



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Investigating the Formation of Helical States in the Process of Homopolymer Collapse using Molecular Dynamics Simulations

M. Bouarkat, S.A. Sabeur and R. Bouamrane

Department of Physics, Faculty of Sciences, University of Science and Technology of Oran,
P.O. Box 1505, El M'Naouer Oran, Algeria

Abstract: The molecular process of homopolymer collapse was numerically modelled through isothermal molecular dynamics simulations. The initial polymer chains were constructed, using random walks in continuum space. A simple harmonic potential was used in order to represent short range interactions between monomers. Measurement of the conformational properties of the polymer during the collapse was performed, while different collapse pathways were also observed. Specifically the spontaneous collapse of the polymer to helical states occurred at low temperatures. It may be concluded that the numerical results are in perfect agreement with those of Langevin dynamics simulations conducted in a previous study.

Key words: Molecular dynamics, nosé-hoover thermostat, polymer collapse, helical order

INTRODUCTION

During the last four decades, the collapse of polymer chains has been extensively investigated using both analytical methods and computer simulations. Initially, Flory (1967), Stephen (1975) and De Gennes (1979) have developed the basic concepts of the polymer collapse problem. In a serie of works Dawson *et al.* (1997) have provided numerical analysis for the conformational transitions of polymers. Frish and Verga (2002) studied the effect of the solvent on the collapse pathways of a single flexible homopolymer chain. The results found by this group show that the collapse of an isolated homopolymer is dominated by a coil-to-globule transition. Depending on the quench dept they observed intermediate sausage regime or a set of pearls along the chain followed by shrink in polymer size to a final spherical globule. These results agree with the general scenario for the kinetics of the collapse of a flexible polymer coil presented by De Gennes (1985). In a more recent study, Kikuchi *et al.* (2005) investigated the role of hydrodynamics on the kinetics of polymer collapse transition. This study shows that hydrodynamics interactions speed up the collapse of the polymer and enhance cooperative motion of the monomers.

Although, fully explicit simulations with solvent particles are still very expensive numerically, mainly in three dimensions, Polson and Gallant (2006) have performed molecular dynamics simulations of a polymer chain immersed in an explicitly modeled solvent.

They studied the effect of hydrophobic and hydrophilic monomers distribution on the collapse process.

In recent years, new interest in polymer collapse dynamics has emerged due to its important application for understanding the complex process of protein folding in molecular biology and its impact on health sciences as by Kemp and Chen (2002).

Elucidation of the trajectory of polymers in the process of collapse is an important step in understanding the mechanics of coil-globule transition, but the structure that attracts actually researchers is the helix, since this ordered structure plays a dominant role in biology because of its special shape that makes biopolymers functional.

In a earlier study, Sabeur *et al.* (2008) used Langevin simulations for this issue. They have found that simple generic bead-and-spring homopolymer chains in a sufficiently bad solvent spontaneously develop helical order.

The purpose of the present study is to study the effect of the temperature on the collapse pathways of homopolymers using molecular dynamics simulations coupled to the Nosé- Hoover Thermostat (Hoover, 1983) and compare the results to those obtained using Langevin simulations.

MATERIALS AND METHODS

This study was conducted on January-September 2009 at University of Science and Technology of Oran, Algeria.

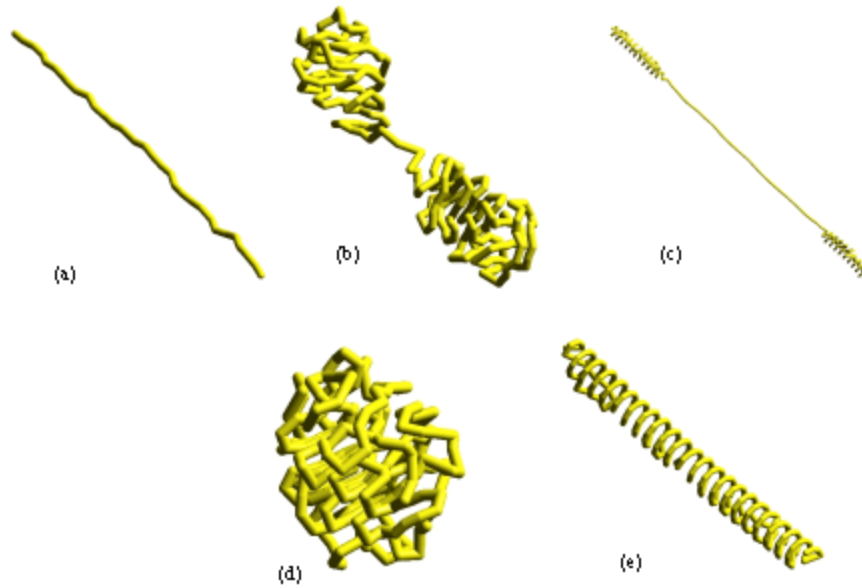


Fig. 1: Snapshots of the configurations obtained from the simulations: (a) Initial stretched configuration $N = 256$, (b) Pearls regime at $t = 4 \times 14^4 \tau$ for the small quench $T = 3.0c/K_B$, $N = 256$, (c) Early stages of helix formation at $t = 15 \times 14^4 \tau$ for the strong quench $T = 0.1c/K_B$, $N = 256$, (d) Globular state at $t = 10^5 \tau$ for the small quench $T = 0.1c/K_B$, $N = 256$ and (e) a well formed helix at $t = 3 \times 10^5 \tau$ for the strong quench $T = 0.1c/K_B$, $N = 256$

Molecular model: We have used the bead spring model to represent a polymer chain of N monomers. A sample of an initial configuration is shown in Fig. 1a. Non bonded monomers interact via a truncated and shifted Lennard-Jones potential:

$$U_{\text{non-bonded}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + C_0 & r < 2.5\sigma \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

where, C_0 ensures that the potential vanishes at the cut-off distance $r_c = 2.5$. We have used standard, reduced units in our calculations, where all distances and energies are expressed in terms of Lennard-Jones parameters σ and ϵ , respectively; mass is expressed in terms of the monomer mass m and the unit of time is $\sqrt{m\sigma^3/\epsilon}$. Temperature and energy are made numerically identical by setting the Boltzmann constant k_B to unity.

The interactions between pairs of bonded monomers are represented only by a harmonic potential of the form:

$$U_{\text{bond}}(r) = \frac{\alpha}{2} (r - r_0)^2 \quad (2)$$

Here, $r_0 = 0.85\sigma$ is the equilibrium distance. We take $\alpha = 100\epsilon/\sigma^2$. This constant characterizes the harmonic interactions as taken by Frisch and Verga (2002).

Numerical simulation: We have performed molecular dynamics simulations in the canonical ensemble. In order to maintain the temperature constant, we have coupled the system to the Nosé-Hoover Thermostat (Hoover, 1985).

This scheme derives from a modified Lagrangian formalism that introduces a new degree of freedom. The equations of motion are then:

$$\begin{cases} \dot{r}_i = p_i/m_i \\ \dot{p}_i = -\frac{\partial V}{\partial r_i} - \xi p_i \\ \dot{\xi} = \frac{1}{Q} \left[\sum_{i=1}^N \frac{p_i^2}{m_i} - 3Nk_B T \right] \end{cases} \quad (3)$$

where, r_i and p_i are respectively the position and momentum of monomer i . Q is a parameter defining thermal inertia in the system. it must be carefully chosen to prevent the simulation from unwanted oscillations. In our simulations, we have chosen $Q = 10$. In this case, the Nosé-Hoover thermostat does provide an ergodic sampling since our value of Q is small relative to the total polymer mass as demonstrated by Legoll *et al.* (2006). K_B represents the Boltzmann constant and ξ is the friction variable. We have solved numerically the equations of

motion, using the Verlet Newton-Raphson algorithm described by Frenkel and Smit (2002) and the time step was set to $\Delta t = 10^{-3}$. A total of 200 independent runs were performed on a cluster of 32 machines to calculate the average quantities. Each run begins with a different initial configuration. The polymer chain was first equilibrated for 10^5 steps at temperature $T = 4.0\epsilon/K_B$, then an abrupt decrease of the temperature (quench) below the Θ -point was applied and the data were sampled for 6×10^5 steps. The temperature was observed for all runs to fluctuate by less than 2%.

RESULTS

Locating the Θ -point: From theoretical point of view, the Θ -point is the temperature at which the distribution of the end-to-end distance of the polymer chain $P(R)$ displays Gaussian statistics:

$$P(R) = 4\pi R^2 A^3 \exp(-\pi A R^2) \quad (4)$$

where, $A = 3/(2\pi \langle R^2 \rangle)$ and \bar{R} is the end-to-end vector defined by:

$$\bar{R} = \sum_{i=1}^N \bar{b}_i \quad (5)$$

where, \bar{b}_i is the bond vector.

We have used a method described by Yong and Clarke (1996) based on Rosenbluth and Rosenbluth (1955)

sampling for locating the Θ -point. The main idea of this method is to compute the distribution of the end to end distance and compare it to the theoretical distribution $P(R)$ for different values of the temperature. In our simulations, we have explored the temperature range from $T = 3.0\epsilon/K_B$ to $T = 4.0\epsilon/K_B$. For a polymer chain size $N = 256$ and the set of parameters used in the molecular model presented above, the end-to-end distance distribution fit closely the theoretical distribution for the temperature $\Theta \approx 3.4\epsilon/K_B$ (Fig. 2).

Collapse kinetics: The quantities of central interest sampled during the simulations are the mean-square radius of gyration R_g^2 of the polymer and the average order parameter S . For a single chain conformation $\{\mathbf{r}_N\}$, the mean-square radius of gyration R_g^2 can be defined as:

$$R_g^2 = \left\langle \frac{1}{N} \sum_{i=1}^N (\bar{r}_i - \bar{r}_{cm})^2 \right\rangle \quad (6)$$

where, \bar{r}_i is the position of the i th monomer, N is the number of monomers and \bar{r}_{cm} is the center of mass position of the polymer chain given by:

$$\bar{r}_{cm} = \frac{1}{N} \sum_{i=1}^N \bar{r}_i \quad (7)$$

The average order parameter S measures the long-range order present in the configurations based on the orientation of the bond vectors \bar{b}_k between adjacent monomers. S can be written as:

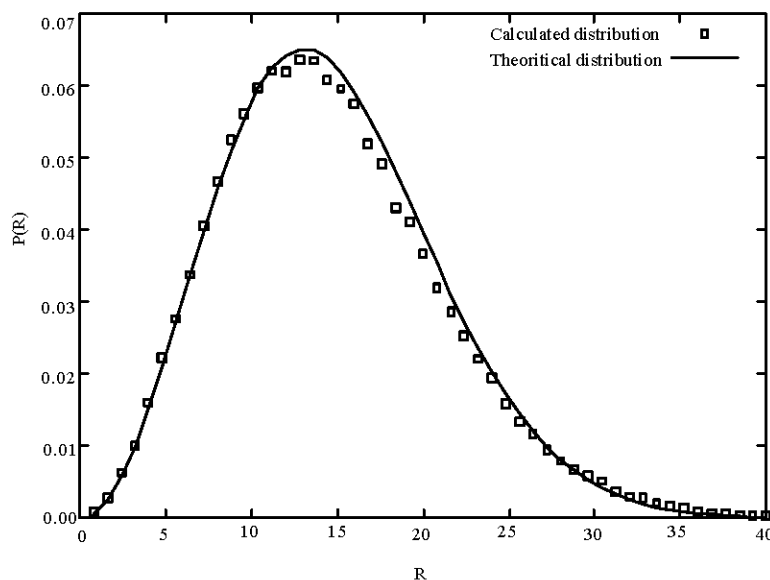


Fig. 2: Distribution of the end-to-end distance corresponding to the temperature $\Theta \approx 3.4\epsilon/K_B$ and $N = 256$

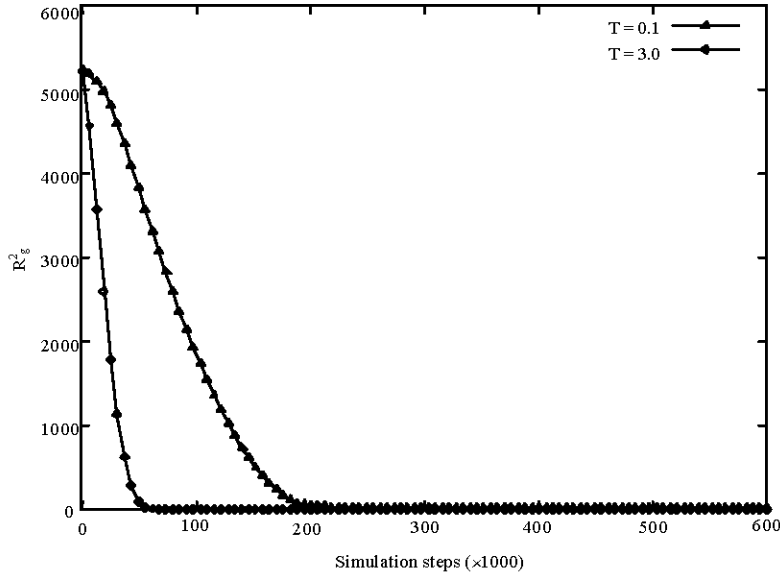


Fig. 3: Mean-square radius of gyration R_g^2 versus time for two different temperature quenches $T = 0.0$ and $T = 3.0$ and for polymer chain size $N = 256$

$$S = \left\langle \frac{1}{(N-2)} \left| \sum_{k=1}^{N-2} (\vec{b}_k \times \vec{b}_{k+1}) \right|^2 \right\rangle \quad (8)$$

For a well-formed helix, Rapaport found that S should have a value close to unity (Rapaport, 2002).

As shown in Fig. 3, the time evolution of the mean-square radius of gyration, respectively for a small temperature quench ($T = 3.0\epsilon/K_B$) and a strong temperature quench ($T = 0.1\epsilon/K_B$). We found that the polymer collapse is characterized by two main stages. In the first stage, we have observed the formation of small pearls that start to grow along the polymer chain in the case of a small quench ($T = 3.0\epsilon/K_B$). This result is in reasonable agreement with results found by Sabeur *et al.* (2008). In the case of a strong quench ($T = 0.1\epsilon/K_B$), monomers tend to form helices that grow symmetrically at the extremities of the polymer chain. Snapshots of the early stages of the collapse are presented in Fig. 1b and c.

To find the collapse time τ_c , we have fitted the data by a stretched exponential function:

$$R_g^2(t) = A + B \exp(-(t/\tau_c)^\gamma) \quad (9)$$

where, γ represents the stretching exponent.

The calculated values of the parameters of the stretched exponential function are shown in Table 1.

Let us first examine the behaviour of the collapse time τ_c for the two types of quenches. The parameter τ_c

Table 1: Calculated values of the parameters of the stretched exponential function used to fit the time evolution of the mean-square radius of gyration for the two temperature quenches

T	R_g^2	τ_c	γ
3.0	53.12±45	25.07±0.10	1.54±0.01
0.1	53.11±35	102.99±0.33	1.73±0.01

increases when the quench is increased showing a slow down of the collapse in the case of the strong quench.

One can see that the stretching exponent γ is also increasing when the quench is increased, which clearly means that the polymer chain is following another collapse pathway (helix formation).

The second stage can be characterized as a slow approach to the final collapsed state. We have observed a compaction of the polymer chain shape to a globule in the case of the small temperature quench and a further optimization of helices in the case of the strong temperature quench. This situation is shown in Fig. 1d and e.

Figure 4 shows the time evolution of the mean energy E for the two temperature quenches. It is clearly seen that the mean energy decreases rapidly during the first stage of the collapse in the first case ($T = 3.0\epsilon/K_B$) due to high mobility of the monomers that helps the pearls to merge rapidly to a compact globule. For the second case ($T = 0.1\epsilon/K_B$), the kinetic energy of each monomer is so small that the polymer chain is dominated by adjacent monomers interactions and the mean energy decreases very slowly. The formation of helices symmetrically at the

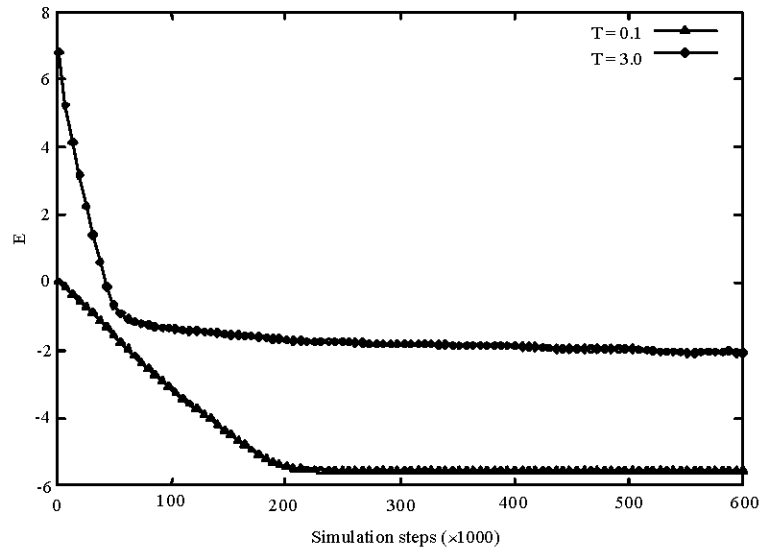


Fig. 4: Mean energy E versus time for two different temperature quenches $T = 0.1 \epsilon/K_B$ and $T = 3.0\epsilon/K_B$ and for polymer chain size $N = 256$

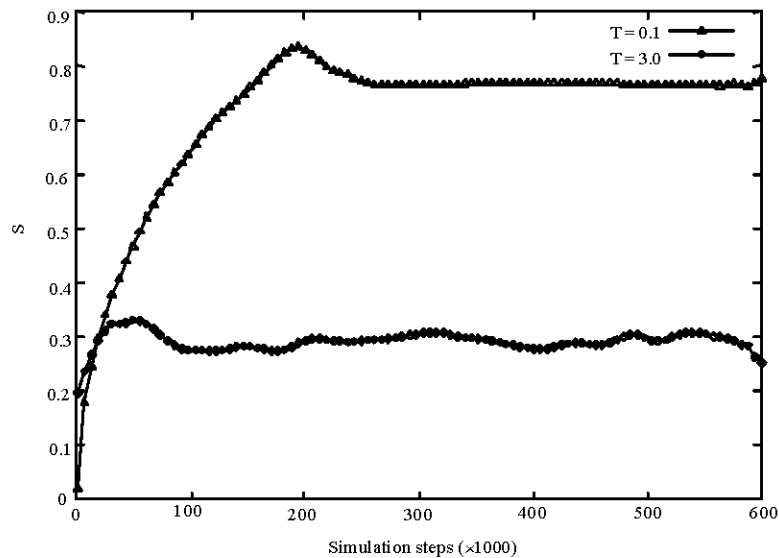


Fig. 5: Average order parameter S versus time for two different temperature quenches $T = 0.1 \epsilon/K_B$ and $T = 3.0\epsilon/K_B$ and for polymer chain size

two extremities of the polymer chain can be explained by the fact that monomers in the extremities of the chain have more degree of freedom than monomers in the middle of the chain. In the two cases, the mean energy vibrates around its equilibrium value in the rest of the simulation time.

Figure 5 compares the time evolution of the average order parameter S for the two temperature quenches. At equilibrium, the value of S fluctuates around 0.3 in the first

case. In the other case, the value of S tends to 0.8, which means that the polymer chain is adopting a helix structure.

DISCUSSION

In this study, we have studied the kinetics of a homopolymer chain during its collapse using molecular dynamics simulations coupled to the Nosé-Hoover thermostat.

In the case of a small temperature quench $T = 3.0\epsilon/K_B$, polymer collapse pathways described by Frish and Verga (2002) are verified. Formation of pearls on a string was observed and at equilibrium these pearls collapse into a single globule.

In the other case investigated, a strong temperature quench $T = 0.1\epsilon/K_B$, the polymer collapses spontaneously to an ordered helix structure without the use of any torsional potential as in (Rapaport, 2002). The helices obtained are metastable but not a true energy minimum and a square-well potential that prefers parallel planes used by Kemp and Chen (2002) was not necessary to observe those long-lived structures. Vogel *et al.* (2009) have shown in a detailed thermodynamic analysis of flexible tubelike polymers that helical structures are clearly visible in the phase diagram. Furthermore, Nguyen and Glotzer (2009) have found that controlling the formation of helical structures can give insights for fabricating switchable nanomaterials.

CONCLUSION

This study shows that the molecular dynamics simulation coupled to the Nosé-Hoover thermostat gives same results as those obtained using Langevin simulations. Although, the collapse kinetics of polymer chains is well-known, the helix formation upon rapid cooling of an originally swollen polymer with simple bead-bead attraction devoid of specific torsion forces seems to be new and might be pointing to interesting unexplored polymer dynamics.

REFERENCES

- Dawson, K.A., E.G. Timoshenko and Y.A. Kuznetsov, 1997. Kinetics of conformational transitions of a single polymer chain. *Physica A.*, 236: 58-74.
- De Gennes, P.G., 1979. *Scaling Concepts in Polymer Physics*. 1st Edn., Cornell University Press, Ithaca, New York, pp: 324.
- De Gennes, P.G., 1985. Kinetics of collapse for a flexible coil. *J. Phys. Lett.*, 46: 639-642.
- Flory, P.J., 1967. *Principles of Polymer Chemistry*. 6th Edn., Cornell University Press, New York, ISBN: 0-8014-0134-8.
- Frenkel, D. and B. Smit, 2002. *Understanding Molecular Simulations*. 2nd Edn., Academic Press, New York, ISBN: 0-12-267351-4.
- Frish, T. and A. Verga, 2002. Slow relaxation and solvent effects in the collapse of a polymer. *Phys. Rev. E*, 66: 041807-041807.
- Hoover, W.G., 1983. Nonequilibrium molecular dynamics. *Ann. Rev. Phys. Chem.*, 34: 103-127.
- Hoover, W.G., 1985. Canonical dynamics: Equilibrium phase-space distributions. *Phys. Rev. A.*, 31: 1695-1697.
- Kemp, J.P. and J.Z.Y. Chen, 2002. Folding dynamics of the helical structure. *Europhys. Lett.*, 59: 721-727.
- Kikuchi, N., J.F. Ryder, C. Pooley and J.M. Yeomans, 2005. Kinetics of the polymer collapse transition: The role of hydrodynamics. *Phys. Rev. E*, 71: 061804-061804.
- Legoll, F., M. Luskin and R. Moeckel, 2006. Non-ergodicity of the nosé-hoover. *Arch. Rational Mech. Anal.*, 184: 449-463.
- Nguyen, T.D. and S.C. Glotzer, 2009. Switchable helical structures formed by the hierarchical self-assembly of laterally tethered nanorods. *Small*, 5: 2092-2098.
- Polson, J.M. and J.P. Gallant, 2006. Equilibrium conformational dynamics of a polymer in a solvent. *J. Chem. Phys.*, 124: 184905-184905.
- Rapaport, D.C., 2002. Molecular dynamics simulation of polymer helix formation using rigid-link methods. *Phys. Rev. E.*, 66: 011906-011906.
- Rosenbluth, M.N. and A.W. Rosenbluth, 1955. Monte Carlo calculation of the average extension of molecular chains. *J. Chem. Phys.*, 23: 356-359.
- Sabeur, S.A., F. Hamdache and F. Schmid, 2008. Kinetically driven helix formation during the homopolymer collapse process. *Phys. Rev. E*, 77: 020802-020802.
- Stephen, M.J., 1975. Collapse of a polymer chain. *Physics Lett. A*, 53: 363-364.
- Vogel, T., T. Neuhaus, M. Bachmann and W. Janke, 2009. Thickness-dependent secondary structure formation of tubelike polymers. *Europhys. Lett.*, 85: 10003-10003.
- Yong, C.W. and J.H.R. Clarke, 1996. The theta condition for linear polymer chains in continuous space and three dimensions. *J. Chem. Phys.*, 105: 9666-9673.