

Monte Carlo simulations of polymer generation

Aboubakr El Mahdaoui *

* Delft, University of Technology

Polymer chain growth has been simulated as a Self Avoiding Walk(SAW) in 3D and 2D using Monte Carlo methods to calculate the Flory exponent that relates the chain size to the number of monomers. A comparison is made of the calculated properties between the algorithms of the Rosenbluth-Rosenbluth Method(RR) and the Pruned-Enriched Rosenbluth Method(PERM) for different lengths of polymers. The polymers are grown attaching monomers one by one while interacting via a Lennard-Jones potential.

Self Avoiding Walk | Monte Carlo simulation | Flory exponent

Abbreviations: SAW, MC; RR, PERM

Introduction

Polymers are macromolecules consisting of a relatively large number of monomers held together by their chemical bonds. In this report we discuss the results of simulations of polymer chains consisting of up to 250 monomers or beads. A Lennard-Jones Potential pair is implemented for the calculation of the potential between the particles:

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

This potential describes the interaction between the monomers themselves, between the solvent molecules and between the monomers and the solvent molecules. The strong short range repulsive term will result in the polymer chain growth to be modeled as a Self-Avoiding Walk[1]. Characteristic measures of the chain size are the end-to-end distance and the radius of gyration for a number of monomers N :

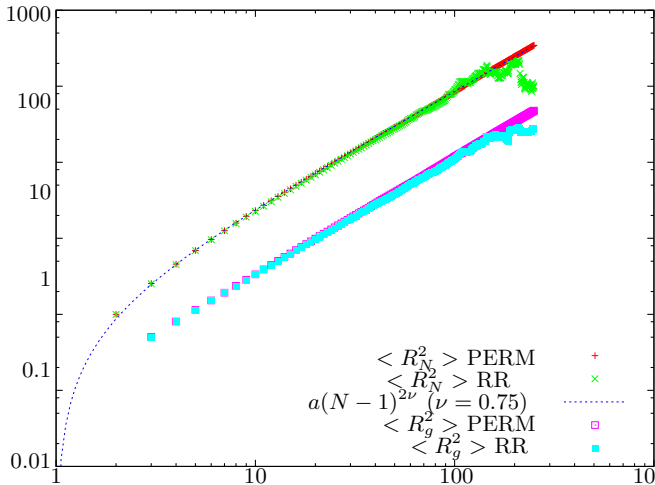


Fig. 1. Weighted average of the end-to-end distance and the radius of gyration as a function of the number of monomers by simulating 20000 polymers up to 250 monomers in 2D comparing PERM with RR. $T = 2$ in reduced units and 10 possible angles to choose from at each next addition of a monomer.

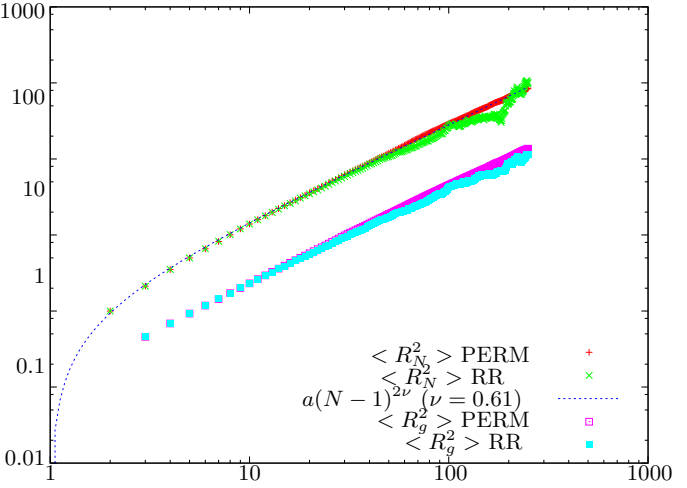


Fig. 2. Weighted average of the end-to-end distance and the radius of gyration as a function of the number of monomers by simulating 20000 polymers up to 250 monomers in 3D comparing PERM with RR. $T = 2.5$ in reduced units and $5(\theta) \times 5(\phi)$ possible angles to choose from at each next addition of a monomer.

$$\langle R_N^2 \rangle = \langle (\mathbf{r}_N - \mathbf{r}_1)^2 \rangle \quad [2]$$

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (\mathbf{r}_i - \mathbf{R}_{com})^2 \quad [3]$$

With \mathbf{R}_{com} denoting the center of mass of the polymer chain:

$$\mathbf{R}_{com} = \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i \quad [4]$$

For polymers, the chain size scales with the number of monomers as follows[2]:

$$\langle R^2 \rangle = aN^{2\nu} \quad [5]$$

Here, a is a proportionality constant that depends on the environment like the solvent used and the temperature, ν is the so called Flory exponent that depends on the dimensionality of the polymers generated and is given by $\nu = \frac{3}{d+2}$ with d the dimensionality of the system[3]. So for 2D polymers the Flory exponent is 0.75, for 3D polymers it is equal to 0.6[2]

Results & Discussion

In this section we will provide the numerical results of the simulations performed for the various calculated properties.

As can be seen in Fig. 1, the PERM algorithm provides a significant improvement in reducing the fluctuations compared to RR for polymers larger than 100 monomers for both distances and provides an estimate of ν in very good agreement with the expected result for 2D polymers. As can be seen in Fig. 2 for 3D polymers, the results of the PERM algorithm provides very reasonable results as well.

Methods

In this section we will discuss the methods used to generate the polymers. To calculate a thermodynamic property in a statistical ensemble, the observable A is averaged over all possible configurations and is calculated and given by:

$$\langle A \rangle = \frac{1}{Z} \sum_i A_i e^{-\beta U_i} \quad [6]$$

With Z the partition function, $\beta = 1/kT$ and U_i the interaction potential.

Rosenbluth-Rosenbluth Method. In the RR method, monomers are added one at a time, choosing from a number of angles N_θ with respect and having a prefixed distance to the last monomer[4]. An angle is chosen randomly with the probability of choosing one particular angle θ_j being controlled by the Boltzmann weights of adding a monomer at that angle:

$$P(\theta_j) = \frac{e^{-E(\theta_j)/kT}}{\sum_{i=1}^{N_\theta} e^{-E(\theta_i)/kT}} = \frac{w_j^{(l)}}{W_l} \quad [7]$$

The total probability of a configuration to occur is then given by:

$$P = \prod_l \frac{w_l^{(l)}}{W_l} \quad [8]$$

In this way it is ensured that high energy conformations are less likely to occur, but the probability of a particular angle should be governed by just the Boltzmann weights:

$$P(\theta_i) = e^{-E(\theta_i)/kT} \quad [9]$$

This is compensated for by calculating a weighted average of the thermodynamic property:

$$\langle A \rangle = \frac{\sum_i A_i P_i}{\sum_i P_i} \quad [10]$$

With $P_i = \prod_l W_l$.

Pruned-Enhanced Rosenbluth Method. The biggest problem in the Rosenbluth-Rosenbluth method is attrition. As the number of good conformations decrease exponentially with the number of beads, the average will be dominated by only a few polymer weights of those conformations causing the relatively high fluctuations of the estimate of the Flory exponent. This problem is sufficiently present for monomers larger than 100.

The PERM algorithm as described by Grassberger et al.[5] is an enhancement of the RR method precisely for solving the problem of attrition in RR. The goal is to remove all the bad configurations early on in the process of generating the polymers and copy the good conformations to double them and

create a tree-like structure of all the polymers generated. To keep the total weight equal for calculating an ensemble average, only 50% of the bad configurations are removed while the other half have their polymer weights doubled. Similarly, if a good configuration is doubled their polymer weights are reduced to half the original polymer weight.

Conclusion

We have seen that the PERM algorithm can provide simulations of SAW's and an excellent estimate of the Flory exponent for 2D and 3D polymers interacting through a Lennard-Jones potential. As the simulations have been done with relatively high temperatures, it would be interesting to see how the temperature dependence is of the Flory exponent. It is expected to behave as an ideal chain and the Flory exponent should tend to 1.

1. A. Sokal, Monte Carlo methods for the Self-Avoiding Walk, (1994).
2. J. M. Thijssen, Computational Physics, Cambridge University Press, 2nd ed. (2007), pp. 374–398.
3. Nakanishi H. Flory approach for polymers in the stiff limit. in Journal de Physique, pp.979-984, (1987)
4. Prellberg T. From Rosenbluth Sampling to PERM - rare event sampling with stochastic growth algorithms. Lecture given at the International Summer School, Modern Computational Science 2012 Optimization, (August 20-31, 2012, Oldenburg, Germany)
5. Grassberger P. , Pruned-enriched Rosenbluth method: Simulations of polymers of chain length up to 1 000 000 Physical Review E 56, 3682 (1997)
6. J. P. Wittmer and H. Meyer, Monte Carlo Simulation of Polymers: Coarse-Grained Models , Vol. 23 (2004)