# Study of thermodynamic and structural properties of a flexible homopolymer chain using advanced Monte Carlo methods

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**Abstract.** We study the thermodynamic and structural properties of a flexible homopolymer chain using both multi canonical Monte Carlo method and Wang-Landau method. In this work, we focus on the coil-globule transition. Starting from a completely random chain, we have obtained a globule for different sizes of the chain. The implementation of these advanced Monte Carlo methods allowed us to obtain a flat histogram in energy space and calculate various thermodynamic quantities such as the density of states, the free energy and the specific heat. Structural quantities such as the radius of gyration where also calculated.

## 1 Introduction

The investigation of thermodynamic properties of complex systems by means of Monte Carlo methods started about 60 years ago with the Metropolis algorithm[1], which emulates the canonical ensemble. The arsenal of algorithms has been extended and more sophisticated methods have been introduced. Among the most powerful simulation techniques are generalized-ensemble methods such us parallel tempering[2] and Wang Landau method[3], which allow in principle to collect all information about the the entire thermodynamic behavior of the investigated system in a single simulation. In this work, we present a comparative study between the multicanonical and the Wang Landau methods to understand the coil-globule transition.

## 2 Monomers interaction model

In our simulations, we employed a model for elastic flexible polymers[4, 5], where non adjacent monomers interact pairwise via a Lennard Jones potential,

$$V_{\mathrm{LJ}}(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] - V_{\mathrm{LJ}}(rc) \qquad (1)$$

r denotes the relative distance between the monomers. $\epsilon$ is set to 1, $r_c = 2.5\sigma$ and $\sigma = r_0 2^{\frac{-1}{6}}$ with the minimum potential distance $r_0 = 0.7$. Covalent bonds are modeled by an additional finite extensible nonlinear elastic(FENE) potential for adjacent monomers:

$$V_{FENE}(r) = -\frac{k}{2}R^2 \ln\{1 - [\frac{r - r_0}{R}]^2\} \qquad (2)$$

The potential possesses a minimum coinciding with $r_0$ and diverges for $r \rightarrow r_0 \pm R$ with $R = 0.3$. Here $k$ is a spring constant set to 40.

## 3 Simulation method

In the first time, the Wang Landau method method is considered. The density of state $g(E)$ is calculated by carrying out a random walk in energy space with an acceptance probability proportional to $\frac{1}{g(E)}$. 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[3, 4, 6] is given by

$$p(E_1 \rightarrow E_2) = min\left(\frac{g(E_1)}{g(E_2)}, 1\right) \qquad (3)$$

Initially, the density of state $g(E)$ is set to 1[7], for each accepted configuration $H(E) \rightarrow H(E) + 1$, $g(E) \rightarrow g(E)f$, $f \rightarrow \sqrt{f}$ Initially, $f = e = 2.7182...$, the process is reapeted; the simulation converges to the true value of $g(E)$ when f is approximately 1.

In the second time, the multicanonical algorithm[8] is implemented. The Boltzmann probability is multiplied by a weight factor $W(E)$ which has to be determined iteratively; in the beginning, the the weights $W^0(E)$ are set to unity. The first run is ausual Metropolis simulation, which yields an estimate $H^0(E)$ for the canonical distribution.

$W^1(E) = \frac{W^0(E)}{H^0(E)}$, the iterative procedure is continued until the weights are appropriate in a way that the multicanonical histogram $H(E)$ is flat.

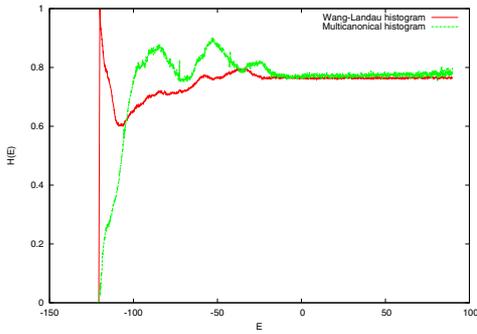Any thermodynamic observable can be obtained by

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**Figure 1.** Comparaison of the histogram evolution for multi-canonical Monte Carlo simulation and a Wang-Landau simulation for a homopolymer chain with 30 monomers.
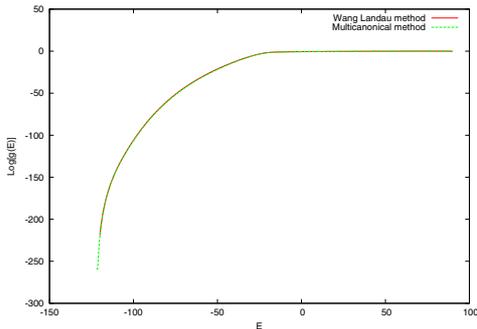


**Figure 2.** Comparison of the density of states obtained by multi-canonical and Wang-Landau simulations.

$$\langle A \rangle_T = \frac{\sum_E A_E g(E) e^{-E/k_B T}}{\sum_E g(E) e^{-E/k_B T}} \qquad (4)$$

## 4 Results

In the following, we present the results obtained by Wang Landau and multicanonical methods for a homopolymer chain whith 30 monomers.

In Figure1, we can see the evolution of the histogram during the Wang-Landau and the multicanonical simulations. For high temperatures, the results obtained are almost the same. For low temperatures, the multicanonical simulation seems to be more stable.
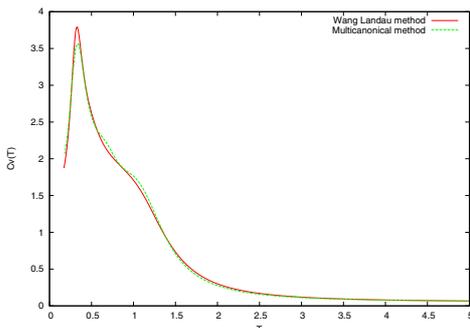
Figure 2 and Figure 3 show repesctively the density of states in logarithmic scale $\log(g(E))$ and the specific heat $C_v$ as a function of the temperature $T$. For both methods, the results obtained are similar.

In the case of a homopolymer chain with 30 monomers, we can observe a small shoulded around $T \approx 1.5$ and a sharp pic around $T \approx 0.5$. These transition signatures are in accordance with the results obtained by Bachmann et al[9].

## 5 Conclusion

We have presented the general behavior of a flexible homopolymer chain using The Wang Landau and the multicanonical Monte Carlo methods. The results obtained allowed us to observe the coil-globule and liquid-solid transitions through the calculation of the specific heat. The computer code developed suffer from some over flows in the calculation of the thermodynamic properties at very low temperatures and will be improved in a future work. The results obtained are almost similar to those obtained in the literature[9].

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**Figure 3.** Specific heat as a function of temperature obtained by multicanonical and Wang-Landau Monte Carlo simulations for a homopolymer chain with 30 monomers.