Understanding a Singular Limit of Path Sampling

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In this work, we consider a particle moving in the presence of thermal fluctuations and via a conservative force. Historically, Onsager and Machlup described this situation within the picture of Brownian dynamics. Here we present an alternative approach based on the Hybrid (or Hamiltonian) Monte-Carlo (HMC) method. The physically interesting situation is when the particle moves from one potential basin to another, across an energy barrier that is large compared to the thermal energy. We concentrate on "double-ended" transition paths; paths that begin in one basin and end in a different basin. The novel HMC approach presented here relies on using a discrete representation of the path. For long paths, the method is consistent with the Boltzmann distribution, and the errors due to this representation are clear. In addition, we compare this novel approach to the continuous time limit of Brownian dynamics and uncover a singular behavior.

Overview

- The intent of this work is to develop an efficient computational algorithm to characterize how a molecule undergoes a transition between long lived states.
- We focus on *double ended* path space methods, where the paths are constrained to begin and end at specified positions.
- Two methods are presented:
  - The continuous time limit algorithm, which has roots in Brownian dynamics.
  - A novel finite time method based on Hybrid Monte-Carlo (HMC).

Brownian Dynamics

The systems of interest reside in the over-damped Langevin regime (Brownian), where all particles have reached terminal velocity. The particles are governed by a conservative force, $F(x)$, at a temperature ε and obey the following equation of motion

$$dx = F(x)\,dt + \sqrt{2\varepsilon}\,dW_t \qquad\qquad x_1 = x_0 + F_0\,\Delta t + \sqrt{2\varepsilon\Delta t}\,\xi_i$$

Using the result of Onsager and Machlup[1], we can define the probability of any path by looking at the underlying random fluctuations of the particles. For any given path, this probability is expressed as

$$-\ln\mathcal{P} \propto \sum \frac{\xi^2}{2} = \frac{\Delta t}{2\varepsilon}\sum \frac{1}{2}\left|\frac{\Delta x}{\Delta t} - F(x)\right|^2 \tag{1}$$

The methods we are developing attempt to sample double ended paths which obey this probability.

Continuous Time Representiation

In the continuous time limit the path probability[2][3] is derived using the Ito calculus and the Girsanov theorem (infinity in the probability is regularized by the probability with $F = 0$, $\mathcal{P}_0$)

$$-\ln\frac{\mathcal{P}}{\mathcal{P}_0} \propto \frac{1}{2\varepsilon}\int_0^T dt\left(\frac{1}{2}|F(x)|^2 - \varepsilon\nabla^2 V(x)\right) \tag{2}$$

Implication: Some paths are more probable than others. This violates equilibrium thermodynamics, as we show below.

Finite Time-Step Hybrid Monte-Carlo

To gain insight into the limiting process we explore a HMC method[4] where the finite-time-step errors are known. The Leap-Frog (velocity-Verlet) integrator gives the following prescription (Note: identify $\Delta t = h^2/2$, choose v_i from Maxwell-Boltzmann distribution, and ignore rejections to recover Browninan dynamics).

$$x_{i+1} = x_i + hv_i + \frac{h^2}{2}F(x_i) \qquad\qquad \tilde{v}_{i+1} = v_i + \frac{h}{2}\Big(F(x_{i+1}) + F(x_i)\Big)$$

The finite time probability for this path is found by expanding the OM probability (eq 1):

$$-\ln\mathcal{P} \propto \frac{\Delta t}{2\varepsilon}\sum_i\left(\frac{1}{4}\left|\frac{x_{i+1}-x_i}{\Delta t} + F_{i+1}\right|^2 + \frac{1}{4}\left|\frac{x_i - x_{i+1}}{\Delta t} - F_i\right|^2 - \frac{\delta e_i}{\Delta t}\right) \tag{3}$$

$$\frac{\delta e_i}{\Delta t} = \frac{U_{i+1}-U_i}{\Delta t} + \frac{x_{i+1}-x_i}{\Delta t}\frac{F_{i+1}+F_i}{2} + \frac{1}{4}(F_{i+1}^2 - F_i^2)$$

The energy error made in this sampling violates detailed balance. In the limit $\Delta t \to 0$, the quadratic variation is satisfied and $\delta e \to 0$, and the cross terms reduce to the continuous time result:

$$\Delta x^2 \to 2\varepsilon\Delta t \qquad\qquad \frac{1}{2}\frac{\Delta x}{\Delta t}(F_{i+1} - F_i) \to \frac{1}{2}\frac{\Delta x^2}{\Delta t}\frac{\Delta F}{\Delta x} \to \varepsilon\nabla F$$

[1] S. Machlup and L. Onsager, Physical Review 91, 1512 (1953).
[2] A. Bach and D. Dürr, Physics Letters A 69, 244 (1978).
[3] R. Graham, Z Physik B 26, 281 (1977).
[4] S. Duane et al. , Physics Letters B 195, 216 (1987).
[5] U. Seifert, Phys. Rev. Lett. 95, 040602 (2005).

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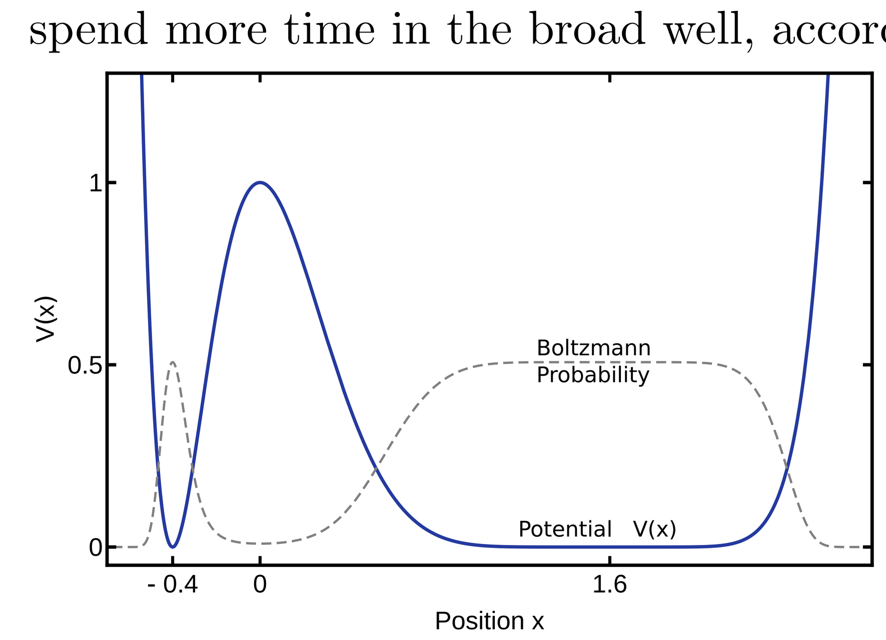
1D Model

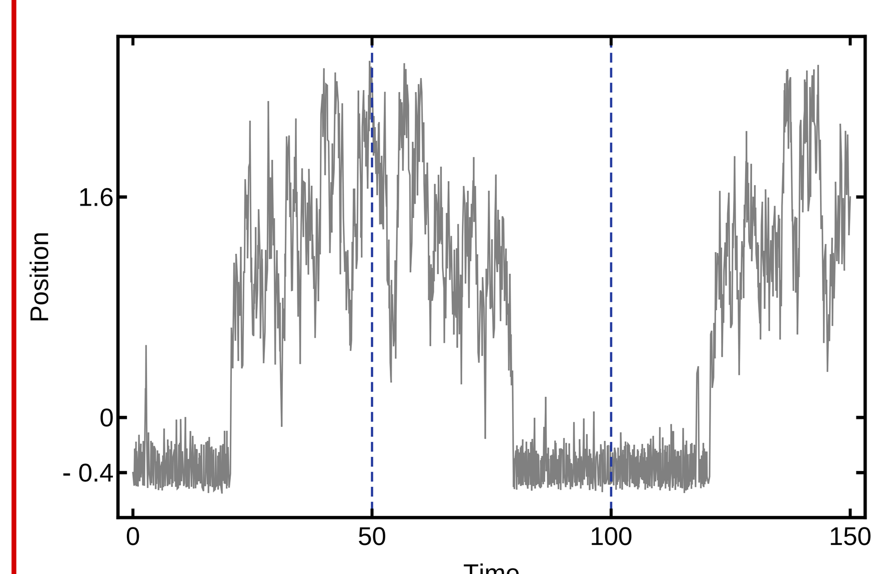
We will use a simple one dimensional potential to illustrate our results. The potential wells are degenerate in energy, but entropy drives the particle to spend more time in the broad well, according to the Bolzmann probability.



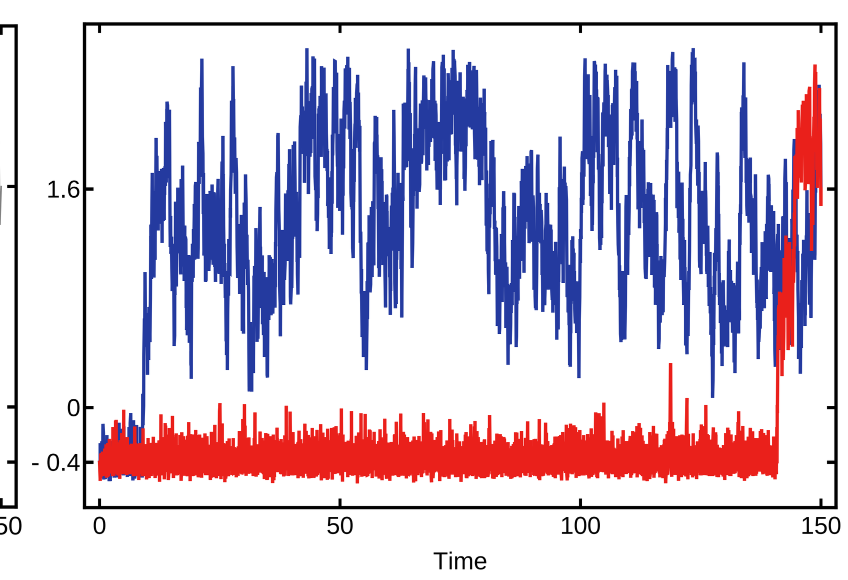
$$V(x) = \frac{(8-5x)^8\,(2+5x)^2}{2^{26}}$$

- Minima: $x = -2/5$ and $x = 8/5$
- Barrier Height: $V_B = 1$
- $P(x > 0) \approx 0.92$ at $\varepsilon = 0.25$

1D Model Results

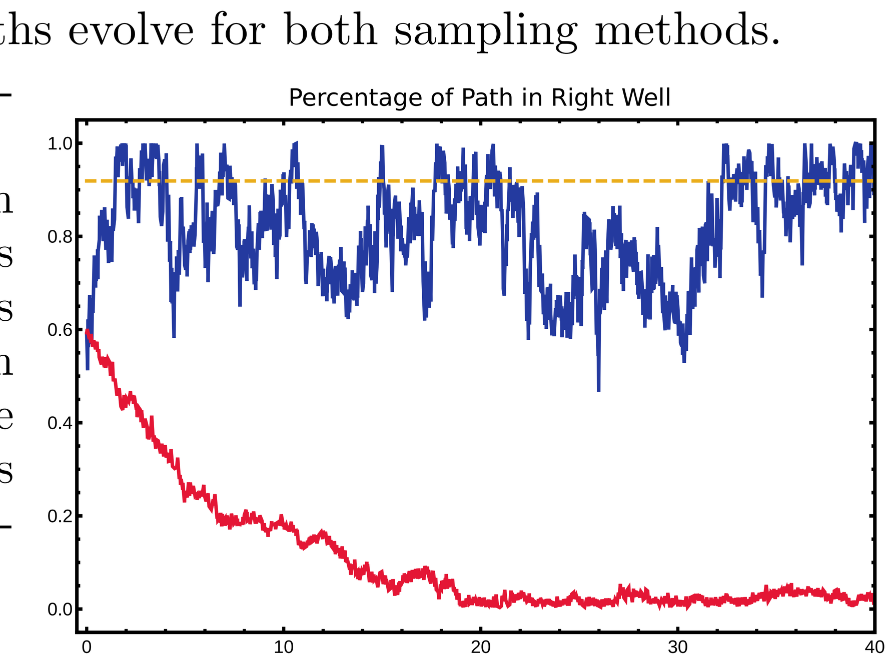


Initial path: (grey ▬) generated by flipping 3 shorter paths end to end, forming a path in a non-Boltzmann state with multiple transitions.



Ending Paths: Aged paths showing the extraneous solution of the continuous time limit (red ▬) and the Boltzmann path generated with finite-time HMC (blue ▬).

Examples of aged paths generated by sampling the two methods (eq 2 and 3) are shown above. Understanding how the sequence of paths evolve can be clearly seen by monitoring the amount of the path which is in the wide, entropy preferred basin, $P(x > 0)$, as the paths evolve for both sampling methods.



Both methods start with identical initial paths, with $P(x>0) \approx 0.6$.
Using the continuous-time expression (red ▬), the path quickly shifts into the skinny (low-entropy) well. This contrasts to the evolution of the path when sampling from the finite-time expressions (blue ▬), which is near the expected Boltzmann probability (yellow ▬).

Discussion and Conclusion

Barrier hopping occurs rarely, but it is still consistent with thermodynamics. Other, extremely rare events (such as all of the molecules in a room ending up in a single corner) are so rare that they violate thermodynamics. We are not interested in those extremely rare events. In particular, for long paths, we expect to recover equilibrium thermodynamics, even for paths with a double ended constraint.

Using the probability that comes from the continuous time limit, leads to unphysical paths which are forced into the narrow well, which is not consistent with entropic considerations. This effect can be traced back to the form of the probability (eq 2). The noise originates from the thermal bath and is independent of the details of the deterministic force. Thus the Integral Fluctuation Theorem[5] states that all paths (of the same length) will have the same probability. By its very nature, the continuous time probability (eq 2) implies that some paths are more probable than others.

Furthermore, sampling with this probability introduces correlation between the noise and positions. This skews the velocity distribution, and produces a non-Maxwell-Boltzmann velocity distribution. We thus argue that **the continuous-time formulation (eq 2) cannot be used as a probability measure to sample physical paths.**

On the other hand, we obtain "physical results" using the probability distribution that comes from using any small but non-zero time step. The HMC picture explicitly describes the errors made in the Brownian picture, which in turn has unphysical consequences. Improving the integrator in the HMC method improves the fidelity of the paths.