MENG 255 Problem Set 3: Wang-Landau MC and Umbrella Sampling

Noah Dohrmann

(Dated: For: 9 March 2022)

Please see the accompanying code that goes along with this report.

I. QUESTION 1

In this question we a given a potential energy curve for a bounded system in $x \in [-3,3]$, namely:

$$V(x) = x^4 - 4x^2 + 1 \tag{1}$$

We will attempt to reconstruct this curve via the use of the Wang-Landau[1] algorithm for Monte Carlo, in which a histogram of the density of states $g(E)$ is iteratively found over the bounds of interest. A second histogram $H(E)$ is used to keep track of the Markov Chain visits to each x and its corresponding energy $E(x)$. At the start of the simulation, H is uniformly initialized to 0 and g likewise to 1. The modified Wang-Landau acceptance probabilities outlined in the lecture notes are:

$$P_{\text{acc}} = \min\left(1, \exp(-\beta\Delta E)\frac{g(E^{\text{old}})}{g(E^{\text{new}})}\right) \tag{2}$$

Each time a certain $E(x)$ is visited, the corresponding $g(E)$ is multiplied by the current iteration's value of a parameter f, usually set to $f_0 = e$ and modified such that $f_{n+1} = \sqrt{f_n}$ until f becomes sufficiently close to 1 after N iterations (in this case, 27). Each new "iteration" is determined when the histogram H becomes sufficiently uniform such that $H(i) \not< 0.8\langle H\rangle \ \forall i$. At this point, H is reset but g is not modified, and f is adjusted according to the above prescription.

It is noted that in practice[2], the values of g often become too large to be dealt with directly, so instead $\ln(g)$ is tracked and is instead updated as $\ln(g) \to \ln(g) + \ln(f)$. This way, the final values that are reported for the density of states will suffer from fewer avoidable numerical inaccuracies. When a final $\ln(g)$ is reached, this value is returned by the main function of the python module, and the shape of the energy curve may be approximated (up to a constant) with $-\ln(g) + \varepsilon$, as seen with Fig. 1

The final DOS $g(E)$ can also be included in a detailed-balance satisfying (up to an error associated with $\ln(f)^2$ random walk MC run with acceptance probabilities scaled by the fixed ratios $\frac{g(E_1)}{g(E_2)}$. A new histogram was recorded for this run for the number of times each site is visited. The probabilities associated with this histogram (i.e. the histogram values normalized by the total number of trial visits) and their respective negative logarithms are used to obtain the following reconstruction in Fig. 2.

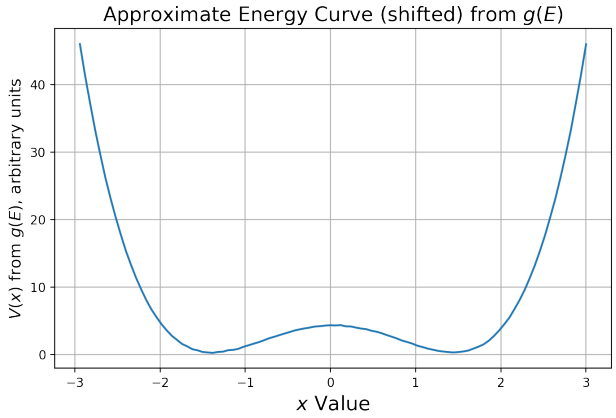

FIG. 1. An approximation of the shape of $V(x)$ from the values of $-\ln(g) + \varepsilon$, where in this case the shift was chosen to approximate the true roots of the equation.

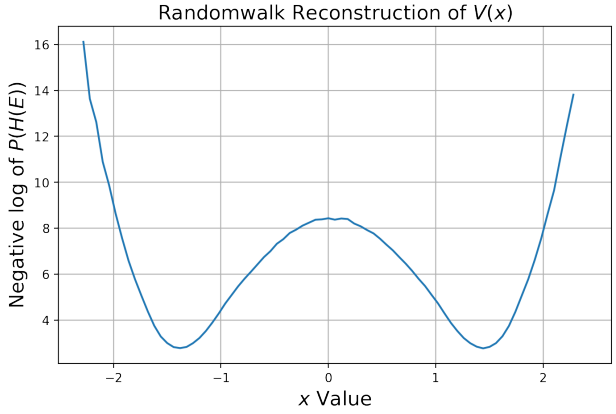

FIG. 2. An approximation of the shape of $V(x)$ from the values of $P(H(E))$, where in this case the random walk is performed with a fixed set of weights $g(E)$ from the previous part of the question..

II. QUESTION 2

For this question, we use HOOMD-Blue in conjunction with PYSAGES in order to run a series of simulations to obtain the energy landscape as a function of the torsional angle between the backbone carbon atoms of a single butane molecule. The tutorials from class as well as documents from the following repository[3] were used to prepare the simulation code.

From Kästner's review on Umbrella Sampling,[5] the free energy A of a window i can be found from a biased distribution

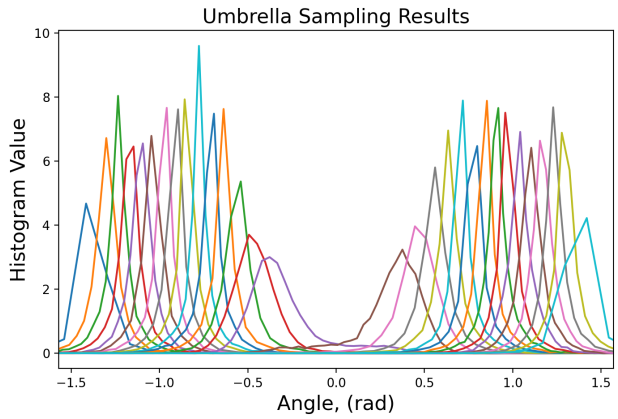

FIG. 3. The total histogram results for the HOOMD-Blue/PYSAGES simulation. There are 30 replicas of 10^6 steps for the collective variable of the torsional angle across the above range.

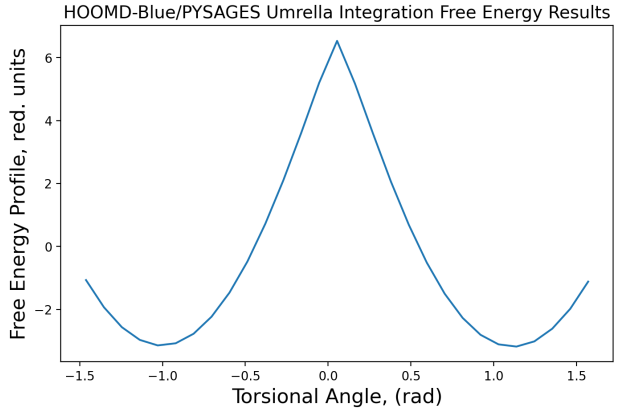

FIG. 4. The free energy profile of the torsional angle φ of the background carbons of butane obtained from umbrella integration of the previous figure's histogram results.

P^b, a set of biased potentials w and additive constants F_i

$$A_i(\zeta) = -(1/\beta)\ln P_i^b(\zeta) - w_i(\zeta) + F_i \tag{3}$$

and then a total unbiased distribution can be attained via the Weighted Histogram Analysis Method(WHAM).

For a collective variable as the torsional angle on atoms $0,4,7,$ and 10 with a range of $-\pi/2$ to $\pi/2$ (results are periodic past this), a total simulation of 30 replicas of 10^6 steps each was run, using a spring constant value of $k = 50$. The total run time was approximately 8.5 hours, or about 17 minutes per replica. In Fig. 3, we see the results of the 30 histogram curves which are combined via umbrella integration to produce the free energy landscape of Fig. 4. Indeed, we see that there is a maximum in energy at $\varphi = 0$, which then decreases until approximately ± 1 radians. Beyond this, there is periodic behavior in the free energy associated with the torsional angle of the backbone carbons due to the symmetry of the molecule.

[1] F. Wang and D. P. Landau, "Efficient, multiple-range random walk algorithm to calculate the density of states," Phys. Rev. Lett. **86**, 2050–2053 (2001).

[2] D. P. Landau, S.-H. Tsai, and M. Exler, "A new approach to monte carlo simulations in statistical physics: Wang-landau sampling," American Journal of Physics **72**, 1294–1302 (2004), https://doi.org/10.1119/1.1707017.

[3] B. Dice, "Hoomd-blue umbrella sampling example," `https://github.com/SSAGESproject/SSAGES/tree/release-0.9/Examples/User/Umbrella/HOOMD` (2018).

[4] R. E. Belardinelli and V. D. Pereyra, "Wang-landau algorithm: A theoretical analysis of the saturation of the error," The Journal of Chemical Physics **127**, 184105 (2007), https://doi.org/10.1063/1.2803061.

[5] J. Kästner, "Umbrella sampling," WIREs Computational Molecular Science **1**, 932–942 (2011), https://wires.onlinelibrary.wiley.com/doi/pdf/10.1002/wcms.66.

Appendix A: Optimized $g(E)$ Data

This section (may appear on the next page) includes the logarithmic values of the optimized weights from Question 1. Note that the first index is left empty due to the way in which values are sorted into the available bins (all values falling under the minimum bound are placed by the program into index 0).

Bins	Weights (Log)
-3.00	0.000000
-2.94	192.437969
-2.88	197.046920
-2.82	201.226101
-2.76	205.239909
-2.70	208.854600
-2.64	212.303640
-2.58	215.318509
-2.52	218.117391
-2.46	220.688590
-2.40	223.102168
-2.34	225.176323
-2.28	227.115765
-2.22	228.813949
-2.16	230.405323
-2.10	231.792728
-2.04	232.934087
-1.98	233.995444
-1.92	234.894866
-1.86	235.690774
-1.80	236.292097
-1.74	236.899669
-1.68	237.247648
-1.62	237.669539
-1.56	237.832150
-1.50	238.081198
-1.44	238.152460
-1.38	238.210875
-1.32	238.076533
-1.26	238.029327
-1.20	237.816134
-1.14	237.766002
-1.08	237.608359
-1.02	237.308667
-0.96	237.083841
-0.90	236.844895
-0.84	236.623338
-0.78	236.344006
-0.72	236.048629
-0.66	235.830685
-0.60	235.584125
-0.54	235.356765
-0.48	235.128313
-0.42	234.893243
-0.36	234.721500
-0.30	234.582212
-0.24	234.455628
-0.18	234.306352
-0.12	234.254628
-0.06	234.162309

Bins	Weights (Log)
0.00	234.118476
0.06	234.150991
0.12	234.095215
0.18	234.280911
0.24	234.295027
0.30	234.465519
0.36	234.607399
0.42	234.699101
0.48	234.924545
0.54	235.072052
0.60	235.292659
0.66	235.569338
0.72	235.815647
0.78	236.078489
0.84	236.386155
0.90	236.595531
0.96	236.836301
1.02	237.145699
1.08	237.349353
1.14	237.570597
1.20	237.736727
1.26	237.906124
1.32	238.009400
1.38	238.087791
1.44	238.151985
1.50	238.097253
1.56	238.002765
1.62	237.862673
1.68	237.572371
1.74	237.283570
1.80	236.929691
1.86	236.394357
1.92	235.698761
1.98	234.892517
2.04	233.974133
2.10	232.996731
2.16	231.719073
2.22	230.375872
2.28	228.864884
2.34	227.098821
2.40	225.197425
2.46	223.047956
2.52	220.715080
2.58	218.072943
2.64	215.334546
2.70	212.212991
2.76	208.873583
2.82	205.284823
2.88	201.211090
2.94	197.038935
3.00	192.466670