

STUDY OF THERMODYNAMIC AND STRUCTURAL PROPERTIES OF A FLEXIBLE HOMOPOLYMER CHAIN USING MULTICANONICAL MONTE CARLO METHOD

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ABSTRACT

We study the thermodynamic and structural properties of a flexible homopolymer chain by means of multi-canonical Monte Carlo 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 method 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 were also calculated.

INTRODUCTION

Monte Carlo methods are very efficient to study the behavior of complex systems. However, the Metropolis method[1] in the canonical ensemble is not able to sample all possible conformations. Especially at low temperatures, the system will be trapped in local energy minima. The simulation in generalised ensemble[2] is the best way to avoid such problems. Recently, the multicanonical Monte Carlo method[3; 4], the Wang-Landau and the parallel tempering methods[5; 6] became very popular in statistical physics. Their approaches allow the system to visit all possible energy states in a single simulation in order to produce a flat histogram in the energy landscape.

In this work, we present a multicanonical Monte Carlo study to understand the coil-globule transitions in homopolymer systems. The model and the simulation method are described in Sec. II and III respectively. The results are given in Sec. IV and we conclude in Sec. V.

MODEL AND SIMULATION METHOD

The polymer chain is described by a coarse grained off lattice flexible homopolymer model that contains N identical monomers (the same model used in references[7; 8; 9]). The non bonded monomers interact pairwise via a truncated shifted Lennard Jones potential given by

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] - U_{LJ}(r_c) \quad (1)$$

here r denotes the relative distance between the monomers. ϵ is set to 1, $r_c = 2.5\sigma$ and $\sigma = r_0 2^{-\frac{1}{6}}$ with the minimum potential distance $r_0 = 0.7$, and the bonded interaction between nearest

neighbors is given by the FENE potential,

$$U_{FENE}(r) = -\frac{k}{2} R^2 \ln \left\{ 1 - \left[\frac{r-r_0}{R} \right]^2 \right\} \quad (2)$$

k is a spring constant set to 40 and $R = 0.3$.

The total energy is given by

$$E_{tot} = \sum_{i=1}^N \sum_{j=i+1}^N U_{LJ}(r_{ij}) + \sum_{i=1}^{N-1} U_{FENE}(r_{ii+1}) \quad (3)$$

The curves of the potentials as a function of the distance between two monomers are shown in figure 1.

In the present work, we employ the multicanonical Monte Carlo algorithm[3; 4] that consists of performing a random walk in energy space. The Boltzmann energy distribution $P_{can}(E) = g(E) \exp(-\beta E)$ is deformed by introducing weight factors $W(E)$ which are unknown a priori and have to be determined iteratively. Thereby, the multicanonical energy distribution will be $P_{muca}(E) = g(E) \exp(-\beta E) W(E) = H(E)$. Where $H(E)$ denotes the multicanonical histogram.

Initially, the weight factors $W^0(E) = 1$ are set to unit. We start by performing a simulation at infinite temperature under canonical distribution which yields an estimate histogram $H^0(E)$. The estimation $W^1(E)$ is given by $W^1(E) = \frac{W^0(E)}{H^0(E)}$. Then, in the next run yield an estimate of $H^1(E)$ and $W^2(E) = \frac{W^1(E)}{H^1(E)}$ and so on. The iterative procedure is continued until the multicanonical histogram is flat.

After having estimated the appropriate weights $W(E)$, a long production run is performed to determine different statistical quantities which can be obtained by the following equation

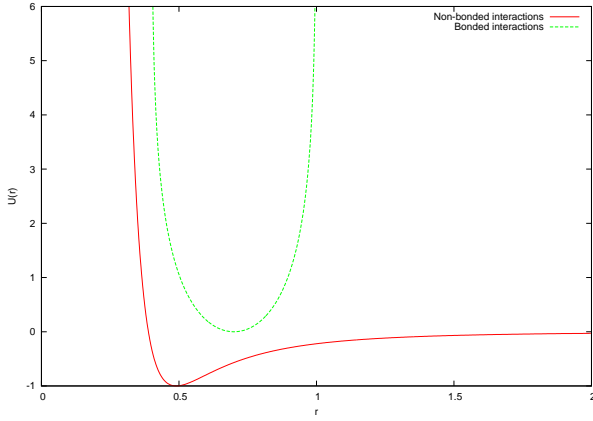


Figure 1. Bonded and Non-bonded potentials versus the distance between two monomers

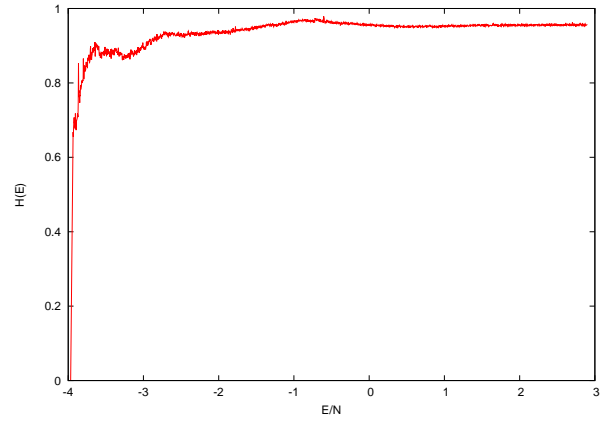


Figure 2. Flat multicanonical histogram obtained for a homopolymer chain with $N=43$ monomers.

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

RESULTS

In the following, we present results of the multicanonical simulation for homopolymer chains for $N = 19, 43$ and 51 . to obtain the multicanonical weights we performed 300 iterations with 10^5 sweeps at each iteration. One sweep is N displacements updates. The simulation has been performed over an energy range in $E/N \in [-3, 4]$ which is divided in bins with bin resolution $dE = 0.1$ and temperature range in $[0.01; 5]$ A long simulation with 3×10^8 sweeps is performed to obtain thermodynamic and structural quantities.

In figure 2 we show the multicanonical histogram obtained at the end of simulation for homopolymer chain with $N = 43$ monomers. In figure 3, we plot the specific heat obtained for different length of the chain. The coil-globule transition is characterized by a peak that appears at approximately $T \simeq 0.5$.

In our simulation we used the shift monomer update, that type of displacement does not allow the detection of the transition signatures at low temperatures. More sophisticated moves are required such as crankshaft move, end bridging move, reptation move[10] and the bond exchange move[11]. We are implementing these types of displacements.

The radius of gyration (structural quantity) is shown in figure 5 for the different lengths of the chain.

CONCLUSION

The coil-globule transition for homopolymer systems is studied by means of multicanonical Monte Carlo simulation for $N = 19, 43$ and 51 chain sizes. To improve our results, It would be more efficient to use more sophisticated displacement algorithm. Especially at low temperature, where transition signatures are still difficult to detect.

Our code was validated for $N = 30$ with the results of another group[8].

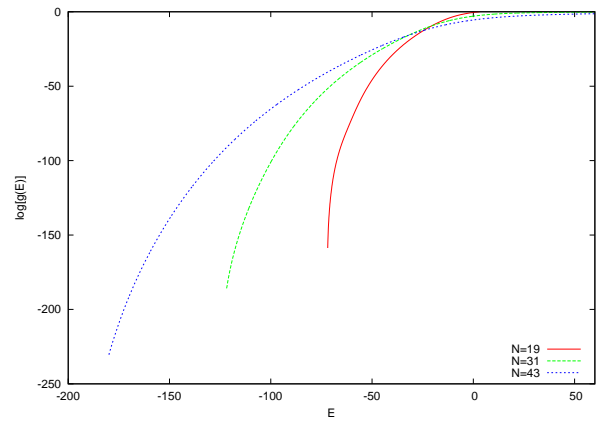


Figure 3. Density of states obtained for homopolymer chains with different length of the chains $N=19, 43$ and 51 .

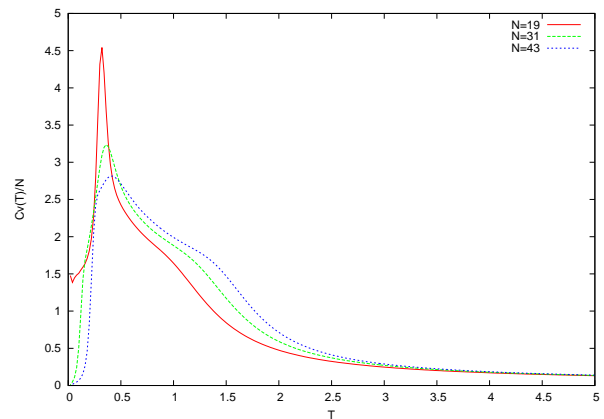


Figure 4. Specific heat per monomers with different lengths $N=19, 43$ and 51 versus temperature in range $[0, 5]$.

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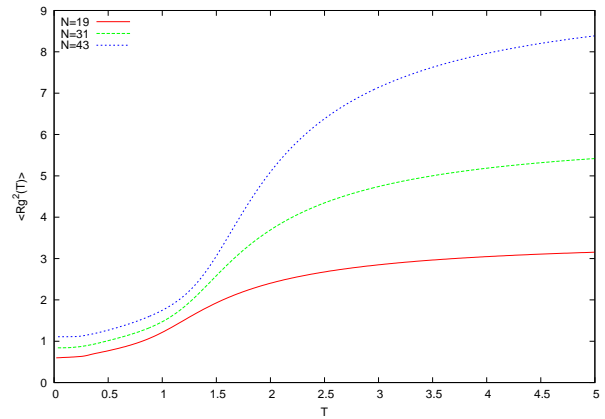


Figure 5. Radius of gyration obtained for $N = 19, 43$ and 51 vs temperature.

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