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Numerical Calculation of Polymer Modeling Using *Monte Carlo* Methods: The Case for Fractional Brownian Motion

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ABSTRACT

In this study, we confirmed the Flory index formula via numerical calculation in two dimensions using *Monte Carlo* methods and the Metropolis algorithm. Results revealed that the simulation in two dimensions is successful in confirming the Flory index formula for short polymers. In addition, using a small value of g which is the penalizing factor to avoid self-crossing within polymers, the simulated value of Flory index agrees with the theoretical prediction. However, when simulating beyond $N = 200$ monomers, significant outliers of the result which cause a great mismatch of the simulated and theoretical values of the Flory index are observed. Results showed from the simulation that the Flory index holds true for short polymers or N, number of monomers below 300. It is recommended that in future work of this research, the coupling constant g must be slowly increased from zero until the result will eliminate the outliers and stabilize the scaling index.

Keywords*: fractional Brownian motion, Monte Carlo methods, polymer modeling, Flory index*

INTRODUCTION

Many studies have been intensively done in understanding and unlocking the mystery behind the mechanical properties of polymers. Polymers such as DNA, proteins and enzymes capture the interest of many biophysicists and other related fields. DNA for example, exhibits several deformations such as twisting, coiling and stretching inside a micron-size nucleus of a cell. Each deformation, which in turn determines its specific conformation, greatly affects and influences its biological functions (Zhou Haijun, et. al., 2000). Nowadays, having the knowledge of DNA's stretching and twisting allows one to study its biological processes such as replication and transcription (Bustamante, et. al., 2000).

Theoretically, probing its mechanical properties have been made possible through the use of various model, i.e. Wormlike Chain (WLC) model that can realistically describe its characteristics analytically (Bouchiat, et. al., 1999). In the WLC model, its ``path'' is treated to be Brownian motion in nature, see the paper (Allison, 1986). That is, its correlation between two successive point in question is always zero (Karatzas, et. al., 2012). In other words, each successive points of the polymer is independent from each other. However, when one looks at these polymers in vitro, it is less likely to be observed as Brownian motion. The polymer will either be in extended or compact form. Thus, the polymer tends to have an interaction with each of the subunits or monomers or a Brownian motion with memory in mathematical terms. Hence, a generalization of the Brownian motion which is termed as the Fractional Brownian motion was developed in describing polymer properties. This endeavor has been one of the great interests especially in the field of polymer physics. This concept of fractional Brownian motion is now used in analyzing the probability distribution of the end-to-end distance and radius of gyration of polymers (McCrackin, et. al., 1973). Generally, knowing these two properties significantly contributes to the understanding of the mechanical properties of the polymer. Coincidentally, these properties, the radius of gyration and end-to-end distance, can be approximated using the Flory's mean field approach which yield a scaling index of N^{ν}, where N and ν are the number of bond segments and Flory index respectively (De Gennes, 1979). In the paper of Bornales, et. al., the Flory index in Brownian motion can then be theoretically generalized in its fractional Brownian form. However, proving this generalized Flory index in closed form is cumbersome and challenging as of now. Thus, a numerical calculation will be a viable approach in getting a concrete answer if one wants to validate the correctness of the said generalization of the Flory index. Therefore, it is the goal of this study to evaluate the validity of the generalized Flory index by comparing it with our numerical calculation using *Monte Carlo* method.

Fractional Brownian Motion

The Edward's model

Fractional Brownian motion, B^H, is a generalization of Brownian motion where H runs from 0 to 1, is the Hurst parameter. This parameter ultimately describes the correlation of each of the points in the path of the polymer. This so-called correlation is expressed in its covariance function as

$$\mathbb{E}(B_t^H B_s^H) = \frac{1}{2}(s^{2H} + t^{2H} - |t-s|^{2H}). \quad (1)$$

It is interesting to note in this case that when $H = 0.5$, it reduces to Brownian motion. Because of this property of fractional Brownian motion, one can fundamentally apply its concept in modeling polymer interaction and conformations. Single chain polymer, which is considered to be a Gaussian chain, exhibits a characteristic of an excluded volume effect. This effect is accountable for the polymer entanglement or swelling. Mathematically, one can describe it using the Edward's model (Wolfgang, et. al., 2013). In this particular model, self-crossing is suppressed by introducing the factor

$$\exp(-gL) \quad (1)$$

where g is the coupling constant and L is the self-intersection local time vented as

$$L = \int\int dsdt\delta(B(s) - B(t)). \quad (2)$$

In this case of fractional Brownian motion, this Gaussian chain can then be generalized as

$$L_H = \int\int dsdt\delta(B^H(t) - B^H(t)), \quad (3)$$

So that the probability density of a given polymer is given as

$$\rho_H \sim \exp\left(-\frac{1}{2}(x, A^{-1}, x) - gL_H\right) \quad (4)$$

Where A is the inverse matrix of the covariance function calculated in Eq. [1].

The Flory Index

A partition function $Z(R)$ for a freely jointed chain of N segments for which the end-to-end length has fixed modulus R is given by

$$Z(R) = aR^{d-1}\exp\left(-\frac{dR^2}{2N}\right), \quad (5)$$

and leads to a free energy

$$F_1 = -\ln Z \approx \frac{dR^2}{2N} - (d-1)\ln R. \quad (6)$$

Instead of such chain a continuous model is that of a Brownian trajectory from time zero to time N for which one computes to

$$\mathbb{E}(\delta(B(N) - \mathbf{R})) = (2\pi N)^{-d/2}\exp\left(-\frac{R^2}{2N}\right). \quad (7)$$

For the fBm case this formula generalizes to

$$\mathbb{E}\left(\delta(B^H(N) - \mathbf{R})\right) = (2\pi N^{2H})^{-d/2}\exp\left(-\frac{R^2}{2N^{2H}}\right). \quad (9)$$

From which we see that $N \to N^{2H}$, and hence we should consider

$$Z(R) = aR^{d-1}\exp\left(-\frac{dR^2}{2N^{2H}}\right) \quad (8)$$

i.e.

$$F_1 = -\ln Z \approx \frac{dR^2}{2N^{2H}} - (d-1)\ln \quad (9)$$

For the repulsive excluded volume energy of fBm paths x with $x(N) = \mathbf{R}$,

$$F_2 = -\ln \mathbb{E}_{x(N)=R}\left(\exp\left(-g\int_0^N ds\int_0^N dt\delta(x(x)-x(t))\right)\right) \quad (12)$$

Dimensional considerations and mean field arguments suggest that

$$F_2 \approx \text{const}\frac{N^2}{R^d} \quad (10)$$

Maximizing

$$F(N,R) = F_1(N,R) + F_2(N,R) \quad (11)$$

with regard to R leads to

$$0 = \frac{dR}{N^{2H}} - \frac{d-1}{R} - \text{constant}\, N^2 R^{-d-1} \quad (15)$$

Assuming that the 2nd term is negligible one finds

$$R^{d+2} \approx N^{2H+2} \quad (12)$$

i.e.

$$R \approx N^{\nu_H} \quad (13)$$

with

$$\nu_H(d) = \frac{2H+2}{d+2} \quad (14)$$

Monte Carlo Simulation of the Generalized Flory index using Matlab software

This paper numerically derives and validates the generalized Flory index and compares it in theory using *Monte Carlo* simulation via Matlab software. That is, we want to know the scaling component ν, which is the Flory index in the case of fractional Brownian motion. In the simulation process, we used the Metropolis algorithm that is fed into the Matlab software. We keep in mind that the main goal of the study is to determine the scaling exponent (Flory index) of an end-to-end distance in the light of fractional Brownian motion. The generalized Flory index is expressed as

$$\nu_H = \frac{2H+2}{d+2} \quad (15)$$

Proving the validity of the above expression is carried out through computer simulation using *Monte Carlo* sampling.

Metropolis Algorithm

We discretized the fractional random walk with non-self-crossing using *Monte Carlo* methods based on the Metropolis algorithm. The Metropolis algorithm is used to update the bonds or the increments of each path of the polymer. Initially, we introduce a random polymer configuration of Hurst index, H given as

$$x_j = B^H(j), \quad j = 0, \dots, N-1 \quad (16)$$

and $N-1$ bond vectors expressed as

$$y_j = B^H(j+1) - B^H(j) \quad (17)$$

From these equations, Eq. [20] and Eq. [21], we define the probability density of the distribution as

$$\rho(y) = \frac{1}{\sqrt{(2N)^{N-1}\det A}} \exp\left(\frac{1}{2}(y, A^{-1}y)\right) = C\exp(y, H_0 y) \quad (22)$$

From the probability density, the Metropolis algorithm is used to produce updates of the configurations by updating randomly chosen $x \to x_k$, so that the initial conformation $x^0(x_1, x_2, \dots, x_k, \dots x_{N-1})$ becomes $x^1(x_1, x_2, \dots, x_k, \dots x_{N-1})$ and so on. Through this algorithm we compute and produce a conformation to a polymer. Iterating this process to a particular number of updates will eventually produce an equilibrium distribution of conformations. From these conformations, we get the simulated value of the Flory index and compare it with the natural logarithm of the root mean square of R and natural logarithm of N.

Self-avoiding fractional random walk

One can obtain of a model of polymer with weakly self-avoiding fractional random walk by penalizing the self-crossings of the polymer as indicated in the previous section. The goal in mind is to discretize the self-intersection local time:

$$L = \int_0^N d\tau \int_0^N dt\delta\left(B^H(\tau) - B^H(t)\right) = \int_{\mathbb{R}} du L_u^2, \quad (23)$$

with

$$L_u = \int_0^N dt\delta(B^H(t) - u), \qquad u \in \mathbb{R} \quad (18)$$

The discretized version of the self-interaction local time is given by

$$L_u = \#\{x_j | x_j \in I_n\} \quad (19)$$

where we decompose the $\mathbb{R}$ into I_n intervals of equal length l. So that

$$L = \sum_n L_n^2. \quad (20)$$

Thus, the unnormalized probability density of conformations becomes

$$\rho(x) \sim \exp\left(-\frac{1}{2}(y, H_0 y) - gL(y)\right). \quad (21)$$

RESULTS AND DISCUSSIONS

In the simulation done in this paper, the number of monomers N is chosen between the range of 100 and 200. The choice of the range was chosen by two considerations. N should be large to approximate the asymptotic regime. The upper bound limit is chosen to be 200 to allow smooth running of the program up to 3 days. This will be enough for the first preliminary results of the study.

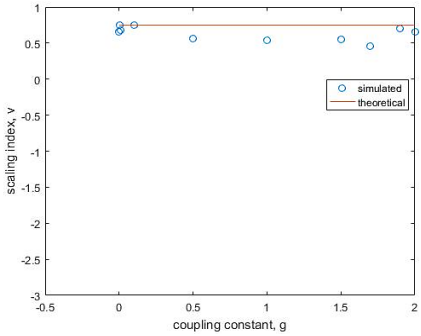

Figure 1: Dependence of the scaling exponent from the penalizing strength for $H = 0{,}5, N = 100,$ and $s = 10^6$ updates.

In figure 1, the limiting case of Brownian motion is observed having a value of $H = 0.5$ with a penalizing factor of zero ($g = 0$). For ($g = 0$) the walks have no penalization and will scale as fBm-path. For small positive values of g the scaling index ν seemingly varies and drops below it for larger g. Scrutiny of the end-to-end length, i.e., conformations that did not unfold to equilibrium conformations during the simulation (relaxation period).

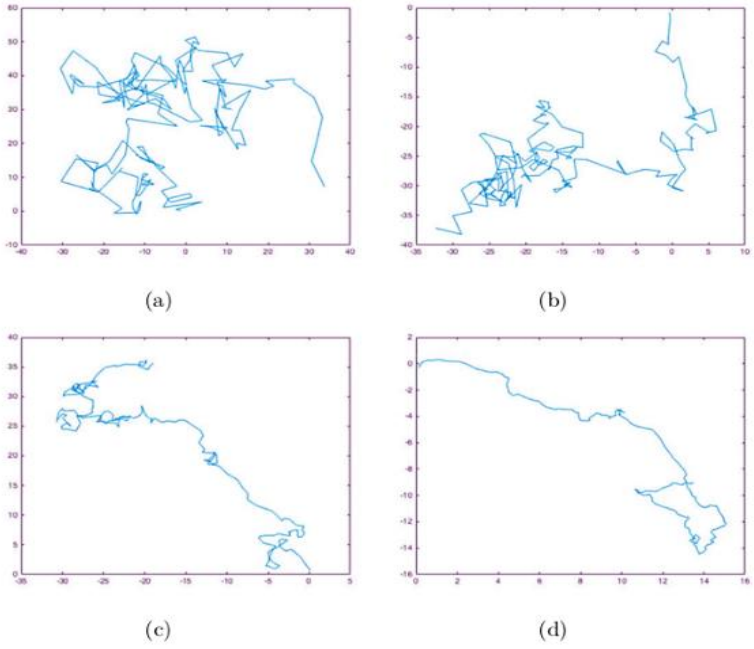

Figure 2. Polymer configuration after 10^6 updates with $N = 200, g = 0.005,$ and (a) $H = 0.3$, (b) $H = 0.6$, (c) $H = 0.7$, and (d) $H = 0.9$.

The results of the simulation of the polymer under varying Hurst exponent *H* for lengths 100 and 200 are outlined and presented in table 1. The table reflects the values of the simulated values of the Flory index for polymer $N = 100, 200$ vs the theoretical value calculated from the Flory index formula. The simulation using our model has successfully reproduced and confirmed the Flory index formula for short polymers, i.e., 100 to 200 number of monomers.

Table 1. Theoretical and simulated values of Flory index ν for polymer of $N = 100, 200$ under varying H with $g = 0.056$.

H	Scaling index (Theory)	Number of monomers			
		N = 100		N = 200	
		Simulated	% error	Simulated	% error
0.1	0.55	0.5300	3.636	0.5600	1.818
0.2	0.60	0.6620	10.33	0.6210	3.500
0.3	0.65	0.6800	4.615	0.6470	0.462
0.4	0.70	0.6905	1.357	0.6054	13.510
0.5	0.75	0.7486	0.187	0.7670	2.267
0.6	0.80	0.8474	5.925	0.8632	7.900
0.7	0.85	0.8388	1.318	0.8225	3.235
0.8	0.90	0.8995	0.056	0.8907	1.033
0.9	0.95	1.0041	5.695	1.1669	22.83

The polymer confirmation after 10^6 updates with $H = 0.3, 0.6, 0.9$ and $N = 200$ monomers are shown in figure 4.2. It can be inferred from the plots that the polymer starts off in a wrinkled state. In this system, the increments or the monomers of the polymers are negatively correlated thus giving us the appearance as shown in Fig. 4.2 (a). Notice that the polymer slowly unknots itself as the Hurst index (H) is gradually increased. For $H = 0.9$, the polymer is fully extended as shown in figure 4.2 (c) since the increments of each monomer are positively correlated.

However, the model fails if we do the simulation for the polymer with $N = 300$ and above. In this range, we begin to observe significant outliers of the result which cause a great mismatch of the simulated and theoretical values of the Flory index. These outliers are significantly different from all others in one or more ways. In other terms, these outlier data deviate from normalcy and can (and most likely will) create anomalies in algorithm and analytical system outputs. To amend this problem, relaxations with a constant g should not be performed but instead slowly increase the coupling constant from zero until the result will eliminate the outliers and stabilize the scaling index.

CONCLUSIONS AND RECOMMENDATIONS

In this paper, the concept of Brownian motion has been generalized into fractional Brownian motion. Results that the simulation of polymer in two dimensions is successful in confirming the Flory index formula for small length of polymers, in this

case, $N = 100,200$. Also, for small value of g, the simulated value of Flory index agrees with the theoretical prediction. However, the success of our model is limited only to short polymers not more than $N = 200$ monomers. Moreover, the results in this paper showed the relationship between N, R and the Flory index which is given in equation (17) and (18). The simulation only accurately describes equation (18) for small scale N which is below 300 monomers. We might be able to describe the scaling of polymers for large N (above 300 monomers) if we set g (coupling constant that appears in the penalizing factor) gradually. That is, g must be slowly increased from zero until the result will eliminate the outliers and stabilize the scaling index.

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