MODELING AND SIMULATION OF THE TWO DIMENSIONAL SCATTERING FACTOR OF STAR POLYMERS

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Abstract

We have designed a computer simulation of ideal star polymers in two dimensions which is well-suited for an independent project in a modeling and simulation course. The polymers are moved by the Monte Carlo Pivot algorithm. The scattering factor has been computed and compared to the theoretical predictions for linear and star polymers with three to six branches. There is good agreement for all polymers studied. This type of project is suitable for junior/senior majors in engineering, mathematics or science.

Introduction

In a previous article in this journal Dunn and Bishop [1] described a modeling and simulation project which computed some of the properties of two dimensional star polymers. The mean-square radius of gyration, $<S^2>$, which characterizes an overall polymer shape was found to be well represented by theoretical predictions. Here, the same model is employed. All the atoms making up the detailed monomer building blocks of a polymer are grouped into circular "beads" and individual beads are linked together to form the polymer. These beads are joined by starting with a central core bead. A star polymer is generated by envisioning F branches extending from this central bead. Hence, if m is the number of beads in one branch of the star, the total number of beads in the polymer, N, is given by

$$N = Fm + 1 \qquad (1)$$

This two dimensional model is further simplified by allowing the bead units to pass through each other and even to overlap. This ideal model is known as the non-excluded volume (NEV) model and it serves as a first approximation of real polymers.

An important structural property of polymers is the scattering factor, S(k), which can be obtained by light or neutron scattering techniques. The scattering factor provides information about the spatial monomer distribution of polymer materials. It is defined [2] as the Fourier transform of the density-density autocorrelation function and is given by

$$S(k) = (1/N^2) \sum_{m,n}^{N} < \exp[i\mathbf{k} \bullet (\mathbf{R}n - \mathbf{R}m)]> \qquad (2)$$

where N is the total number of monomers, **k** is the momentum transfer of the scattering experiment, **R**m and **R**n are the positions of the m-th and n-th monomers and <> denotes an average over all polymer configurations.

In an NEV polymer model the configurations obey random statistics and have a Gaussian distribution. Then the scattering factor for a star polymer with uniform branches is given by the Benoit [3] function

$$S(k) = 2 [X – F (1 – \exp(- X / F)) + 0.5 F (F - 1) (1 – \exp(- X / F))^2] / X^2 \qquad (3)$$

In two dimensions [4]

$$X = (3/2) k^2 <S^2> \text{ linear} \qquad (4)$$

A linear polymer is a star polymer with F = 2. The radius of gyration of a linear polymer is related to that of a star polymer by the g-ratio which is defined as

$$g = \langle S^2 \rangle_{star} / \langle S^2 \rangle_{linear} \quad (5)$$

An equation for the g-ratio of uniform NEV star polymers has been obtained by Zimm and Stockmeyer [5]. Their result is

$$g = (3F - 2) / F^2 \quad (6)$$

Tiglias and Bishop [6] re-derived the Fourier transform equation in two dimensions. It involves J0, the zero-th order Bessel function. Using this relationship to perform the average in Eq.2 over the angle between **k** and **R**n - **R**m yields

$$S(k) = (1/N^2) \sum_{m,n}^{N} \langle J0[k(Rn - Rm)] \rangle \quad (7)$$

Method

The Monte Carlo computer simulation details are contained in Dunn and Bishop [1]. The central bead is set as the origin of the coordinate system and the distance between two connected beads is assumed to be a constant of magnitude one. The beads are moved in continuous space by the Pivot algorithm [7]. The first 1×10^6 attempted pivot moves are used for equilibration. The scattering factor is sampled thereafter every 500 moves, providing a total of 8000 samples for averaging. J0 is calculated using the computer routines provided by Press et al [8]. The function, J0[k(Rn - Rm)], has been computed from each configuration in the system and the average S(k) obtained using Eq. (7).

Results

Polymer systems with N = 601 have been simulated. Hence, the polymers studied contain from 300 beads/branch when F = 2 down to 100 beads/branch when F = 6. In these systems the number of beads/branch is large enough to be meaningfully compared to the theoretical predictions which are for infinite N. The simulation results are compared to those predicted by the Benoit function, Eq. (3), in Figure 1. The reciprocal of the scattering factor is plotted versus X in order to emphasize the differences between the different star polymers. For low values of X (or k), the agreement between the theoretical prediction, Eq. (3), and the simulations is very good. Some discrepancy is observed as X increases and F increases. This may be a result of keeping N constant and decreasing the number of beads/branch as F increases.

Conclusions

The Monte Carlo Pivot algorithm has been used to simulate ideal star polymers in two dimensions. The scattering factor has been determined for a variety of star polymers. It is found that the simulation data are in good agreement with the Benoit theoretical predictions. These types of simulations provide interesting projects in which students can get experience in computational science. They involve knowledge from a number of different areas: chemistry, computer programming, model development and testing. This experience will be very useful in a student's future career.

Appendix: The Manhattan College Undergraduate Research Program

Manhattan College has a long tradition of involving undergraduates in research and was one of the original members of the Oberlin 50 [8]. This is a group of undergraduate institutions whose students have produced many PhDs in engineering and science. At Manhattan College, students can elect to take an independent study course for 3 credits during the academic year. In addition, the College provides grant support to the students for 10 weeks of work during the summer. I have personally recruited the students from my junior level course in Systems Programming. Previously published articles in this journal by Manhattan College student co-authors are a very effective recruitment tool. The students have also presented their results at a variety of undergraduate research conferences including the Hudson River Undergraduate Mathematics Conference and the Spuyten Duyvil Undergraduate Mathematics Conference.

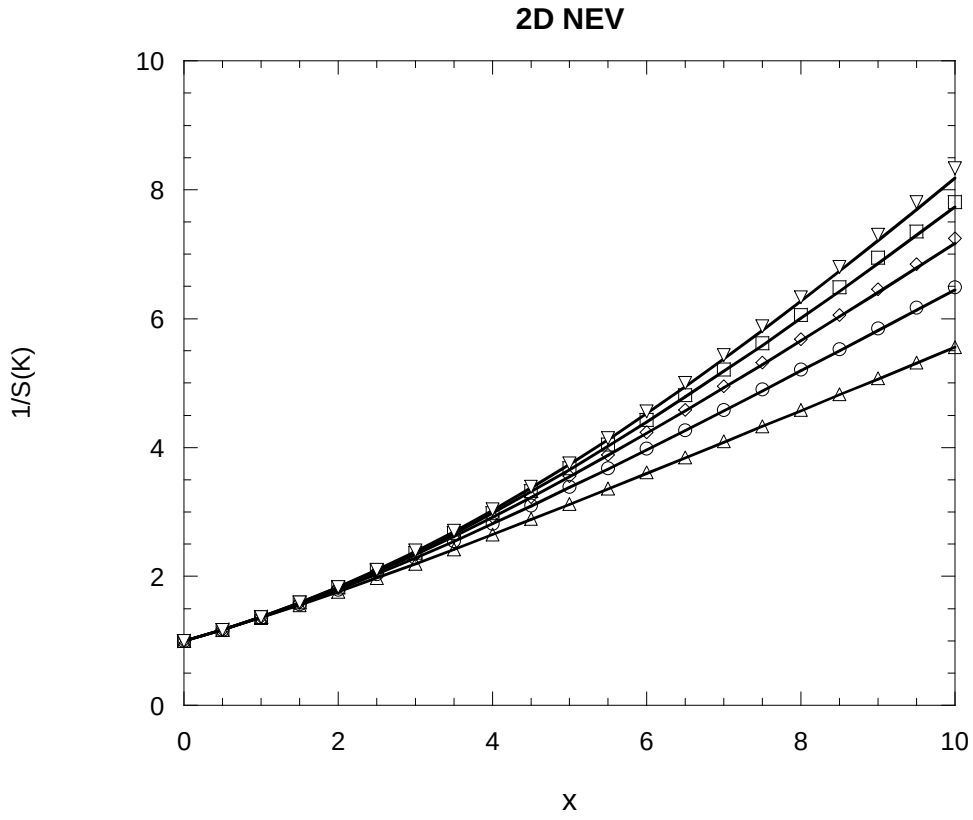

Figure 1: The reciprocal of the scattering factor for star polymers is plotted versus X defined in Eq. (4). The lines are the Benoit predictions, Eq. (3), and the symbols are the Pivot Monte Carlo simulations. The upward pointing triangles are for F=2, the circles for F=3, the diamonds for F=4, the squares for F=5 and the downward pointing triangles are for F=6.

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9. The Oberlin 50 institutions are: Albion College, Alma College, Amherst College, Antioch University, Barnard College, Bates College, Beloit College, Bowdoin College, Bryn Mawr College, Bucknell University, Carleton College, Colgate University, Colorado College, Davidson College, Denison University, DePauw University, Earlham College, Franklin and Marshall College, Grinnell College, Hamilton College, Hampton University, Harvey Mudd College, Haverford College, College of the Holy Cross, Hope College, Kalamazoo College, Kenyon College, Lafayette College, Macalester College, Manhattan College, Middlebury College, Mount Holyoke College, Oberlin College, Occidental College, Ohio Wesleyan University, Pomona College, Reed College, Smith College, St. Olaf College, Swarthmore College, Trinity College (CT), Union College (NY), Vassar College, Wabash College, Wellesley College, Wesleyan University, Wheaton College (IL), Whitman College, Williams College, and College of Wooster.

Biographical Information

Thomas Forzaglia is currently an undergraduate student in the computer science program at Manhattan College. He will complete a B.S. in computer science at Manhattan College in 2011.

Marvin Bishop is a Professor in the Department of Mathematics and Computer Science at Manhattan College. He received his PhD from Columbia University, his M.S. from New York University and his B.S. from City College of New York. His research interests include simulation and modeling and parallel processing.