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Hydrodynamic factors for linear and star polymers on lattice under the theta condition

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Abstract

Monte Carlo calculations were made to evaluate the intrinsic viscosity $[\eta]$ and hydrodynamic radius R_H along with the mean square radius of gyration $\langle S^2 \rangle$ for linear and star polymers with the arm number $f = 3$, 4, 6, and 8 on a simple cubic lattice. For the hydrodynamic calculation, Zimm's method based on the rigid-body approximation was used. The ensemble averages were taken according to the Boltzman factor with the contacting energy between segments, which was chosen to be 0.275 for the theta condition, multiplied by the number of contacts among the chain. The ratios $g_\eta \equiv [\eta]_\mathrm{star}/[\eta]_\mathrm{linear}$ and $g_\mathrm{H} \equiv (R_\mathrm{H})_\mathrm{star}/(R_\mathrm{H})_\mathrm{linear}$ calculated agreed with experimental data for theta solvent systems within 3.5 and 2.5%, respectively, where the subscripts describe the structure of polymer chain. The hydrodynamic factors Φ and ρ defined by $[\eta]M/(6\langle S^2 \rangle)^{3/2}$ and $\langle S^2 \rangle^{1/2}/R_\mathrm{H}$, respectively, with the molecular weight M obtained from the simulation for linear and star polymers with $f = 4$ and 6 were also close to experimental values. It was concluded that most of the error of analytical theories, which fail to predict hydrodynamic properties for star polymers, comes from the preaveraging approximation of the Oseen tensor.

Keywords: Monte Carlo calculation; Hydrodynamic property; Star polymer

1. Introduction

The intrinsic viscosity $[\eta]$ and the hydrodynamic radius R_H are basic hydrodynamic properties useful for characterizing polymer molecules in dilute solution. The hydrodynamic factors [1–3] $\Phi = [\eta]M/(6\langle S^2 \rangle)^{3/2}$ (the Flory–Fox factor [4]) and $\rho = \langle S^2 \rangle^{1/2}/R_\mathrm{H}$ relating to these properties are known to change with polymer architecture [5–8], where M is the molecular weight and $\langle S^2 \rangle$ the mean-square radius of gyration. Although it is important to establish the relationship between these factors and the branching structure of polymer, available theories for hydrodynamic properties fail to predict experimental results even for star polymers [9,10], which may be considered to have the simplest branched architecture.

These theories invoke some approximations in solving the hydrodynamic equation. Among the approximations, preaveraging of the Oseen hydrodynamic tensor is thought to cause serious errors in the results. For linear chains, the errors from the preaveraging Oseen tensor on Φ and ρ were estimated to be about 10% [11–14]. The theoretical errors seem much more serious for star polymers than those for linear polymers. The deviation of the theoretical values for the factors g_η ($\equiv [\eta]_\mathrm{star}/[\eta]_\mathrm{linear}$ at constant M) and g_H ($\equiv (R_\mathrm{H})_\mathrm{star}/(R_\mathrm{H})_\mathrm{linear}$ at constant M) based on the preaveraging approximation from the experimental values becomes larger [5–8] with increasing the number of arm f, where the subscripts, star and linear, show the type of polymer.

Zimm [14] showed that the Kirkwood–Riseman equation [15] can be solved without preaveraging the Oseen tensor to obtain the dimensionless intrinsic viscosity E (see Eq. (2) for the definition) and R_H, if the chain conformation is once determined by the Monte Carlo method, under the assumption that the conformation is not changed under the shear flow (the rigid-body approximation). Although this method was applied to star polymer systems [14,16], the values for Φ and ρ without preaveraging Oseen tensor are not established yet as functions of f.

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We made Monte Carlo calculations [17] to evaluate E and R_H for linear and star polymers on a simple cubic lattice in the self-avoiding condition according to Zimm's scheme. The resulted values for Φ and ρ extrapolated to the infinitely large segment number N were very close to the experimental values for good solvent systems to reach the conclusion that the preaveraging of the Oseen tensor causes the most of the error and that the rigid-body approximation is less serious. To confirm this, it is important to do similar calculations on polymers in the Θ condition to compare the results with the theoretical values for $[\eta]$ and R_H, which ignore the intramolecular excluded-volume effects.

In this paper, we evaluate E and R_H for linear and star polymers with $f = 3$, 4, 6, and 8 on a simple cubic lattice at the theta condition to determine the values of Φ and ρ without the preaveraging approximation as functions of f, which are compared with the theoretical and experimental values.

2. Calculation method

Self-avoiding linear and three-, four-, six-, and eight-arm star chains were generated on a simple cubic lattice by the enrichment algorithm [18,19], which enables us to produce star polymer samples efficiently. In this algorithm, the production of stars begins at a polyhedral core with f segments set on a simple cubic lattice. In the first step of the production, one segment is added to each segment on the core according to a pseudorandom number, to obtain a group of a large number of samples with the length of an arm being 1. In the next step, an appropriate number of samples are randomly chosen from the group and one more segment is added to each arm. This operation is repeated until another group of samples is made. After l steps, a group consisting of m_l polymers having arms with the length l is obtained for the calculation of physical quantities. At each step, all the polymers are checked to fulfil the self-avoiding condition and those which do not satisfy the condition are discarded. The sample number m_l was increased with increasing l and kept from 30,000 to 75,000.

For each sample, the number of contacts between non-bonding segments and $\langle S^2 \rangle$ were calculated. Then, the Kirkwood–Riseman equation [15] was solved according to the Zimm method [14] to obtain the velocity u_z (in the z direction) of the center of the mass and the dimensionless intrinsic viscosity E. The former is related to the hydrodynamic radius R_H by

$$R_H = F_z / 6\pi\eta_0 u_z \tag{1}$$

where F_z and η_0 are the force exerted on the polymer in the z-direction (set to be N) and the solvent viscosity (set to be 1), respectively. The latter is related to $[\eta]$ by

$$[\eta] = N_A N b^3 E / 2M \tag{2}$$

where M is the molecular weight, N_A the Avogadro constant, N, the number of segments in a molecule, and b is the bond length (set to be 1). Computations were made for the hydrodynamic radius a of each segment to be 0.25 and 0.5. Zimm [14] used the Oseen hydrodynamic tensor for the segment–segment distance r lager than the cross over value $R_c = 1.707a$ and used a constant tensor for $r < R_c$. However, in our calculation, we need not consider the latter case because R_c is smaller than 1 for both a values and r is always larger than 1. When $a = 0.5$, we sometimes (less than 1% of the results) obtained negative values of E. In such cases, the polymer chains took crumpled shapes. Probably, the hydrodynamic equation cannot be solved correctly for such polymer conformations. Those unphysical values were ignored.

To realize the theta condition on a lattice, it is essential to consider the interaction between segments which are placed on neighboring sites. Assuming the interaction energy $-\varepsilon$ for the contact of two segments, the total energy for the ith chain can be evaluated multiplying the number of intramolecular contacts by $-\varepsilon$. Then, the ensemble average of the quantity A ($\langle S^2 \rangle$, E, and u_z) was taken by

$$A = \sum_i A_i \exp(\varepsilon q_i / kT) / \sum_i \exp(\varepsilon q_i / kT) \tag{3}$$

with the aid of the Boltzman factor, where A_i is A for the ith chain, q_i the number of contacts among non-bonding segments in the chain, and kT has the usual meaning.

It is known that $\langle S^2 \rangle^{1/2}$ of lattice chains with $\varepsilon/kT = 0.275$ scales according to $N^{0.5}$ [20–22], as is that for the Gaussian chains. Janssens and Bellemans [23] calculated the second virial coefficient A_2 for linear chains on a simple cubic lattice and found that A_2 for the infinite segment number vanishes by choosing $\varepsilon/kT = 0.27$, which essentially agrees with the value determined from $\langle S^2 \rangle^{1/2}$. Then, we use $\varepsilon/kT = 0.275$ as the Θ condition for the present calculation.

3. Results and discussion

Fig. 1 shows the plots of $\langle S^2 \rangle / N$ against N for different f. It can be seen that $\langle S^2 \rangle / N$ for linear chains ($f = 2$) increases with N and approaching 0.33, as was observed by Bruns [24]. This can be regarded as the non-Gaussian behavior until the polymer reaches the asymptotic behavior. On the other hand, $\langle S^2 \rangle / N$ of star polymers for each f is almost constant. This may be due to the cancellation of the non-Gaussian behavior and the core effect, which increases $\langle S^2 \rangle$ at small N. The values of $\langle S^2 \rangle / N$ for different f are given in the second column of Table 1. The factor g_S defined by $\langle S^2 \rangle_{\text{star}} / \langle S^2 \rangle_{\text{linear}}$ (at constant N) were calculated from these $\langle S^2 \rangle / N$ values to be 0.76, 0.61, 0.45, and 0.33 for $f = 3$, 4, 6, and 8, respectively. These g_S values obtained are close to those for star polymers with flexible arms (0.778, 0.625, 0.444, and 0.344 for $f = 3$, 4, 6 and 8, respectively)

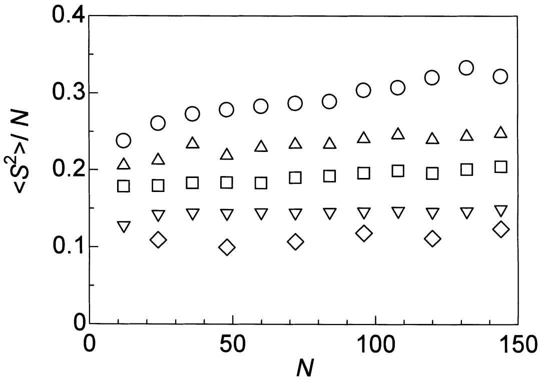

Fig. 1. Mean-square radii of gyration $\langle S^2\rangle$ divided by the segment number N for linear and star polymers on the simple cubic lattice with different arm number f plotted against N : circles, linear chain; triangles up, $f = 3$; squares, $f = 4$; triangles down, $f = 6$; diamonds, $f = 8$.

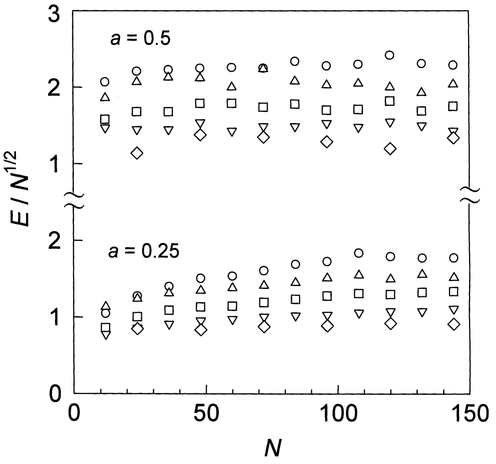

Fig. 2. Dimensionless intrinsic viscosities E divided by $N^{1/2}$ for linear and star polymers on the simple cubic lattice with different f plotted against N. Symbols are the same as those in Fig. 1.

calculated from the Zimm–Stockmayer equation [25]

$$g_S = (3f - 2)/f^2 \tag{4}$$

Then, we confirm that this simulation corresponds to the theta condition.

Fig. 2 represents $E/N^{1/2}$ plotted against N for $a = 0.5$ and 0.25. For $a = 0.5$, it is seen that the values for each f are almost constant regardless of N being consistent with the behavior of flexible polymers in the theta condition. However, for $a = 0.25$, $E/N^{1/2}$ at each f increases with N. It seems that larger segment number is needed for this a to observe the asymptotic behavior. The numerical results of $[\eta]$ based on Zimm's bead-spring model [26] also show that the segment number at which $[\eta]$ reaches its asymptotic behavior depends on a [27]. The values of $E/N^{1/2}$ at $a = 0.5$ for different f are given in the third column of Table 1. They enable us to calculate g_η, which is plotted against f (unfilled circles) in Fig. 3. We note that close values were obtained when we calculated g_η from $E/N^{1/2}$ for $a = 0.25$ at large N. The solid line in Fig. 3 indicates the calculated values from the Zimm–Kilb theory [9]

$$g_\eta = (2/f)^{3/2}[0.390(f - 1) + 0.196]/0.586 \tag{5}$$

which is based on the preaveraging approximation of the Oseen tensor. It can be seen that the theoretical values overestimate g_η as was already pointed out [5–8]. The values from the current simulation agree with the experimental values [6,8] represented by the filled symbols within 3.5%. The dashed line in the figure indicates the values from Roovers' empirical equation [6]

$$g_\eta = [(3f - 2)/f^2]^{0.58} \tag{6}$$

which describes the experimental data and our simulation values as well.

Table 1
Results of mean-square radius of gyration, dimensionless intrinsic viscosity, and hydrodynamic radius from the Monte Carlo calculations for $a = 0.5$

f	$\langle S^2\rangle/N$	$E/N^{1/2}$	$R_H/N^{1/2}$
2	0.33	2.3	0.45
3	0.25	2.0	0.44
4	0.20	1.7	0.43
6	0.15	1.5	0.41
8	0.11	1.3	0.38

Segment number dependence of $R_H/N^{1/2}$ for $a = 0.25$ and 0.5 is shown in Fig. 4. As is the case of E, the values for each f with $a = 0.5$ are almost constant, although those with $a = 0.25$ increase with N. The values of $R_H/N^{1/2}$ for $a = 0.5$ are given in the fourth column of Table 1, which allow us to calculate g_H. The g_H values for $a = 0.25$ estimated at large N essentially agree with those for $a = 0.5$. Plots of g_H against f are shown by the unfilled circles in Fig. 5, in which some experimental values [6,8] are indicated by the filled circles. The Monte Carlo values agree with the experimental values within 2.5% except the data for $f = 3$. The solid line in the figure shows the calculated values from the

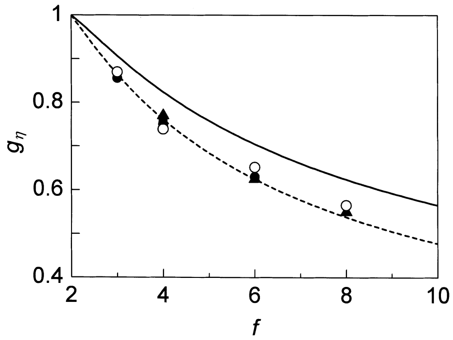

Fig. 3. Plots of g_η vs. f for star chains on a simple cubic lattice (unfilled circles). The other symbols represent experimental data [6,8] for theta solvent systems: filled circles, polystyrene in cyclohexane; filled triangles, polyisoprene in dioxane; filled squares, polybutadiene in dioxane. Solid and dashed lines indicate calculated values from Eqs (5) and (6), respectively.

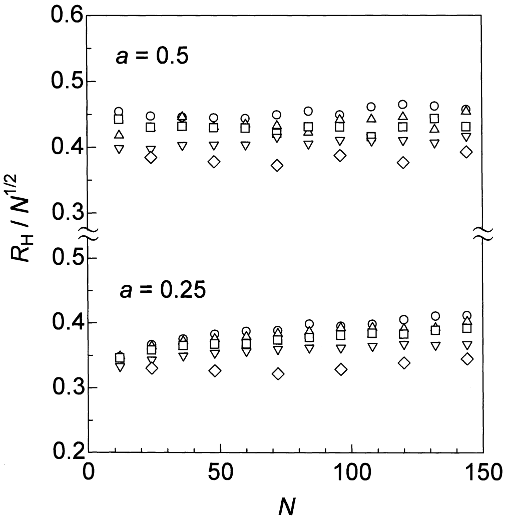

Fig. 4. Hydrodynamic radii R_H divided by $N^{1/2}$ for linear and star polymers on the simple cubic lattice with different f plotted against N. Symbols are the same as those in Fig. 1.

Stockmayer and Fixman equation [10]

$$g_H = f^{1/2}/[2 - f + 2^{1/2}(f - 1)] \tag{7}$$

which is based on the preaveraging approximation. The theoretical curve is far below the current Monte Carlo values. On the other hand, the Roovers empirical equation [6]

$$g_H = f^{1/4}/[2 - f + 2^{1/2}(f - 1)]^{1/2} \tag{8}$$

fits the Monte Carlo and experimental values very well as is shown by the dashed line in the figure.

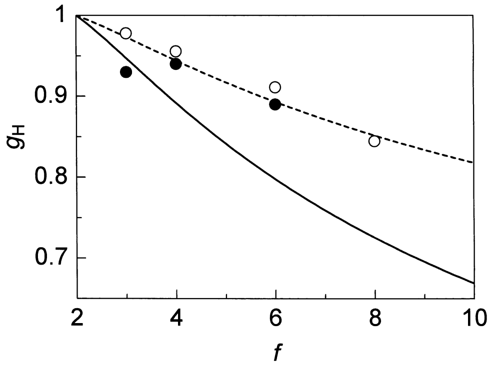

Fig. 5. Plots of g_H vs. f for star chains on a simple cubic lattice. Symbols are the same as those in Fig. 3. Solid and dashed lines indicate calculated values from Eqs. (7) and (8), respectively.

Table 2
Φ and ρ obtained from the Monte Carlo calculations compared with values for the preaveraged theories

f	$\Phi/10^{23}$ mol^{-1}		ρ	
	Monte Carlo	Theoretical	Monte Carlo	Theoretical
2	2.5	2.87	1.28	1.48
3	3.5	3.79	1.11	1.38
4	3.9	4.78	1.04	1.31
6	5.3	6.81	0.94	1.23
8	7.3	8.87	0.87	1.19

The values of Φ and ρ calculated from the values $E/N^{1/2}$ and $R_H/N^{1/2}$, respectively, along with $\langle S^2\rangle/N$ are summarized in Table 2. The table also contains the preaveraging-approximation values evaluated from $\Phi_{\text{star}} = \Phi_{\text{linear}}(g_\eta/g_S^{3/2})$ and $\rho_{\text{star}} = \rho_{\text{linear}}(g_S^{1/2}/g_H)$ with Eqs. (4), (5) and (7) and the original Kirkwood–Riseman values [1] of $\Phi_{\text{linear}} = 2.87 \times 10^{23}$ mol^{-1} and $\rho_{\text{linear}} = 1.48$. For $f = 2$, the value of Φ by the simulation is about 13% larger and that of ρ is about 14% smaller than the theoretical value being consistent with the results of Zimm [14].

For both Φ and ρ, difference between the values from the preaveraged theories and those from the simulation increases with increasing f. Freire et al. [16] made similar calculations on linear and star polymers with Gaussian arms according to the rigid-body approximation (called upper bound calculation) and obtained $\Phi/10^{23}$ mol^{-1} = 2.54 (for $f = 2$) and 4.9 (for $f = 6$) and $\rho = 1.27$ (for $f = 2$) and 0.98 (for $f = 6$) in the limit of $N \to \infty$. Their values are quite close to our results. They also made another calculation [28] (called lower bound calculation) based on Fixman's method [29] without using the rigid-body approximation. They obtained $\Phi/10^{23}$ mol^{-1} = 2.54 for linear flexible chains whose segments interact with the Lennard-Jones potential. However, their value of $\Phi/10^{23}$ mol^{-1} = 2.15 in the same paper for the non-interacting linear Gaussian chain is too small compared to experimental values for flexible polymers in theta solvents.

In comparison with linear polymers, Φ and ρ for star polymers in the theta state are as yet investigated very much neither experimentally nor theoretically. Experimental values [30–38] in theta solvents are summarized in Table 3. The literature values of Φ for star-polystyrene (PS) in cyclohexane (CH) with $f = 3$ and 4 are around 3.0 and 3.7 (except Berry's old data [31]), respectively, which are close to our Monte Carlo results. Values of Roovers and Bywater [32] for six-arm PS in CH are close to the Monte Carlo

Table 3
Experimental values of Φ and ρ for star polymers with f arms in theta solvents

f	System	$\Phi/10^{23}$ mol^{-1}	ρ	No. of samples	References
3	PS/CH	3.0	–	4	[30]
3	PS/CH	–	1.13	2	[38]
4	PS/CH	4.6	–	1	[31]
4	PS/CH	3.7	1.09	3	[32,33]
4	PS/CH	3.7	–	4	[34]
4	PIP/Diox	3.6	–	3	[35]
6	PS/CH	5.4	–	3	[32]
6	PS/CH	4.4	–	4	[36]
6	PIP/Diox	4.9	–	3	[35]
6	PS/CH	–	0.92	1	[33]
8	PS/CH	4.6	–	5	[37]

value, although they are somewhat larger than the values of Okumoto et al. [36] for PS in CH and Hadjichristidis and Roovers [35] for polyisoprene (PIP) in Dioxiane (Diox). The experimental value of Bauer et al. [37] for eight-arm star PIP in Diox seems rather small. The values for ρ in Table 3 are quite close to our Monte Carlo values.

In conclusion, our hydrodynamic calculations using the Zimm method based on the rigid-body approximation gave very close values of Φ and ρ to the experimental ones for star polymers in theta solvents, although theories invoking the preaveraging approximation give values far from the experimental values. This shows that the preaveraging approximation of the Oseen tensor made most of the error on these hydrodynamic factors and that the error from the rigid-body approximation is minor. Theories of Φ and ρ for star polymers without invoking the preaveraging approximation have not been submitted yet and are eagerly desired.

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