Can we learn something important from wormy apples?

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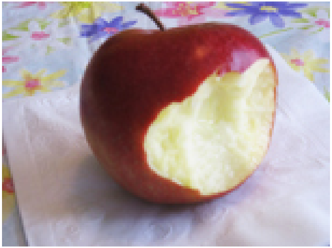
Abstract

I report on a series of computer experiments to test our understanding of classical path integrals. In particular, I examine calculations of doubly-constrained paths for a particle undergoing Brownian dynamics and moving in an external potential.

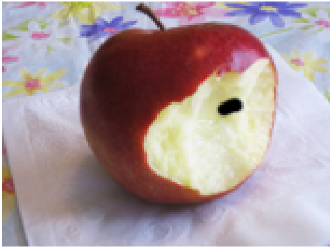
Apples - A tasty treat



Consider an apple.

If one bites into it, and only sees the flesh of the apple, one enjoys the experience.

Apples - A tasty treat

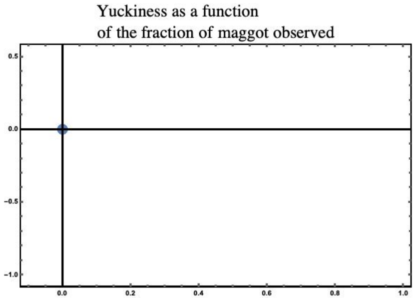


On the other hand if one sees part of a maggot, one is disgusted. Define the *yuckiness* function as a measure of the revulsion one feels when one sees part of a maggot in the apple.

The *yuckiness* Function

The *yuckiness* function **Y(R)**
depends on **R**, the remaining part of the maggot.

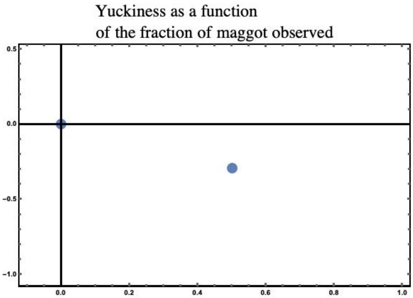
The first value we have is when no maggot is seen in the apple.



The *yuckiness* Function

The *yuckiness* function **Y(R)**
depends on **R**, the remaining part of the maggot.

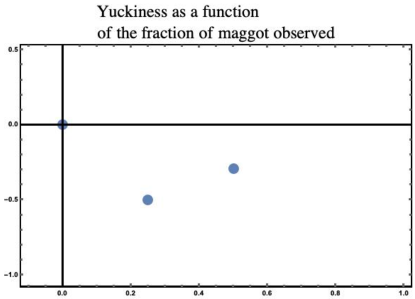
The next value: a half of a maggot is found in the apple.



The *yuckiness* Function

The *yuckiness* function **Y(R)**
depends on **R**, the remaining part of the maggot.

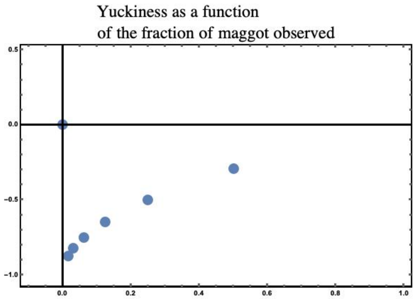
What's worse than finding half a maggot?
Discovering only a quarter of one.



The *yuckiness* Function

The *yuckiness* function **Y(R)**
depends on **R**, the remaining part of the maggot.

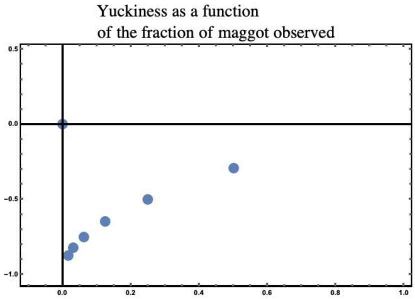
Away from $R = 0$, the *yuckiness* function is monotonic when viewed as a function of the fraction of the remaining maggot.



The *yuckiness* Function has a singular limit (Berry)

The *yuckiness* function **Y(R)**
depends on **R**, the remaining part of the maggot.

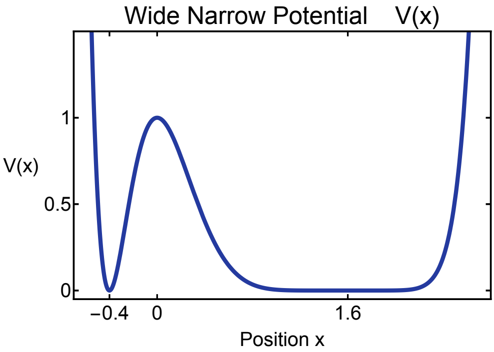
Clearly as $\mathbf{R} \Rightarrow 0$, $\lim \mathbf{Y(R)} \neq \mathbf{Y(0)}$



Note that if one does not see a maggot in the uneaten part of the apple, one cannot tell if one ate a whole maggot or not.

A Singular Limit in thermodynamics

I explore a particle moving in a simple one dimensional potential



$$V(x) = (1 + \frac{5}{2}x)^2 \, (1 - \frac{5}{8}x)^8$$

- Minima: $-\frac{2}{5}$ and $\frac{8}{5}$
- Barrier Height: $V_{\text{bar}} = 1$

The ground state is degenerate: at **zero temperature** the particle is equally likely to be in either well.

A Singular Limit in thermodynamics

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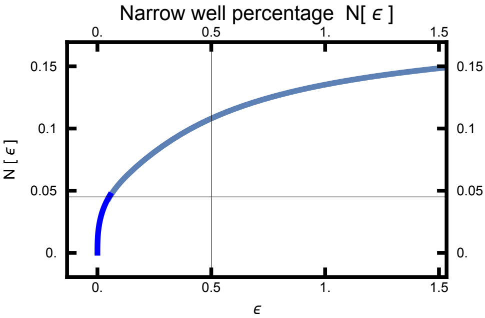


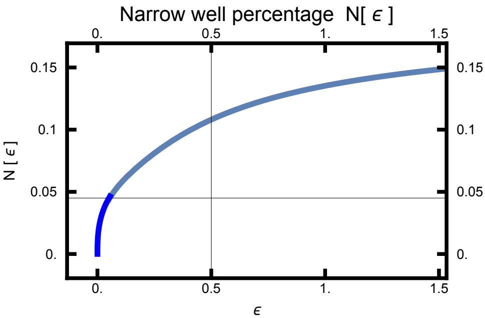
$$V(x) = (1 + \frac{5}{2}x)^2\ (1 - \frac{5}{8}x)^8$$

- Minima: $-\frac{2}{5}$ and $\frac{8}{5}$
- Barrier Height: $V_{\text{bar}} = 1$
- Temperature: ε

$$N[\epsilon] = \int_{left} \exp[-V(x)/\epsilon]\, dx \Big/ \int_{all} \exp[-V(x)/\epsilon]\, dx$$

A Singular Limit in thermodynamics

I explore a particle moving in a simple one dimensional potential

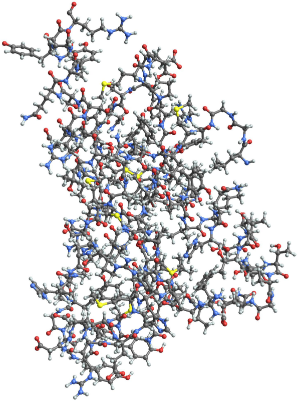


$$V(x) = (1 + \frac{5}{2}x)^2\,(1 - \frac{5}{8}x)^8$$

- Minima: $-\frac{2}{5}$ and $\frac{8}{5}$
- Barrier Height: $V_{\text{bar}} = 1$
- Temperature: ε

Equilibrium Thermodynamics
The zero temperature limit is singular.

The Big Picture
Protein Folding



Proteins are horribly complex structures. We are interested in constructing efficient methods to probe how proteins fold. To accomplish this, we start with very simple systems.

We never got beyond a single particle in two dimensions.

Focus: Rare Events

- Transitions – ultimate goal: Protein Folding
- Rare Events (seen) vs extremely rare (never seen in the life of the universe)

- Transitions driven by Thermodynamical fluctuations (Folding)
- Violating Thermodynamics (atoms into a corner of the room)

- Brownian Dynamics - Onsager and Machlup (1953)

Brownian Dynamics $\qquad \epsilon \Rightarrow k_B$ Temperature

Particle buffeted by random forces – modeled by White Noise

$$dx_t \;=\; F(x_t)\,dt \,+\, \sqrt{2\,\epsilon}\;dW_t \qquad\qquad F(x) = -\frac{dU}{dx}$$

For a finite time step, Δt, (Euler-Maruyama Method)

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

where ξ is a Gaussian random variate: mean zero and unit variance.

Paths are continuous but almost nowhere differentiable.

Quadratic Variation $\qquad \sum \left(x_{i+1} - x_i\right)^2 \;\approx\; 2\,\epsilon\,T$

where T is the length of the path, $T \;=\; N_t\,\Delta t$.

Brownian Trajectory $\quad \epsilon \Rightarrow k_B$ Temperature

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

Iterate to get a **Trajectory** $\{x_0, x_1, x_2, x_3, \ldots x_{N_t}\}$

Path probability $\mathbb{P}_{path} \propto \Pi_i \exp\big(-\xi_i^2/2\big) = \exp\big(-\sum_i \xi_i^2/2\big)$

Onsager-Machlup functional (1953) $\mathbb{P}_{path} \propto \exp\big(-\mathbb{I}_{OM}\big)$

$$\mathbb{I}_{OM} = \frac{1}{4\,\epsilon}\sum_{i=1}^{N_t} \Delta t \left| \frac{\Delta x}{\Delta t} - F(x_i) \right|^2$$

Doubly Constrained Paths $\quad \epsilon \Rightarrow k_B$ Temperature

Fixed beginning and end points $x_0 = x_-$ and $x_{N_t} = x_+$

Onsager-Machlup functional $\Rightarrow$ "Thermodynamic Action"

Graham (1977) Minimize to find Most Probable Path (MPP)

$$\mathbb{I}_{OM} = \frac{1}{4\,\epsilon} \sum_{i=1}^{N_t} \Delta t \left| \frac{\Delta x}{\Delta t} - F(x_i) \right|^2$$

In the continuous time limit: Radon-Nikodym derivative, Girsanov theorem and Ito's lemma: with $T = N_t\,\Delta t$

$$-\log \frac{\mathbb{P}_{path}}{\mathbb{P}_0} = \mathbb{C} + \frac{U(x_+) - U(x_-)}{2\,\epsilon} + \frac{1}{2\,\epsilon} \int_0^T dt\; G(x_t)$$

$$G(x) = \frac{1}{2} U'(x)^2 - \epsilon\, U''(x)$$

where $\mathbb{P}_0$ is the Free Brownian Measure.

Note: Maruyama's 1954 paper predates Girsanov's Theorem (1960).

Girsanov Theorem and Ito's Lemma

Onsager-Machlup functional (1953) $\qquad \mathbb{P}_{path} \propto \exp\big(-\mathbb{I}_{OM}\big)$

$$\mathbb{I}_{OM} = \frac{1}{4\,\epsilon}\sum_{i=1}^{N_t} \Delta t \left| \frac{\Delta x}{\Delta t} \; - \; F(x_i) \right|^2$$

$$\mathbb{I}_{OM} = \frac{1}{4\,\epsilon}\sum_{i=1}^{N_t} \Delta t \left| \frac{\Delta x}{\Delta t} \right|^2 + \frac{1}{2\,\epsilon}\sum_{i=1}^{N_t} \Delta t \left(\frac{1}{2}\left| F(x_i) \right|^2 - \frac{\Delta x}{\Delta t} F(x_i) \right)$$

Cross Term (use a Taylor Expansion)

$$-\Delta x\, F(x_i) = \Delta x\, V'(x_i) \approx U(x_{i+1}) - U(x_i) - \frac{\Delta x^2}{2} U''(x_i)$$

Ito's Result (continuous time limit)

Use the definition of the Quadratic Variation

$$\frac{1}{2}\frac{\Delta x^2}{\Delta t} U''(x_i) \Rightarrow \epsilon\, U''(x_i) \qquad\qquad G(x) = \frac{1}{2} U'(x)^2 - \epsilon\, U''(x)$$

Simple Example – Forward Integration

Follow the motion of a particle as

it tries to hop from one well to the other.

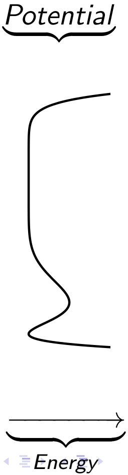
Brownian Dynamics, Temperature: $\epsilon = 0.25$

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

Path Sampling Results: Ito-Girsanov $\epsilon = 0.25$

$$I_{OM}^{Ito} = \frac{1}{2\,\epsilon} \sum_i \Delta t \left(\frac{1}{2} \left| \frac{\Delta x}{\Delta t} \right|^2 + G(x_i) \right) \qquad G(x) = \frac{1}{2} F(x)^2 - \epsilon\, U''(x)$$

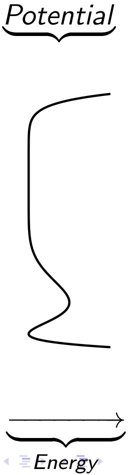
Use the Path-Space HMC machinery
to sample double ended paths.



Path Sampling: away from the Continuous-Time-Limit

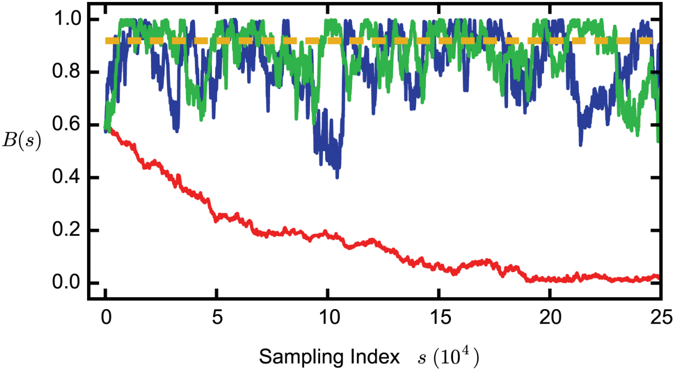
$$I_{OM} = \frac{1}{2\,\epsilon} \sum_i \Delta t \left(\frac{1}{2} \left| \frac{\Delta x}{\Delta t} - F(\overline{x}_i) \right|^2 - J_i \right) \quad J_i = \text{Jacobian}$$

Use the Path-Space HMC machinery
to sample double ended paths.



Numerical Tests: Comparisons

$$B(s) = \frac{1}{T}\int_0^T dt\ \Theta(x_t^{(s)}) \approx \frac{1}{N}\sum_i \Theta(x_i^{(s)})$$



Red: Ito-Girsanov Green: OM Blue: Midpoint
Orange Dashed Line: Equilibrium Thermodynamics

Question

What do these results show?
Is the continuous time limit singular ?

To answer this: first examine Brownian trajectories.

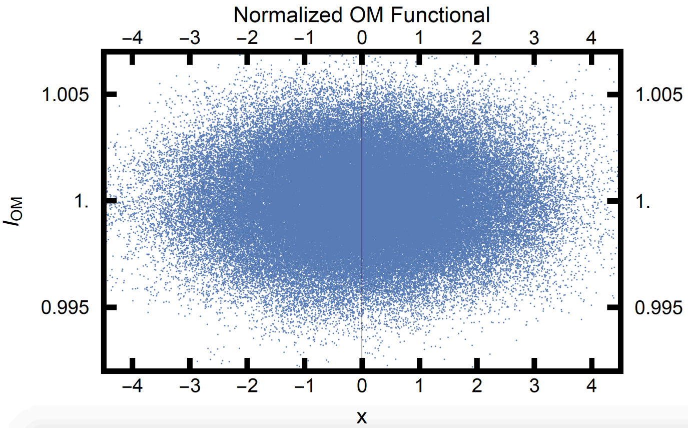
$$x_{i+1} = x_i + F(x_i)\,\Delta t + \sqrt{2\,\epsilon\,\Delta t}\;\xi_i$$

Iterate the Euler-Maruyama equation for a fixed time period.

- Plot a Histogram of the endpoints.
- For each trajectory, plot the value of the Osager-Machlup function vs. the ending position.

OM functional is effectively "flat"

Do many "forward" integrations of Brownian Motion, fixed starting point. Form many free trajectories and look at $\mathbb{I}_{OM}$ as a function of the endpoint.

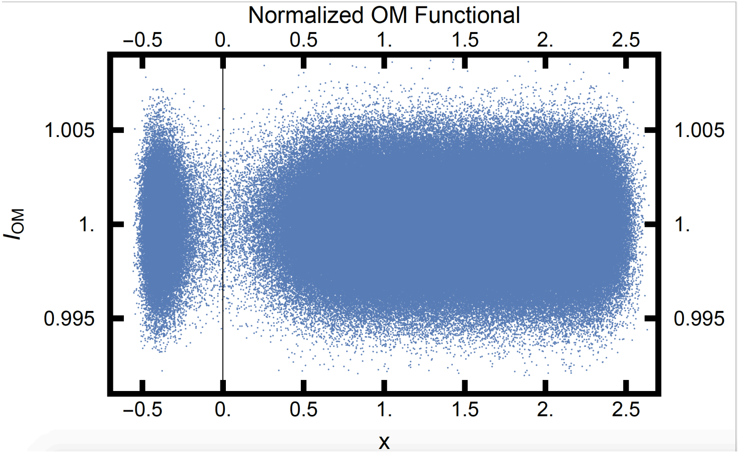


Brownian Dynamics: sampling the Boltzmann distribution

Perform many "forward" (numerical) integrations of Brownian Dynamics (using the discrete SDE) with a fixed starting point. Look at a histogram of the ending positions of these trajectories.

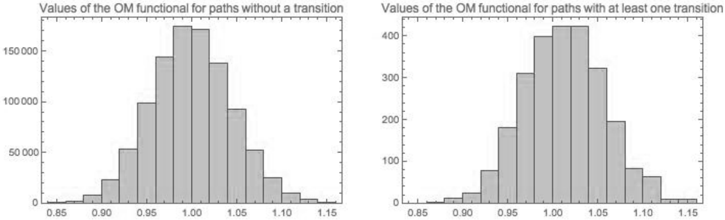
OM functional is effectively "flat"

Perform many "forward" integrations of Brownian Dynamics.
Look at $\mathbb{I}_{OM}$ as a function of the endpoint of these trajectories.



What about short trajectories?

Do many "forward" integrations of Brownian Motion, with a fixed starting point. Compare values of $\mathbb{I}_{OM}$ for trajectories that contain at least one transition from those that do not contain any.



Clearly the values of $\mathbb{I}_{OM}$ are distributed similarly for both types of trajectories. $\mathbb{I}_{OM}$ cannot be used to discriminate between the two.

Observations – for any iterative sequence with $\Delta t > 0$

- The value of the OM functional is effectively flat.
- One cannot use the value of the OM function to differentiate paths that contain a transition from those that do not.
- No path is more probable than another.
- The multiplicity determines the probability of ending at a particular place - reproducing the Boltzmann distribution.
- For sampling doubly-constrained paths, the Ito-Girsanov measure produces unphysical results.

Next: Explore the underlying mathematics.

Compare the OM functional with its continuous time limit.

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

$$I_{OM}^{IG} = \frac{1}{2\,\epsilon} \sum_i \Delta t \, \left(\frac{1}{2} \left| \frac{\Delta x}{\Delta t} \right|^2 + G(x_i) \right)$$

To understand what is going on, it is illustrative to concentrate on how the cross term becomes proportional to the Laplacian of the Potential in the continuous time limit.

When does $\sum_i \Delta t \, \frac{\Delta x^2}{\Delta t} \, U''(x_i)$ become $\frac{< \Delta x^2 >}{\Delta t} \sum_i \Delta t \, U''(x_i)$?

Answer: When Δx is uncorrelated with the position of the particle.

In the continuous time limit, Ito proved that this is indeed the case.

Compare the OM functional with its continuous time limit.

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

$$I_{OM}^{IG} = \frac{1}{2\,\epsilon}\sum_i \Delta t \left(\frac{1}{2}\left|\frac{\Delta x}{\Delta t}\right|^2 + G(x_i)\right)$$

In the sampling process, a successful algorithm will generate paths that minimizes I_{OM}.
Using I_{OM}^{IG} the sampling algorithm evidently finds paths that are similar to the "MPP," where the Laplacian of U dominates,
The multiplicity of such paths is large, and becomes infinite in the continuous time limit.
The unphysical MPP-like paths differ from the uncorrelated paths in (only) a small number of low frequency modes.
The expression for I_{OM} does not contain such pathologies.

Consider free Brownian Motion.

- I_{OM} diverges in the continuous time limit.
- The function $P(x,\, t;\, x',\, t')$ is only conditionally convergent.
- Specifically $P(x,\, t;\, x',\, t' > t)$ is conditionally convergent.

$$P = \left(\frac{1}{\sqrt{4\,\pi\,\epsilon\,\Delta t}}\right)^{N_t} \int \mathcal{D}[x] \;\exp\left(-\frac{1}{4\epsilon} \sum \Delta t \left| \frac{\Delta x}{\Delta t} \right|^2 \right)$$

- In the continuous time limit, both the numerator and denominator diverge.
- One can get something sensible if one integrates over each intermediate position in turn: forward integration.
- Interchanging the order of operations
  $\Rightarrow$ one can get an indeterminate value.

The continuous time limit is singular!

What happens in the Continuous Time Limit ?

$$P_{\Delta t} = \Big(\frac{1}{\sqrt{4\,\pi\,\epsilon\,\Delta t}}\Big)^{N_t} \int \mathcal{D}[x]\, \exp\Bigg(-\frac{1}{4\epsilon} \sum \Delta t \left|\frac{\Delta x}{\Delta t} - F(x_i)\right|^2 \Bigg)$$

- Both the numerator and denominator diverge.
- Integrating forward in time $\Rightarrow$ the noise and the particle position are uncorrelated $\Rightarrow$ Ito's Theorem holds.
- Interchanging the order of operations
  $\Rightarrow$ one can get an indeterminate value.

Now consider: $$\frac{P}{P_0} = \lim \prod \int dx_i \;\exp\Big(-\frac{1}{2\epsilon}\Delta t\, G(x_i)\Big)$$

or this $$\frac{P}{P_0} = \int \mathcal{D}[x]\; \exp\Big(-\frac{1}{2\epsilon} \sum \Delta t\, G(x_i)\Big)$$

Does changing the order of operations, change the answer?
This is the wrong question to ask.

Conclusions

- The Onsager-Maclup (OM) functional is the same for for thermodynamically-allowed paths.
- The OM functional is **not** the Thermodynamic Action. It cannot be used to differentiate paths that contain a transition from those that do not.
- The continuous-time limit is only conditionally convergent. (Not to be confused with the Radon-Nikodym derivative.)
- The continuous-time limit is singular; the limit sequence has a noncommutative map.
- Ramifications in other areas: control theory, uncertainty quantification (UQ), finance, etc..
- Double ended Quantum paths behave differently from their classical analog.
- The quantum single particle propagator is better behaved than the classical equivalent: $\mathbb{P}(x_-, 0; x_+, t)$

What I would like you to take home

Here I presented a series of numerical calculations that make one question some long-held ideas.

- The OM functional has the same value for each physically allowed path. A MPP (most probable path) does not exist.
- Using a HMC algorithm with the Ito-Girsanov measure, we found that an ensemble of paths that are similar in nature to the mislabeled unphysical MPP.

The Crux of the Problem

The premise that the function $P\left(x,\,0;\,x',\,T\right)$ exists.
When $T>0$, $P\left(x,\,0;\,x',\,T\right)$ is conditionally convergent.
When $T<0$, $P\left(x,\,0;\,x',\,T\right)$ has an indeterminant form.

The continuous time limit for path measures is singular.

Using a "bimodal' noise

Use $s_n = \pm 1$: $$x_{n+1} = x_n + \Delta t\, F(x_n) + \sqrt{2\epsilon\,\Delta t}\; s_n$$

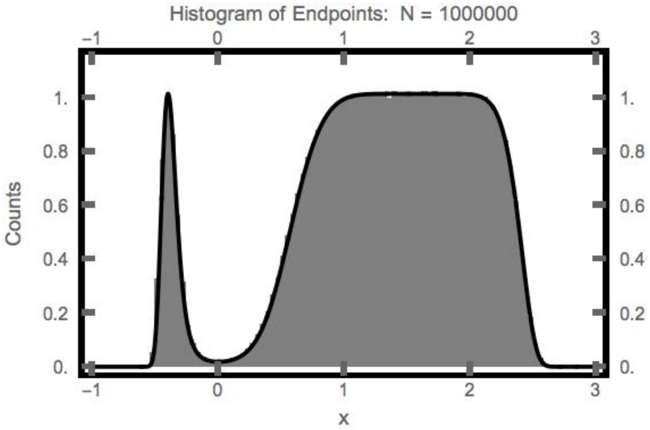


Figure: Histogram of endpoints from iterating the above equation plotted along with the Boltzmann factor (solid line) using the "narrow-broad" potential. Calculation used $\epsilon = 0.25$, $T = 100$, and $\Delta t = 1 \times 10^{-3}$.

Using the continuous time measure

Results from path sampling

Expected histogram
(partition function)