Monte Carlo Calculation of the Friction Coefficient and Viscosity Number of Wormlike Star Molecules

Bruno H. Zimm

Department of Chemistry, B-017, University of California (San Diego), La Jolla, California 92093. *Received July 28, 1983*

ABSTRACT: We report Monte Carlo calculations on the hydrodynamics of star molecules to survey the effects of chain stiffness and Kirkwood–Riseman preaveraging of the interaction tensor. An ensemble of rigid random-chain star molecules with two, four, or six arms was generated by Monte Carlo methods, the translational friction coefficients and viscosity numbers of the individual chains were calculated numerically, with and without preaveraging of the interaction tensor, and the results were finally averaged. The results suggest that the deviations of experimental measurements on star molecules from the commonly used theoretical formulas can be explained partly as the effect of preaveraging and partly as the effect of chain stiffness and mutual repulsion of the chains as they emanate from the branch point.

Introduction

The physicochemical determination of the amount of long-chain branching in high polymers usually employs theoretical relations between measurable hydrodynamic properties, most commonly viscosity number or translational friction coefficient, and the degree of branching. The most commonly used theoretical relations, by Stockmayer and Fixman[1] for the friction coefficient and by Zimm and Kilb for the viscosity number,[2] were obtained with the use of several simplifications: (1) simple Gaussian chains with no excluded-volume effects, (2) chain hydrodynamics in the nondraining limit only, (3) use of the Kirkwood–Riseman preaveraged form of the hydrodynamic formulas, and (4) molecules in the form of a star with a fixed number of arms of equal length. The theoretical expressions have been critically compared with experimental data by Berry,[3] by Roovers and Bywater,[4] and by Roovers, Hadjichristidis, and Fetters[5] on synthetic equal-armed stars in Θ solvents. Their results show perceptible quantitative differences between theory and experiment. Also, Mansfield and Stockmayer[6] have suggested that, rather than the Gaussian chain, the wormlike chain is a better simple model to use for star molecules, reproducing approximately the Monte Carlo simulations of the rotational isomeric state model by Tonelli,[7] by Mattice and Carpenter,[8] by Mattice,[9] and by Oka and Nakajima.[10] See also Mattice.[11]

We report here some preliminary Monte Carlo calculations on the hydrodynamics of star molecules to survey the possible effects of chain stiffness and of Kirkwood–Riseman preaveraging. We have done this by generating an ensemble of random-chain star molecules by Monte Carlo methods and then calculating numerically hydrodynamic properties of each molecule. The properties were then averaged to give the final results. The methods were used in an earlier paper on linear molecules,[12] but their meaning and limitations have been clarified considerably by later work by Wilemski and Tanaka,[13], Fixman,[14] and Zimm.[15] In brief, two parallel calculations were carried out on the ensemble, one using the nonpreaveraged (Oseen–Burgers) hydrodynamic interaction between the chain elements, and one using the Kirkwood–Riseman preaveraged form of this interaction. The latter method is exactly the familiar method that has been used before,[1,2] except that here we are extending the calculation to (approximately) wormlike chains, and we using Monte Carlo instead of analytical procedures. The difficulty is that in both calculations the individual molecules are assumed to be rigid rather than flexible. We now understand that while the assumption of rigidity is inconsequential when preaveraging is used, it does not give exact results in general. What it does, when preaveraging is not used, is to give an upper limit to the viscosity number and to the translational friction coefficient,[13–15] and hence a lower limit to the sedimentation rate.

Thus we have two methods of calculation, neither of which is exact, but which give results that are rather close to each other, and which give definite limiting values of the desired hydrodynamic quantity. It therefore seems worthwhile to see what these methods show when applied to star molecules of wormlike chains.

Methods

The branches of the star are represented by strings of beads connected by bonds. The bonds were generated by an algorithm that is quick and convenient and that produces chains that are close to, but not exactly, wormlike. Assume that a chain is desired with a certain persistence length, a', and contour length, L. We shall approximate this by a chain of N unit bonds connected by flexible joints. First an initial direction is chosen in the form of a unit vector, $\mathbf{s}_0$. This vector is multiplied by a "persistence factor", $p = a'/(1 + a')$, to generate one part of the first bond of the chain. Then a normally distributed random vector of root-mean-square length $(1 - p^2)^{1/2}$ is generated by a pseudo-random-number generator and is added to the above vector to complete the first bond of the chain. The result is a vector of unit root-mean-square length that "remembers" the initial direction to an extent determined by p. Subsequent bonds are created by repeating the process with the preceding bond as the initial direction. If the vector representing the ith bond is represented by $\mathbf{s}_i$, then we have

$$\mathbf{s}_i = p^i\mathbf{s}_0 + R_i \tag{1}$$

where R_i represents a linear combination of random numbers that averages to zero. The persistence length is defined[17] as the average of

$$\sum_{i=1}^{\infty} \mathbf{s}_0 \cdot \mathbf{s}_i = \frac{p}{1-p} = a' \tag{2}$$

The last results come from remembering that the average of R_i vanishes. Thus the persistence length is indeed a', as required. When a' is zero the model reduces exactly to the random-flights chain of N flights, and when a' is infinity it becomes exactly a rigid straight rod of length N. It deviates somewhat from the wormlike model, except when $a' = \infty$, in that the contour length fluctuates instead

0024-9297/84/2217-0795$01.50/0

Table I
Comparison of Persistence Chain to Wormlike Chain

N	L	h^2 eq 3	h^2 eq 4
	$p = 0.1, a' = 0.11111$		
1	5.2632	1.0000	1.1449
5	26.3158	5.8642	5.8233
10	52.6316	11.9753	11.6712
	$p = 0.5, a' = 1$		
1	1.3333	1.0000	1.1939
5	6.6667	11.1250	11.3359
10	13.3333	26.0039	24.6667
	$p = 0.9, a' = 9$		
1	1.0101	1.0000	0.9832
5	5.0505	21.2882	21.3370
10	10.1010	72.7621	72.5523

of remaining rigidly fixed. The root-mean-square end-to-end length, h, is given by the formula

$$h^2 = \frac{N(1 - p^2) - 2(p - p^{N+1})}{(1 - p)^2} \quad (3)$$

whereas for the wormlike coil the formula is

$$h^2 = 2a'^2(\exp(-L/a') - 1 + L/a') \quad (4)$$

where L is the contour length. The differences between these two formulas are not great if we set L proportional to N with the right scaling factor; thus if we choose $L = N/(2p - p^2)$, we get the results shown in Table I, where the differences are seen never to exceed 20% and usually to be much less. So our algorithm produces chains that are close approximations to wormlike chains. (It is also possible to produce still closer approximations to wormlike chains by a method that we have previously published,[18] but with the use of much more computer time.)

Two, four, or six branches were made to emanate from one central bead to form the star. Following Mansfield and Stockmayer,[6] the initial directions were symmetrically arranged, so that the sum of the cosines between the initial directions adds to $-f/2$, where f is the number of branches; this "is what one might expect for molecules in which steric effects force the rays to be symmetrically disposed".[6] The orientation in space of the first initial direction was chosen at random, and the others were then arranged opposite, or tetrahedrally, or cubically around it, according to whether f was two, four, or six. In order to make the case of $f = 2$ represent exactly a linear chain, the first bond of the first branch in this case was allowed to fluctuate only in length, and not in direction, so that the distribution of the angle between the first bonds of the two branches should be exactly the same as the distribution of angles between all other neighboring bonds in the chain.

Since we do not have analytical formulas for the averages of the reciprocals of the intersegment distances either for this model or for the wormlike chain, except when $a' = 0$ or $a' = \infty$, it was necessary to calculate the Kirkwood–Riseman preaverages by averaging over the ensembles as actually generated before doing any calculations of properties. For $a' = 0$, the averages of the reciprocals for linear chains ($f = 2$) were, within the expected sampling error, close to the analytical formula.[12]

The hydrodynamic calculations were carried out as described previously,[12] using the same program, modified only enough to run on a different computer (Digital Equipment Corp. VAX 11-780, using the Pascal language). The same modified Oseen–Burgers interaction tensor was used, both with and without preaveraging, as previously.

Results

Calculations were performed on molecules with 25 beads and two, four, or six branches. Four values of the persistence length, a', were used, including the two extremes of Gaussian chains ($a' = 0$) and rigid straight rods ($a' = \infty$). The results for Gaussian molecules with two branches agree closely with those obtained[12] previously for linear chains of the same size, as they should. Since this work was intended as a preliminary survey, rather small sample sizes were used.

The results are shown in Table II, where the conventions are the same as those previously employed;[12] u and E are dimensionless numbers proportional to the sedimentation coefficient and viscosity number, respectively, N' is Avogadro's number, R^2 is the mean-square "central radius of gyration", P and Φ are the coefficients that Flory[19] introduced to describe the dependence of sedimentation and viscosity on molecular weight and size, and $B \times 10^{19} = P^{3/2}/(10\Phi/N')^{1/2}$. The digraph kr designates those quantities calculated with the use of Kirkwood–Riseman preaveraging. The plus/minus values are the standard deviations of the means of the preceding numbers, that is, the standard deviations in the ensemble divided by the square root of the number in the ensemble, except in the case of the ratios g, g', and h, for which see below. A blank for the standard deviation indicates that statistics were not gathered.

We have to remember that our results have been obtained from chains with only 25 beads. These are hydrodynamically partially draining, as can be seen from the sedimentation rates, u and u,kr, which are actually only 2–4 times greater than the free-draining value,[12] 0.1955. However, in our previous work on linear chains[12] we found that the relations among the various hydrodynamic quantities were already well established at $N = 25$. Also, Osaki and Schrag[20] have carried out the preaveraged calculation of g',kr for many values of N above 40 for various values of a certain hydrodynamic parameter h^*. They find that there is very little change of g' with N if h^* has values in the neighborhood of 0.25; our value is 0.2652. We are therefore encouraged to believe that our numbers may be meaningful for molecules much larger than is suggested by the number 25.

As a partial check on the calculations we can compare R^2 for the case of $a' = 0$ with the theoretical expectation, R^2,th. This was found by extending the formulas of a much earlier paper[21] to the case of finite N. (The actual working out of the rather complicated algebra was done by an "artificial intelligence" program[22] on a microcomputer.) The formula for R^2,th for star molecules is

$$R^2 = (-2 + 8N + 5f - 18Nf + 14Nf^2 - 4Nf^3 + 24N^2f - 16N^2f^2 + 3N^2f^3 - 14N^3f + 6N^3f^2 + 3N^4f - 12N^2 + 8N^3 - 2N^4 - 4f^2 + f^3)/(6N^2f^2(-1 + f + N)) \quad (5)$$

The agreement between this formula and the Monte Carlo values is good (third and fourth rows of Table II).

Of particular interest for seeing the effects of branching are the ratios of the ensemble averages: $g = R^2/R_2^2$, $h = u_2/u$, and $g' = E/E_2$, where the subscript 2 in every case indicates the linear molecule ($f = 2$); h, of course, also equals the ratio of the translational diffusion coefficients. These quantities are given in the bottom rows of each section of the table; their error measures were estimated, by the square-root-of-sum-of-squares method, from the standard deviations of the primary quantities in the rows above.

Table II

	$a' = 0$			$a' = 0.6$		
f	2	4	6	2	4	6
no. of molecules	99	50	50	50	50	50
R^2	4.101 ± 0.2	2.682 ± 0.1	2.061 ± 0.1	7.405 ± 0.7	4.865 ± 0.3	3.249 ± 0.1
R^2,th	4.16	2.778	2.112			
u	0.846 ± 0.01	0.904 ± 0.02	0.933 ± 0.01	0.749 ± 0.02	0.777 ± 0.02	0.836 ± 0.01
u,kr	0.944 ± 0.01	1.046 ± 0.02	1.085 ± 0.02	0.813 ± 0.02	0.883 ± 0.02	0.973 ± 0.02
E	4.041 ± 0.2	3.216 ± 0.2	2.528 ± 0.1	6.528 ± 0.6	5.298 ± 0.3	4.048 ± 0.2
E,kr	4.574 ± 0.2	3.97 ± 0.3	3.322 ± 0.2	7.323 ± 0.7	5.981 ± 0.4	4.786 ± 0.2
P	5.973 ± 0.1	6.889 ± 0.2	7.62 ± 0.1	5.008 ± 0.1	5.953 ± 0.1	6.773 ± 0.1
P,kr	5.352	5.959	6.552	4.615	5.242	5.819
Φ/N'	0.417 ± 0.02	0.623 ± 0.03	0.727 ± 0.02	0.276 ± 0.02	0.42 ± 0.02	0.578 ± 0.03
Φ/N',kr	0.473	0.769	0.955	0.309	0.474	0.695
$B \times 10^{19}$	7.162 ± 0.1	7.247 ± 0.2	7.803 ± 0.1	6.751 ± 0.2	7.088 ± 0.2	7.27 ± 0.2
$B \times 10^{19}$,kr	5.707	5.248	5.428	5.639	5.513	5.326
g	1	0.654 ± 0.04	0.502 ± 0.03	1	0.657 ± 0.07	0.438 ± 0.04
h	1	0.935 ± 0.02	0.906 ± 0.01	1	0.964 ± 0.04	0.895 ± 0.03
h,kr	1	0.902 ± 0.02	0.870 ± 0.02	1	0.920 ± 0.03	0.835 ± 0.03
g'	1	0.795 ± 0.06	0.625 ± 0.04	1	0.811 ± 0.09	0.620 ± 0.06
g',kr	1	0.867 ± 0.08	0.726 ± 0.05	1	0.816 ± 0.10	0.653 ± 0.07
$g^{1/2}$	1	0.808 ± 0.02	0.708 ± 0.02	1	0.810 ± 0.05	0.662 ± 0.03

	$a' = 6$			$a' = \infty$		
f	2	4	6	2	4	6
no. of molecules	50	50	50	25	25	25
R^2	26.51 ± 3	11.51 ± 0.6	5.938 ± 0.2	52 ± 0.000	14.56 ± 0.001	7.2 ± 0.001
u	0.582 ± 0.01	0.611 ± 0.01	0.681 ± 0.01	0.469 ± 0.01	0.523 ± 0.000	0.591 ± 0.000
u,kr	0.630 ± 0.02	0.691 ± 0.02	0.787 ± 0.01	0.474 ± 0.01	0.567 ± 0.000	0.654 ± 0.000
E	22.04 ± 3	13.00 ± 0.8	7.698 ± 0.4	44.96 ± 3	18.68 ± 0.2	9.571 ± 0.2
E,kr	21.0 ± 2	12.26 ± 0.7	7.831 ± 0.4	42.92 ± 3	17.24 ± 0.001	9.745 ± 0.000
P	3.406 ± 0.1	4.924 ± 0.07	6.152 ± 0.06	3.018 ± 0.05	5.11 ± 0.000	6.431 ± 0.000
P,kr	3.149	4.354	5.324	2.985	4.716	5.816
Φ/N'	0.137 ± 0.01	0.283 ± 0.02	0.453 ± 0.01	0.102 ± 0.01	0.286 ± 0.003	0.421 ± 0.01
Φ/N',kr	0.131	0.267	0.46	0.097	0.264	0.429
$B \times 10^{19}$	5.363 ± 0.2	6.491 ± 0.2	7.173 ± 0.2	5.191 ± 0.4	6.831 ± 0.03	7.946 ± 0.08
$B \times 10^{19}$,kr	4.885	5.56	5.727	5.228	6.305	6.772
g	1	0.434 ± 0.05	0.224 ± 0.03	1	0.280 ± 0.000	0.139 ± 0.000
h	1	0.953 ± 0.02	0.855 ± 0.02	1	0.897 ± 0.02	0.794 ± 0.02
h,kr	1	0.912 ± 0.04	0.801 ± 0.03	1	0.836 ± 0.02	0.725 ± 0.01
g'	1	0.590 ± 0.09	0.349 ± 0.05	1	0.416 ± 0.03	0.213 ± 0.02
g',kr	1	0.584 ± 0.06	0.373 ± 0.04	1	0.402 ± 0.03	0.227 ± 0.02
$g^{1/2}$	1	0.659 ± 0.04	0.473 ± 0.03	1	0.529 ± 0.000	0.372 ± 0.000

In a certain respect these error measures are misleading, however, because of the strong correlations between the preaveraged and the nonpreaveraged quantities in the ensemble and between the viscosity numbers and the mean-square radii; in fact, the fluctuation of the difference between, say, E and E,kr is only about one-fourth of the fluctuation of either in the case of linear molecules.[12] Thus g' is nearly always less than g',kr, for example, even though the error measures of either alone would suggest that the difference was not significant; in fact, the overall trend appears to be strongly significant. Regretfully, we did not anticipate this result, so the statistics necessary to compute a realistic measure of the error of, say, the ratio of g' to g were not gathered. In this respect, as in several others, these results must be considered as preliminary to a more definitive study.

Discussion

The numbers that correspond most closely to the old theoretical formulas for g' and h are g',kr and h,kr for the case of $a' = 0$; these involve some of the same assumptions as the old formulas, namely, Gaussian chains and Kirkwood–Riseman preaveraging. The difference is the small value of N in contrast to infinite N. Consider first the viscosity ratio, g'. The old theoretical result[2] had g' approximately equal to $g^{1/2}$; it can be seen that this relation is not generally true for these finite wormlike chains. There is a tendency for g' and g',kr, especially g', to depend more strongly on f than $g^{1/2}$ does. This interesting in view of the experimental results,[3-5] where the same tendency appears. The actual experimental values by Roovers et al.[4,5] for g' in the Θ solvent are 0.76 for four-armed stars and 0.63 for six-armed stars, which are close to the corresponding values in Table II with $a = 0$ or 0.6. The nonpreaveraged values are closer than the preaveraged ones. Berry's[3] results are similar.

With the frictional ratios, h and h,kr, there is also an interesting parallelism to the experimental results, as summarized in ref 5. The latter show less dependence on f than does the Stockmayer–Fixman formula based on preaveraging.[1] Likewise the nonpreaveraged ratios, h, show less dependence on f than do the preaveraged ones, h,kr.

In further parallelism to the experiments, the dimensionless factors P and Φ are seen to increase significantly with increase of f. On the other hand, the factor B is much more nearly constant. B, which is related to the Flory–Scheraga–Mandelkern factor β, is useful for correlating the three quantities sedimentation coefficient, viscosity number, and molecular weight with each other, so that it is interesting to see that it is not much dependent on molecular structure.

These results suggest that the deviations of the experimental results from the older formulas can be explained partly as the effect of Kirkwood–Riseman preaveraging and partly as the effect of some wormlike character and mutual repulsion of the chains as they emanate from the branch point. Because the effects of the finiteness of N may also be present, however, it is not yet clear how much

of the deviations is to be attrributed to each cause.

Acknowledgment. This work was supported by Grant GM-11916 from NIH.

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Diffusion of Labeled Macromolecules in Molten Polystyrenes Studied by a Holographic Grating Technique†

Markus Antonietti, Jochen Coutandin, Roland Grütter, and Hans Sillescu*

Institut für Physikalische Chemie der Universität Mainz, D-6500 Mainz, West Germany.
Received July 25, 1983

ABSTRACT: A holographic technique for measuring small diffusion coefficients has been applied to polystyrene (PS) labeled with fluorescein, which is thermally stable at 180 °C but can be bleached with light (λ = 458 or 488 nm) from an Ar ion laser. The diffusion of short chains (M_w = 4000) decreases in a surrounding matrix of higher molecular weight, as predicted by the WLF equation taking into account the end-group free volume. For labeled PS chains of $1.8 \leq M_n \times 10^{-4} \leq 16.1$ in a high molecular weight matrix we find diffusion coefficients $4.2 \times 10^{-11} \geq D/\mathrm{cm}^2\,\mathrm{s}^{-1} \geq 4 \times 10^{-13}$ and $D \sim M_n^{-2.2}$ at 177 °C. The diffusion of labeled PS rings in the same matrix of linear PS depends upon sample preparation. We conclude that the rings can exist in a twisted pseudolinear shape that allows for rapid diffusion and in an open shape where a network is formed when long chains thread through more than one ring.

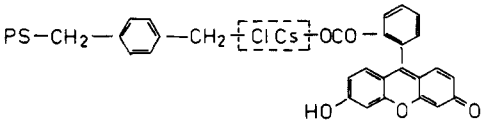
Introduction

In recent years, experimental studies of dynamical phenomena in matter have had increasing recourse to a laser technique[1] in which, by interference of two coherent beams, a grating is induced in the sample and the time evolution of this grating is monitored by light scattering. The terms *forced Rayleigh scattering*[2-4] and *holography*[5-7] have been used by different authors. We prefer the latter expression since we create the simplest possible hologram by partially bleaching the dye used for labeling the macromolecules, and we "read" this hologram as it changes due to macromolecular diffusion. There is some resemblance to the fluorescence bleaching technique where gratings have also been generated recently by interference of coherent light beams[8] or by applying an appropriate mask to the sample.[9] In holography, the diffusion length x can, in principle, be as small as the wavelength λ of the light. Thus, the lower limit of the diffusion coefficient D as given by eq 1 is $D \gtrsim (x/2\pi)^2 t^{-1} \sim 10^{-14}$ cm^2 s^{-1} if the diffusion time t is of the order of hours.

There are a huge number of problems related to macromolecular diffusion that can be solved after straightforward experimental methods have become available. The diffusants can be linear chains, rings, stars, combs, or block copolymers where the different blocks may vary drastically with respect to compatibility. The environment of the diffusants may consist of high or low molecular weight chains of the same or of different species, where the latter may be compatible or heterogeneous on a microscopic scale. Further, macromolecular diffusion in networks, porous systems, membranes, polymer liquid crystals, polyelectrolyte solutions, and many other environments is of interest. In the present paper, we describe the holographic technique as applied to diffusion of fluorescein-labeled molecules in molten polystyrene.[7] The first applications address the dependence upon the amount of labeling, the molecular weight, and the shape of the diffusant, as well as changes in the surrounding matrix.

Experimental Section

1. **Fluorescein Labeling.** Two different methods have been used in order to obtain polystyrene (PS) samples of narrow molecular weight (MW) distribution and labeled with fluorescein (FL). Labeling at the end group was achieved by terminating the anionic polymerization of styrene with dichloroxylylene and subsequent reaction of the chloromethyl end group with the cesium salt of fluorescein:[10]



Typically, a tetrahydrofuran (THF) solution of about 10 g of living PS in 200 cm^3 was terminated with a 40-fold surplus of di-

† Dedicated to Professor W. H. Stockmayer on occasion of his 70th birthday.

0024-9297/84/2217-0798$01.50/0