Fractional Brownian Modeled Linear Polymer Chains with One Dimensional Metropolis Monte Carlo Simulation

Jan Philippe B. Sambo, Jinky B. Bornales, Beverly V. Gemao

Minadanao State University – Iligan Institute of Technology

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Polymer Applications

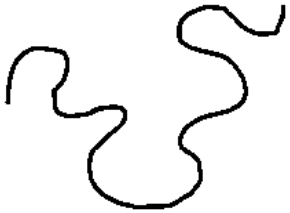
Source: http://greenliving4live.com/wp-content/uploads/2013/06/biodegradable-plastic.jpg

Source://http://www.popularmechanics.com/cm/popularmechanics/images/aE/dendrimer1-lg.jpg.

Source:http://upload.wikimedia.org/wikipedia/commons/8/82/Selfassembly_Organic_Semiconductor_Trixler_LMU.jpg.

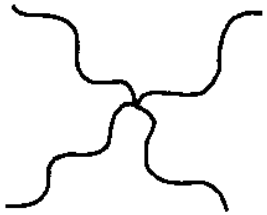
Source: http://images.motorcycle-superstore.com/ProductImages/OG/0000-Bridgestone-Battlax-BT-023-GT-Sport-Touring-Rear-Tire.jpg

Polymer Architectures

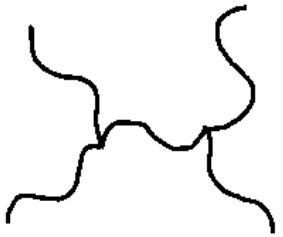


Linear

Ring

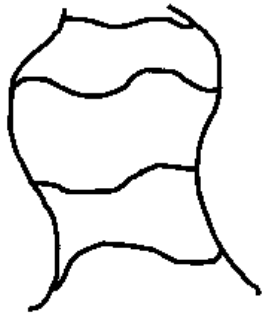


Star

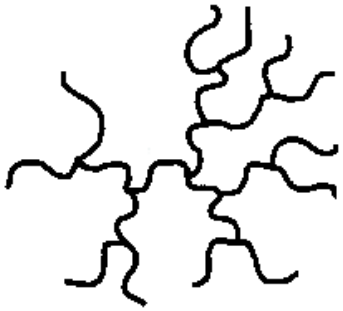


H

Comb



Ladder



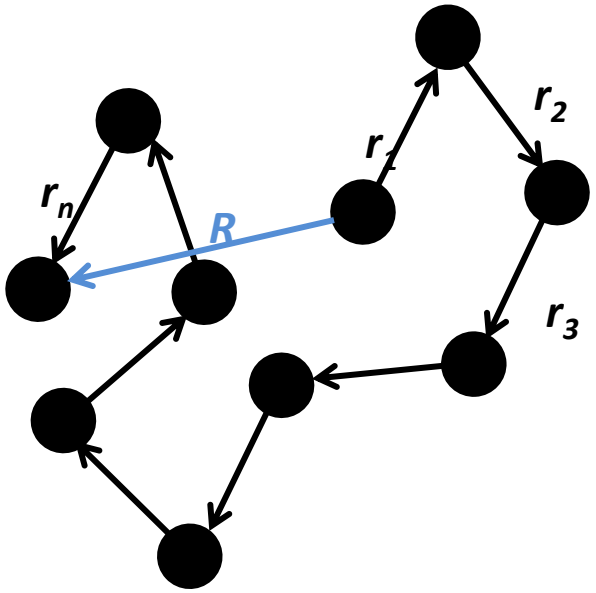
Dendrimer

Randomly Branched

Reference: Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press

Polymer Models

- **Ideal Chain Models**
  - Freely Jointed Chain
  - Freely Rotating Chain
  - Worm-like Chain
- **Real Chain Models**
  - Edwards Model
  - Excluded Volume Effect



Freely Jointed Chain

- A collection of *N* statistically independent but connected rigid segments, with length *l*

$$\begin{aligned} R &= R_N - R_0 \\ &= (R_N - R_{N-1}) + (R_{N-1} - R_{N-2}) + \ldots \\ &\quad + (R_1 - R_0) \\ &= \sum_{i=1}^{N} r_i \end{aligned} \qquad (1)$$

Reference: Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press

Properties of R (Brownian Case)

- First we look at ‹*R*› :

$$\langle R \rangle = \langle \sum_{i=1}^{N} r_i \rangle \qquad (2)$$

$$= \sum_{i=1}^{N} \langle r_i \rangle$$

$$= \langle r_1 \rangle + \langle r_2 \rangle + \langle r_3 \rangle + \ldots + \langle r_N \rangle$$

$$\langle R \rangle = 0 \qquad (3)$$

- Next we look at ‹R^2›:

$$\langle R^2 \rangle = \langle R \cdot R \rangle \qquad (4)$$

$$= \sum_{i=1}^{N} \langle r_i \rangle \cdot \sum_{j=1}^{N} \langle r_j \rangle$$

$$\langle R^2 \rangle = \langle \sum_{i=1}^{N} r_i^2 \rangle + 2 \sum_{i=1}^{N} \sum_{j=1}^{j \neq =1} \langle r_i . r_j \rangle$$

$$= Nl^2$$

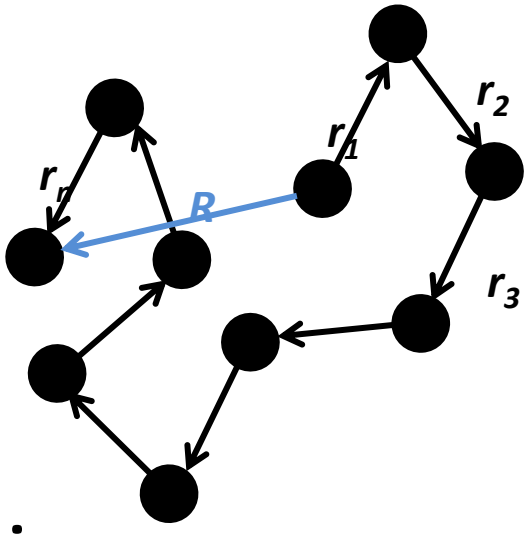
$$R_{rms} = \sqrt{\langle R^2 \rangle} = \sqrt{N} l \qquad (5)$$

Reference: Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press

Scaling Theory for Polymers

- ***Expression:***

$$R \sim N^{\upsilon} \qquad (6)$$



– > **R – end-to-end distance**

– > **N – number of monomers**

- ***Flory Index*** **(real chain models in Brownian Case):**

$$\upsilon = \frac{3}{d+2} \qquad (7)$$

- > d – dimension

Reference: [1]Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press
[2] P.-G. de Gennes, Scaling Concepts in Polymer Physics, Cornell University Press, Ithaca, NY, 1979.
[3] J. Bois, Rudiments of Polymer Physics, California Institute of Technology, Pasadena, California, 2012

The Brownian Model

- **Scaling Expression:**
  - ➢ **for Ideal Chains:** $R \sim N^{\frac{1}{2}}$
  - ➢ **w/ excluded volume:** $R \sim N^{\frac{3}{d+2}}$ **(Flory index)**
- **Expression for Probability Distribution:**

$$P(N,x) = \frac{1}{\sqrt{2\pi\langle x^2\rangle}} \exp\left(-\frac{x^2}{2\langle x^2\rangle}\right) \qquad (8)$$

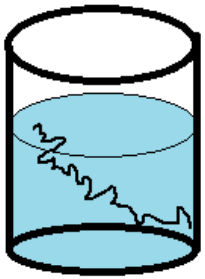
Reference: [1]Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press
[2] J. Bois, Rudiments of Polymer Physics, California Institute of Technology, Pasadena, California, 2012

Polymer Solvents

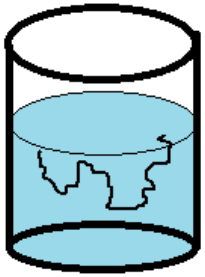
- **2 Key Factors**

  Temperature* and *Concentration

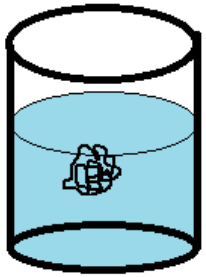
Long-Range Repulsion Solvents



Good Solvent



Poor Solvent



- **for good solvents**

  → Brownian Case

  → monomer units are randomly placed

  → can be modeled as a random walk

But this is not always the general case!

How about for other solvent-types? →

Fractional Brownian Model!

Reference: Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press

Fractional Brownian Motion

- **a Gaussian chain:**

$$P(N,x) \sim \frac{1}{\sqrt{2\pi\langle x^2\rangle}} \exp\left(-\frac{x^2}{2\langle x^2\rangle}\right) \qquad (9)$$

- **self-similarity:**

$$\frac{1}{a^H} B_{at}^H = b_t^H, \qquad t \geq 0; a > 0 \qquad (10)$$

(where H is the Hurst Parameter)

Reference: [1]Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press
[2] Hammond, A. and Sheffield S., Power law Pólya's urn and fractional Brownian motion, Springer-Verlag, Berlin, 2012.
[3] S. Sarkar, Fractional Brownian Motion: Long range dependency, Markov property, Simulation strategy-A review, Term Paper submitted for Stochastic Process Course in Spring 2008
[4] Bornales, J., Oliveira, M. and Streit, L. Self-Repelling fractional Brownian motion – a generalized Edwards model for chain polymers. December 13, 2011

Fractional Brownian Motion

- **stationary increments:**

$$\langle (B_t^H - B_s^H)^2 \rangle = E[(B_t^H - B_s^H)^2] = |t-s|^{2H} \quad (11)$$

$$E[(B_t^H\ B_s^H)^2] = \frac{1}{2}(t^{2H} + s^{2H} - |t-s|^{2H}) \quad (12)$$

Note: *H* has values *0<H<1*

→ becomes the basis for different solvents

Reference: [1]Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press
[2] Hammond, A. and Sheffield S., Power law Pólya's urn and fractional Brownian motion, Springer-Verlag, Berlin, 2012.
[3] S. Sarkar, Fractional Brownian Motion: Long range dependency, Markov property, Simulation strategy-A review, Term Paper submitted for Stochastic Process Course in Spring 2008
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The Hurst Parameter

- **For H = 1/2** → **Relaxed Chain (Good Solvent)**

  Brownian Case – monomer units are not correlated

- **For 0<H<1/2** → **Anti-persistent Chain (Poor Solvent)**

  negative correlation between monomer units

  Ex: High Concentration

- **For 1/2<H<1** → **Persistent Chain (Repulsive Solvent)**

  positive correlation between monomer units

  Ex: High Temperature

Reference [1] S. Sarkar, Fractional Brownian Motion: Long range dependency, Markov property, Simulation strategy-A review, Term Paper submitted for Stochastic Process Course in Spring 2008
[2] Bornales, J., Oliveira, M. and Streit, L. Self-Repelling fractional Brownian motion – a generalized Edwards model for chain polymers. December 13, 2011

Scaling Theory for fBm

- **Average value of R^2 (in terms of Probability Distribution):**

$$\langle R^2 \rangle = Z \int_0^N x^2 \exp\left(-\beta \frac{(x_t, H_0 x_s)}{2}\right) \qquad (13)$$

where $$E[(x_t \cdot x_s)^2]^{-1} = H_0 \qquad (14)$$

using change of variables:

$$x = \beta^{-\frac{1}{2}} a \qquad \rightarrow \qquad x^2 = \beta^{-1} a^2$$

$$\langle R^2 \rangle = Z \int_0^N a^2 \exp\left(-\frac{H_0 a^2}{2}\right) \qquad (15)$$

Reference: [1]Rubinstein, M. & Colby, R. H. (2003). Polymer Physics. Great Clarendon Street, Oxford, United Kingdom: Oxford University Press
[2] Hammond, A. and Sheffield S., Power law Pólya's urn and fractional Brownian motion, Springer-Verlag, Berlin, 2012.
[3] Bornales, J., Oliveira, M. and Streit, L. Self-Repelling fractional Brownian motion – a generalized Edwards model for chain polymers. December 13, 2011

Scaling Theory for fBm

Note that:

$$\langle x^2 \rangle \sim \int a^2 \exp\left[-\frac{c^2}{2}x^2\right] dx \qquad (16)$$

Now eq. (15) becomes,

$$\langle R^2 \rangle \sim ZE[a^2] = ZE[(B_N^H)^2] \qquad (17)$$

FBm is Self-Similar: $B_N^H = N^H b^H$

$$\langle R^2 \rangle \sim ZE[N^{2H}(b^H)^2] = ZN^{2H}E[(b^H)^2] \qquad (18)$$

$$\boxed{\langle R^2 \rangle \sim N^{2H}} \qquad (19)$$

Numerical Methods

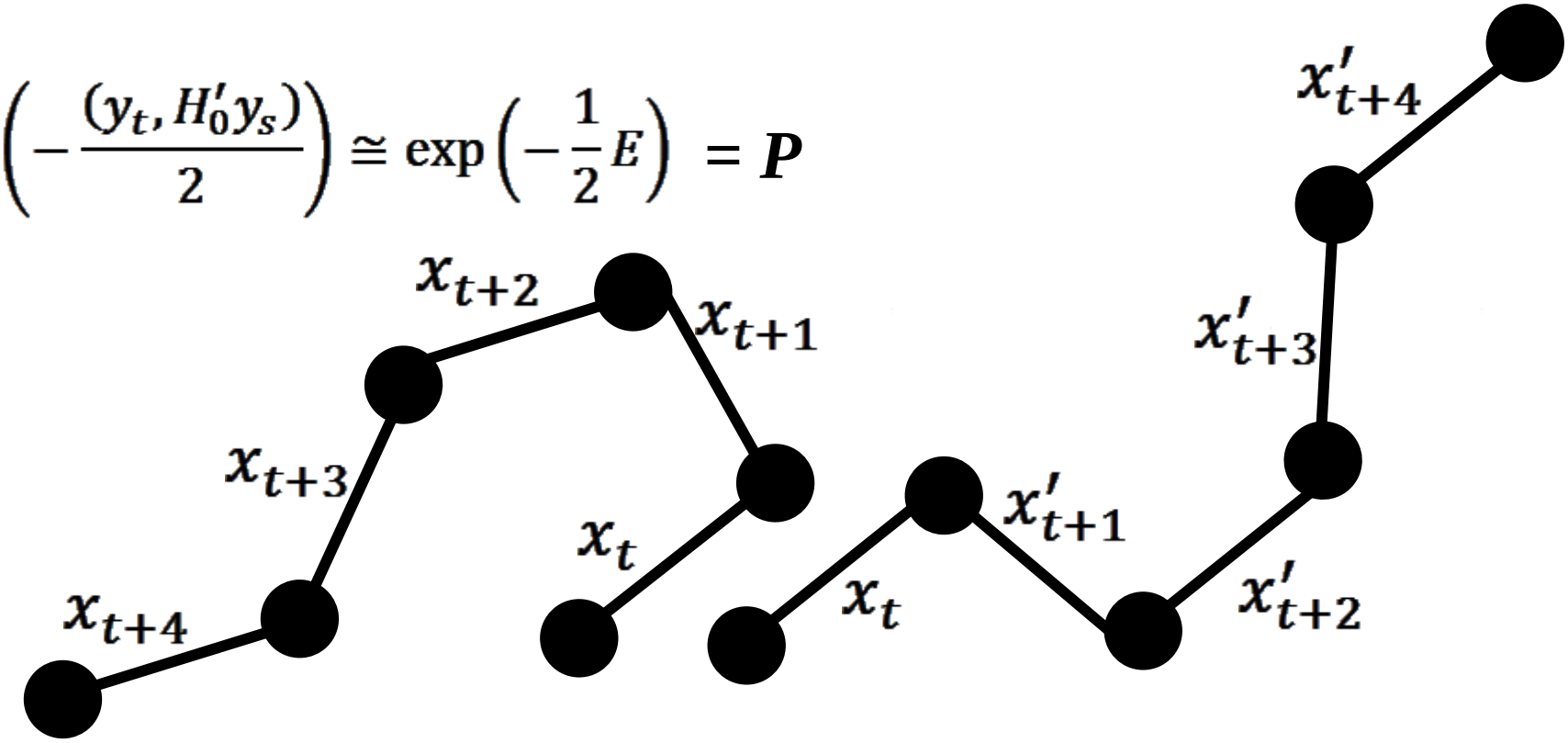
- **Monte Carlo Simulation**
  - a method used for precise approximation
  - widely used in polymer simulations
  - makes use of random generation of monomer positions
  - With the help of a filtering process, the process is iterated multiple times to reach close approximation

Reference: [1] Binder, K. Applications of Monte Carlo Methods to Statistical Physics. Rep. Prog. Physics, 1997.
[2] Besold, G., Guo, H. and Zuckermann, M. Off-Lattice Monte Carlo Simulation of the Discrete Edwards model. Journal of Polymer Science, 2000
[3] Bhanot, G. 1988. The Metropolis algorithm. Rep. Prog. Phys. 51:429-457

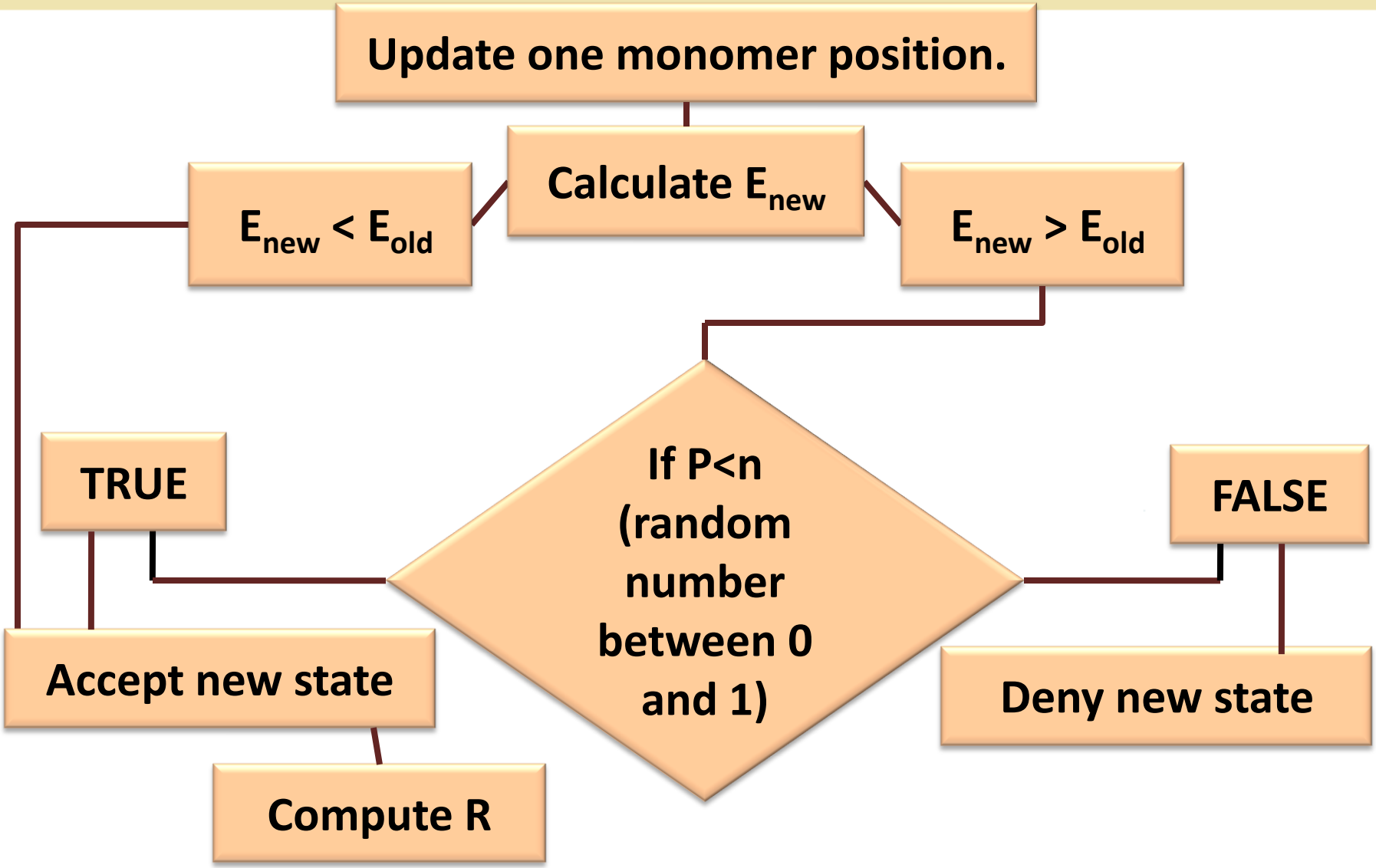
Monomer Randomization

- **alteration of a single monomer position/ bond vector has the effect as illustrated:**

$$\exp\left(-\frac{(y_t, H_0' y_s)}{2}\right) \cong \exp\left(-\frac{1}{2}E\right) = \boldsymbol{P}$$



The Metropolis Algorithm



Extraction of Scaling Expression

- **Results from the simulation give the values for:**

$$\ln\left(\langle R^2\rangle^{\frac{1}{2}}\right)$$

- **To get scaling expression, the ff. is employed:**

$$\ln\left(\langle R^2\rangle^{\frac{1}{2}}\right) \approx \upsilon_H \ln(N) \quad (20)$$

$$\langle R^2\rangle^{\frac{1}{2}} \approx N^{\upsilon_H}$$

$$\langle R^2\rangle \sim N^{2\upsilon_H} \quad (21)$$

Actual Simulation Codes

- **Codes were written by *Wolfgang Bock* and his team in Germany for their collaboration with the Physics Department – CSM, MSU-IIT.**

- **Simulation is run using C programming language**

Summary of Results

$\langle R^2 \rangle \sim N^{2\upsilon_H}$

- **Theoretical Prediction:** $\langle R^2 \rangle \sim N^{2H}$

Hurst Parameter (H)	Simulation Results for N=200-450	Simulation Results for N=500-850	Theoretical Result ($\upsilon_H = H$)
0.1	0.1205783	0.11700828	0.1
0.2	0.2262343	0.21894096	0.2
0.3	0.3400670	0.33257905	0.3
0.4	0.4436808	0.44101619	0.4
0.5	0.4997110	0.50125228	0.5

Summary of Results

$$\langle R^2 \rangle \sim N^{2\upsilon_H}$$

- **Theoretical Prediction:** $\langle R^2 \rangle \sim N^{2H}$

Hurst Parameter (H)	Simulation Results for N=200-450	Simulation Results for N=500-850	Theoretical Result ($\upsilon_H = H$)
0.6	0.51088970	0.50792676	0.6
0.7	0.50875442	0.50840673	0.7
0.8	0.50321720	0.49895897	0.8
0.9	0.50334768	0.50119497	0.9

Conclusions

- **The scaling expression for fractional Brownian model for linear polymer chains has been theoretically derived.**

$$\langle R^2 \rangle \sim N^{2H}$$

- **This result is similar to that shown in the study by Sarkar (Pennsylvania State University, Pennsylvania, USA) where the expectation value for is given by a general formula:**

$$E\left[\left(B_t^H - B_s^H\right)^2\right] = c(H)|t-s|^{2H}$$

Reference S. Sarkar, Fractional Brownian Motion: Long range dependency, Markov property, Simulation strategy-A review, Term Paper submitted for Stochastic Process Course in Spring 2008

Conclusions

- **Simulation results give a very close value or the Brownian case, H=0.5 (about 0.2% error). H-values less than 0.5 have approximately 10 - 20% difference from the theoretical prediction.**

- **For the case of H>1/2, the scaling constants remain to be the same as that of H=0.5, which is similar to that as theoretically predicted by the Bornales et al. in their work due to the limitations of scaling in one dimension**

Reference : [1] Bornales, J., Oliveira, M. and Streit, L. Self-Repelling fractional Brownian motion – a generalized Edwards model for chain polymers. December 13, 2011

Acknowledgements

- **Dr. Wolfgang Bock of University of Kaiserslautern, Germany and Dr. Samuel Eleuterio of Unibersidade Tecnica de Lisboa, Portugal for the codes.**

- **Sim Bantayan, Roel Bayabayon, and Cresente Cabahug for their help with the simulations.**

Acknowledgements

- **Dr. Ludwig Streit (BiBoS, Univ. Bielefeld and CCM, Univ. da Madeira) for initiating and providing new studies of Fractional Brownian motion in the field Polymer Science.**

Thank You!