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Monte Carlo Calculation of the Hydrodynamic Radius at the Θ Point. Deviations from Analytical Gaussian Behavior

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I. Introduction

A number of recent papers have been published comparing theoretical[1,2] expressions for the diffusion coefficient for a polymer at infinite dilution with the diffusion coefficient obtained from quasi-elastic light scattering.[3-6]

In a recent comprehensive comparison of theory and experiment, Schmidt and Burchard[3] found that there is a discrepancy between the predicted and theoretical values of the dimensionless parameter ρ_E

$$\rho_E = R_G/R_H \tag{1}$$

where R_G is the *z*-average radius of gyration of a polymer chain, usually obtained from light scattering or neutron scattering experiments, and R_H is the experimentally obtained mean reciprocal hydrodynamic radius defined[3] in terms of the Stokes law expression

$$1/R_H \equiv \left(\frac{6\pi\eta_0}{kT}\right)D \tag{2}$$

where η_0 is the solvent viscosity, kT the thermal energy, and D the measured *z*-average translational diffusion coefficient for the polymer obtained from quasi-elastic light scattering. Schmidt and Burchard[3] found ρ_E to be 1.27 ± 0.05 for a large number of experiments on polystyrene in Θ solvents. The above ρ_E deviates from the 1.504 theoretical value of ρ predicted by Kirkwood theory[1] for the analytical Gaussian coil model of the polymer.

These deviations of experiment and theory have yet to be explained, although usually the inadequacies of the Kirkwood dynamical formulation are considered to be the cause of the discrepancy.[2-9]

In this paper, we approach the observed deviation of theory and experiment from a point of view different from what has been proposed before. We compute the diffusion coefficient from the Kirkwood theory with preaveraging for polymer chains at the Θ point by calculating the $1/R$ moment of these chains created by a Monte Carlo simulation in which both excluded volume and nearest-neighbor interaction are included.[10] The value of ρ obtained for such chains is closer to the experimentally obtained ρ and differs from that obtained for an analytical Gaussian coil. The value of ρ obtained from this Monte Carlo calculation, ρ_{MC}, is 1.40 ± 0.01 for chains with an infinite number of monomers.

II. Gaussian Coil Inverse Radius: Slow Approach to Asymptotic Value

In Kirkwood[1] theory, the diffusion constant, D, is given by

$$D = \frac{kT}{N\zeta} + \frac{kT}{6\pi\eta_0}\left\langle\frac{1}{R}\right\rangle \tag{3}$$

where the first term is the free-draining limit, which depends on the friction coefficient (ζ) and the number of statistical segments in the chain (N). Substituting eq 3 in eq 2 yields

$$\frac{1}{R_H} = \left(\frac{3}{\pi}\right)^{1/2}\frac{1}{h^*b'N} + \left\langle\frac{1}{R}\right\rangle \tag{4}$$

where

$$h^* = \frac{\zeta}{(12\pi^3)^{1/2}b'\eta} \tag{5}$$

The value of h^* has been estimated in a variety of ways for various models of the chain. For chain models where b' and N refer to quantities defined in the spring-and-bead model of a polymer chain, Wang[11] considers values of h^* in the range 0.12–0.40.

Because the term involving h^*, the free-draining term, is considered small compared to the $\langle 1/R\rangle$ term for large N, Schmidt and Burchard[3] did not consider it in their estimation of $1/R_H$. For the moment, we, too, shall not consider this term further but rather focus on the calculation of $\langle 1/R\rangle$.

The term $\langle 1/R\rangle$ in Kirkwood theory is defined as

$$\left\langle\frac{1}{R}\right\rangle = \frac{1}{(n+1)^2}\sum_{i\neq j}^{n+1}\left\langle\frac{1}{r_{ij}}\right\rangle \tag{6}$$

where r_{ij} is the distance between beads i and j and n is the number of bonds in the chain. For the analytical Gaussian coil model one has[12]

$$\left\langle\frac{1}{r_{ij}}\right\rangle = \left(\frac{6}{\pi}\right)^{1/2}\left(\frac{1}{|i-j|^{1/2}}\right)\frac{1}{b'} \tag{7}$$

The Gaussian $\langle 1/R\rangle$ was obtained from eq 6 and 7 by replacing the sum by its trapezoid rule integral. The approximate formula

$$\left\langle\frac{1}{R}\right\rangle_G \doteq \left(\frac{6}{\pi}\right)^{1/2}\frac{8}{3b'N^{1/2}}\left[1 - \frac{9}{8N^{1/2}}\right] \tag{8}$$

to order $1/N$ was obtained. Equation 8 gives the term in $1/N^{1/2}$ exactly but gives the coefficient of the $1/N$ only approximately.

Although inexact, the above result shows the slow approach to the asymptotic value of the Gaussian $\langle 1/R\rangle$, $\langle 1/R\rangle_G$, to its limiting value. The mean reciprocal inverse radius has also been computed for values of N to 100000 using eq 6 and 7 by performing the summation on a com-

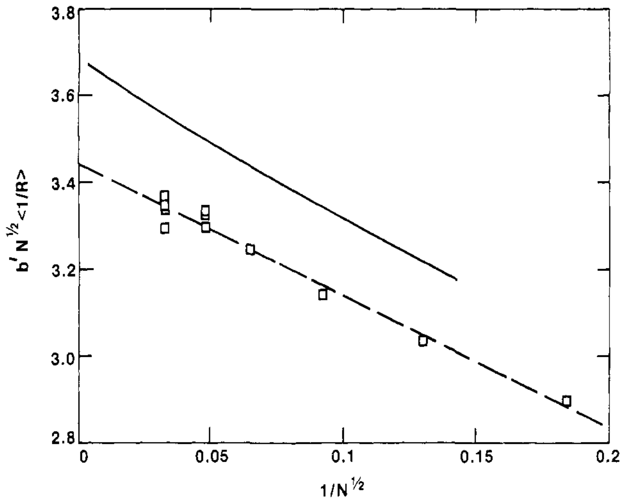

Figure 1. Calculated normalized values of the average inverse radius of the Gaussian coil model (solid line) and the Monte Carlo model (squares and dashed line).

puter. In Figure 1, $N^{1/2}\langle 1/R\rangle_G$ is plotted vs. $1/N^{1/2}$ as the solid curve. The curve is straight for large N, has an intercept given by eq 8, and has a slope of −3.8, which is in satisfactory agreement with the value of −4.1 given by eq 8. It should be noted that Akcasu and Higgins[13] saw a similar $1/N^{1/2}$ approach to the asymptotic of $N^{1/2}\langle 1/R\rangle$ in their calculation of the short-time diffusion coefficient for a freely jointed chain. The $1/N^{1/2}$ approach to its asymptotic function for $\langle 1/R\rangle$ is to be compared to the more rapid $1/N$ approach of R_G for the analytical Gaussian coil to its asymptotic value.

Using eq 4, 6, and 8, we obtain for the Gaussian coil the approximate equation

$$\frac{1}{R_H} = \left(\frac{6}{\pi}\right)^{1/2}\frac{8}{3b'N^{1/2}} + \frac{1}{Nb'}\left[\left(\frac{3}{\pi}\right)^{1/2}/h^* - 3\left(\frac{6}{\pi}\right)^{1/2}\right] \qquad (9)$$

Thus the contribution from the free-draining term is of the same order as the correction to the $\langle 1/R\rangle$ term but of opposite sign. For certain values of h^* the sum of these two terms is zero. Both Wang[11] and Osaki[15] noticed such a compensation in their efforts to extend the Zimm bead-and-spring models of viscoelastic properties of the chain to finite N.

III. Monte Carlo Calculation of $\langle 1/R\rangle$

In an earlier paper[10] we presented Monte Carlo calculations of the mean-squared radius of gyration and of the mean-squared end-to-end distance of a lattice model of a polymer chain with excluded volume and nearest-neighbor attractive energies ϵ. In the present work the chain generation technique was identical with that used previously. However, for the present calculation, we were only interested in chains at the Θ point (the value of ϵ/kT at which $R_G{}^2$ is proportional to the length of the chain for long chains), which corresponds to $-\epsilon/kT = 0.275$ for chains on a cubic lattice. Description of calculational procedures for $\langle 1/R\rangle$ will be given in a later paper.

Since we wish to compare our results with experimental values of R_H, we introduce the usual concept of statistical step.[16] This yields

$$b' = C_n b \qquad (10)$$

$$N = n/C_n \qquad (11)$$

where b is the length of a bond, b' is the length of a statistical step, N is the number of statistical steps, and n is the number of bonds in the polymer, for both the Monte Carlo model and a real polymer. C_n is the characteristic ratio of the polymer. For the Gaussian coil, $C_n = 1$. For the Monte Carlo chains on a cubic lattice at the Θ point from ref 10, C_n is 1.69.

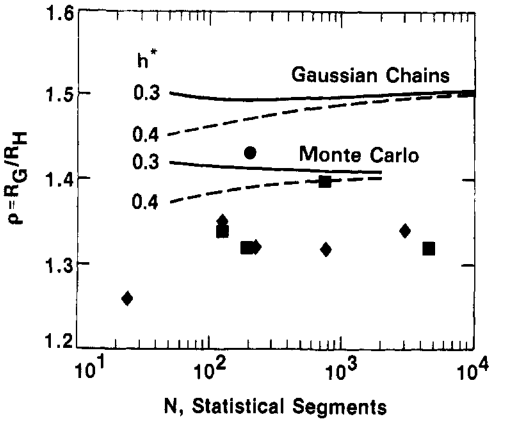

Figure 2. Values of $\rho \equiv R_G/R_H$ vs. number of statistical segments and molecular weight of polystyrene. The values from ref 26 are plotted as squares, the value from ref 25 is indicated as a circle, and the values from ref 24 are plotted as diamonds. The ρ obtained for a Gaussian coil and Monte Carlo chain are shown in the curves in the figure. The solid lines are for $h^* = 0.3$ and the dashed curves for $h^* = 0.4$.

The dimensionless product $b'N^{1/2}\langle 1/R\rangle$ is plotted in Figure 1 vs. $1/N^{1/2}$ as squares for the Monte Carlo data and fit by the dashed line

$$\langle 1/R\rangle = 3.44N^{-1/2}(1 - 0.879N^{-1/2})/b' \qquad (12)$$

Consistent with our findings for the Gaussian coil model, the coefficient of the $N^{-1/2}$ correction term in the parentheses is about 1.

From eq 12 and 4, we have

$$b'/R_H = 3.44N^{-1/2} + (0.98/h^* - 3.02)N^{-1} \qquad (13)$$

The product $\rho = R_G/R_H$ for the Monte Carlo results and for the Gaussian chains is shown in Figure 2. For the solid curves, $h^* = 0.3$, a value of h^* near the midpoint of the range that has been proposed for h^*, and the dashed curves are for $h^* = 0.4$, the maximum value proposed for h^*. The Gaussian chains are seen to give larger values of ρ than the Monte Carlo chains. Also larger values of h^* are seen to give smaller values of ρ. The infinite N limit of the Monte Carlo curve for ρ is 1.40 and is independent of h^*. The value of 1.40 found for the Monte Carlo chains is less than the value of 1.504 found for the analytical Gaussian coil model.

One might worry that effects of different lattices or small changes in ϵ on the cubic lattice would change the above conclusion. We are currently investigating these possibilities and shall report on them in a future paper. Suffice it to say our preliminary investigation into these matters supports the view that our present conclusions are, in the main, unaltered by these changes.

In our earlier work we computed distance moments higher than $\langle R^2\rangle$ and R_G and obtained their ratios to $\langle R^2\rangle$ and R_G (for example, $\langle R^2\rangle/\langle R^4\rangle^{1/2}$). At the Θ point none of these Monte Carlo moment ratios obtained in the earlier work showed significant deviation from Gaussian behavior within the error of the Monte Carlo experiment. Thus, this present result is the first time we have observed non-Gaussian behavior for distance moments at the Θ point. Significantly, we do not see any deviation from the $1/N^{1/2}$ behavior expected from Gaussian statistics for $\langle 1/R\rangle$, although a small deviation from this behavior would

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Table I
Experimental Values of ρ of Polystyrene in Cyclohexane (except for the Last Value) at the Θ Temperature

M	N	R_H, nm	R_G, nm	ρ	ref
4.1×10^6	4660	45.4	59.9	1.32	26
6.7×10^5	761	17.29	24.2	1.40	26
1.79×10^5	203	9.44	12.5	1.32	26
1.1×10^5	125	7.31	9.82	1.34	26
2.7×10^6	3068	36.28	48.6	1.34	24
6.7×10^5	761	18.36	24.2	1.32	24
2.0×10^5	227	9.99	13.2	1.32	24
1.1×10^5	125	7.26	9.82	1.35	24
2.1×10^4	24	3.41	4.29	1.26	24
1.79×10^5	203	9.11	13.0	1.43	25

be difficult to see in the presence of the $1/N^{1/2}$ approach to the asymptotic behavior. In particular, correction terms of order ln N, as de Gennes[17] found for $\langle R^2 \rangle$, or N^δ (for $\delta < {}^1/_2$) would be nearly impossible to detect by our Monte Carlo calculations. In the same vein, such weak N variations would be difficult to detect experimentally.

We should remark, however, that in our earlier work[10] we did notice that the partition function of the Monte Carlo generated chain did not go to the expected Gaussian value of 1 at the Θ temperature; rather, it reached 1 at a value of $\epsilon/RT = 0.250$, somewhat lower than the Θ temperature. This observation is consistent with theoretical results[17,18] that the third virial is finite for N approaching infinity at the Θ point (the temperature at which $R_G{}^2 \sim N$). However, we are unaware of any earlier arguments that any of the distance moments themselves show non-Gaussian behavior.

IV. Comparison with Experiment

The ρ_E factor was computed for polystyrene of various molecular weights in cyclohexane at the Θ temperature from values of R_G obtained from elastic light scattering and values of $1/R_H$ obtained from quasi-elastic light scattering using eq 1 and 2.

Recent experimental values[19–21] of the root-mean-square radius of gyration of polystyrene in cyclohexane at the Θ temperature were fit to the equation

$$R_G = 0.0296M^{1/2} \quad \text{(nm)} \qquad (14)$$

This value of 0.0296 is slightly larger than that of 0.0290 used by Schmidt and Burchard[3] because we used only data for cyclohexane while they used data for several solvents. The values of R_H were measured for four polystyrene samples in cyclohexane at the Θ temperature by using the experimental method given in ref 22. These measurements and others from the literature with the calculated values of ρ_E are given in Table I.

The number of statistical steps in these polystyrene samples must be determined before their values of ρ_E may be compared to Monte Carlo and analytical Gaussian coil values. The number of monomers, n, in a polystyrene molecule is $M/104$ and the length, b, of the monomer for the molecule in the extended (trans) configuration is[23] 0.255 nm. Therefore

$$C_n = 8.41 \qquad (15)$$

and

$$N = n/8.41 = M/874 \qquad (16)$$

The number of statistical steps, N, of the polystyrene samples computed by eq 16 is given in Table I and the experimental values of ρ in Table I are plotted in Figure 2 vs. N. The previously computed values of ρ are also shown for the Gaussian coil and Monte Carlo models, each with values of h^* of 0.3 and 0.4, in Figure 2. It is clear the Monte Carlo model is in better agreement with the experimental values than the analytical Gaussian coil model.

As we have indicated earlier in this paper, the result reported here is only one possible explanation for the disagreement between the experimental ρ_E and the analytical Gaussian coil value of ρ. The Kirkwood theory with its many assumptions may be in error. Our model of the chain used for Monte Carlo simulation may not be realistic enough. Or the errors in extrapolation discussed in section IV may be important. Therefore our results should be viewed as tentative.

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Conformational Analysis of Syndiotactic Polymer Chains in the Crystalline State: Polypropylene and 1,2-Poly(1,3-butadiene)

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Conformational energy maps for the isolated chain of syndiotactic polypropylene were calculated by Natta, Corradini, and Ganis[1] under the restriction of a periodic repetition. The calculations were performed under the approximation of constant valence angles; moreover, for the interactions between nonbonded atoms, the methyl and

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