

# Wang-Landau Sampling in Three-Dimensional Polymers

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Monte Carlo simulations using Wang-Landau sampling are performed to study three-dimensional chains of homopolymers on a lattice. We confirm the accuracy of the method by calculating the thermodynamic properties of this system. Our results are in good agreement with those obtained using Metropolis importance sampling. This algorithm enables one to accurately simulate the usually hardly accessible low-temperature regions since it determines the density of states in a single simulation.

Keywords: Homopolymers; Wang-Landau sampling; Interaction self avoiding walk

## I. INTRODUCTION

With the rapid development of computer processors, numerical simulations using the Monte Carlo method have become a well established tool for the study of proteins, polymers and spin-glass models. When a Monte Carlo simulation using Metropolis importance sampling [1] is carried out at a fixed temperature, the quality of the data depends on the distance from criticality, and therefore, multiple computer runs should be performed for each temperature. In order to speed up the simulation several methods have been suggested to overcome problems such as slow dynamics which makes the Metropolis algorithm inefficient, and to study systems with a rough energy landscape with multiple local minima in free energy. Important examples are the cluster-flip Swendsen-Wang algorithm [2], which has been used to reduce critical slowing down at second order phase transitions, the multicanonical method [3] which was introduced to overcome the barrier between coexisting phases at first order phase transitions, the broad histogram method [4] which directly calculates the density of states with only one computer run, and the flat histogram method [5] which generates a flat histogram in energy space similar to multicanonical simulations. The drawback of the flat histogram method is the slow diffusion of the random walk which is the same as in the multicanonical method. Nevertheless, no method is more efficient than that recently proposed by Wang and Landau [6–9] which allows one to get around these difficulties even for large systems.

In this work we present results of simulations of three-dimensional lattice polymer chains [10] using Wang-Landau sampling, and calculate thermodynamic properties of the system. The method is described in Sec. II. Sec. III provides a brief background on the algorithm. The results are given in Sec. IV and we summarize and conclude in Sec. V.

## II. THE MODEL

We consider a homopolymer consisting of  $N$  monomers which may assume any self avoiding walk (SAW) config-

uration on a three-dimensional lattice. Assuming that the polymer is in a bad solvent, there is an effective monomer-monomer attraction in addition to the self-avoidance constraint representing excluded volume. For every pair of non-bonded nearest-neighbor monomers the energy of the polymer is reduced by  $\varepsilon$  (See Fig. 1).

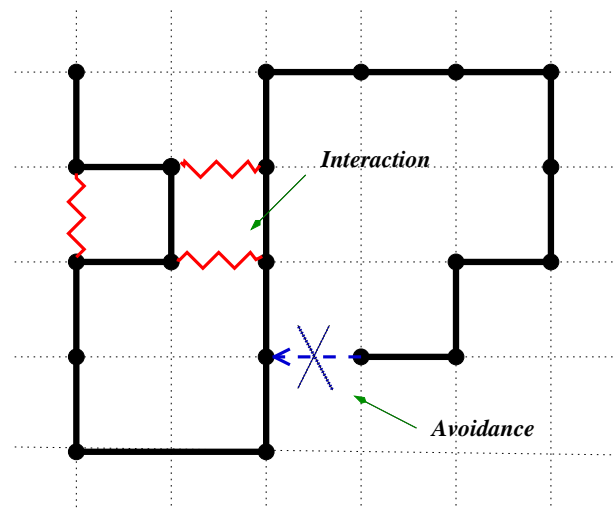


FIG. 1: Interaction Self Avoiding Walk.

Therefore, the interaction between two nonbonded monomers  $i$  and  $j$  is given by

$$u_{i,j} = \begin{cases} \infty & r < \delta \\ -\varepsilon & r = \delta \\ 0 & r > \delta \end{cases} \quad (1)$$

where  $\delta$  is the lattice constant.

The Hamiltonian for the model can be written as

$$\mathcal{H} = -\varepsilon \sum_{\langle i,j \rangle} \sigma_i \sigma_j \quad (2)$$

where  $\sigma = 1$  (0) if the site  $i$  is occupied (vacant), and the sum is over nearest-neighbor pairs [11]. (The sum is understood

to exclude pairs of bonded segments along the chain). We are interested in the equilibrium properties at temperature  $T$ . (In the following, temperature is measured in units of  $\varepsilon/k_B$ , where  $k_B$  is the Boltzman's constant.)

In order to generate a Markov process for sampling configurations we have first to define a protocol of movements. We used the so-called reptation or “slithering snake” move which consists of randomly adding a monomer to one end of the chain and removing a monomer from the other end, maintaining the size of the polymer constant. We define one Monte Carlo step as  $N$  attempted moves. At certain moments, one end of the chain may not be able to move, but successive motions of the other end release it from the trap.

### III. THE METHOD

The Wang-Landau algorithm calculates the density of states  $g(E)$  by carrying out a random walk in energy space with an acceptance probability proportional to  $1/g(E)$  instead of the usual Boltzmann weight  $e^{-E/k_B T}$  used in the conventional Monte Carlo simulation. The probability of energy  $E$  changes therefore from  $g(E)e^{-E/k_B T}$  in the Metropolis scheme to an almost constant probability in the Wang-Landau method. As a result the probability minimum which appears at first order phase transitions, for example, practically vanishes. The simulation is performed such that if  $E_1$  is the energy of the current configuration and  $E_2$  is the energy of a possible new configuration, the acceptance probability is given by

$$p(E_1 \rightarrow E_2) = \min \left[ \frac{g(E_1)}{g(E_2)}, 1 \right]. \quad (3)$$

For each accepted configuration we accumulate an energy histogram  $H(E)$ . Since the density of states is not known *a priori*, Wang and Landau proposed to set  $g(E) = 1$  initially, for all energy levels.

To study large systems the energy space is divided into bins and the random walk is carried out independently in each segment. As the random walk in energy space is performed, whenever a move to a configuration with energy  $E$  is accepted the density of states is updated by multiplying it by a “modification factor”  $f > 1$  that accelerates the diffusion of the random walk, and an unit is added to the histogram  $H(E)$ , i.e.

$$g(E) \rightarrow g(E) \cdot f; \quad \text{and} \quad H(E) \rightarrow H(E) + 1. \quad (4)$$

The initial choice of  $f$  is  $f_0 = e = 2.71828\dots$ . The density of states is multiplied by  $f$  until the accumulated histogram  $H(E)$  is flat. We then reduce  $f$  by setting

$$f \rightarrow \sqrt{f}, \quad (5)$$

and resetting  $H(E) = 0$  for all energy values.

This process is repeated; the simulation converges to the true value of  $g(E)$  when  $f$  is approximately 1. In our simulations the criterion of flatness was taken as each value of the histogram reaching at least 80% of the mean value  $\langle H(E) \rangle$ . The histograms are generally checked after each 1000 Monte Carlo steps.

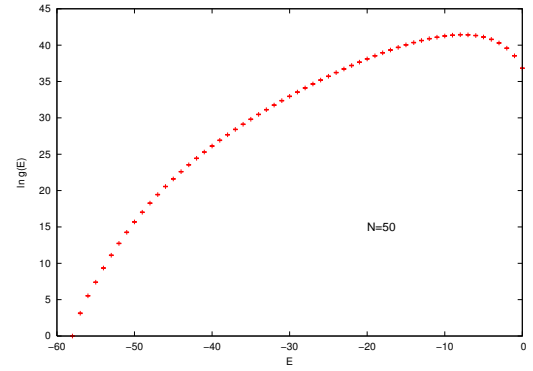


FIG. 2: Density of states for a chain of  $N = 50$  monomers. The ground state of this chain is  $E_g = -58$ .

### IV. RESULTS

In this section we present results obtained for chains of lattice homopolymers using the Wang-Landau algorithm and compare them with those obtained using Metropolis algorithm importance sampling. In Fig. 2 we show the density of states for a chain of 50 monomers.

The ground state is achieved by shaping a configuration rolled up like a snail (see Fig. 3). The energy of this configuration is obtained by counting the number of nonbonded nearest-neighbor pairs. In our simulations the polymer was always set initially in this configuration and, using the algorithm described above, the density of states was estimated as a result of a random walk in the energy space.

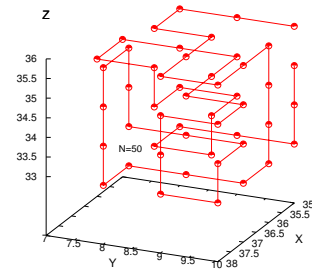


FIG. 3: A ground state configuration for  $N = 50$ . In this case the energy is  $E_g = -58$ .

Knowing the density of states, one can calculate any thermodynamic property  $A$  of the system through the canonical average

$$\langle A \rangle_T = \frac{\sum_E \langle A \rangle_E g(E) e^{-E/k_B T}}{Z} \quad (6)$$

where  $\langle A \rangle_E$  is the microcanonical average of observable  $A$  obtained during the simulation,  $g(E)$  is the density of states for

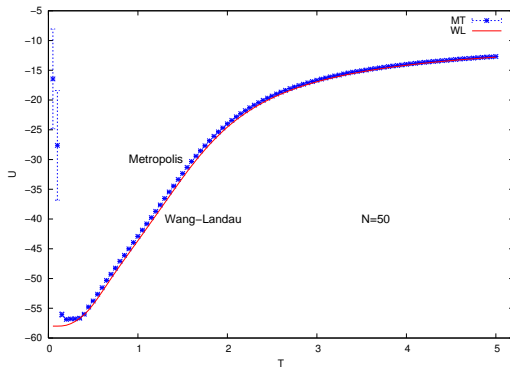


FIG. 4: Temperature dependence of the internal energy for a chain of  $N = 50$  monomers.

each energy level  $E$ , and  $Z$  is the partition function

$$Z = \sum_E g(E) e^{-E/k_B T}. \quad (7)$$

In Monte Carlo simulations using Metropolis sampling we fix the temperature and determine the thermodynamic average  $\langle A \rangle_T$ . Therefore a new simulation is needed for each value of temperature. In Wang-Landau sampling we estimate the density of states and then calculate any thermodynamic property of interest by means of a simple algebraic operation. The computational time in our simulations was about ten times smaller using the Wang-Landau method as compared with the Metropolis algorithm.

In Fig. 4 we show the result for the internal energy via Wang-Landau sampling, evaluated using the relation

$$U(T) = \frac{\sum_E E g(E) e^{-E/k_B T}}{\sum_E g(E) e^{-E/k_B T}} \equiv \langle E \rangle, \quad (8)$$

and compare it with that obtained via the Metropolis algorithm.

The specific heat can be determined from the fluctuations in the internal energy

$$C_v(T) = \frac{\langle E^2 \rangle_T - \langle E \rangle_T^2}{k_B T^2}. \quad (9)$$

The temperature dependence of the specific heat is shown in Fig. 5. Much more CPU time would be needed to obtain significantly better results using the Metropolis algorithm. One can see clearly from these results that the Wang-Landau method yields a better description in the low-temperature regime.

The temperature dependence of the mean square end-to-end distance, given by

$$\langle R^2 \rangle = \langle [(x_N - x_0)^2 + (y_N - y_0)^2 + (z_N - z_0)^2] \rangle \quad (10)$$

is shown in Fig. 6.

Differentiating expression 6 with regard to temperature using  $\langle R^2 \rangle$  as the observable  $A$ , we obtain the fluctuation of the mean square end-to-end distance as

$$\frac{d \langle R^2 \rangle_T}{dT} = \frac{\langle E R^2 \rangle_T - \langle E \rangle_T \langle R^2 \rangle_T}{T^2}. \quad (11)$$

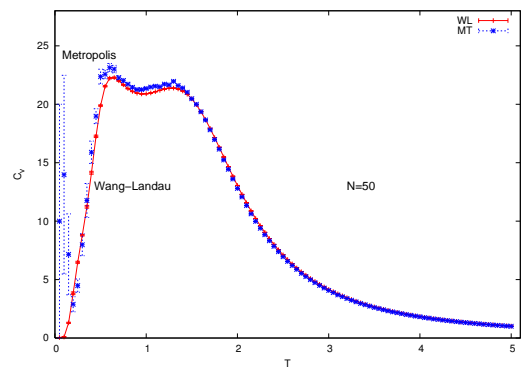


FIG. 5: Specific heat vs. temperature for a chain of  $N = 50$  monomers.

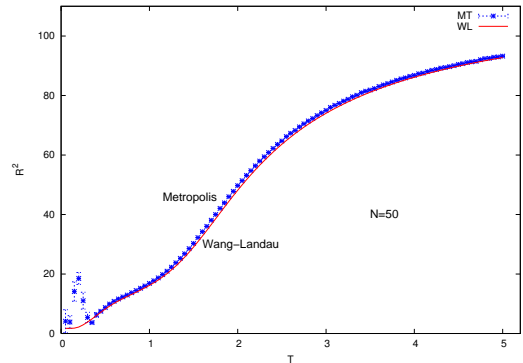


FIG. 6: Mean square end-to-end distance vs. temperature for a chain of  $N = 50$  monomers.

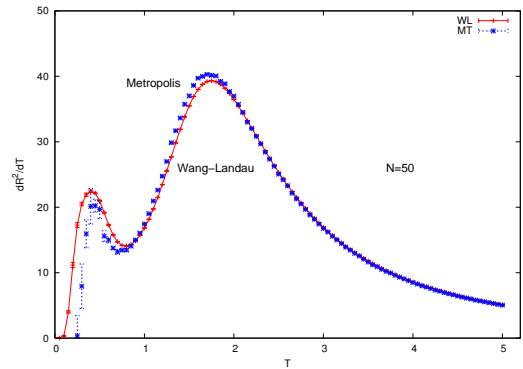


FIG. 7: Derivative of the mean square end-to-end distance vs. temperature. The curve with a peak resembles a second-order phase transition.

The temperature dependence of the derivative of the mean square end-to-end distance is shown in Fig. 7. The coil-globule phase transition is characterized by a peak in the derivative of  $\langle R^2 \rangle$  similar to the specific heat. We believe that the low-temperature peak corresponds to excitations of the surface of the typically compact, folded configuration. This effect is more pronounced in short chains.

An advantage of this algorithm is that we can readily calcu-

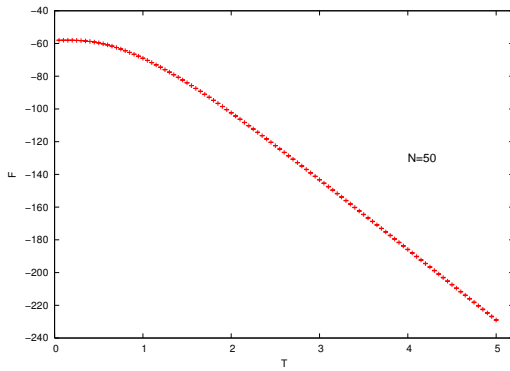


FIG. 8: Free energy vs. temperature for a chain of  $N = 50$  monomers.

late the free energy and entropy, quantities that are not directly accessible in conventional Monte Carlo simulations. In terms of the density of states, the free energy can be calculated from the partition function

$$F(T) = -k_B T \ln(Z) = -k_B T \ln \left( \sum_E g(E) e^{-E/k_B T} \right). \quad (12)$$

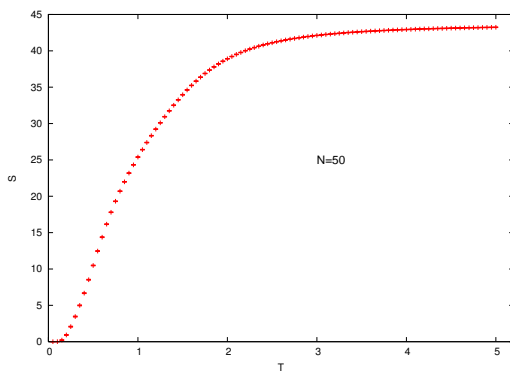


FIG. 9: Entropy vs. temperature for a chain of  $N = 50$  monomers.

The temperature dependence of the free energy obtained

from our simulation is shown in Fig. 8 for a homopolymer with  $N = 50$  monomers.

The entropy is a key thermodynamic quantity that cannot be calculated directly by conventional Monte Carlo simulation. It can be estimated by integration over other thermodynamic quantities, such as specific heat, but these calculations are somewhat unreliable since the specific heat itself is not easy to estimate accurately. With an accurate density of states estimated by the Wang-Landau method, the entropy can be calculated simply using

$$S(T) = \frac{E(T) - F(T)}{T}. \quad (13)$$

In Fig. 9 we show our result for the temperature dependence of the entropy for a homopolymer chain of  $N = 50$  monomers.

## V. CONCLUSIONS

We study the thermodynamic behavior of a three-dimensional homopolymer chain in lattice using the Wang-Landau sampling. We show that the density of states directly obtained by this algorithm enables one to calculate thermodynamic properties even for large systems with only one computer run. We also note from the temperature dependence of the specific heat and the mean square end-to-end distance that the low-temperature region is better explored by this method than by standard Monte Carlo simulation. Finally, thermodynamic quantities such as the free energy and the entropy, which are not easily accessible by conventional methods, are directly estimated from the density of states.

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