On the existence of helical structures during the collapse of flexible homopolymers: A Wang-Landau study

Sid Ahmed Sabeur\textsuperscript{a,*}, Mounira Bouarkat\textsuperscript{a}, Fatima Hamdache\textsuperscript{a}

\textsuperscript{a}Laboratoire de Physique des Plasmas, des Matériaux Conducteurs et de leurs Applications, Département de Physique, Faculté des Sciences, USTOMB, BP 1505 El M’naouer, Oran, Algeria

Abstract

In this work, we report our results on the phase transition of a flexible homopolymer from a stretched chain to a compact globule. The Wang-Landau method is used to study the thermodynamic properties of a the chain up to 512 monomers. We believe that the peak in the specific heat at low temperature \( T \approx 0.05 \) for small chain sizes \( N < 100 \) is a clear evidence of the existence of metastable helical structures observed in a previous study.

Keywords: Helical Structures, Wang-Landau Algorithm, Homopolymer Collapse

1. Introduction

In recent years, designing functional polymers at nanometers scales has gained increasing interest\cite{1}. However, it is challenging to control structures that have the ability to undergo cooperative transitions between random conformations (globules) and ordered conformations (\( \alpha \)--helices and \( \beta \)--sheets). There has been a spate of theoretical studies dealing with this issue, commonly achieved using Monte Carlo and molecular dynamics simulations\cite{2,3}. These works have offered rewarding insights for understanding the dynamics and the phase transition of polymers and there is still a big interest in investigating them until today\cite{4}. In a previous work, we have found that flexible homopolymers spontaneously develop helical order during the process of collapsing from an initially stretched conformation. We have also demonstrated that the helices are long lived transient states at low temperatures\cite{7}, but with "borrowing" energy from their surrounding solvent particles, they overcome the energetic barrier and collapse into a stable globule (Fig. 1 shows typical configurations in the process of a homopolymer collapse). Here, we extend our study to the thermodynamic behavior of a flexible homopolymer using the Wang-Landau method\cite{8}. Our main goal is to confirm the existence of the helical structures during the collapse, and to characterize the temperature regions corresponding to those structures. The paper is organized as follows. In Sec. II we introduce the model. In Sec. III the simulation method and the parameters used to quantify the thermodynamic properties are presented. The simulations results are summarized in Sec. IV. Finally, conclusions and appropriate acknowledgments are given in Sec. V.

\textsuperscript{*}Corresponding author.
Email address: aminesabeur@yahoo.fr (Sid Ahmed Sabeur)

Preprint submitted to Comp. Phys. Comm. January 27, 2011
2. Model

In the simulation, we have used a simple bead-spring model. The polymer chain consists of \( N \) identical monomers where each monomer position varies continuously in three dimensions. There are two types of interactions: a harmonic interaction between adjacent monomers

\[
U_{\text{bond}}(r) = a(r - r_0)^2, \quad (1)
\]

with \( a = 100\epsilon/\sigma^2 \) and \( r_0 = 0.85\sigma \)

and a truncated Lennard-Jones potential between non adjacent monomers

\[
V_{\text{LJ}}(r) = \begin{cases} 
4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6 + c_0] & \text{for } r < 2.5\sigma \\
0 & \text{otherwise},
\end{cases} \quad (2)
\]

where the constant \( c_0 \) is chosen such that the potential is continuous everywhere.

Dimensionless units are used during the simulation and are defined in terms of the bead size \( \sigma \) and the Lennard-Jones energy \( \epsilon \).

3. Method

We have implemented the Wang-Landau algorithm to study the thermodynamic behavior of the flexible homo-polymer. This method is a temperature independent Monte Carlo technique for exploring the energy landscape. By calculating the density of states \( g(E) \), where \( E \) is the energy of the polymer chain, any thermodynamic observable \( A \) can be obtained with one single simulation for a wide range of temperatures through the canonical average

\[
\langle A \rangle_T = \frac{\sum_E \langle A \rangle_E g(E) e^{-E/k_B T}}{Z} \quad (3)
\]

Where \( Z \) is the partition function and can be determined by

\[
Z = \sum_E g(E) e^{-E/k_B T} \quad (4)
\]

Using Eq. 3 one can calculate the internal energy \( \langle E \rangle_T \) of the homopolymer.
\begin{equation}
\langle E \rangle_T = \frac{E g(E) e^{-E/k_B T}}{Z} \tag{5}
\end{equation}

and thus the specific heat \( C_v \)

\begin{equation}
C_v = \frac{\langle E^2 \rangle_T - \langle E \rangle_T^2}{k_B T^2} \tag{6}
\end{equation}

Initially, we start the simulation by taking a stretched configuration for the homopolymer chain. We set the density of states \( g(E) = 1.0 \). Then, we proceed by generating trial states, using appropriate "moves", and accepting them with transition probability

\begin{equation}
p(E_i \rightarrow E_f) = \min \left( \frac{g(E_i)}{g(E_f)}, 1 \right) \tag{7}
\end{equation}

where \( E_i \) is the initial energy and \( E_f \) is the energy of the trial state.

Each Monte Carlo sweep in the simulation consists of the following moves: \( N \) diffusion moves, one reptation move, one single-bead crankshaft move and one pivot move. The moves are chosen identical to those of reference[10].

If the trial move is accepted, the density of states is multiplied by a modification factor \( f \), i.e. \( g(E_f) \rightarrow g(E_f) \times f \), and a histogram \( H(E) \) is also updated, \( H(E_f) \rightarrow H(E_f) + 1 \).

If the trial state is rejected, the same procedure is followed for the initial energy \( E_i \).

This process is repeated until the histogram \( H(E) \) is sufficiently flat, at which point the histogram is reset to zero, the modification factor is reduced by \( f \rightarrow \sqrt{f} \), and the random walk continues. The initial value of the modification factor is set to \( f = e^1 \) and is eventually reduced to a value which is \( f_{\text{final}} \approx 1 \). The flatness of \( H(E) \) is defined as its minimum divided by its average, and in this study, the flatness criterion is set to 0.6. To prevent overflow during the simulations, the logarithm of the density of states \( \ln[g(E)] \) is used instead of \( g(E) \). More details about the Wang-Landau algorithm can be found in reference[8].

In this study we have defined the energy range per monomer \( E/N = [-3.75, 3.0] \).

4. Simulation results

The temperature dependence of the specific heat for chain lengths smaller then \( N = 100 \) are shown in Fig. 2. The large peak around \( T \approx 0.4 \) corresponds to the coil-globule transition.

At lower temperatures, for \( N = 64 \), a sharp peak forms around \( T \approx 0.05 \), indicating another transition. We believe that this transition corresponds to the formation of helical structures. The peak becomes smaller for \( N = 96 \).

Fig. 3 also shows the temperature dependence of the specific heat but for chain sizes greater than \( N = 100 \). At low temperature, for chain lengths \( N = 128 \) and \( N = 256 \), we observed large shoulders. This can be explained by the fact that it is difficult for
helical structures to form correctly for longer chain sizes. Those shoulders are rapidly vanishing for greater chain sizes ($N = 512$) because of the metastable nature of the helical structures.

5. Conclusions

We have studied the thermodynamic behavior of a flexible homopolymer using the Wang-Landau method for chain sizes up to $N = 512$. Our results show two kind of transitions. The coil-globule transition is observed around the temperature $T \approx 0.4$, for all the chain sizes studied. At low temperature $T \approx 0.05$, a second transition appears and depends on the homopolymer chain size. For small chain sizes $N < 100$, a sharp peak appear corresponding to a long lived helical structures. However, for $N > 100$ we observe a shoulder that become small as the chain size increases. We believe that for infinite chain sizes, this transition vanishes and that the formation of helical structures occurs only for finite chain sizes. Although, the potential model used for the flexible homopolymer is different from the one used by Seaton et al.\cite{11}, our results tend to have some similarities.

Acknowledgments

This work has been supported by the Algerian Ministry of Higher Education and Scientific Research, within the frame work of projects [cnepru-d0192001054].

References

[1] Trung Dac Nguyen and Sharon C. Glotzer, small 5(18) (2009) 2092.
[2] E.G Timoshenko, Yu. A. Kuznetsov and K.A. Dawson, J. Chem. Phys. 102 (1995) 1816.
Figure 3: Specific heat versus temperature for chain lengths $N = 128, 256$ and $512$. These chain lengths offer two features: a large peak in $C_v$ indicative of the coil-globule transition and a shoulder indicative of rapidly vanishing metastable states.

[3] E.G. Timoshenko, Yu. A. Kuznetsov and K.A. Dawson, J. Chem. Phys. 104 (1996) 3338.
[4] E.G. Timoshenko, Yu. A. Kuznetsov and K.A. Dawson, Phys. Rev. E 51 (1996) 3381.
[5] T. Frisch and A. Verga, Phys. Rev. E 66 (2002) 041807.
[6] D. T. Seaton, T. Wüst and D. P. Landau, Phys. Rev. E 81 (2010) 011802.
[7] S. A. Sabeur, F. Hamdache and F. Schmid, Phys. Rev. E 77 (2008) 020802.
[8] F. Wang and D. P. Landau, Phys. Rev. E 64 (2001) 056101.
[9] F. Wang and D. P. Landau, Phys. Rev. Lett. 86(10) (2001) 2050.
[10] D. T. Seaton, S. J. Mitchell, D. P. Landau, Braz. J. Phys. 38 (2007) 1.
[11] D.T. Seaton, T. Wüst and D.P. Landau, Comput. Phys. Comm. 180 (2009) 587.