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Numerical Study of Hydrodynamic Radii of Polymer Chains in Θ Solvent

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ABSTRACT: We simulated polymer chains in Θ solvent by a random walk model and calculated the translational friction coefficients and the hydrodynamic radii of these chains by solving the hydrodynamic equations numerically. Thus the preaveraging approximation in the Kirkwood–Riseman theory is avoided. More than 25 polymer chains of size 900 segments were calculated. The average ratio $\langle R_h/R_g \rangle$ for long chains approaches 0.87 and the averaged $\langle R_h^{-1} \rangle^{-1}$ vs root-mean-square averaged R_g approaches 0.79; thus they agree well with the measurement.

The hydrodynamic behavior of polymer chains is an important subject in macromolecule science and has been studied extensively. By considering the hydrodynamic interactions between segments, Kirkwood and Riseman[1] have calculated the intrinsic viscosity and the translational diffusion coefficient of polymer chains. Their theory has shown that the scaling exponent β of the translational friction coefficient (and hence the hydrodynamic radius R_h) vs the molecular weight of polymer N ($R_h \sim N^{\beta}$) decreases from 1 to 0.5 describing the transition from free-draining to nondraining limit. Thus the ratio of the hydrodynamic radius vs the radius of gyration approaches a constant for large polymers. Efforts have been made to improve the original K-R theory by considering the flexibility of the chains and improving or avoiding the preaveraging approximation.[2-7] On the other hand, the rapid development in light scattering techniques has furnished highly accurate measurement of the translational friction coefficient,[8] and the result indicated that the Kirkwood–Riseman theory[1] and Zimm's theory[2] underestimated the ratio between the hydrodynamic radius and the radius of gyration. Zimm's Monte Carlo calculation has indicated that by avoiding the preaverage approximation the extrapolated value from numerical calculations did raise this ratio significantly.[9] Since Zimm's result is extrapolated from calculations that were limited to 50 segments, it is essential to extend the calculation to polymers of large sizes. In this paper we numerically solved the hydrodynamic interactions between chain segments and calculated the translation friction coefficient and the hydrodynamic radius. By directly solving the hydrodynamic equations, we avoided the preaveraging approximation used in the K–R theory and some other theories, and thus the fluctuations are considered. Our work is in the same line as Zimm's Monte Carlo study of the hydrodynamic property of polymer chains.[9] The major differences are that we used a different model to generate the configurations of the chains and we extended the calculation to larger chains of 900 segments as compared to 50 segments calculated by Zimm. The other difference is that we have used a modified Oseen tensor. As in Zimm's Monte Carlo calculation our model also neglected the flexibility of the chains and the internal friction proposed by Fixman.[10]

We generate random walks in a three-dimensional lattice, and the monomers are modeled by spherical beads at each lattice point where the walker passes. The walk is allowed to cross itself or to take an immediate back step, though only one bead is located on each crossing point. The diameter of the bead is chosen to be the lattice constant. This simple model retains the essential

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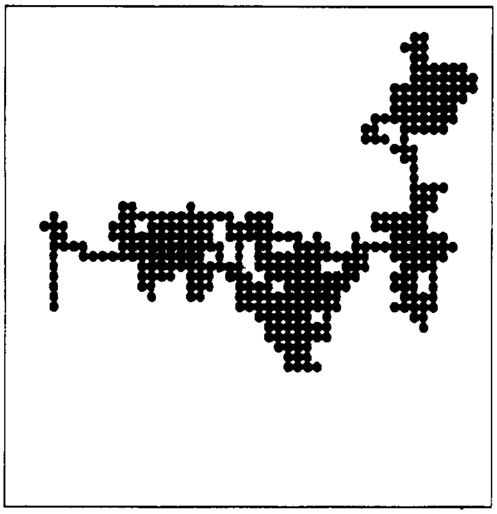

Figure 1. Illustrative projection of a polymer chain generated by the random walk model.

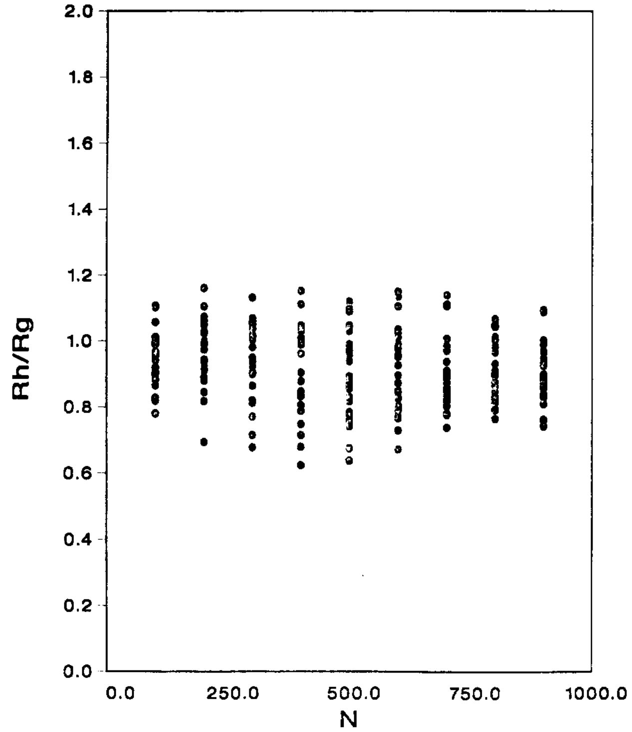

Figure 2. The calculated ratio between the hydrodynamic radius and the radius of gyration, R_h/R_g, vs the molecular weight of the chains N.

static scaling feature of polymers; i.e., $R_g \sim N^{0.5}$. Compared with the Gaussian chain model used by Zimm, this model features constant bond length and a finite-sized monomer. The latter facilitates the application of a modified Oseen tensor that considers the hydrodynamic interaction between a pair of spheres instead of two points. The real polymers, of course, have various monomer structures for different chemical compositions, but they all obey a similar scaling law. A projection of this kind of chain is given in Figure 1.

Following Kirkwood and Riseman the forces at each segment are determined by solving the following equations

$$\tilde{F}_i + \zeta_0 \sum_{\substack{j=1 \\ i \neq j}}^{n} \tilde{\tilde{T}}_{ij} \tilde{F}_j = \zeta_0 \tilde{U}_i \qquad i = 1, 2, ..., N \tag{1}$$

where $\tilde{F}_i$ is the force exerted by the ith particle on the solvent, ζ_0 ($= 6\pi\eta_0 a$) is the friction coefficient of a particle with radius a, $\tilde{U}_i$ is the velocity of ith particle, η_0 is the solvent viscosity, and $\tilde{\tilde{T}}_{ij}$ is the hydrodynamic interaction tensor.

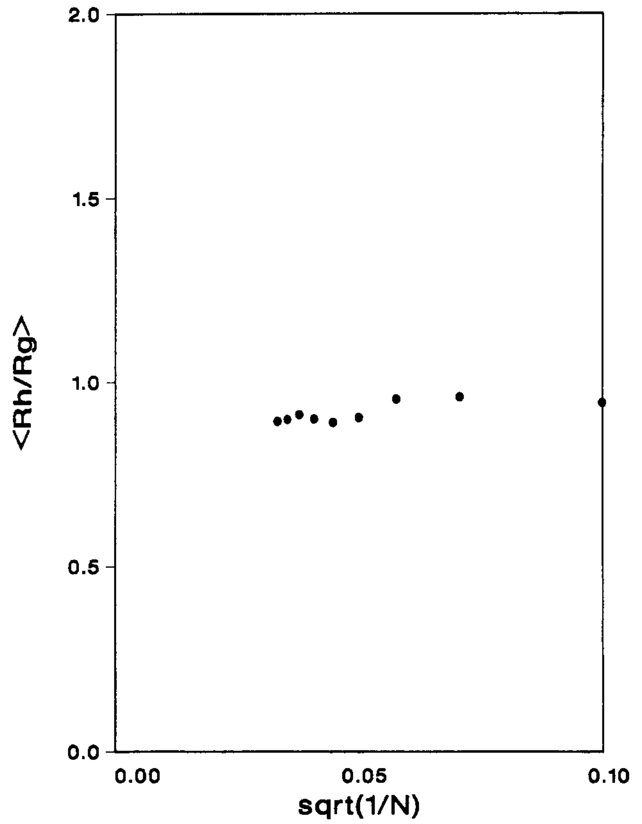

Figure 3. The averaged ratio between the hydrodynamic radius and the radius of gyration $\langle R_h/R_g \rangle$ vs $(1/N)^{1/2}$.

A modified version of the Oseen tensor as suggested by Ronte and Prager[13] and Yamakawa[14] is used in our calculation

$$\tilde{\tilde{T}}_{ij} = 1/8\pi\eta_0 r_{ij}\{\tilde{\tilde{I}} + (\tilde{r}_{ij}\tilde{r}_{ij}/r_{ij}^2) + (2a^2/r_{ij}^2)[{}^1/{}_3\tilde{\tilde{I}} - \tilde{r}_{ij}\tilde{r}_{ij}/r_{ij}^2]\} \tag{2}$$

where $\tilde{r}_{ij}$ is the difference in position between particle i and j. This formula considers the finite-size effect of monomers and represents the interaction between two spheres of radius a and separated by $\tilde{r}_{ij}$ up to the second order. The cluster is not permitted to rotate, and the total force, $\tilde{F}_{\mathrm{T}} = \sum_{i=1}^{n} \tilde{F}_i$, is determined in response to a uniform velocity, $\tilde{U}_\alpha$, in a specific direction, $\alpha = x, y, z$. The friction coefficient f_α is determined by the ratio between the total force and the velocity of the chain, $F_T{}^\alpha = f_\alpha U_\alpha$, and the average friction coefficient f is determined according to $f = 3/\sum_\alpha 1/f_\alpha$. This scheme has been used by McCammon and Deutch[11] to calculate chains with simple geometric shapes and by Chen, Deutch, and Meakin to calculate the friction coefficient and the hydrodynamic radius of diffusion-limited aggregates and other fractal clusters.[12]

The hydrodynamic radius is determined through the following relation

$$f = 6\pi\eta_0 R_h \tag{3}$$

$3N$ equations (eq 1) are solved numerically on the Cray at the Pittsburgh Super Computer Center. The friction coefficient and thus the hydrodynamic radius are calculated for chains up to 900 particles. The calculation was performed for intervals of 100 particles. Twenty-five chains were calculated, and averaged ratios of R_h/R_g were obtained.

Table I
Averaged R_h/R_g for Different Sizes of Polymer Chains

N	100	200	300	400	500	600	700	800	900
$\langle R_h/R_g \rangle$	0.942	0.959	0.949	0.909	0.896	0.903	0.909	0.896	0.891
$\langle R_h^{-1} \rangle^{-1}/\langle R_g \rangle_{rms}$	0.942	0.909	0.889	0.833	0.823	0.840	0.862	0.860	0.850

Table II
R_h/R_g for a Same Chain by Using Two Different Oseen Tensors: the Original Oseen Tensor and the Modified Oseen Tensor Given by Rotne, Prager, etc.

N	100	200	300	400	500	600	700	800	900
R_h/R_g (orig Oseen)	1.017	1.122	0.998	1.046	0.983	0.883	0.870	0.838	0.827
R_h/R_g (mod Oseen)	1.005	1.101	0.986	1.035	0.975	0.871	0.860	0.828	0.818

Table III
R_h/R_g for Two Chains Having the Same Lattice Configuration but with Different Bead Diameters: the First One (a) Has a Diameter of Two-Thirds of the Lattice Constant and the Second (b) Has a Diameter Equal to the Lattice Constant

N	100	200	300	400	500	600	700	800	900
R_h/R_g (a)	0.943	1.047	0.944	0.996	0.940	0.842	0.833	0.802	0.794
R_h/R_g (b)	1.005	1.101	0.986	1.035	0.975	0.871	0.860	0.828	0.818

The results of 25 chains are plotted in Figure 2 where each point represents a calculated R_h/R_g value for a specific chain configuration. The fluctuation in R_h/R_g is mostly related to the fluctuation in R_g, a typical phenomenon in random walks. The averaged R_h/R_g value is equal to 0.91 ± 0.11 for all points are calculated ($N = 100$–900). The average ratio of R_h/R_g for 25 chains are given in the Figure 3 and Table I. Two average schemes are used. One is the average value of R_h/R_g. The other gives a ratio of averages, $\langle R_h^{-1} \rangle^{-1}/\langle R_g \rangle_{rms}$. The latter is closer to the real measurement, where the experimental average of R_h is obtained from the average sedimentation or diffusion velocity, which is an average of R_h^{-1}, and light or neutron scattering gives a root-mean-square average of R_g.

Both the measured data and the Kirkwood–Riseman theory showed that the scaling exponent of the hydrodynamic radius vs molecular weight, β ($R_h \sim N^{\beta}$), varies from 1 at small N to 0.5 at large N. Thus R_h/R_g would increase, then decrease as N increases, and reach a stable value when N becomes large enough. This tendency can be observed in Figure 3. Because of limited computer capability at the present time, it is difficult to carry the calculation to large N. Extrapolating the data vs $1/(N)^{1/2}$ in Figure 3, we find the value of $\langle R_h/R_g \rangle$ for large N equals 0.871 ± 0.016 and $\langle R_h^{-1} \rangle^{-1}/\langle R_g \rangle_{rms}$ equals 0.788 ± 0.020. The limiting value for R_h/R_g certainly depends on the extrapolation scheme. Fixman and Mansfield suggested that there is a slower varying term proportional to $\ln N/(N)^{1/2}$ from their perturbation analysis.[15] If extrapolating the data vs $\ln N/(N)^{1/2}$, the value of $\langle R_h/R_g \rangle$ for large N will be 0.838 ± 0.015 and $\langle R_h^{-1} \rangle^{-1}/\langle R_g \rangle_{rms}$ will be 0.740 ± 0.02. Because the results of Fixman and Mansfield are based on the Kirkwood approximation for translational diffusion and because the discrepancies between two extrapolating schemes are within 5%, we chose to use the values extrapolated vs $1/(N)^{1/2}$ in order to compare with other results that are based on the same extrapolating scheme. The values from different theories and calculations are listed below:

K–R[1]	Zimm[2]	Zimm's Monte Carlo[9] extrapolated from $N = 50$	current calculation extrapolated from $N = 900$
0.66	0.67	0.78	0.79 $\langle R_h^{-1} \rangle^{-1}/\langle R_g \rangle_{rms}$, 0.87 $\langle R_h/R_g \rangle$

There are extensive measurements of R_h/R_g from light scattering. For polystyrene in Θ solvent the averaged value from measurement is 0.787 ± 0.06[8] while for PMMA in Θ solvent the value is around 0.86.[16] Compared to the measurement, our result, depending on average schemes, falls in the same range of the measured data of two types of polymers and thus gives a very good prediction. These data show that the calculation based on chains of random walk beads and the solution of the hydrodynamic interaction using the modified Oseen tensor can be a good model to describe the hydrodynamic radius of polymers in Θ solvent.

In order to compare with Zimm's result, we ran a test calculation for the same cluster by using the original Oseen tensor used by Zimm. The result is about 1% higher than the result obtained by the modified Oseen tensor for most cases (see Table II). This indicates that the different forms of the Oseen tensor will not cause a significant difference in calculating the hydrodynamic radius for lattice models. It is interesting to note that if we use the same average scheme as Zimm's calculation, i.e., the averaged R_h vs root-mean-square average of R_g, then the ratio from our calculation would be $\langle R_h \rangle/\langle R_g \rangle_{rms}$ 0.798 ± 0.02 which is quite close to Zimm's result of 0.78.[9] Thus we found that Zimm's Monte Carlo calculations, although they were limited to 50 segments, still gave a very good prediction.

Because of the limited computing time, our calculation is limited to 25 chains and the fluctuations are still quite significant. We note that the measurement data also have quite large fluctuations (for example, for polystyrene, the measured average value is 0.787 ± 0.06). Thus we are not going to search the detailed differences between our results and the measurement. As a general discussion we know that there are still two factors needed to be considered: first, the flexibility of the chains is neglected in our model; second, the detailed structures of segments may have sizable effects on the asymptotic value of R_h/R_g, though they still have a similar scaling behavior. As a small test of the second effect, we ran two separate calculations for two polymers with the same lattice configuration but with different monomer sizes: one type of monomer is represented by beads with a diameter equal to the lattice constant; the other type of monomer is represented by beads with a diameter equal to two-thirds of the lattice constant. The ratio of R_h/R_g of the second polymer is about 3% smaller than the first polymer (see Table III). Another effect related to both the structure and the rigidity is the internal friction discussed by Fixman.[10] He estimated that this effect seems to be within the order of 5%. Despite the simplicity of our model we are glad to see that the numerical results fall in the range of measured data.

In summary, our result shows that by avoiding preaveraging approximations numerical solutions give a better agreement with the measured data than Kirkwood and Zimm's theory for polymer chains. This result also is close to Zimm's Monte Carlo study based on 50 segments. These agreements confirm that the numerical method that sums up two-particle interactions (Oseen tensor) to calculate the hydrodynamic frictions gives a good prediction; thus the scheme used here can serve as a good method to calculate hydrodynamic properties of other more complicated aggregates such as various fractal clusters where the measurement is still lacking.[17]

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Thermal Analysis of the Volume Phase Transition with *N*-Isopropylacrylamide Gels

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ABSTRACT: Experimental work was done to study the thermoshrinking-type volume phase transition of *N*-isopropylacrylamide (NIPA) gel in aqueous solutions. The experiments principally consisted of the application of thermal analysis with a differential scanning calorimeter (DSC) to NIPA gels and to aqueous solutions of linear NIPA polymer (PNIPA) and poly(vinyl methyl ether) (PVME), whose gel is characteristic of the thermoshrinking type. The transition temperatures of NIPA gel obtained from DSC analysis were compared with those usually obtained from standard swelling experiments. This comparison clarified the efficiency of DSC for the determination of the transition temperature. For the linear polymer solutions, the transition temperatures obtained from DSC were satisfactorily consistent with their cloud points. Both the transition temperature and heat of the collapse of the NIPA gel showed similar values to those of the PNIPA solutions, which permitted the inference that the volume phase transition is controlled primarily by the same factors as the coil-globule transition of the linear polymer. The transition heat of collapse of the gel was endothermic and its absolute value was larger than those reported for nonpolar organic solution systems. Similar results were obtained with the linear polymer solutions. The experimental results were interpreted by using the concept of hydrophobic interaction. The addition of low molecular weight substances changed the transition temperature. This can be explained through the viscosity *B* coefficient.

I. Introduction

The volume phase transition of hydrogels[1] has been attracting much attention because of its technological and scientific importance. A gel can change in volume discontinuously as much as 1000-fold when surrounding conditions such as solvent composition,[2-4] salt concentration,[5] pH,[6] and temperature[1,3] vary continuously. With respect to temperature dependence, three types of phase transitions have been reported. The first is the thermoswelling type, or expansion with temperature;[1] the second is the thermoshrinking type, or collapse with temperature;[3] and the third is the "convexo" type, a mixture of the two types described above.[4]

It has been reported that the type of transition depends largely on the affinity of the monomers for water.[7] Therefore, for an explanation of temperature dependence, it would be important to consider the molecular structure of monomer units in a gel. Thermoswelling hydrogels mostly contain hydrophilic monomers such as acrylamide, acrylic acid, and methacrylic acid, and their transition can be explained by Tanaka's thermal mixing model.[1,3,4] On the other hand, the main examples of thermoshrinking hydrogels are composed of monomers like *N*-methylacrylamide, *N,N*-diethylacrylamide, and *N*-isopropylacrylamide (NIPA), whose hydrophobic substituents make them less hydrophilic. Transition in their cases cannot be precisely depicted by the Tanaka model.

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