

Size of a Flexible Polymer as a Function of the Number of Monomers

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Introduction

Polymers are long chains of covalently bonded units called monomers. When placed in a solution, a polymer will coil due to interactions with the solvent, as well as between monomers. The polymer will take different configurations depending on the solvent itself. The configurations of the polymer chains are characterized in terms of the following two length scales:

End-To-End Vector (R_L): the root-mean-square distance between the first and last monomers

Radius of Gyration (R_G): the average distance between the center of mass of a polymer and each monomer

Theory predicts the following exponential relationships for polymer size:

Ideal Polymer: $R_L \sim R_G \sim N^{1/2}$

Real Polymer (Good Solvent): $R_L \sim R_G \sim N^{3/5}$

Real Polymer (Poor Solvent): $R_L \sim R_G \sim N^{1/3}$

Goal of the Study: to confirm the exponential relationship between the number of monomers in a polymer and its size, measured by both the end-to-end vector and the radius of gyration, through a computational approach rather than a mathematical deduction

Experimental Design: Polymer chains were simulated using FORTRAN code to calculate position and velocity values for individual monomers, which ultimately leads to the two measurements of polymer size. The molecular bonds were modeled as harmonic springs to simplify calculations.

Method

Forces

Elastic Force (F_E): force between consecutive (bonded) monomers

$$\bullet F_E = k(r - l)$$

Dissipative Force (F_D): frictional force between polymer and solvent

$$\bullet F_D = \gamma v$$

Random Force (F_R): randomly adds or removes energy from the polymer

$$\bullet F_R = \sqrt{\frac{6 \cdot k_b \cdot T \cdot \gamma}{\Delta t}} \cdot N, -1 \leq N \leq 1$$

Real-Polymer Force (F_N): force experienced between non-consecutive monomers exclusively in real polymers

$$\bullet F_N = \begin{cases} 2Ar+B, & 0 < r < \alpha \\ 3Ar^2+2B'r+C', & \alpha \leq r < \beta \\ 0, & r \geq \beta \end{cases}$$

Velocity Verlet

Velocity and position of each monomer are approximated with a modified second-degree Taylor polynomial, where each calculation is done twice over two half-time-steps before being read into data files. After forces are initially calculated, the velocity and position are run through the first half-time-step. The forces are then updated to these new values, and the process repeats over a loop of time-steps.

1. $v(t+\frac{\Delta t}{2}) = v(t) + \frac{\sum F}{m} \cdot \frac{\Delta t}{2}$
2. $x(t+\frac{\Delta t}{2}) = x(t) + v(t) \cdot \frac{\Delta t}{2}$
3. Re-calculation of Forces
4. $v(t+\Delta t) = v(t+\frac{\Delta t}{2}) + \frac{\sum F}{m} \cdot \frac{\Delta t}{2}$

References

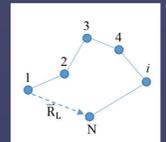
- [1] Alexander Yu. Grosberg and Alexei P. Khokhlov, "Giant Molecules: Here, There, and Everywhere..." Massachusetts Institute of Technology and Moscow State University, 1997 [2] "The Verlet Algorithm", University of Udine, 1997, <<http://www.fisica.uniud.it/~ercolessi/md/md/node21.html>> [3] Chinedum Osuji, "Ideal Chain Conformations and Statistics" Yale University, 2013 <http://www.eng.yale.edu/polymers/docs/classes/polyphys/lecture_notes/2/handout2.pdf> [4] Chinedum Osuji, "Non-Ideal Chains: Size, Statistics, Free-Energy" Yale University, 2013 <http://www.eng.yale.edu/polymers/docs/classes/polyphys/lecture_notes/4/handout4.pdf>

Method, cont.

End-To-End Vector

The square distance between the first and last monomers is averaged over the number of time-steps taken, after removing an initial "transient period" before the polymer reaches its equilibrium configuration.

$$\bullet \overline{R_L^2} = (x_N - x_1)^2 + (y_N - y_1)^2 + (z_N - z_1)^2$$

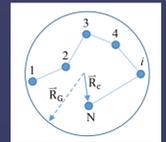


Radius of Gyration

The center of mass is first measured by calculating the average distance of each monomer from the origin. The square radius of gyration is calculated as the average distance of each monomer from the center of mass.

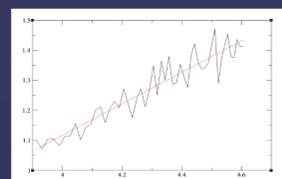
$$\bullet \overline{R_{cm}} = \frac{1}{N} \cdot \sum_{c=1}^N (\overline{R_c})$$

$$\bullet \overline{R_G^2} = \frac{1}{N} \cdot \sum_{c=1}^N (\overline{R_c} - \overline{R_{cm}})^2$$

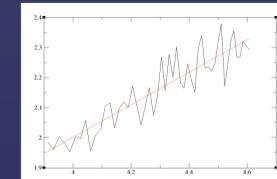


Results

Ideal Polymer:



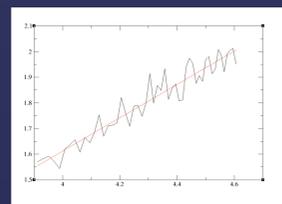
$\ln(R_G)$ v. $\ln(N)$



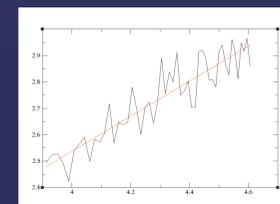
$\ln(R_L)$ v. $\ln(N)$



Real Polymer (Good Solvent):



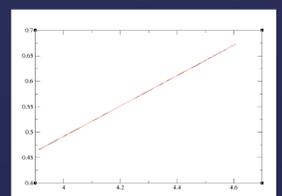
$\ln(R_G)$ v. $\ln(N)$



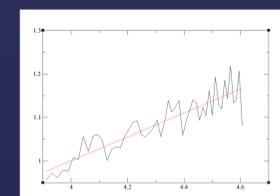
$\ln(R_L)$ v. $\ln(N)$



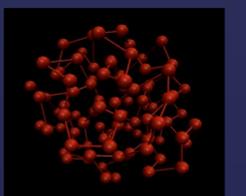
Real Polymer (Poor Solvent):



$\ln(R_G)$ v. $\ln(N)$



$\ln(R_L)$ v. $\ln(N)$



Polymer Type	Radius of Gyration	End-to-End Vector
Ideal	$R_G \sim N^{0.5232}$	$R_L \sim N^{0.54}$
Real (Good Solvent)	$R_G \sim N^{0.6502}$	$R_L \sim N^{0.6652}$
Real (Poor Solvent)	$R_G \sim N^{0.2988}$	$R_L \sim N^{0.2744}$

Conclusion and Future Work

Despite a slight degree of error compared to the theoretical predictions, the overall results are relatively consistent with the expected exponential relationships between polymer size and the number of monomers. Given further improvements to the code to create more accurate simulations, these computationally created polymers can be utilized to study specific polymers, such as cell membranes, and their behavior under various circumstances.

Acknowledgments

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