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Free Energy Computations Employing Jarzynski Identity And Wang – Landau Algorithm

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Abstract. We introduce a simple method to compute free energy differences employing Jarzynski identity in conjunction with Wang – Landau algorithm. We demonstrate this method on Ising spin system by comparing the results with those obtained from canonical sampling.

Keywords: Free energy, Jarzynski identity, Monte Carlo methods, Wang – Landau algorithm, Ising model
PACS: 05.70.Ce, 05.50.+q, 87.55.K-,

INTRODUCTION

Calculation of free energy differences has become very important in different fields of science. This is because free energy determines the behaviour of the systems, like polymer conformational changes, ligand attachment to protein, drug designing and many more. Several methods have been proposed to calculate free energy differences between two equilibrium states of a system. These include methods based on perturbation [1], thermodynamic integration [2] and adaptive integration [3] which are categorised as equilibrium sampling methods. Jarzynski identity [4], Crooks fluctuation theorem [5] and fast switching method [6] are known as nonequilibrium sampling methods. Another way of estimating free energy differences is by using path-sampling ensembles [7]. Jarzynski identity (JI) is the first nonequilibrium sampling method that was proposed. JI is given by

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F} \qquad (1)$$

where $\beta = 1/k_B T$ with k_B Boltzmann constant and T the temperature; W is the work done on the system. The advantage of this method over equilibrium sampling methods is that the system need not be in equilibrium or near equilibrium during the process. However it should be in equilibrium at the beginning of the process. It has been shown that the results obtained from JI suffer from large statistical fluctuations during the instantaneous switching process due to the biasing in unidirectional averaging. This is usually overcome by applying Bennet averaging [8] to JI. In this paper, we introduce a way to calculate ΔF using JI from an entropic ensemble generated by employing Wang-Landau algorithm [9]. We show that despite instantaneous switching, the results obtained from our method do not suffer from large statistical fluctuations.

NON – BOLTZMANN MONTE CARLO SIMULATION

The proposed method consists of two steps. In the first step, we estimate the density of states (DoS) denoted by $g(E)$ using Wang - Landau algorithm. In the second step we unweight the entropic ensemble to a uniform ensemble and reweight it to a canonical ensemble; the quantity $\langle \exp(-\beta W) \rangle$ is obtained by averaging over the canonical ensemble. Here W denotes the work done by instantaneous switching. Estimation of $g(E)$ is done as follows.

At first, we set $g(E_i)=1$, $\forall\ i$ and $H(E_i)=0\ \forall\ i$. H is the histogram of visited microstates. Consider an initial microstate C_i. Calculate the energy of the configuration, say E_i. Generate a trial configuration C_t by making a small change in C_i. For example, flip a randomly selected spin in case of Ising spin system or change the position of a monomer in case of polymers. Calculate energy of the trial state say E_t. We accept this trial state with the probability p given by,

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$$p = \min\left(1, \frac{g(E_i)}{g(E_t)}\right) \qquad (2)$$

If trial state is accepted, $C_{i+1} \rightarrow C_t$; we update the DoS and histogram corresponding to trial state as

$$g(E_t) \rightarrow g(E_t) \times f_0$$
$$H(E_t) \rightarrow H(E_t) + 1$$

where f_0 is called Wang-Landau factor. Usually we take f_0 as *exp(1)*. If trial state is rejected, $C_{i+1} \rightarrow C_i$ and we update the DoS and histogram accordingly. This constitutes a Monte Carlo step. *N* such Monte Carlo steps constitutes a Monte Carlo sweep, where *N* is size of the system under consideration. We carry out several Monte Carlo sweeps. Typically we check for a flat histogram after every 10,000 Monte Carlo sweeps. We say a histogram is flat when the highest and lowest of its entries do not differ from each other by more than 20%. When the histogram is flat we stop. This constitutes one Wang – Landau iteration. We reduce modification factor to $f_1 = \sqrt{f_0}$ and reset histogram $H(E_i) = 0 \; \forall \; i$, and carry out the Wang – Landau run with f_1. We repeat this till f_n takes a value close to unity. We collect converged DoS, $g(E_i)$ and use to generate an entropic ensemble. In the production run, we start with a random configuration C_0 and generate a sequence of microstates

$$C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow \ldots C_i \rightarrow C_{i+1} \rightarrow \ldots \; C_N$$

employing Wang – Landau algorithm with converged DoS $g(E_i)$. We do not update DoS in production run. After generating every microstate we calculate the possible work done on the system with the desired applied external field and collect $W(C_i)=W_i \; \forall \; i$ and also the energy of that microstate $E(C_i)=E_i \; \forall \; i$.

Calculation of Free Energy Differences

Once we collect an ensemble of microstates belonging to an entropic ensemble, ΔF can be calculated using JI as follows.

We unweight (divide with $g(E)^{-1}$) and reweight (multiply with Boltzmann factor). The average of $\exp(-\beta W)$ over canonical ensemble is calculated after applying and reweighting factors, see below.

$$\langle \exp(-\beta W) \rangle = \frac{\sum_C \exp(-\beta W(C)) g(E(C)) \exp(-\beta E(C))}{\sum_C g(E(C)) \exp(-\beta E(C))} \qquad (3)$$

In the above *C* belongs to entropic ensemble. Then we calculate ΔF using JI.

The advantage of this method is, with the converged DoS, we can perform a production run with different applied fields and calculate ΔF at any desired temperature. Since DoS contains whole information of the system, the ΔF calculated with this method is statistically accurate despite instantaneous switching. We have applied above described method to a Ising spin system [10]. We have also calculated ΔF through JE and Crooks fluctuation theorem employing canonical sampling method.

CANONICAL MONTE CARLO SIMULATION

In this section, we describe canonical sampling method which is often used to calculate ΔF through JI. First we equilibrate the system at desired temperature using metropolis algorithm [11]. Consider a microstate C_0 from equilibrium ensemble and calculate energy E_0. Apply small external field Δε. Calculate the energy E_1. The difference between E_1 and E_0 gives small work done ω_1. This we call a work step. Then we perform a Monte Carlo sweep with the field Δε. In canonical sampling, the acceptance probability is $p = \min\{1, \exp[-\beta(E_t - E_i)]\}$, where E_t and E_i are energies of trial and current states. This acceptance/rejection step is called Monte Carlo step and *N* Monte Carlo steps constitutes a Monte Carlo sweep. This is called a heat step. We perform alternate work and heat steps till external field ε reaches predetermined value, say ε_f. Let *n* be the number of work steps required to switch the field from an initial value of ε_0 to a final value ε_f. In other words,

$$\varepsilon_n = \varepsilon_f = \varepsilon_0 + n\Delta\varepsilon$$

where $\Delta\varepsilon = (\varepsilon_f - \varepsilon_0)/n$. *n* is called switching time. if *n* is small, the process is irreversible; when $n \rightarrow \infty$, we get a quasi-static reversible process. We have,

$$W = \sum_{i=1}^{n} \omega_i \qquad (4)$$

We carry out the simulation independently for a large number of times with the same switching protocol and construct an ensemble $\{W_i\}$ of work values from which we calculate the free energy difference using JI. In the simulation we have taken $\varepsilon_0 = 0$ and $\varepsilon_f = 0.1$. The size of the Monte Carlo ensemble is one million.

ISING SPIN SYSTEM

We have considered an 32×32 Ising spin system on a square lattice to demonstrate the both the methods described above. A spin takes a value of +1 if it points upwards and -1 if it points downwards. The interaction energy between two spins S_i and S_j which are located at nearest neighbour sites *i* and *j* is given by $\varepsilon_{ij} = -JS_iS_j$, where *J* is the strength of spin-spin

interaction. For a two dimensional lattice, each spin interacts with four nearest neighbours. The total energy of the system is given by

$$H = -J\sum_{\langle i,j\rangle} S_i S_j \qquad (5)$$

where $\langle i,j\rangle$ denotes that i and j are nearest neighbour sites and the summation runs over all the distinct nearest neighbour pairs with periodic boundary conditions.

RESULTS AND DISCUSSIONS

We have calculated the free energy differences at various temperatures through JI using both the non – Boltzmann and canonical sampling methods described above. Let ΔF^{WL} and ΔF^{C} be the free energy differences calculated from Wang – Landau algorithm and canonical sampling respectively. We have collected an entropic work ensemble of one million size to calculate ΔF^{WL}. In canonical sampling, for the applied field $\varepsilon_f = 0.1$, ΔF^{C} converged for switching time $n = 16$. In FIGURE 1, we have plotted ΔF^{WL} and ΔF^{C} as a function of temperature. We observe that the results show a good agreement with each other.

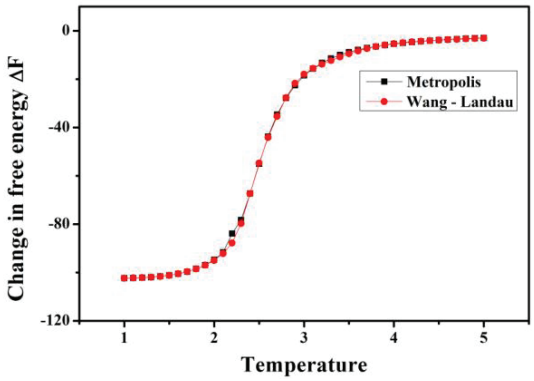

FIGURE 1. Comparison between of free energy differences calculated from Jarzynski identity employing Metropolis and Wang – Landau algorithm at different temperatures.

FIGURE 2 shows probability density of work for forward process $\rho(W)$ and backward process $\rho(-W)$ for switching times $n = 16$ and $n = 32$. A Forward process is a process that described in canonical sampling method and the backward process similar to that described in canonical sampling method but in reverse direction *i.e.,* we equilibrate the system at $\mathcal{E}_f$ and turn it to $\mathcal{E}_0$ and the remaining procedure is same. According to Crooks fluctuation theorem, free energy difference is given by the intersection of these two distributions. The ΔF obtained from these distributions is well matched with the value obtained from the proposed method.

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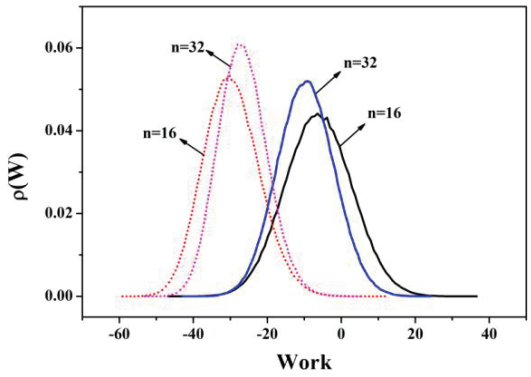

FIGURE 2. Probability density of work for switching times n=16 and n=32 at temperature T=3. Dashed lines are for backward process and solid lines are for forward process.

CONCLUSIONS

In summary, we have proposed a simple method to calculate free energy differences using Jarzynski idenity employing Wang – Landau algorithm. We compared the results with those obtained from canonical Monte Carlo techniques and they are in very good agreement.

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REFERENCES

1. R. W. Zwanzig, *J. Chem. Phys.* **22**, 1420 (1954).
2. J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).
3. M. Fasnacht, R. H. Swendsen and J. M. Rosenberg, *Phys. Rev. E* **69**, 056704 (2004).
4. C. Jarzynski, *Phys. Rev. E* **56**, 5018 (1997).
5. G. E. Crooks, *Phys. Rev. E* **61**, 2361 (2000).
6. W. Lechnar, Harald Oberhofer, Christoph Dellago and P.L. Geissler, *J. Chem Phys.* **124**, 044113 (2006).
7. F. M. Ytreberg and D. M. Zuckerman, *J. Chem. Phys.* **120**, 1086 (2004); **121**, 5022 (2004).
8. C. H. Bennett, *J. Comp. Phys.* **22**, 245 (1976).
9. F. Wang and D. P. Landau, *Phys. Rev. Lett.* **86**, 2050 (2001).
10. Stephen G. Brush, *Rev. Mod. Phys.* **39**, 883 (1967).
11. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).