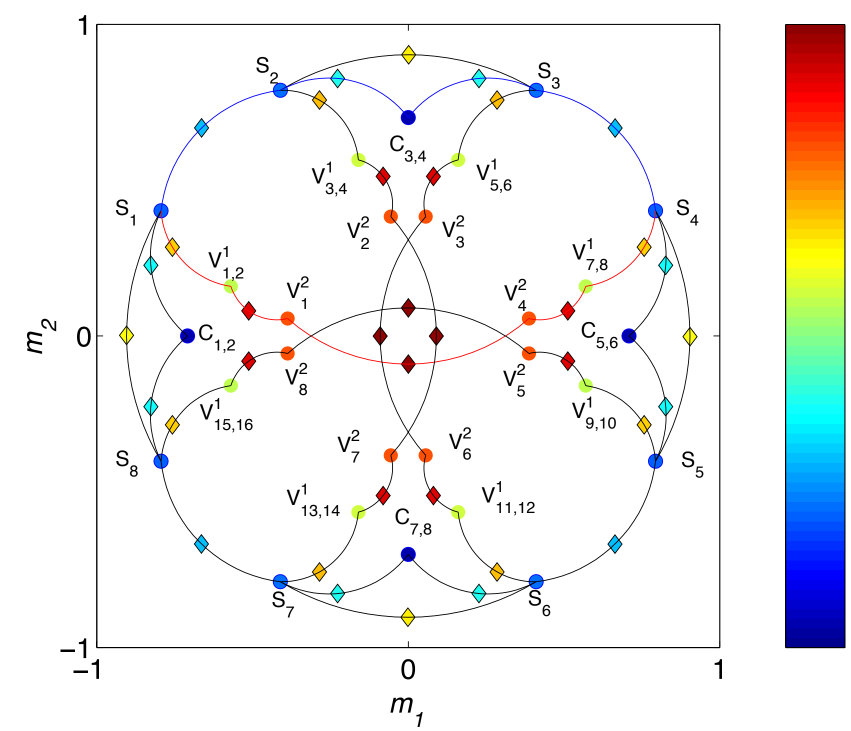
- TPT can be used to focus and analyze a specific `reaction'.
- Gives rate (mean frequency of transition) and mechanism via analysis of current.
- No small parameter needed - reduces to LDT or Bovier's approach in right limits, but can be used outside the range of applicability of these asymptotic theories.
- Can be and has been used in many other examples.

Some other applications

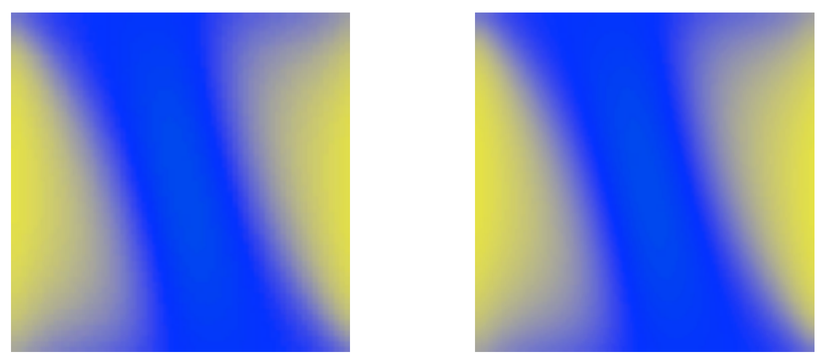
▷ Thermally induced magnetization reversal in submicron ferromagnetic elements



with Weinan E and Weiqing Ren



Practical side of LDT - Dynamics can be reduced to a Markov jump process on energy map, whose nodes are the energy minima and whose edges are the minimum energy paths.



▷ Hydrophobic collapse of a polymeric chain by dewetting transition

with Tommy Miller and David Chandler

Rate limiting step is entropic - creation of a water bubble