An Application of a Hybrid Monte Carlo Method in Path Space

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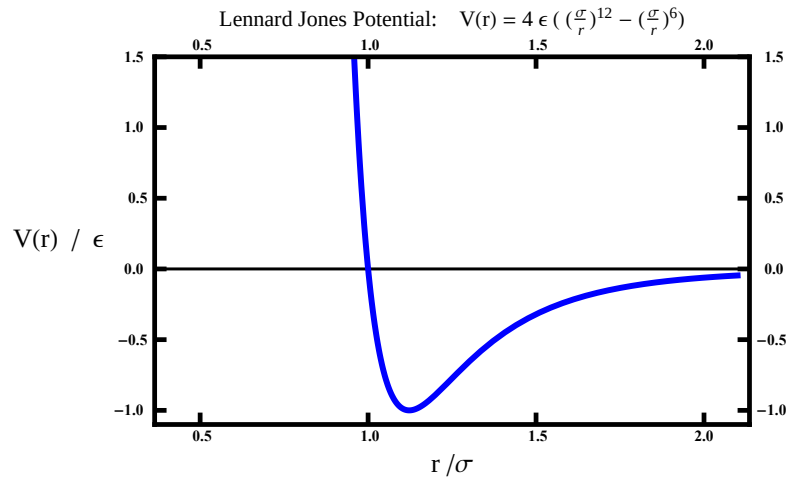
The General Problem

Consider molecules, or clusters of atoms: The Free-Energy Landscape has many wells which are separated by barriers. Some may be large and all may shift with temperature or external field.

Such transitions are rare when the barrier is large compared to the available thermal energy. **How do we find the paths that describe the transitions to the new equilibrium state when such events are rare?** A possible solution: constrain paths to make the desired transition, sample these paths in a thermodynamic significant manner.

Here we use a Hybrid Monte Carlo Method to sample transitions in small clusters interacting via two-body Lennard-Jones potentials.



Lennard-Jones: 13 atoms

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Jellinek, Beck and Berry, J. Chem. Phys., 1987.

Outline

1. The General Problem
2. The Starting Point - Brownian Dynamics
   - Quadratic Variation
3. Onsager-Machlup Functional
4. The Continuum Limit
5. Sampling the Measure
   - Langevin Hairer, Stuart, Voss, Wiberg, Comm. in Math. Sciences, 2005
   - Preconditioning
   - Metropolis Adjusted Beskos, Roberts, Stuart, Voss, Stoch. & Dyn., 2008
   - Hybrid Monte Carlo Beskos, Pinski, Sanz-Serna, Stuart, Stoch. Proc. Applic. 2011 and previous talk
6. Results
7. Conclusion and Discussion

Starting Point - Brownian Dynamics

Sample Boltmann Distribution: $P_B \propto \exp(-V/T)$

$$dx = F\,du + \sqrt{2\,T}\,dW = T\,D \log P_B\,du + \sqrt{2\,T}\,dW$$

F is the force $F = -DV$
T is the temperature
u is the **time along the path**
U is the **time length of the path**
dW is the standard Wiener Process

If a large energy barrier exists, the transition becomes a **rare event**.

The aim of this work is to find an efficient way of sampling the transition paths themselves in a thermodynamically significant manner.

Brownian Paths

Finite Representation of a path

$$x_{i+1} - x_i = F_i \Delta u + \sqrt{2\,T\,\Delta u}\;\xi_i \quad \text{with} \quad P_G(\xi) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\xi^2}{2}\right)$$

Note: Path is continuous and almost nowhere differentiable.

Quadratic Variation

$$Q_v = \sum_i \left(x_{i+1} - x_i\right)^2 = 2\,T\,U$$

U is the length of the path and T is the temperature

The grid space Δu must be sufficiently small to resolve the quadratic variation.

The high-frequency modes are dominated by noise.

Onsager-Machlup Functional

$$x_{i+1} - x_i = F_i \Delta u + \sqrt{2\,T\,\Delta u}\;\xi_i \quad \text{with} \quad P_G(\xi) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\xi^2}{2}\right)$$

The path probability can be constructed (OM functional)

$$\pi_{path} \propto \prod_i \exp\left(-\frac{\xi_i^2}{2}\right) = \exp\left(-\frac{\Delta u}{4T} \sum_i \left(\frac{\Delta x}{\Delta u} - F_i\right)^2\right)$$

Now consider a double ended path: fix both ends. These boundary conditions are chosen so that the starting configuration lies in one free-energy basin, and the other end lies in another basin.

The relative probability of such a path is expressed in terms of the path positions themselves. The noise history is implicitly included in the expression.

Continuum Limit

OM Functional: $\pi_{path} \propto \exp\left(-\frac{\Delta u}{4T}\sum_i \left(\frac{\Delta x}{\Delta u} - F_i\right)^2\right)$

Continuum Limit (The Measure – informally)

$\pi_{path} \propto \exp\left(-\frac{\mathbb{I}_0}{2T}\right)$ where $\mathbb{I}_0 = -\frac{1}{2}\langle x,\, Lx\rangle + \langle 1,\, G(x)\,\rangle$

$\langle ...\rangle$ is the usual inner product,
$L = d^2/du^2$ (non-positive) and
$G = \frac{1}{2}|DV|^2 - T\,\triangle V$

The function G is sometimes denoted as the path potential.
In the continuum limit, G contains the Laplacian of the particle potential. Note, that in equilibrium, $\mathbb{E}\left(|DV|^2\right) = T\,\mathbb{E}\left(\triangle V\right)$,

Need Girsanov's theorem and Ito's formula to justify these steps.

Langevin Sampling

Let the path evolve as a function of algorithmic time t:

$$\frac{\partial x}{\partial t} = 2\,T\,D \log \pi_{path} + \sqrt{4\,T}\,\frac{\partial w}{\partial t} = \frac{\partial^2 x}{\partial u^2} + DG + \sqrt{4\,T}\,\frac{\partial w}{\partial t}$$

This is subject to the imposed Boundary Conditions.

Stiff: different modes have different relaxation times.

Use "preconditioning," to arrive at the SPDE:

$$\frac{\partial x}{\partial t} = -x + L^{-1}\,DG + \sqrt{4\,T}\,\frac{dB}{dt}$$

with the last term being the unit Brownian Bridge, and again $L = d^2/du^2$

All modes evolve at the same rate (democratic).

Metropolis Adjusted - Smart Monte Carlo

We want to sample paths from the measure (almost surely infinite), that we can write informally as $\pi_{path} \propto \exp\left(-\frac{\mathbb{I}_0}{2\,T}\right)$
with $\mathbb{I}_0 = -\frac{1}{2}\langle x,\ L\,x\rangle + \langle 1,\ G(x)\,\rangle$

Use an approximation to $\frac{\partial x}{\partial t} = -x + L^{-1}\,DG + \sqrt{4\,T}\ B(t)$
as a (biased) way of generating a proposed path evolution.
Use a Metropolis-Hasting criterion to accept or reject the proposal.

Set Δt in the approximation of the SPDE to allow efficient movement through path space.

Proposed moves using small values of Δt tend to be accepted but a large number of steps are needed to move appreciably far away from current path.
Proposed moves using large values of Δt tend to be rejected as the integration errors become prohibitively large.

Hybrid Monte Carlo (HMC)

We want to sample paths from the measure

$$\pi_{path} \propto \exp\left(-\frac{\mathbb{I}_0}{2\,T}\right) \qquad \text{and} \qquad \mathbb{I}_0 = -\tfrac{1}{2}\langle x,\ L\,x\rangle + \langle 1,\ G(x)\,\rangle$$

Augment $\mathbb{I}_0$ to include "Kinetic Energy" thereby forming $\mathbb{I}$:

$$\mathbb{I} = \tfrac{1}{2}\langle p,\ M^{-1}p\rangle - \tfrac{1}{2}\langle x,\ L\,x\rangle + \langle 1,\ G(x)\,\rangle$$

where M is the mass matrix.

The path p is composed of auxiliary variables, corresponding to momenta: they are conjugate to x, they do not alter the stationary distribution of paths and their (Gaussian) distribution is known.

HMC has four (4) ingredients.

1. Choice of mass Matrix M.
2. Hamiltonian Flow
3. Integrator that is reversible and volume conserving
4. Accept/reject criteria (based on "energy drift")

HMC - Mass Matrix

The effective Hamiltonian can be informally written as

$$\mathbb{I} = \tfrac{1}{2}\langle p,\, M^{-1}p\rangle - \tfrac{1}{2}\langle x,\, L\,x\rangle + \langle 1,\, G(x)\,\rangle$$

We choose $M = -L$. (non-negative)

$$\mathbb{I} = -\tfrac{1}{2}\langle v,\, Lv\rangle - \tfrac{1}{2}\langle x,\, L\,x\rangle + \langle 1,\, G(x)\,\rangle$$

By inspecting the above equation for $\mathbb{I}$, we see that we get the desired feature that the modes evolve at the same rate in the absence of G.

The paths x and v are conditioned bridges, both having the same quadratic variation.

HMC - Hamiltonian Flow

The effective Hamiltonian can be informally written as

$$\mathbb{I} = -\tfrac{1}{2}\langle p,\ L^{-1}p\rangle - \tfrac{1}{2}\langle x,\ Lx\rangle + \langle 1,\ G(x)\,\rangle$$

Use Hamilton's equations:

$$\frac{\partial x}{\partial t} = \frac{\partial\,\mathbb{I}}{\partial p} = -L^{-1}\,p$$

$$\frac{\partial p}{\partial t} = -\frac{\partial\,\mathbb{I}}{\partial x} = L\,x - DG$$

We can combine these and get

$$\frac{\partial^2 x}{\partial t^2} = -x + L^{-1}DG$$

Note: we have seen something similar to the above equation.

HMC - Integrator

Consider the second order equation and convert it to

$$v = \frac{\partial x}{\partial t} \qquad \textit{and} \qquad \frac{\partial v}{\partial t} = -x + L^{-1} DG$$

Splitting of the Verlet integrator:

1. Half step $\qquad w_i = v_i + \frac{h}{2}\, L^{-1} DG_i$
2. Full step – Rotation

$$\begin{pmatrix} x_{i+1} \\ w_{i+1} \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x_i \\ w_i \end{pmatrix}$$

3. Half step $\qquad v_{i+1} = w_{i+1} + \frac{h}{2}\, L^{-1} DG_{i+1}$

$$\cos\theta = \cos h \quad \textit{or} \quad \frac{4 - h^2}{4 + h^2} \qquad \sin\theta = \sin h \quad \textit{or} \quad \frac{4\,h}{4 + h^2}$$

Integration scheme is Reversible and Volume Conserving.
For finite representations, this Verlet splitting preserves the Quadratic Variation of the evolving path.

HMC: Metropolis-Hastings Criterion

The value of $\mathbb{I}$ is almost surely infinite in the continuum limit.
Must devise a method to calculate differences in $\mathbb{I}$ as the path evolves without subtracting large (possibly infinite) numbers.
At the end of MD step, $i+1$, $\Delta\mathbb{I} = \mathbb{I}_{i+1} - \mathbb{I}_i$ can be tracked.

$$\Delta\mathbb{I} = \langle 1, G_{i+1}\rangle - \langle 1, G_i\rangle + \frac{h^2}{8}\Big(\langle DG_i,\, L^{-1}DG_i\rangle - \langle DG_{i+1},\, L^{-1}DG_{i+1}\rangle\Big)$$

$$-\frac{h}{2\,\sin\theta}\Big(\langle DG_{i+1},\, x_{i+1} - x_i\rangle - \langle DG_i,\, x_i - x_{i+1}\rangle\Big)$$

Accumulate the changes as one performs MD integration.
Note the first terms in $\Delta\mathbb{I}$ "telescope."
If step size, h, is small, drift in $\mathbb{I}$ is minimal, the evolved path will be accepted. For large step sizes, the integration error will be substantial, and the entire sequence of paths will be rejected.

Lennard-Jones: building the 13-atom cluster

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Lennard-Jones Clusters: $kT/\epsilon = 0.13$

For the 13-atom cluster, we considered the transition from its ground state to a conformation where one atom sits on the surface, and a "dimple" exists on the opposite side.
For the 14-atom cluster, we considered the process that starts with the "extra" atom on one side of the cluster and ends with the "extra" atom on the other side.

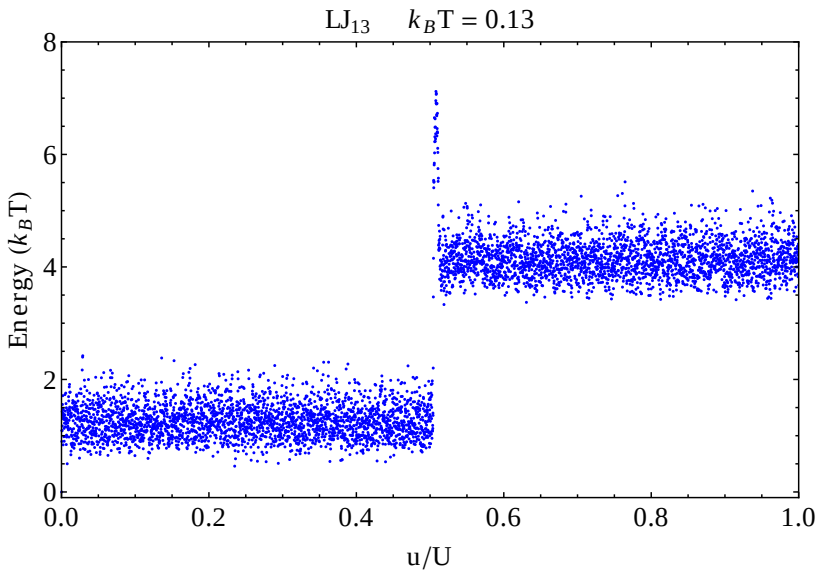

Figure: LJ_{13}: Energy along the path.

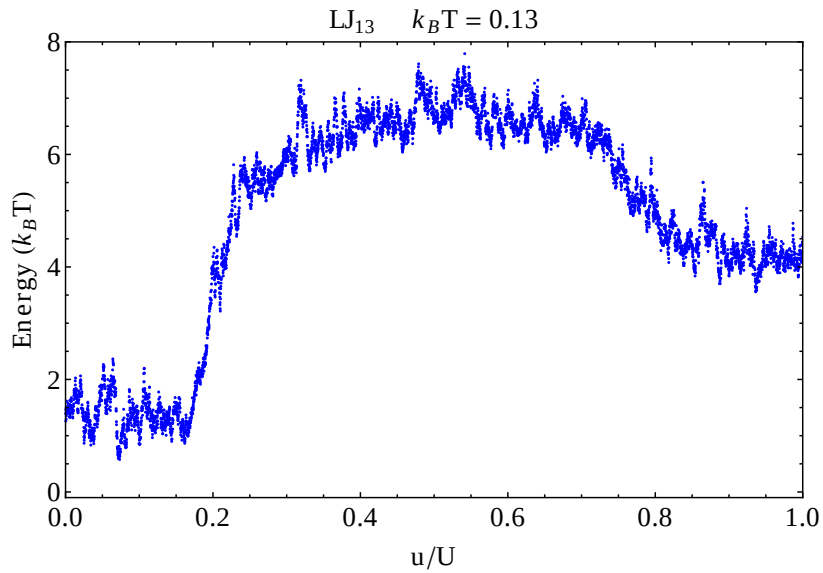

Figure: LJ_{13}: Energy along the path.

Lennard-Jones cluster: inspecting the transition

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HMC - Some Numerical Aspects

The effective Hamiltonian for N_p in N_d dimensions can be written as $\mathbb{I} = \sum_{i\,\alpha} \left(-\frac{1}{2}\langle v_{i\,\alpha},\ Lv_{i\,\alpha}\rangle - \frac{1}{2}\langle x_{i\,\alpha}\,, Lx_{i\,\alpha}\rangle \right) + \langle 1,\ G(x)\,\rangle$.
On a finite grid, using the quadratic variation of the conditioned Brownian Bridges, both the first and second terms become $N_u \times T$, where T is the temperature and N_u is the number of divisions along the path. To keep the quadratic variation of the path nearly constant, the last term must be small compared to the other two. If one uses $\bar{G}$ as an average value of G, then $\Delta u = \frac{U}{N_u} >> \frac{\bar{G}}{N_p N_d T}$.
The value of $\bar{G}$ can be approximated by its equilibrium average. Thus for these clusters we take $\Delta u \approx 0.0001$, with $N_u \approx \frac{1}{2}\,10^6$.

For the time step h used in the deterministic integration, we have chosen $h = 0.00024$ which gives an acceptance rate of over 90%. We then integrate over N_{MD} steps. We chose $N_{MD} \approx 15000$ to give the product $N_{MD}h$ a value somewhere between 1 and 3.

Messages to take Home

- Discussed the general problem: sampling transition paths, when the starting and ending configurations are known.
- Explained how to implement a Hybrid Monte Method in Path Space to do such sampling
- Studied small Lennard-Jones clusters (13 and 14)
- Showed how the sampling was able to describe a transition, even though the initial path was quite naive (expansion of the belt of 10)
- The Lennard-Jones systems at *low temperature* are a severe test of the method – the r^{-12} part of the potential is quite steep: the resulting equations are very stiff
- Even for such simple systems: HMC in path space provides new physical insights
- Next step: transitions in larger molecules (softer potentials)

Lennard-Jones Clusters: $kT/\epsilon = 0.13$

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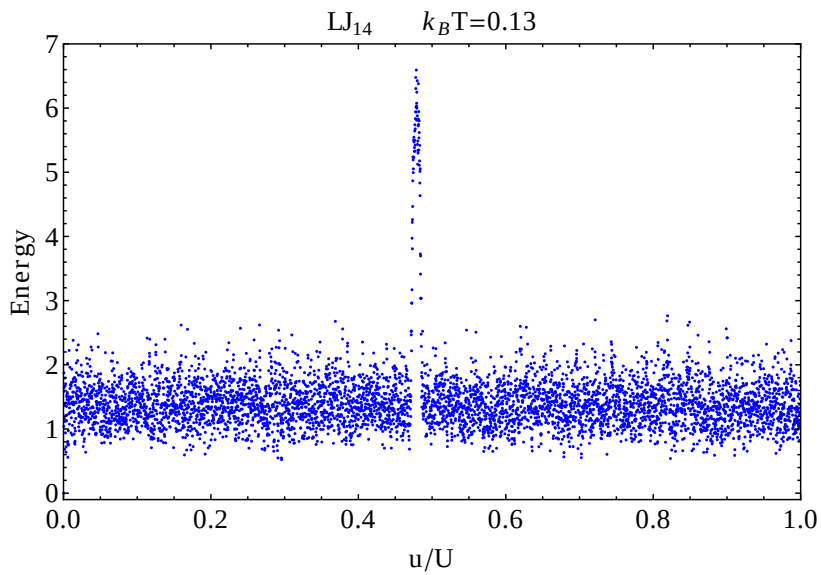

Figure: LJ_{14}: Energy along the path.

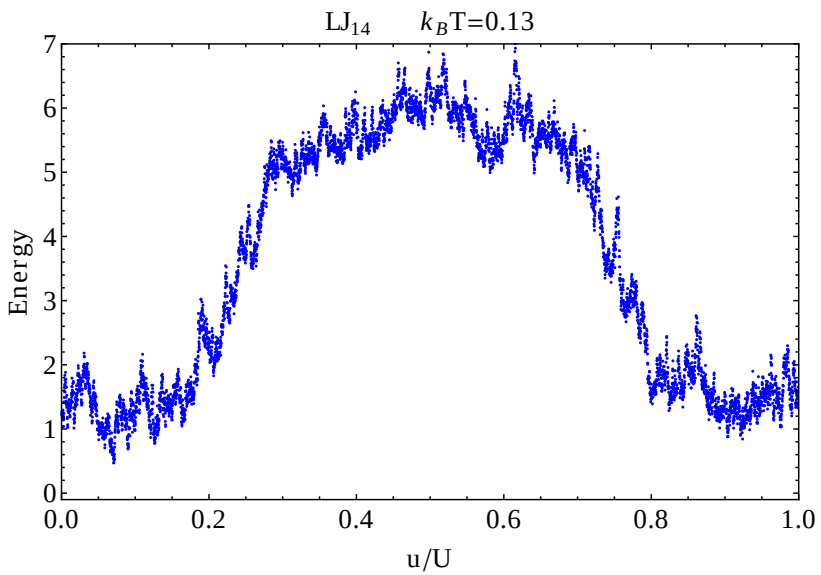

Figure: LJ_{14}: Energy along the path.

Lennard-Jones cluster: inspecting the transition

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