SFG Final report

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1 Introduction

The goal of the project was to develop a machine learning methodology to find the reaction pathways of chemical reactions. At the start, we are given a multi-dimensional potential $U(\mathbf{x})$ and minima of this potential, and we want to produce the most likely path between two given minima. The most likely path is the one minimizing the Onsager-Machlup action[1]

$$S[\mathbf{x}(t)] = \frac{\Delta U}{\zeta} + \frac{1}{2}\int_0^\tau \left(|\dot{\mathbf{x}}|^2 + \left(\frac{\nabla U}{\zeta}\right)^2 - \frac{2D}{\zeta}\nabla^2 U \right) dt$$

We minimize the OM action using neural networks in PyTorch. Two potential landscapes are considered: Müller Brown potential (Figure 1) and Lennard Jones potential (Figure 2).

Our OM functional includes the laplace term, since for our purposes it is the correct form[2].

2 Methodology

We rewrite the OM action to a more convenient form. Since the $\frac{\Delta U}{\zeta}$ term does not effect minimization, we drop it, and make all other variables dimensionless, denoting $\bar{x}, \bar{t}, \bar{U}$ the characteristic size, time and energy respectively. We get

$$S[\mathbf{x}(t)] = \int_0^1 \left(|\dot{\mathbf{x}}|^2 + \alpha(\nabla U)^2 + \beta \nabla^2 U \right) dt, \quad \alpha = \frac{\bar{U}^2\bar{t}^2}{\zeta^2\bar{x}^4}, \ \beta = \frac{-2D\bar{U}\bar{t}^2}{\zeta\bar{x}^4}$$

We encode the path using a neural network with 1 input, the reaction coordinate, and as output the configuration of particle(s) at the given time, 2-dimensional for Müller Brown and $3 \times 7 = 21$-dimensional for Lennard Jones with 7 atoms (LJ7). We therefore compute the continuous path and not just a

[1] Mauri, Roberto. Non-Equilibrium Thermodynamics in Multiphase Flows. Netherlands: Springer Netherlands, 2013.

[2] Adib, Artur B. Stochastic Actions for Diffusive Dynamics: Reweighting, Sampling, and Minimization. Journal of Physical Chemistry B, vol. 112, no. 19, 2008, pp. 5910–5914. DOI: 10.1021/jp0751458.

sequence of points, unlike in other methods[3]. This has the advantage that there is no need for spring terms, interpolation, resampling and so on. Discretization is then used to compute the integral $S[\mathbf{x}(t)]$ and when drawing the paths. We use two hidden layers of size 16 and the Adam optimizer with learnig rate 0.001.

We check convergence of the optimization by computing the Hamiltonian. Since we are minimizing an action where the integrand is a function of $\mathbf{x}$ and $\dot{\mathbf{x}}$ (Lagrangian), we can make a Legendre transformation

$$L(\mathbf{x}, \dot{\mathbf{x}}) = \left(|\dot{\mathbf{x}}|^2 + \alpha(\nabla U)^2 + \beta \nabla^2 U\right) \rightarrow H(\mathbf{x}, \mathbf{p}(\mathbf{x}, \dot{\mathbf{x}})) = \left(|\dot{\mathbf{x}}|^2 - \alpha(\nabla U)^2 - \beta \nabla^2 U\right)$$

and the associated Hamiltonian should be conserved. When calculated at each point of a path, the Hamiltonian turned out to have a standard deviation of about 1% of its mean value for discretization of just 50 points, which indicates good convergence. This applies to both MB and LJ potentials.

2.1 Müller Brown

The Müller Brown potential is a toy example in 2D used to benchmark different path-finding algorithms. The expression is:[4] (see in Figure 1).

$$U(x, y) = \sum_{\mu=1}^{4} A_\mu e^{a_\mu \left(x - x_\mu^0\right)^2 + b_\mu \left(x - x_\mu^0\right)\left(y - y_\mu^0\right) + c_\mu \left(y - y_\mu^0\right)^2}$$

We rewrote the inhouse code, since it had multiple issues, like interchanged x and y axes and wrong sign of the β coeficient. Now that all is corrected, the path is very close to going through the saddle for $\beta = 0$, which is a check for correctness.

2.2 Lennard Jones

The Lennard Jones potential is an interatomic potential describing van der Walls interactions.

$$U(\mathbf{x}) = 4\epsilon \sum_{i<j} \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}$$

Here ϵ, σ are the energy and length scales, set to 1 for convenience, r_{ij} is the distance between i-th and j-th atom. We considered the case of 7 atoms (i.e. an Ar_7 cluster), which is well known to have 4 minima and 11 saddles[5].

We also compare the point of highest energy with of the computed reaction path and compare with the known saddles of the potential landscape. The green-black structure in Figure 4 is the saddle, and at maximum energy the square L2 distance from the saddle is $5.322 \cdot 10^{-2}$.

[3] Luca Maragliano, Alexander Fischer, Eric Vanden-Eijnden, Giovanni Ciccotti; String method in collective variables: Minimum free energy paths and isocommittor surfaces. J. Chem. Phys. 14 July 2006; 125 (2): 024106.

[4] https://taps0313.readthedocs.io/en/latest/about.html

[5] https://doye.chem.ox.ac.uk/networks/LJn.html

3 Results

3.1 Müller Brown

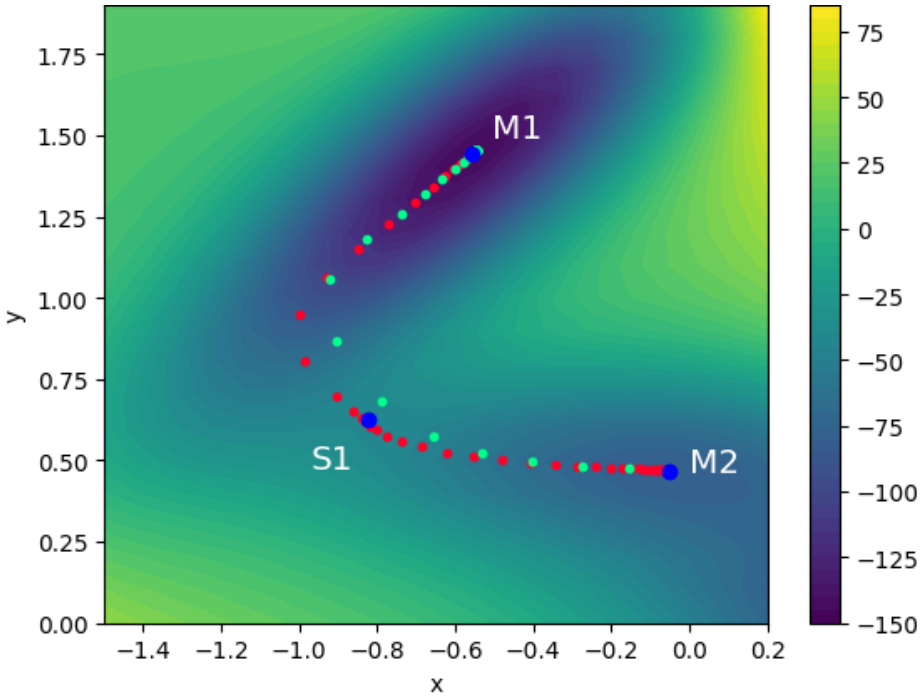

Figure 1: M1, M2 are minima, S1 is saddle. Red path: $\alpha = 0.01, \beta = 0$, Green path: $\alpha = 0.01, \beta = -0.05$, trained for 10000 epochs. The effect of diffusive term controlled by β can be seen. Nonzero β corresponds to nonzero temperature by the Stokes relation $D\zeta = k_B T$, so we see that for nonzero temperature the particle "cuts corners."

3.2 Lennard Jones

We chose as beginning and end points two minima with lowest energy:

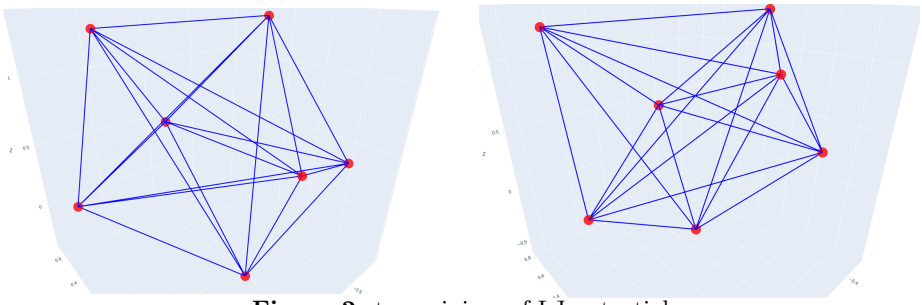

Figure 2: two minima of LJ potential

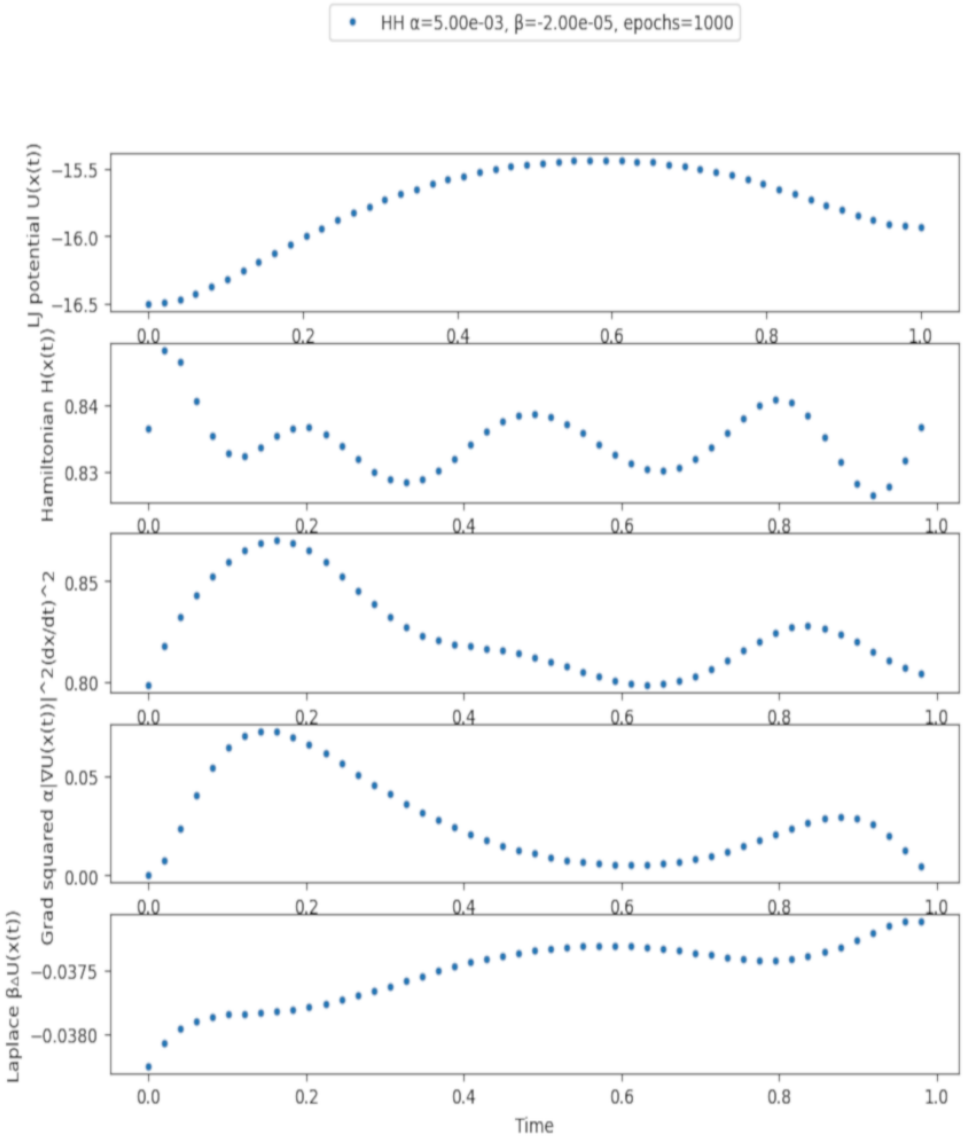

Figure 3: From top to bottom: energy U, Hamiltonian, and the three terms in the OM action $|\dot{\mathbf{x}}|^2,\ \alpha(\nabla U)^2,\ \beta\nabla^2 U$.

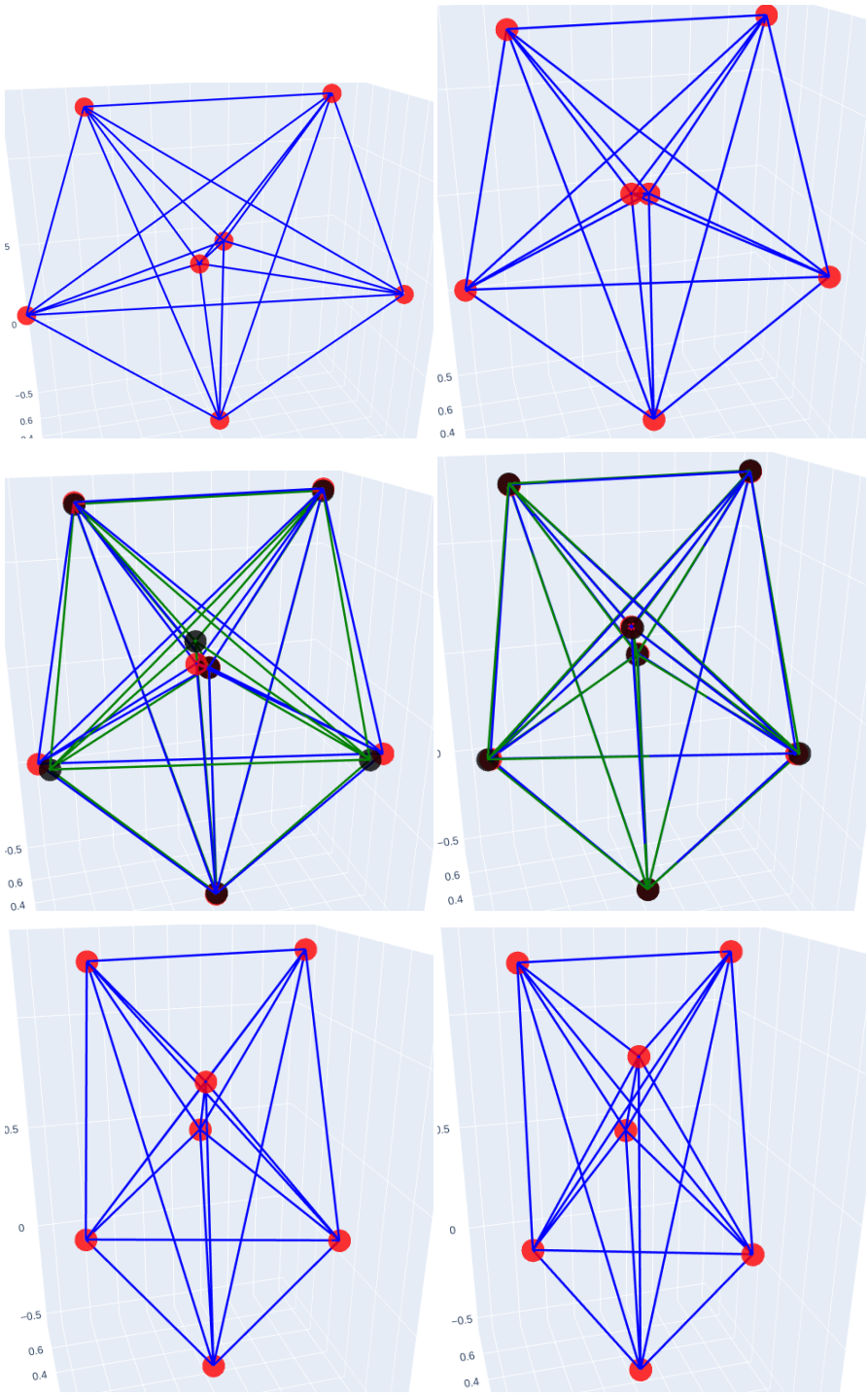

Figure 4: From left to right, top to bottom: isomerization path of LJ7 cluster.

4 Conclusion

We developed a framework for calculating most probable paths in potential landscapes and tested it on the Müller Brown and Lennard Jones potential, yielding plausible results. Our approach gives a continuous path and uses the Onsager-Machlup action with the diffusive term included, which is a physically justified method based on the underlying dynamics.

In the future, we would like to extend this to Physics informed neural networks (PINN) and calculate quantities of interest like the committor function and transition rates.

5 Acknowledgments

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