Hybrid Monte-Carlo in Path Space

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Outline

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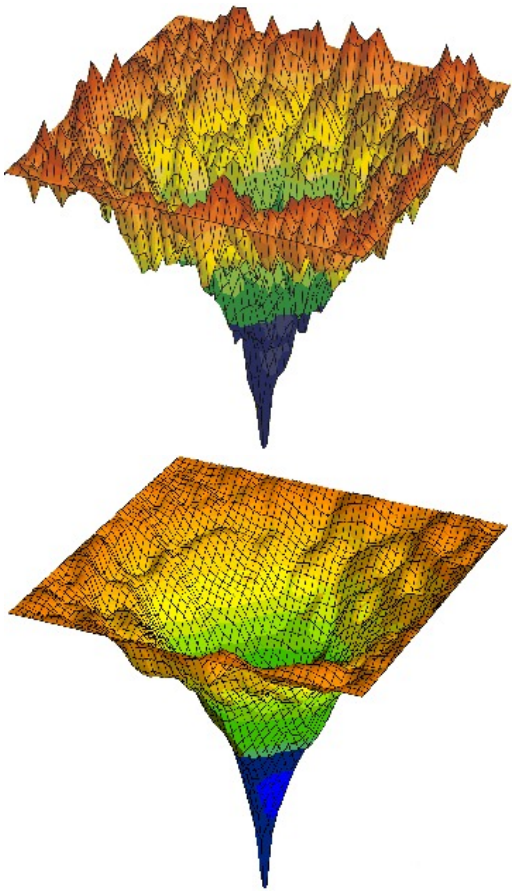
Motivation

- Studying rare transition states of systems of particles is extremely important but can be difficult
- Rare transitions occur in many physical systems, such as proteins and clusters of particles
- The energy landscape of complex systems impedes exploration of transition states
- Development of algorithms that probe these rare transition states is necessary

Free Energy Landscapes



- Goal is to probe finite temperature transitions
- Energy $\neq$ Free Energy
- Energy and free energy landscapes are unknown before simulation
- Classical Equilibrium Statistical Mechanics ($\mathcal{P} \sim e^{-\beta H}$)

http://www.btinternet.com/ martin.chaplin/protein2.html

Equilibrium Statistical Mechanics

- Molecular Dynamics
- Brownian Dynamics
- Monte Carlo
- Combined Methods

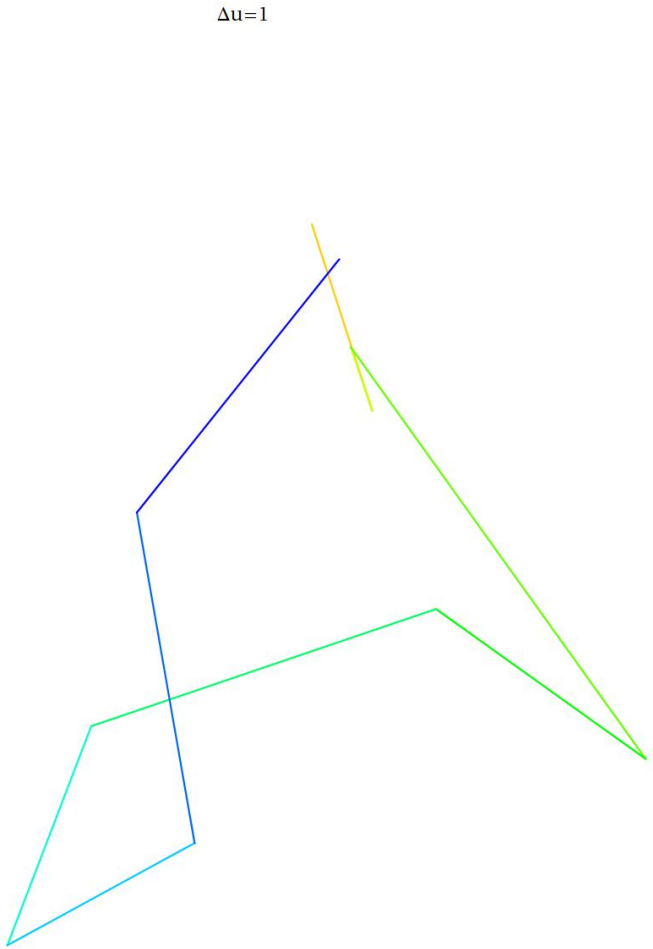
Molecular Dynamics

- Familiar equations for physicists
- $m\frac{d^2x}{dt^2} = F$
- Deterministic and fixed energy
- Long waiting times if $PE > Nk_BT$
- Cooperative movement of particles

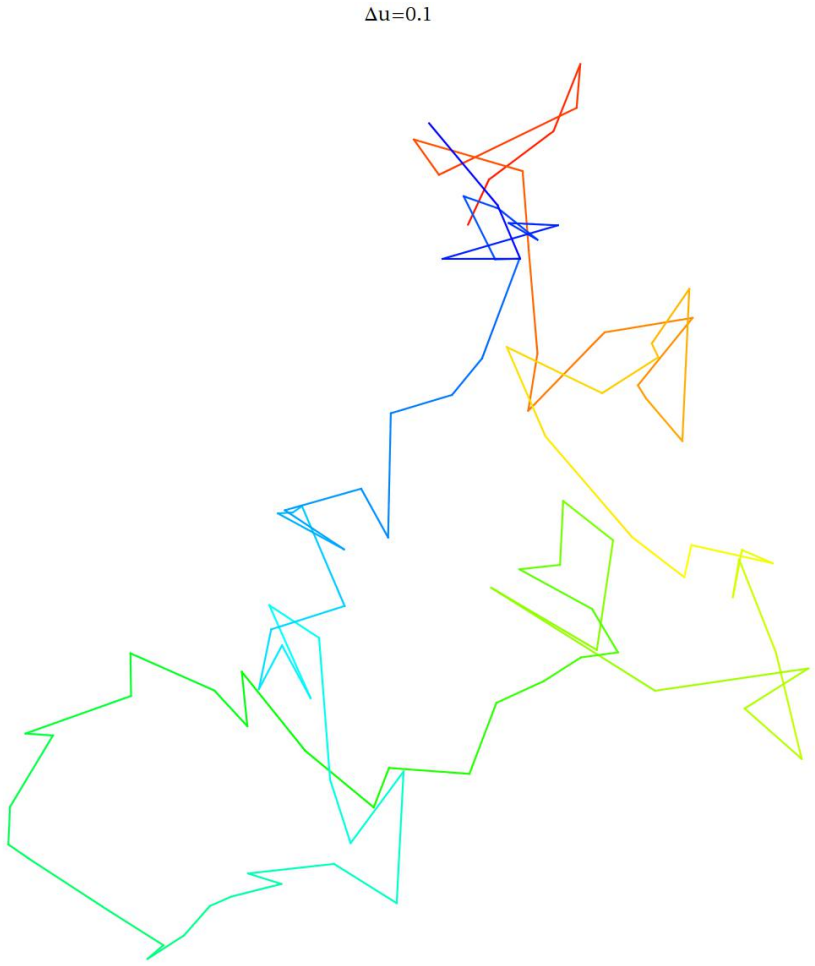
Brownian Dynamics

- Over-damped Langevin dynamics
- $\frac{dx}{du} = F + \sqrt{2k_BT}\ \frac{dW}{du}$
- W is the Wiener process (white noise)
- Quadratic variation: $\sum \Delta x^2 = 2k_BTU$
- Fractal nature

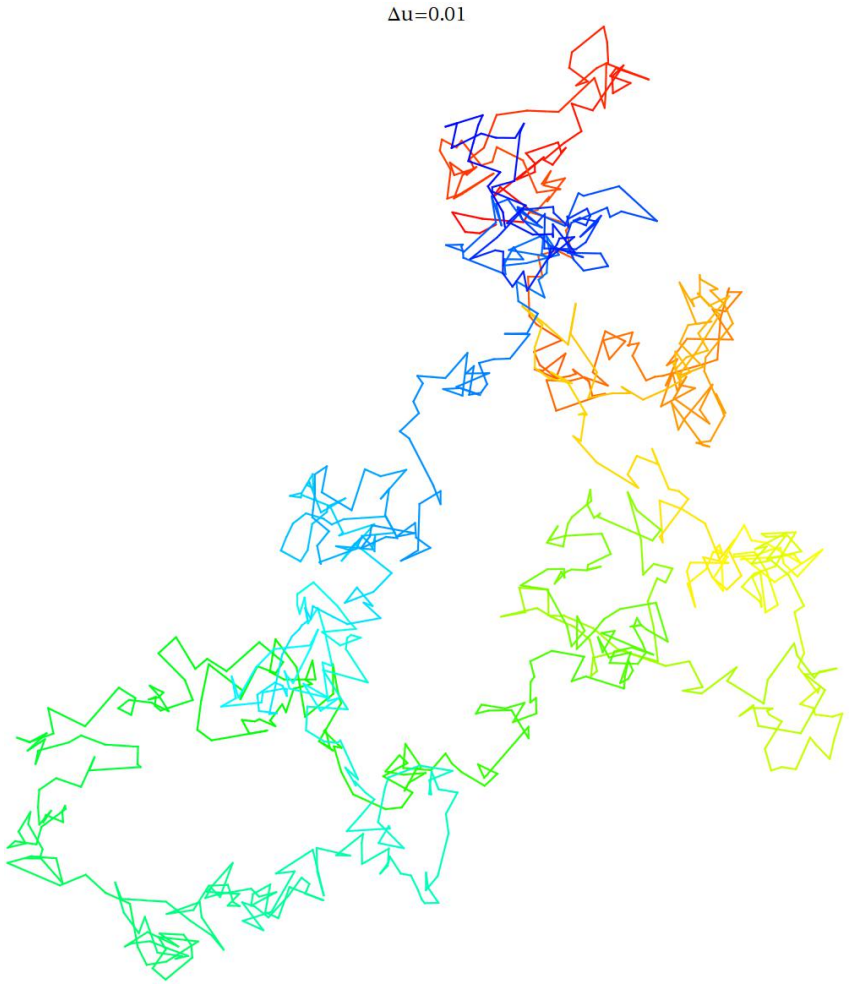
Brownian Dynamics



Brownian Dynamics



Brownian Dynamics



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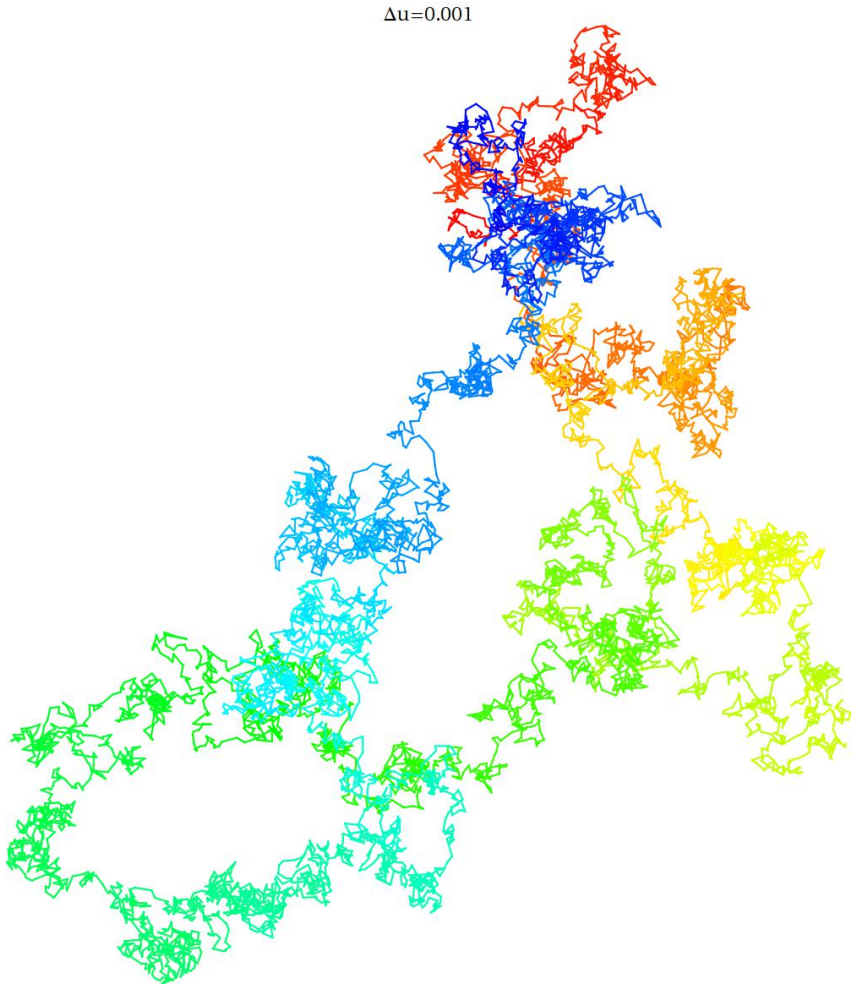

Monte-Carlo

$x \Rightarrow$ current state
$x' \Rightarrow$ proposed move
$\Pi(x, x') \Rightarrow$ the probability of choosing x' given x

Accept/reject based on the Metropolis-like criteria

- Unbiased (Metropolis)
  - $e^{-\beta \Delta H} >$ Rand
- Biased (Metropolis-Hastings)
  - $\exp(-\beta \Delta H) \frac{\Pi(x,x')}{\Pi(x',x)} >$ Rand

Importance sampling with detailed balance

Combined Methods

Smart Monte Carlo

The biased proposed move is generated using Brownian dynamics: Accept/reject with Metropolis-Hastings criteria

Hybrid Monte Carlo

The biased proposed move is generated using molecular dynamics: Accept/reject with Metropolis-Hastings criteria

Error Correction

Monte-Carlo step corrects for the finite step size in BD/MD

Path Space

- Goal: To describe transitions in terms of paths
  - Such transitions can be rare events
  - Paths are inherently infinite dimensional objects
- Route: Create robust and efficient methods to perform sampling in an infinite dimensional space
- Will do the above by imposing boundary conditions and thus forcing the transition of interest

In the next few slides, I will show how to devise one such method. The starting point is the SDE for Brownian dynamics.

Onsager-Machlup Functional

Discreteization of Brownian dynamics: $\frac{\Delta x}{\Delta u} = F + \sqrt{\frac{2k_BT}{\Delta u}}\,\xi_i$

The Onsager-Machlup functional

$$\mathcal{P}_{path} \propto \exp\left(-\frac{1}{2}\sum_i \xi_i^2\right) = \exp\left(-\frac{I}{2k_BT}\right)$$

$$I = \int_0^U du \left\{\frac{1}{2}\left(\frac{\partial x}{\partial u}\right)^2 + G\right\}$$

In the continuum limit the path potential is

$$G = \frac{1}{2}|\nabla V|^2 - k_BT\nabla^2 V$$

The path starts and ends at specified points.
A transition is forced to happen during time interval U.

Path Space Effective Hamiltonian

Transform to k-space (frequency) to facilitate uniform convergence

$$x(u) = \sqrt{2U} \sum_k \frac{A_k}{\pi k} \sin\left(\frac{\pi k u}{U}\right)$$

Remember that $\mathcal{P}_{path} \propto \exp\left[-\frac{I}{2k_B T}\right]$

This allows us to define an effective Hamiltonian

$$H_{eff} = \frac{1}{2}\sum_k \dot{A}_k^2 + I = \frac{1}{2}\sum_k \dot{A}_k^2 + \frac{1}{2}\sum_k A_k^2 + \int_0^U du\ G$$

The masses are chosen to be diagonal in k-space (frequency)
All modes have the same natural frequency (2π)

Overview of the HMC Algorithm

1. Generate zero temperature path by minimizing I
2. Add appropriate thermal fluctuation to the path positions
3. Choose velocities consistent with the temperature
4. Use molecular dynamics to evolve the path
5. Test proposed move using Monte-Carlo
6. Iterate steps 3, 4 and 5

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Implementation of HMC

Molecular Dynamics

- Integrate (deterministic) Hamilton's equations many times
- Use a leap frog algorithm to reduce error
- $N_t \cdot h \approx \pi$ to maximize sampling of phase space

Monte Carlo

- Correct for errors that are introduced with above integration
- Integrate over multiple steps to de-correlate the Markov chain

Lennard-Jones Potential and LJ14 Cluster

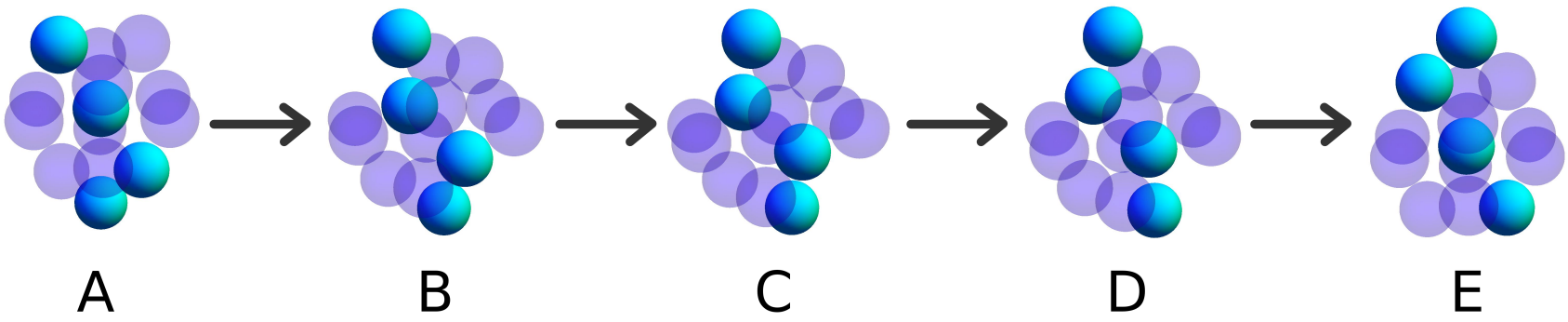
Need for a simple and well understood test problem

$$V_{LJ} = 4 \sum_{i,j}^{N} \left[\left(\frac{1}{r_{ij}} \right)^{12} - \left(\frac{1}{r_{ij}} \right)^{6} \right]$$

Cluster of 13 particles in a hexagonal close-packed configuration

Single nearest neighbor particle on outside of cluster

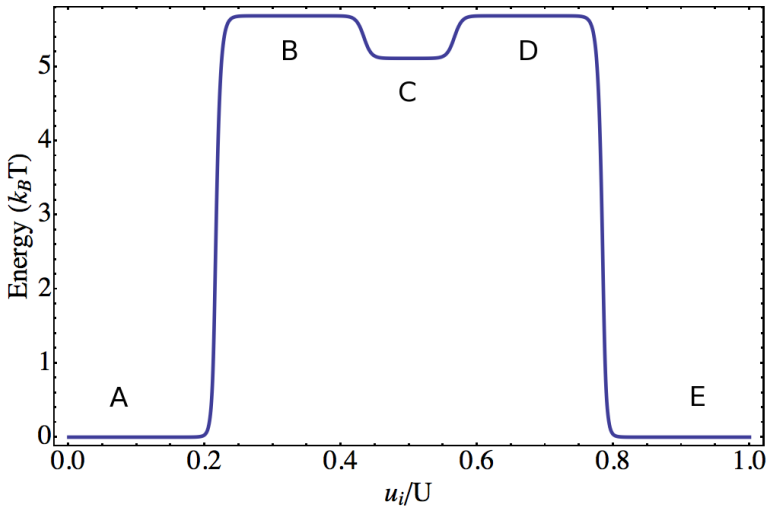
Lennard-Jones Potential and LJ14 Cluster

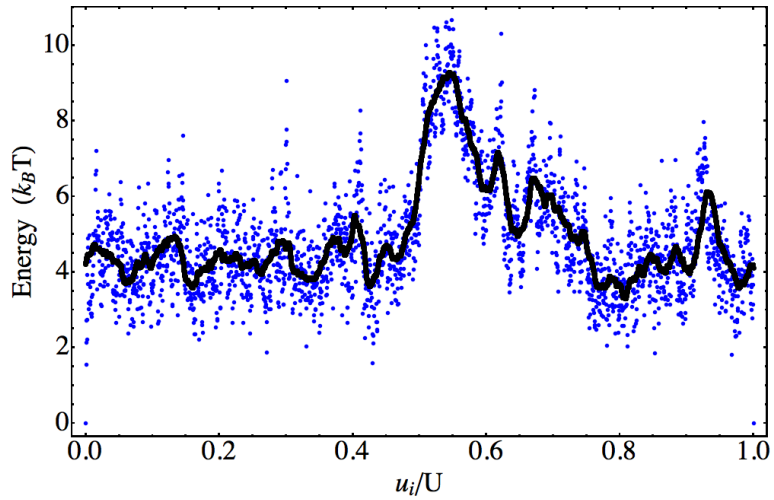


Investigate the low energy mode discovered by Beck *et. al.* [1]

- 5 distinct states for T=0 path
- Two pairs of degenerate states: (A, E) and (B, D).
- Outer group of particles remain approximately static during the transition
- Inner 4 particles form a chain and "snake" through the cluster

The Energy Landscape





Zero Temperature

- Obtained by minimizing I
- Nonphysical solution
- Cluster spends same order of time at each critical point

Finite Temperature $T = 0.35$

- Majority of time spent in low energy state
- Quick transition after traversing the energy barrier

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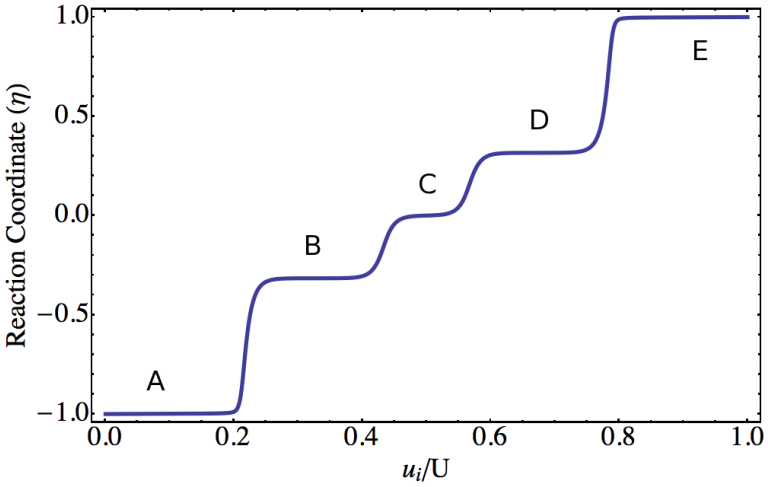
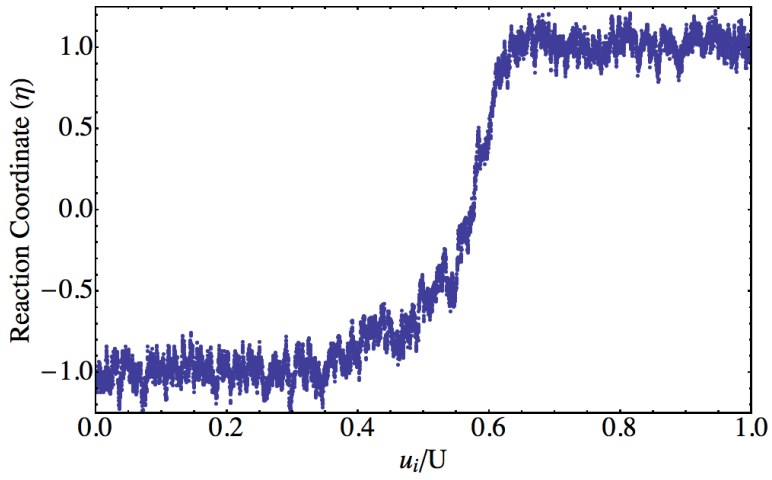
Reaction Coordinate



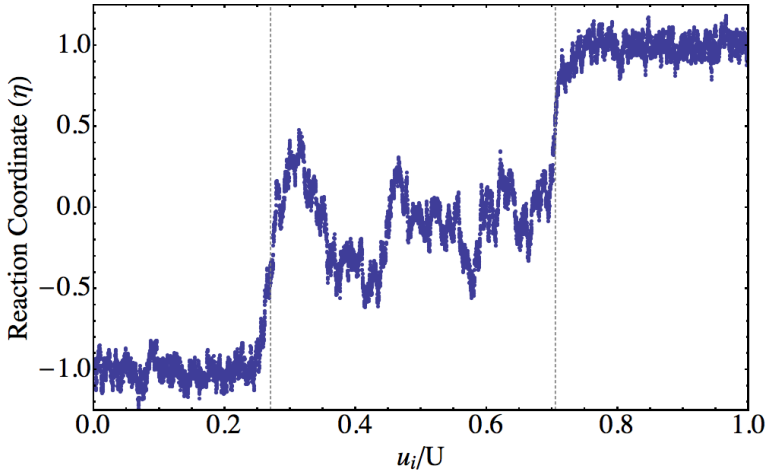


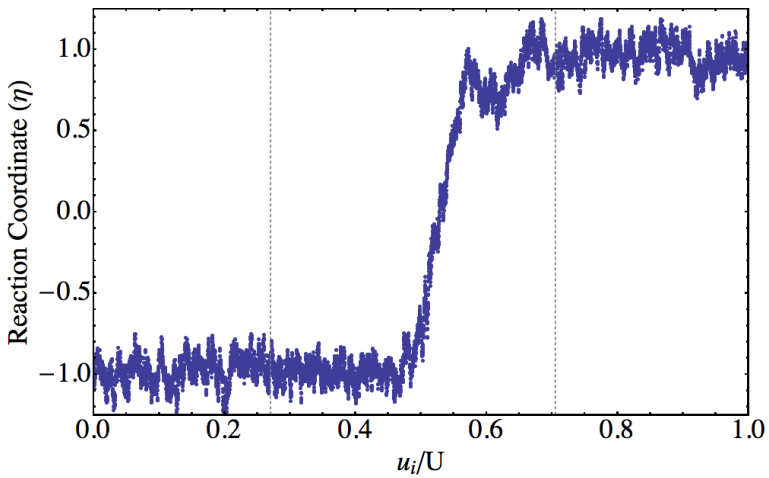
$$\eta = \left(\vec{R}_4 - \vec{R}_{10}\right) \cdot \hat{n}$$

Maps a configuration along the path to the amount the transition has progressed

- $(\vec{R}_4 - \vec{R}_{10})$ difference in center of mass of outside cluster to inside chain
- $\hat{n}$ is the eigenvector corresponding to the minimum eigenvalue of the moment of inertia of the chain

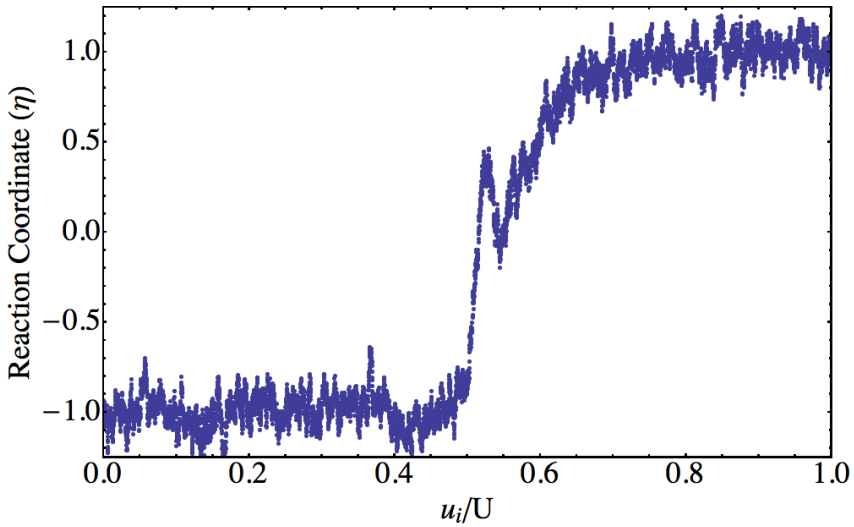
Evolution of the Path





- Strengths
  - Efficient sampling of path space
  - Allows a noise enhanced zero temperature starting path
  - Can characterize the instanton for moderate path sizes
- Weaknesses
  - Transition rates are only accessible in the long path length limit.
  - Risk of inefficient sampling with improper choice of parameters

Intermediate State



- Able to investigate intermediate states efficiently
- No a priori knowledge of any intermediate state(s)
- States B, C and D may not exist as separate entities

Challenges

Boundary Conditions

Algorithm does not supply information about the path
Annealing an unphysical starting path is computationally expensive

Path Length

BC's act as an unphysical external force if path length is too short

Challenges

Thermal Noise

Fractal nature of the path requires calculations of noise
Quadratic variation imposes limit on Δu
Small $\Delta u \Rightarrow$ calculation of noise

Computational Complications

Implementation of parallel algorithm is necessary for large problems
Distributed memory system
Scaling with an increase of system size

Possibilities for Future Work

2D LJ system

Liquid-gas phase transition of Lennard-Jones particles in two dimensions
Size and shape of critical droplets (sufficiently distant from the critical point)[2]

Coarse grained protein models

Very large systems require a coarse-grain model
Uncover intermediate states and impediments to proper folding
Need to understand what an appropriate model might be

References

- H. D. R.S. Berry, T.L. Beck and J. Jellinek *Advances in Chemical Physics, Prigogine, I.; Rice, S. A., Ed(s); Wiley: New York*, vol. 70, pp. 75–138, 1988.
- S. C. M. Santra and B. Bagchi *J. Chem. Phys.*, vol. 129, p. 234704, 2008.

Thank You!

Appendix

Derivation of the Path Potential

Discrete Brownian eqn: $\frac{\Delta x}{\Delta u} = F + \sqrt{\frac{2k_BT}{\Delta u}}\,\xi_i$

Forward: $\frac{k_BT}{2}\sum \xi^2_{i,\rightarrow} = \sum_i \frac{\Delta u}{4}\left[\left(\frac{\Delta x}{\Delta u}\right)^2 + |F_i|^2 - 2F_i\frac{x_{i+1}-x_i}{\Delta u}\right]$

Back: $\frac{k_BT}{2}\sum \xi^2_{i,\leftarrow} = \sum_i \frac{\Delta u}{4}\left[\left(\frac{\Delta x}{\Delta u}\right)^2 + |F_{i+1}|^2 - 2F_{i+1}\frac{x_i-x_{i+1}}{\Delta u}\right]$

Avg: $\frac{k_BT}{4}\sum \left(\xi^2_{i,\rightarrow} + \xi^2_{i,\leftarrow}\right) = \sum_i \frac{\Delta u}{4}\left[\left(\frac{\Delta x}{\Delta u}\right)^2 + F^2 + F'\frac{\Delta x^2}{\Delta u}\right]$

With the substitutions: $F' = -\nabla^2 V$ and $\frac{\Delta x^2}{\Delta u} = 2k_BT$

$$\frac{k_BT}{4}\sum \left(\xi^2_{i,\rightarrow} + \xi^2_{i,\leftarrow}\right) = \frac{1}{2}\int_0^U du \left[\frac{1}{2}\left(\frac{\partial x}{\partial u}\right)^2 + \underbrace{\frac{1}{2}|\nabla V|^2 - k_BT\nabla^2 V}_{G}\right]$$

Controlling Errors in Molecular Dynamics

Errors and Hamilton's Equations

- $\Delta E \sim \mathcal{O}(t^2)$ necessitates a integration with error in t^2
- Hamilton's Equations: $\frac{dp}{dt} = -\frac{dH}{dq}$ and $\frac{dq}{dt} = \frac{dH}{dp}$
- Using H_{eff} we find: $\dot{v} = -A - \text{S.T.}[\nabla G]$ and $\dot{A} = v$

Leap Frog Type Algorithm

Half Step $\Rightarrow$ $v(t + h/2) - v(t) = -\frac{h}{2} \cdot \text{S.T.}[\nabla G]$

Full Step $\Rightarrow$ $\dot{v} = -A$ and $\dot{A} = v$ *(Analytic Rotation)*

Half Step $\Rightarrow$ $v(t + h) - \tilde{v}(t + h/2) = -\frac{h}{2} \cdot \text{S.T.}[\nabla G]$

Transform the above equations from k-space to path space

Quadratic Variation Along the Path

The correct thermal 'noise' along the path is governed by the quadratic variation. From Brownian dynamics:

$$\frac{\Delta x}{\Delta u} = F + \sqrt{\frac{2k_BT}{\Delta u}}\,\xi_i$$

On average, the force (F) is zero. The expectation of $\xi_i^2 = 1$.

$$\sum_i \left(\frac{\Delta x}{\Delta u}\right)^2 = \sum_i \frac{2k_BT}{\Delta u}\,\xi_i^2$$

$$\sum_i (x_i - x_{i-1})^2 = 2k_BTU$$

Equilibrium Average of G

$$G = \sum_{i,\alpha} \left\{ \frac{1}{2} \left(\frac{\partial V}{\partial x_{i\alpha}} \right)^2 - k_B T \left(\frac{\partial^2 V}{\partial x_{i\alpha}^2} \right) \right\}$$

$$\left\langle \left(\frac{\partial V}{\partial x_{i\alpha}} \right)^2 \right\rangle = \frac{1}{Z} \int dx^{dN} \left(\frac{\partial V}{\partial x_{i\alpha}} \right)^2 \exp\left(-\frac{V}{k_B T}\right)$$

$$u = -\exp\left(-\frac{V}{k_B T}\right) \quad \text{then} \quad du = \frac{dx}{k_B T} \frac{\partial V}{\partial x_{i\alpha}} \exp\left(-\frac{V}{k_B T}\right).$$

$$v = \frac{\partial V}{\partial x_{i\alpha}} \quad \text{then} \quad dv = \frac{\partial^2 V}{\partial x_{i\alpha}^2}\, dx.$$

$$\left\langle \left(\frac{\partial V}{\partial x_{i\alpha}} \right)^2 \right\rangle = \frac{k_B T}{Z} \int v\, du = -\frac{k_B T}{Z} \int u\, dv = k_B T \left\langle \frac{\partial^2 V}{\partial x_{i\alpha}^2} \right\rangle$$

$$\langle\, G \,\rangle = -\frac{1}{2} \sum_{i,\alpha} \left\langle \left(\frac{\partial V}{\partial x_{i\alpha}} \right)^2 \right\rangle = -\frac{k_B T}{2} \sum_{i,\alpha} \left\langle \left(\frac{\partial^2 V}{\partial x_{i\alpha}^2} \right) \right\rangle$$

Calculation of an Appropriate Path Length

$$I_1 = \int du \sum_{i,\alpha} \frac{1}{2} \left(\frac{dx}{du} \right)^2 = \left(\frac{1}{\Delta u} \right) \left(\frac{3N_p}{2} \right) 2TU$$

$$I_2 = \int du\, G \approx GU$$

Now for good statistics we impose $I_1 = 100 I_2$

$$\Delta u = \frac{3N_p T}{100G}$$