Sampling Doubly Constrained Brownian Paths using HMC: Exploring Entropic Barriers

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Abstract

I present calculations of doubly-constrained paths for a particle undergoing Brownian dynamics and moving in an external potential. Using the lens of the Metropolis algorithm, I construct Onsager-Machlup-like functionals for a discrete time mesh. I then use the path ensemble to estimate the free energy difference between the starting and ending states.

The Sombrero Potential

Creased

Creased with Bump

Shifted Bump

Creased Sombrero

Creased Sombrero with bump

shifted bump

Outline

- Algebra: Brownian Dynamics and the OM functional
- HMC: review and connection to Brownian Dynamics
- Sampling paths
  - Auxiliary variables, Mass, Splitting, Error
  - Determining how long to integrate Hamiltion's equations
- Results (two-dimensions) Paths and Free energy difference

The Framework

We look at a particle moving in an external potential, $V(x)$, where x denotes the position of the particle.

The components of the force are given by $F_\alpha(x) = -\frac{\partial V}{\partial x_\alpha}$.

The temperature (in energy units) will be represented as ϵ.

The time increment along the path is Δt.

The "length" of the path is the integration time and is given by T.

The evolution of the path will be in steps of $\Delta\tau = \tilde{h}^2/2$.

Brownian Dynamics – Stochastic Differential Equation

The usual discretization of the SDE is

$$x_{i+1} = x_i + \Delta t\, F(x_i) + \sqrt{2\,\epsilon\,\Delta t}\,\xi_i$$

where ξ_i is a Gaussian random variate (unit variance and mean zero). The probability of the path starting at x_0 and $t = 0$, with $T = N_t\,\Delta t$, is

$$P_{\Delta t}(x_0,\, T) = \frac{1}{\sqrt{2\,\pi}} \prod_i \exp\left(-\frac{\xi_i^2}{2}\right)$$

The OM (Onsager-Machlup) functional is given by

$$I_{OM} = \frac{1}{4\,\epsilon} \sum_i \Delta t \left| \frac{(x_{i+1} - x_i)}{\Delta t} - F(x_i) \right|^2$$

With the path probability

$$P_{\Delta t}(x_0,\, T) = \left(\frac{1}{\sqrt{4\,\pi\,\epsilon\,\Delta t}}\right)^{N_t} \exp\Big(-I_{OM}\Big)$$

Path Sampling

Hold the starting and ending positions fixed.

$$\tilde{I}_{OM} = \frac{1}{2} \sum_i \Delta t \left| \frac{(x_{i+1} - x_i)}{\Delta t} - F(x_i) \right|^2$$

Use importance sampling with $\log P = C - \frac{1}{2} \tilde{I}_{OM}/\epsilon$ to create an ensemble of paths.

Here we use a Hybrid Monte Carlo (HMC) algorithm using auxiliary variables.

Next Steps:

- Derive various OM-like functions.
- Describe the HMC method employed.
- Display Results

Configuation Space Sampling using HMC

Boltzmann Probability: $P \propto \exp\big(-V(x)/\epsilon\big)$
Hamiltonian: $H = \frac{1}{2}v^2 + V(x)$
Auxiliary (Gaussian-distributed) variable (velocity): v

Temperature: ϵ Starting position x_0
Choose the velocity: $v = \sqrt{\epsilon}\,\xi$ Evolve Hamilton's equation
Leap-frog (MD time step h)

$$\text{MD step} \qquad x_1 = x_0 + \; h\,v \; + \; \frac{h^2}{2}F(x_0)$$

Iterate "MD step" a number of times, then accept or reject last configuration using the Metropolis-Hastings-Green criterion.

Connection to Brownian dynamics

$$\text{MD step} \qquad x_1 = x_0 + h\,v + \frac{h^2}{2} F(x_0)$$

If we only take a single MD step and define $\Delta t = \frac{h^2}{2}$, we arrive at

$$x_1 = x_0 + \Delta t\, F(x_0) + \sqrt{2\,\epsilon\,\Delta t}\,\xi,$$

which is the Euler-Maruyama equation.

This point explains why Brownian dynamics does such a reasonable job of sampling the Boltzmann distribution for sufficiently small time steps.

Using other quadratures in HMC

Temperature: ϵ Starting position x_0

Choose the velocity: $v = \sqrt{\epsilon}\,\xi$ Evolve Hamilton's equation

General MD step $$x_1 = x_0 + h\,v + \frac{h^2}{2}\tilde{F}(x_0, x_1)$$

Transformation $\{x_0, v\} \Rightarrow \{x_1, v'\}$ is not necessarily symplectic.

The acceptance criterion depends on the Jacobian as well as energy conservation. The midpoint rule gives the highest acceptance rate for a choice of h (of the four methods considered).

Method	Average Force: $\tilde{F}(x_i, x_{i+1})$	Jacobian	ΔE_t
Trapezoid	$\frac{1}{2}\left(F(x_i) + F(x_{i+1})\right)$	$J = 1 + O(h^2)$	$O(h^3)$
Midpoint	$F\left(\frac{x_i + x_{i+1}}{2}\right)$	$J = 1$	$O(h^3)$
Simpson's	$\frac{1}{6}\left(F(x_i) + 4F\left(\frac{x_i + x_{i+1}}{2}\right) + F(x_{i+1})\right)$	$J = 1 + O(h^2)$	$O(h^5)$

Table: The average force $\overline{F}(x_i, x_{i+1})$ that is acting as the system evolves from x_i to x_{i+1} for the three methods.

OM-like functionals: 1-dimensional case

For the transformation $\{x_0,\, v_0\} \Rightarrow \{x_0,\, x_1\}$, the Jacobian, $\mathbb{J} = \partial v_0 / \partial x_1$ is given by

- Trapezoid: $\sqrt{2\,\Delta t}\ \mathbb{J} = 1 - \frac{\Delta t}{2} F'(x_1)$
- Midpoint: $\sqrt{2\,\Delta t}\ \mathbb{J} = 1 - \frac{\Delta t}{2} F'\left(\frac{x_i + x_{i+1}}{2}\right)$
- Simpson's: $\sqrt{2\,\Delta t}\ \mathbb{J} = 1 - \frac{\Delta t}{6}\left(F'(x_0) + 2\,F'\left(\frac{x_i + x_{i+1}}{2}\right)\right)$

Note that $\frac{2\epsilon}{\Delta t}\log(\mathbb{J}) \approx c - \epsilon\,\mathbb{F}'$ which, when provides the Laplacian term in the definition of G in the continuous time limit.

$$\tilde{I}^{Q}_{OM} = \sum_i \Delta t \left(\frac{1}{2}\left|\frac{(x_{i+1} - x_i)}{\Delta t} - \tilde{F}(x_i)\right|^2 + \frac{2\epsilon}{\Delta t}\log\left|\det(\mathbb{J})\right|\right)$$

For dimensions larger than 1 and for systems consisting of more than a single particle, the Jacobian becomes a matrix. The complexity of the calculation quickly increases as one changes either.

Sampling Brownian paths using HMC

The OM functional

$$\tilde{I}^{Q}_{OM} = \sum_{i} \Delta t \left(\frac{1}{2} \left| \frac{(x_{i+1} - x_i)}{\Delta t} - \tilde{F}(x_i, x_{i+1}) \right|^2 + \frac{2\epsilon}{\Delta t} \log \left| \det(\mathbb{J}) \right| \right)$$

Sampling Brownian paths using HMC

The OM functional

$$\tilde{I}^{Q}_{OM} = \sum_{i} \Delta t \left(\frac{1}{2} \left| \frac{(x_{i+1} - x_i)}{\Delta t} - \tilde{F}(x_i, x_{i+1}) \right|^2 + \frac{2\epsilon}{\Delta t} \log \left| \det(\mathbb{J}) \right| \right)$$

$$\tilde{I}^{Q}_{OM} = \frac{1}{2} < X \,|\, L \,|\, X > + < 1 \,|\, \overline{\Phi} >$$

where the operator L is the discrete version of $L = -\partial^2 / \partial t^2$.

Sampling Brownian paths using HMC

$$\tilde{I}^{Q}_{OM} = \frac{1}{2} < X \,|\, L \,|\, X > \; + \; < 1 \,|\, \overline{\Phi} >$$

where the operator L is the discrete version of $L = -\partial^2 / \partial t^2$.

Add Gaussian distributed auxiliary variables (free Brownian Bridge)

$$H_{eff} = \frac{1}{2} < v \,|\, L \,|\, v > \; + \frac{1}{2} < X \,|\, L \,|\, X > \; + \; < 1 \,|\, \overline{\Phi} >$$

where the mass operator M has been chosen to be the same as L.

Hamilton's equations

Mass operator M_{op} is $L = -\partial^2 / \partial t^2$ (the discrete version).
And L^{-1} is defined with the appropriate boundary conditions.

$$H_{eff} = \frac{1}{2} < v \,|\, L \,|\, v > + \frac{1}{2} < X \,|\, L \,|\, X > + < 1 \,|\, \overline{\Phi} >$$

$$L\,\dot{v} = -L\,X - \overline{\Phi}' \qquad \dot{v} = -X - L^{-1}\phi$$

$$\dot{X} = v \qquad \ddot{X} = -X - L^{-1}\phi$$

For $\overline{\Phi} = 0$, these equations reduce to mixing of Brownian Bridges with 100% acceptance.

For $\overline{\Phi} = 0$, all modes have the same frequency $2\,\pi$.

Splitting Hamilton's equations (symplectic)

equations of motion: $\dot{v} = -L^{-1}\phi - X \qquad \dot{X} = v$

Half Step	$\dot{v} = -L^{-1}\phi$	$v_h - v_0 = -\frac{1}{2}\tilde{h}\ L^{-1}\phi(X_0)$
Full Step	$\dot{v} = -X$	$v_h - w_h = -\frac{1}{2}\tilde{h}\Big(X_0 + X_1\Big)$
Crank-Nicolson	$\dot{X} = v$	$X_1 - X_0 = \frac{1}{2}\tilde{h}\Big(v_h + w_h\Big)$
Half Step	$\dot{v} = -L^{-1}\phi$	$v_1 - w_h = -\frac{1}{2}\tilde{h}\ L^{-1}\phi(X_1)$

The middle step ensures that the quadratic variation is preserved, as the step corresponds to mixing Brownian Bridges.

Hybrid Monte Carlo: ingredients

1. Need starting path – with "correct" quadratic variation

$$\sum \left(x_{i+1} - x_i\right)^2 = 2\,\epsilon\,T$$

2. Generate velocities – with "correct" quadratic variation

$$\sum \left(v_{i+1} - v_i\right)^2 = 2\,\epsilon\,T$$

3. Integrate Hamilton's equations: iterate the above method

   Picked number N_s of steps so that $\pi/2 < N_s\tilde{h} < 3\pi/2$

4. Acceptance step: proposed path may be rejected

   Symplectic property ensures that the error in the effective energy is bounded (when $\tilde{h}$ is small).

Error in the "Energy"

Remember that the OM function grows with the number of intervals; thus as $\Delta t \to 0$, the value of the OM functional grows without bounds.

One of the virtues of the numerical scheme is that the error in the effective energy can be calculated without subtracting large numbers.

And that the symplectic nature of the numerical scheme means that this error is bounded.

The numerical scheme is particularly good at handling the high frequency modes. The L^{-1} is a smoothing operator as it corresponds to doubly integrating the function upon which it acts. Thus the Fourier components of $L^{-1}\phi$ become small beyond some cutoff frequency. The numerical scheme is exact when Φ vanishes.

Error in the "Energy"

$$\Delta E_{eff}\left(X_0 \to X_1\right) = < 1 \,|\, \overline{\Phi}(X_1) > - < 1 \,|\, \overline{\Phi}(X_0) >$$

$$-\frac{1}{2} < \phi(X_0) + \phi(X_1) \,|\, X_1 - X_0 >$$

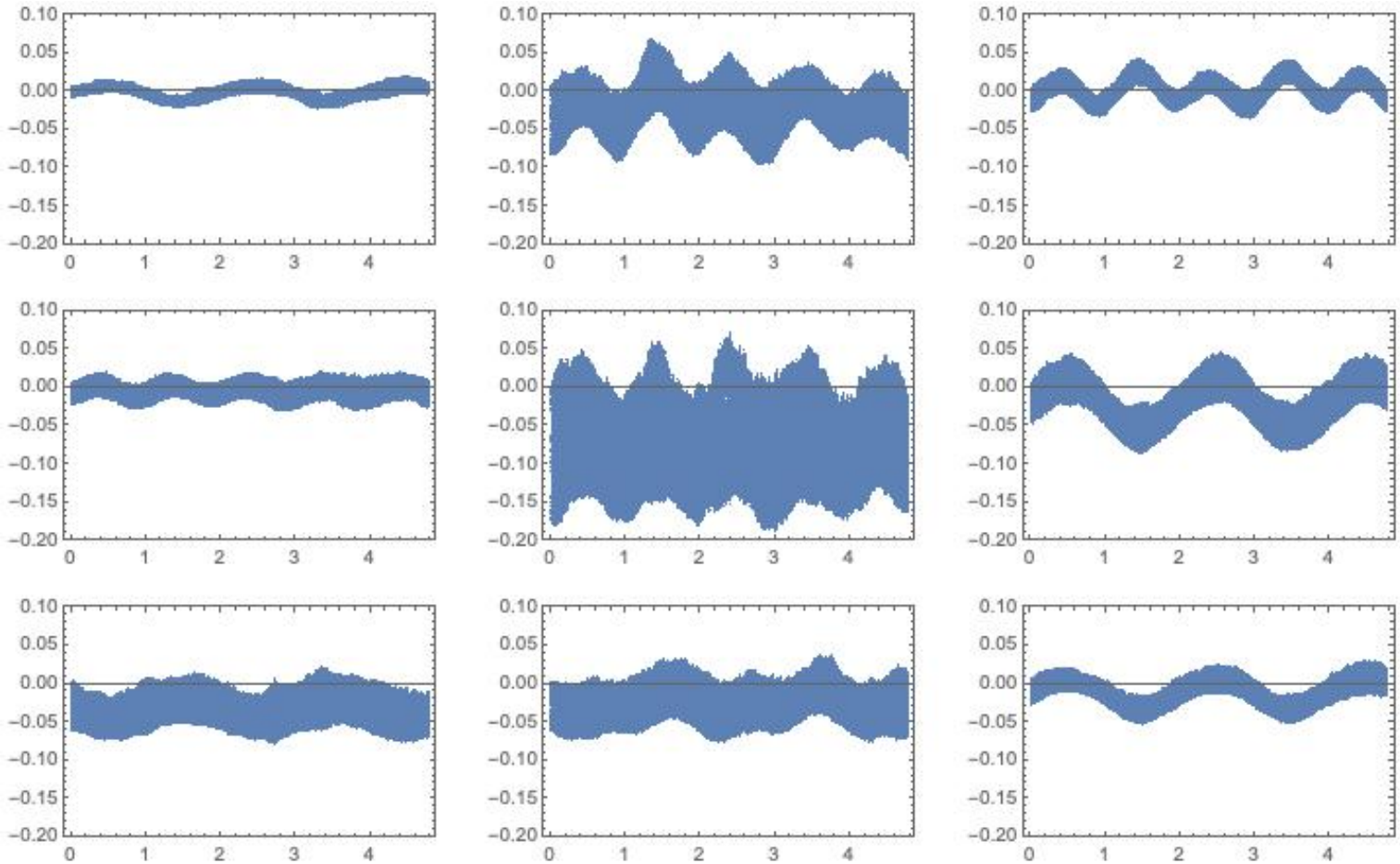
$$-\frac{\tilde{h}^2}{8} < \phi(X_1) - \phi(X_0) \,|\, X_0 + X_1 >$$

$$+\frac{\tilde{h}^2}{8}\left(< \phi(X_1) \,|\, L^{-1}\phi(X_1) > - < \phi(X_0) \,|\, L^{-1}\phi(X_0) > \right)$$

The overall error for the N_s MD steps is simply the sum of the errors for each step. Note that the last term telescopes – and thus leads to the error having an oscillating behavior when viewed as a function of (time) step. This gives the bounded error that was promised by the symplectic nature of the method.

Looking at the error in the effective energy

Error as a function of the number of integration time (determinisitic segment) $\tilde{h} \approx 10^{-4}$

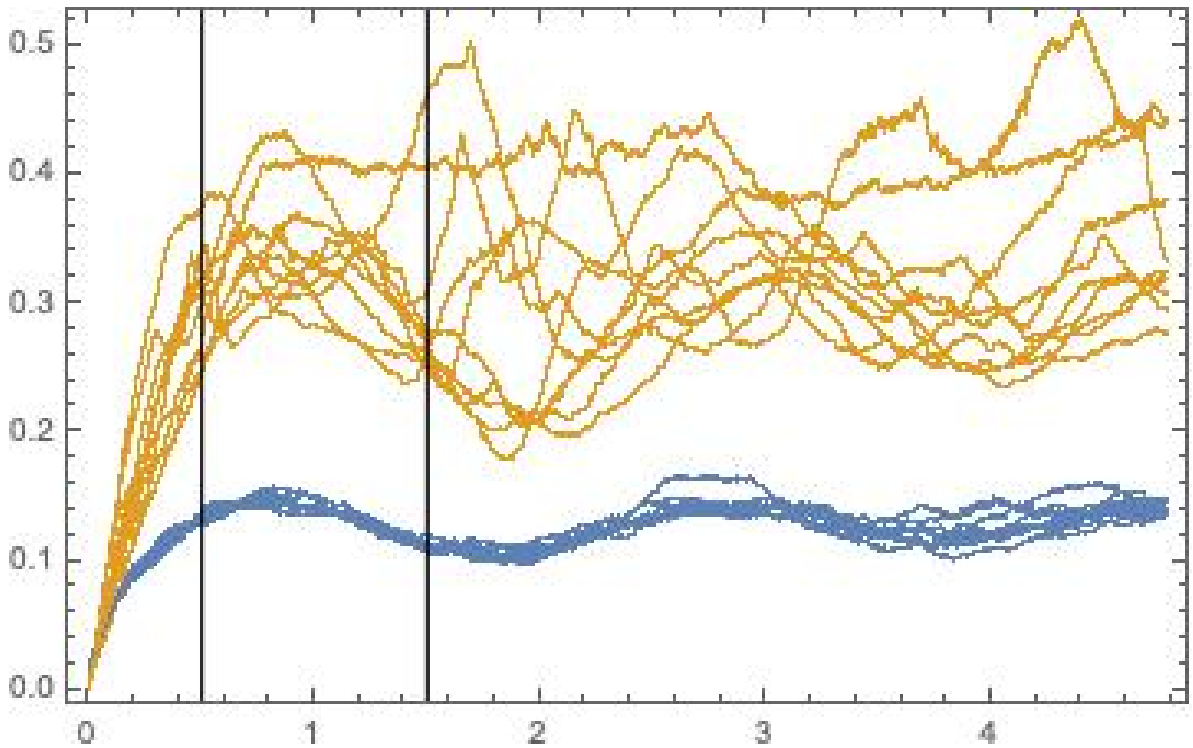


time (multiples of π)

Path Evolution during the deterministic step

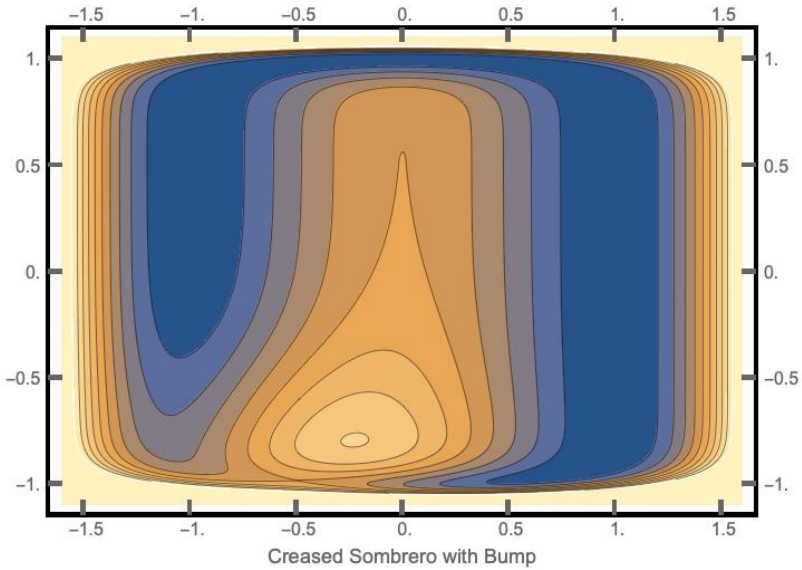
Distance as a function of the number of integration time (determinisitic segment) $\tilde{h} \approx 10^{-4}$

Blue: $d_X \propto \sum_i \Big(x_i(t) - x_i(0)\Big)^2$ Gold: $d_Y \propto \sum_i \Big(y_i(t) - y_i(0)\Big)^2$

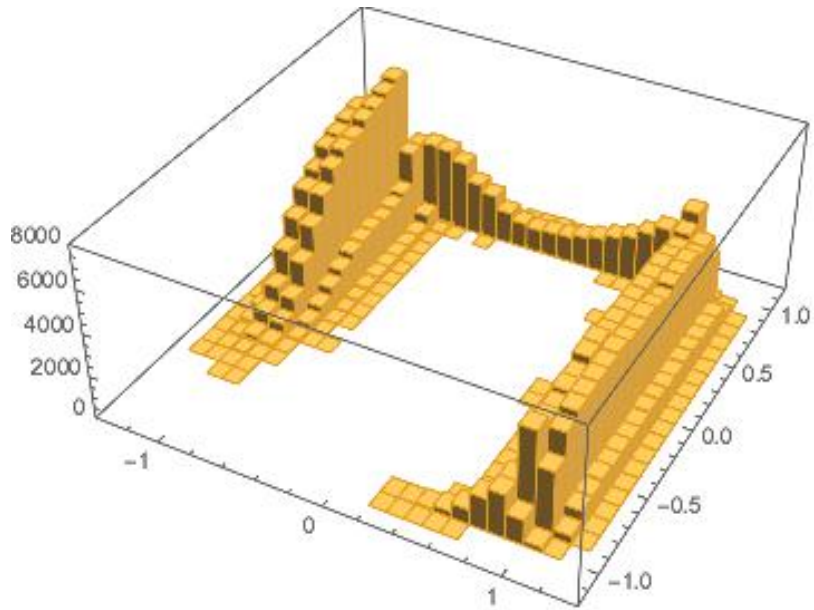


Exploring a two-dimensional case

Potential Contours



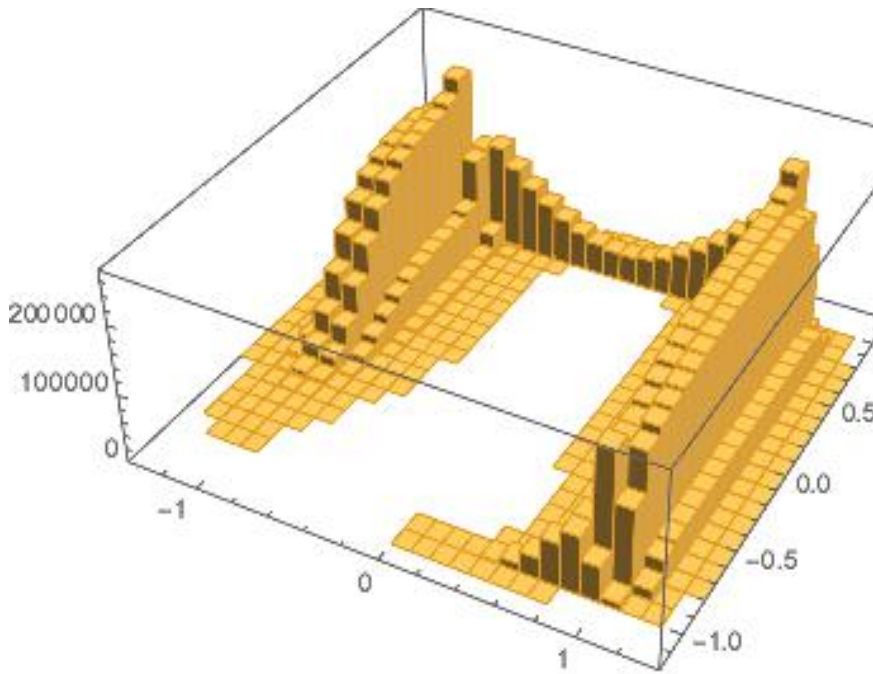
Histogram
(results from forward integration)



Using the midpoint discrete time measure

Results from path sampling

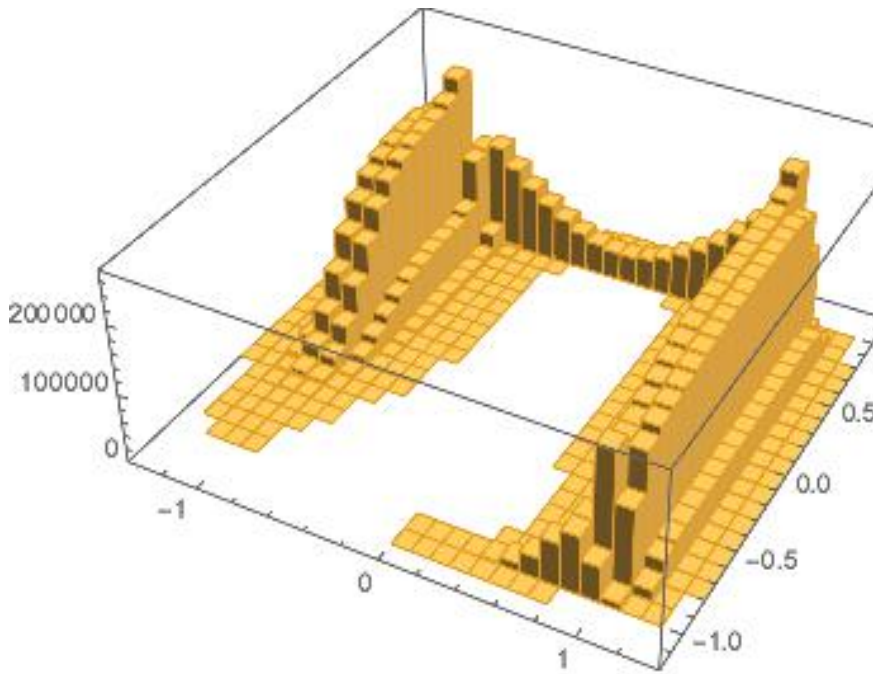
Expected histogram
(partition function)



Using the continuous time measure

Results from path sampling

Expected histogram
(partition function)



Generating Free Energy differences

- Times - doesn't work

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} = \frac{Z_2}{Z_1} \qquad \Delta\mathbb{F} = -\epsilon \log \frac{Z_2}{Z_1}$$

- Explicit Calculation - doesn't work

$$\Delta\mathbb{F} = -\epsilon \log \frac{\sum_2 \exp\left(-U/\epsilon\right)}{\sum_1 \exp\left(-U/\epsilon\right)}$$

- Quasi-Harmonic Approximation - promising

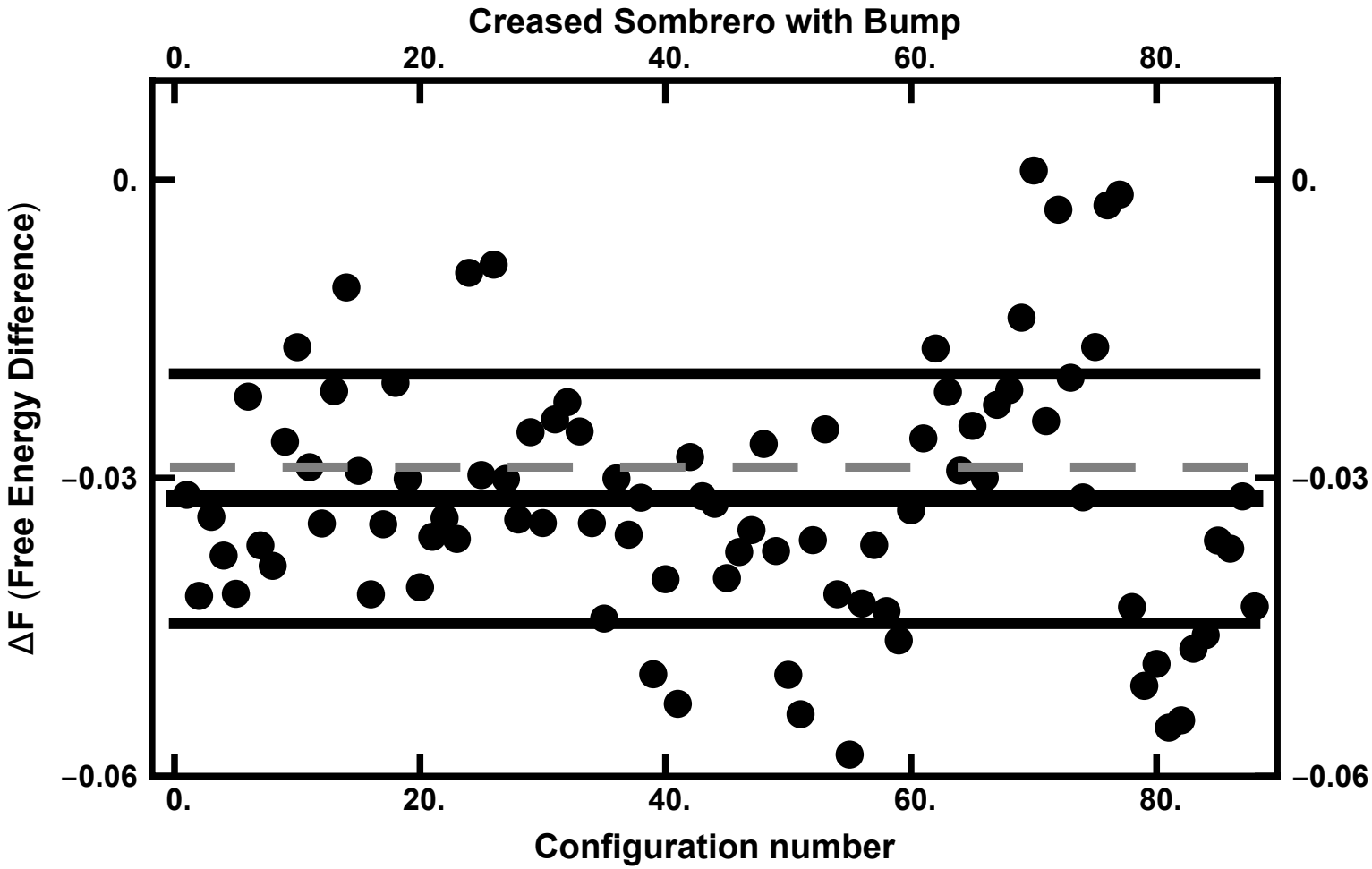
$$\Delta\mathbb{F} = \sum_2 U - \sum_1 U - \frac{\epsilon}{2} \log\left(\frac{\det CoVar_2}{\det CoVar_1}\right)$$

Gibbs-Bogoliubov variational method Jensen's inequality
Cross Entropy method Kullback-Leibler divergence

Generating Free Energy differences

Estimated Free Energy difference: -0.032, Standard Deviation 0.013

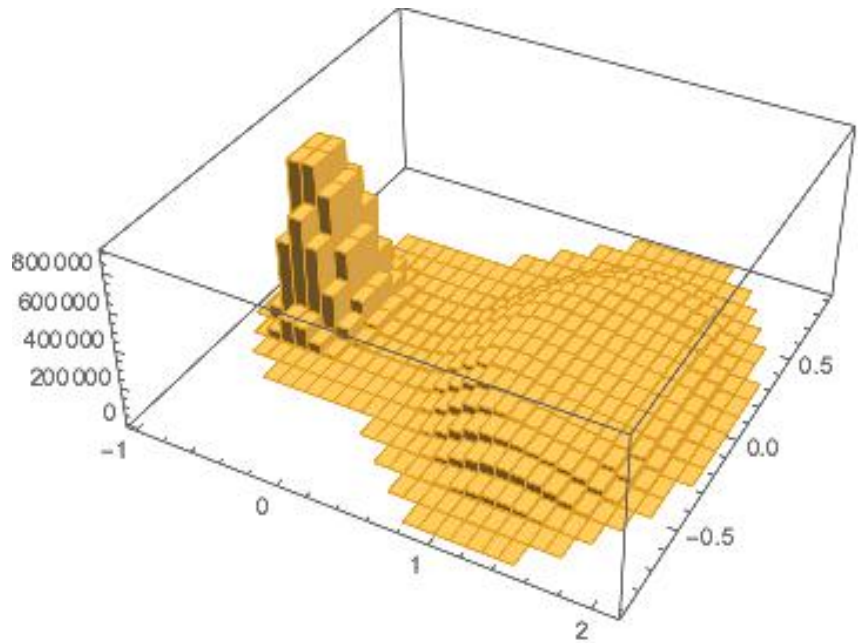
Actual Free Energy difference: -0.029



Deep Narrow Well – Shallow Wide Well

36%

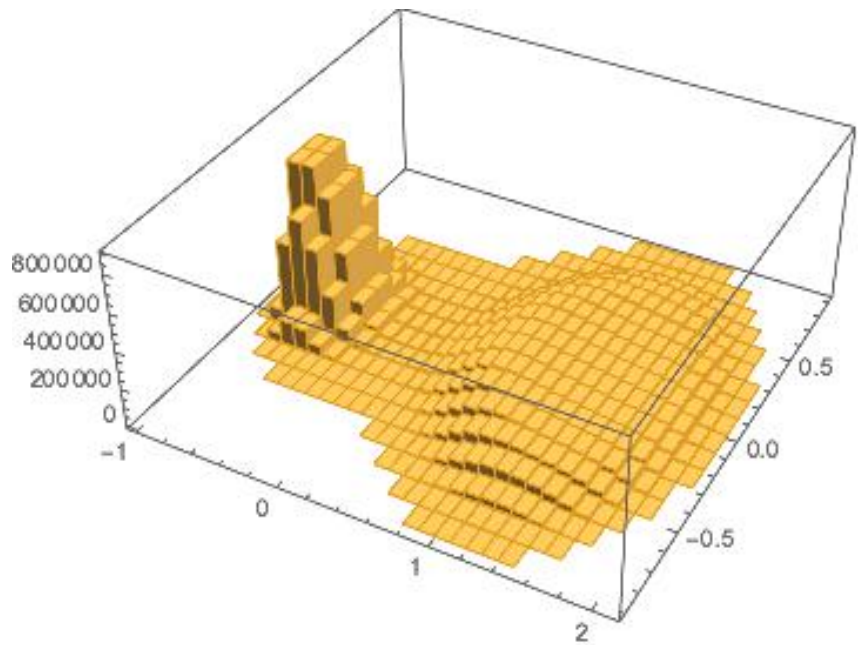
64%



Deep Narrow Well – Shallow Wide Well

Path Sampling

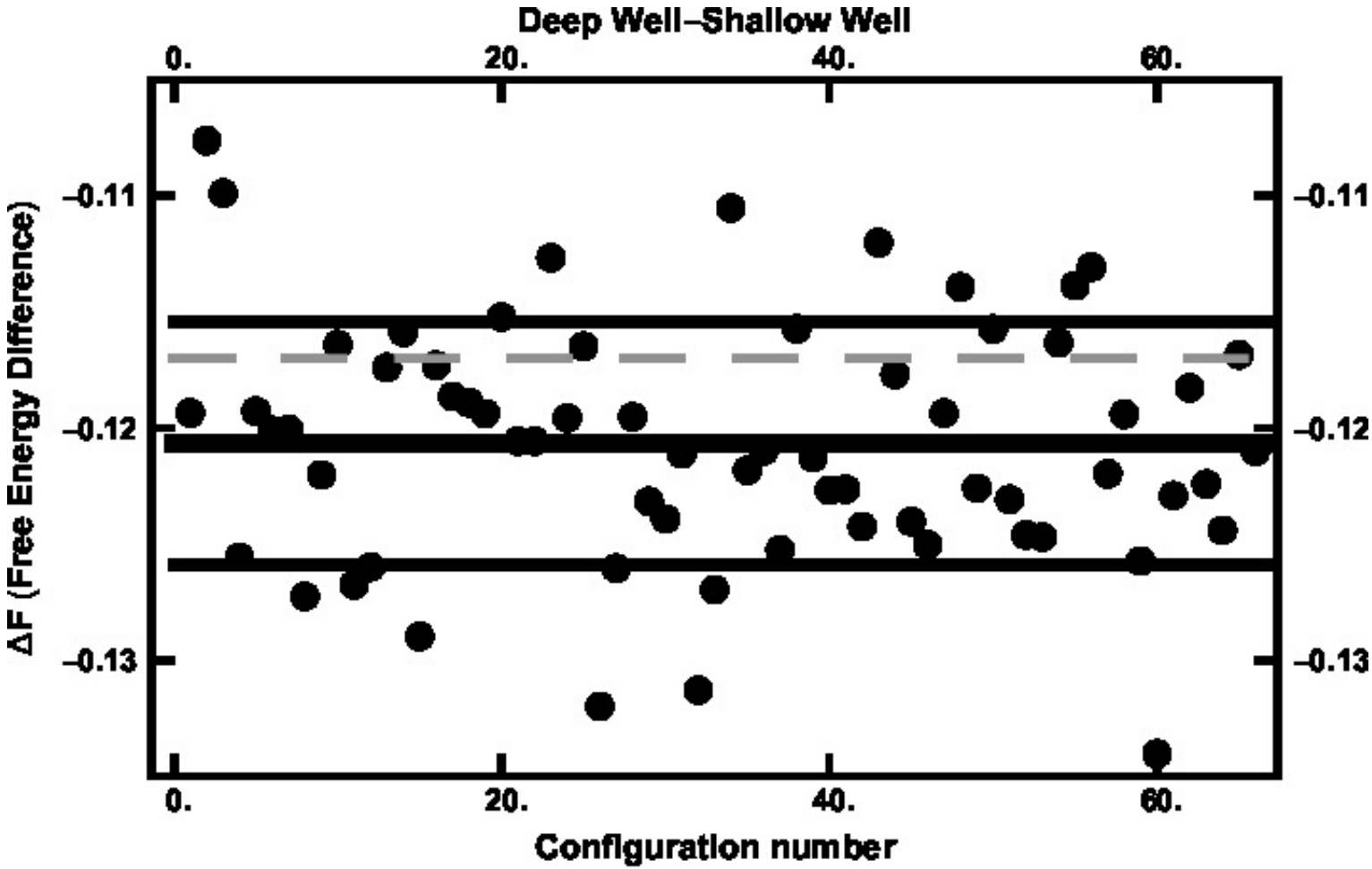
36% 64%



Generating Free Energy differences

Estimated Free Energy difference: -0.121, Standard Deviation 0.005

Actual Free Energy difference: -0.117



Path Sampling

Looked at two types of transitions:
Entropic Barrier and Energy Barrier

- Generated an ensemble of paths
- used a discrete time mesh in the original SDE
- used HMC with a specific choice for the mass matrix
- ensembles are consistent with the Boltzmann distribution
- Approximate Free Energy differences can be extracted

Sampling using the continuous-time limit of the OM functional:
generated unphysical results.