Effects of Fluctuating Hydrodynamic Interaction on the Hydrodynamic-Radius Expansion Factor of Polymer Chains

Hiromi Yamakawa* and Takenao Yoshizaki

Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan

Received December 30, 1994; Revised Manuscript Received March 13, 1995[⊗]

ABSTRACT: The effect of fluctuating (nonpreaveraged) hydrodynamic interaction (HI) on the hydrodynamic-radius expansion factor α_H for the Gaussian chain with excluded volume is theoretically examined in the uniform-expansion approximation within the framework of the theory previously developed for the unperturbed Gaussian chain with fluctuating HI. It is shown that α_H may be given by the product of the Zimm hydrodynamic-radius expansion factor $\alpha_H^{(Z)}$ and a newly introduced factor, which represents the present effect of fluctuating HI on α_H and is generally smaller than unity. Thus it is concluded that the fluctuating HI decreases α_H from $\alpha_H^{(Z)}$. An approximate interpolation formula for α_H is also constructed as a function of the conventional excluded-volume parameter z and is completed by replacing z by the scaled excluded-volume parameter $\tilde{z}$ in the quasi-two-parameter scheme.

I. Introduction

In a series of recent experimental work on the excluded-volume effects in dilute solutions of oligomers and polymers,[1] it has been found that the effects of chain stiffness on the gyration- and viscosity-radius expansion factors α_S and α_η remain large for such large molecular weight M where the ratio of the unperturbed mean-square radius of gyration $\langle S^2\rangle_0$ to M already reaches its coil-limiting value independent of M.[1–5] It has then been shown that such behavior of α_S and α_n, which is inconsistent with the conventional two-parameter theory prediction, may be well explained in the quasi-two-parameter scheme. This scheme assumes that α_S and α_H are functions only of the scaled excluded-volume parameter $\tilde{z}$ (instead of the conventional z), which is defined to become asymptotically identical with z in the Yamakawa–Stockmayer–Shimada theory[6–8] that takes account of the effects of excluded volume and chain stiffness on the basis of the helical wormlike (HW) chain.[9,10] We are now in a position to proceed to examine whether the new scheme is or is not valid for another expansion factor, i.e., the one, which we designate by α_H, for the hydrodynamic radius R_H determined from the translational diffusion coefficient D.

However, there still remains a theoretical problem to be resolved even within the framework of the theory for flexible (Gaussian) chains prior to an experimental study of α_H. Historically, the problem was first presented by Zimm,[11] who showed that the Kirkwood–Riseman–Zimm values[12–14] of the ratio ϱ_0 of $\langle S^2\rangle_0^{1/2}$ to $R_{H,0}$ and of the Flory–Fox factor Φ_0 as defined as the ratio of the (molar) hydrodynamic volume defined from the intrinsic viscosity $[\eta]_0$ to $\langle S^2\rangle_0^{3/2}$ for long unperturbed flexible (Gaussian) chains (without excluded volume) are about 13 and 12% too high, respectively, based on his Monte Carlo evaluation of D_0 and $[\eta]_0$ with fluctuating (nonpreaveraged) hydrodynamic interaction (HI) in the rigid-body ensemble approximation. (Here and hereafter, the subscript 0 refers to the unperturbed value.) Subsequently, Fixman[15,16] has derived the decrease in ϱ_0 below the Kirkwood value 1.505, depending on the local structure and hence the stiffness of polymer chains, from the theoretical evaluation of D_0 at zero time with the fluctuating HI. We ourselves have also investigated[17] possible effects of the fluctuating HI on ϱ_0 by evaluating D_0 at an infinitely long time on the basis of the HW chain, including the Gaussian chain, with partially fluctuating (orientation-dependent) HI to find the decrease (not constant) in ϱ_0. It should however be noted that Fixman and Pyun[18,19] had already shown the possibility of the decrease in Φ_0 below the Kirkwood–Riseman value 2.862×10^{23} mol^{-1} by perturbation theory for Gaussian chains with fluctuating HI but that the nonuniversality of Φ_0 cannot be derived within the framework of our theory, although it has been experimentally found that neither ϱ_0 nor Φ_0 is a universal constant.[20] Thus it seems convincing that the fluctuating HI may also have an effect on α_H. The purpose of the present paper is to examine this effect.

Now recall the previous findings[2–5] that the data for α_η form a single composite curve irrespective of polymer–solvent systems when plotted against $\tilde{z}$ and that the curve may be approximately reproduced by the Barrett equation[21] (with $\tilde{z}$ in place of z). Thus, it may be expected that this is also the case with the corresponding Barrett equation[22] for α_H. From a preliminary analysis of literature data,[23–25] however, it has been found that the experimental values of α_H are appreciably smaller than those predicted by the Barrett equation. Indeed, this difference in the agreement with experiment between his theories of α_η and α_H is the motivation of the present investigation.

In the following paper,[26] we make an experimental study of α_H, taking atactic oligo- and polystyrenes as an example, and compare the results with the present theory.

II. Fluctuating Hydrodynamic Interaction

As mentioned in section I, it is evident that there must be effects of fluctuating HI on α_H, if any, even for (perturbed) Gaussian chains. Thus we first derive a two-parameter theoretical expression for α_H as a function of z for them with fluctuating HI and then simply replace z by the scaled excluded-volume parameter $\tilde{z}$ according to the quasi-two-parameter scheme. It is then convenient to begin by giving a brief summary of the previous results for D_0 for the unperturbed Gaussian chain with fluctuating HI.[17]

In the previous paper,[17] we first derived a length-coarse-grained kinetic equation for the Zimm center of resistance $\mathbf{R}_C$ of the (unperturbed) spring–bead model

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

0024-9297/95/2228-3604$09.00/0 © 1995 American Chemical Society

(Gaussian chain) composed of N identical springs of effective bond length a and of $N + 1$ identical beads, each with the translational friction coefficient $3\pi\eta_0 d$, with η_0 being the viscosity coefficient of the solvent and d being the effective hydrodynamic diameter of the bead, by projecting the diffusion equation in the $3(N + 1)$-dimensional full configurational space onto the 3-dimensional $\mathbf{R}_C$ space. Then, the memory term in the kinetic equation, which represents the coupling between the $\mathbf{R}_C$ space and its complementary one through the fluctuating HI, was evaluated in the limit of time $t \to \infty$, using the Oseen HI tensor (partially) preaveraged only over the magnitude of the vector distance between any two centers of beads with its orientational dependence being retained. (Recall that the Zimm center of resistance is the point $\mathbf{R}_C$ such that the space $\mathbf{R}_C$ is decoupled from its complementary space if the Oseen HI tensor is preaveraged.) Finally, an expression was derived for $D_0(t)$ in the limit of $t \to \infty$, which is the quantity of interest in usual experiments on it.

The result for D_0 may be written in the form

$$D_0 = D_0(\infty) = D_0^{(Z)}(1 - \delta_{1,0}) \qquad (1)$$

where $D_0^{(Z)}$ is the Zimm translational diffusion coefficient[14] given by

$$D_0^{(Z)} = k_B T\Gamma(5/4)/3\pi\Gamma(3/4)\eta_0\langle S^2\rangle_0^{1/2} \qquad \text{(Zimm)} \quad (2)$$

with k_B the Boltzmann constant, T the absolute temperature, Γ the gamma function, and $\delta_{1,0}$ representing the correction term due to the fluctuating HI and being a function of the reduced hydrodynamic thickness d/a of the chain (relative to the effective bond length). It is given by

$$\delta_{1,0}(d/a) = [(3/8)^{1/2}\Gamma(3/4)/\pi\Gamma(5/4)](d/a)N^{-1/2}\sum_{k=1}^{N} S_{0,k}(\lambda_{0,k}^{B})^{-1} \qquad (3)$$

where $\lambda_{0,k}^{B}$ is the kth diagonal element (multiplied by $3\pi\eta_0 d$) of the Fourier representation of the (unperturbed) diffusion matrix in the subspace complementary to the $\mathbf{R}_C$ space, and $S_{0,k}$ is given by

$$S_{0,k} = \frac{\pi a^2}{6}\sin^2\frac{\pi k}{2(N+1)}\sum_{\substack{p,p',q,q'=1\\ p\neq p',q\neq q'}}^{N} w_{p'}w_{q'}\cos\frac{\pi(p-{}^1\!/_2)k}{N+1}\times \cos\frac{\pi(q-{}^1\!/_2)k}{N+1}\langle R_{pp'}^{-1}\rangle_0\langle R_{qq'}^{-1}\rangle_0\langle P_2(\cos\gamma_{pp',qq'})\rangle_0 \qquad (4)$$

In eq 4, $R_{pp'}$ is the magnitude of the vector distance $\mathbf{R}_{pp'}$ from the center of the pth bead to that of the p'th one, P_2 is the Legendre polynomial, $\gamma_{pp',qq'}$ is the angle between the vectors $\mathbf{R}_{pp'}$ and $\mathbf{R}_{qq'}$, $\langle ...\rangle_0$ indicates an equilibrium average in the unperturbed state, and w_p ($p = 1, 2, ..., N + 1$) are the factors determined so that the sum of $w_p\mathbf{R}_p$ with $\mathbf{R}_p$, the vector position of the pth bead, may be identical with $\mathbf{R}_C$ under the condition that $\sum_p w_p = 1$. In practice, the factor w_p has been put

$$w_p = (N+1)^{-1} \qquad (5)$$

independently of p in the numerical evaluation of $S_{k,0}$.[17]

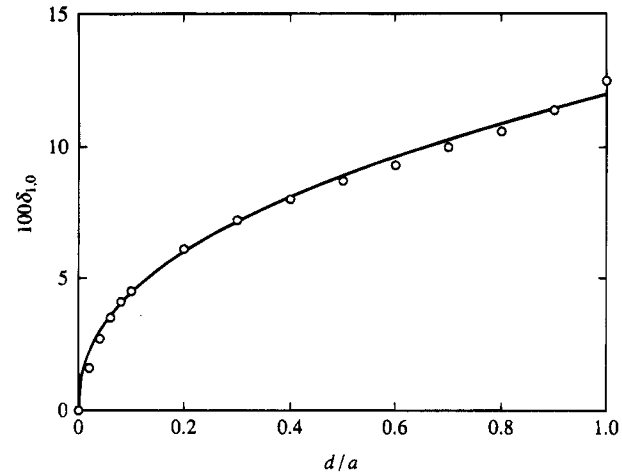

Figure 1. Plots of $\delta_{1,0}$ against d/a for the Gaussian chain. The unfilled circles represent the theoretical values and the solid curve represents the values calculated from the interpolation formula given by eq 6.

Table 1. Values of $\delta_{1,0}$ and ϱ_0 as a Function of the Reduced Hydrodynamic Thickness d/a

d/a	$\delta_{1,0}$	ϱ_0	d/a	$\delta_{1,0}$	ϱ_0
0	0	1.479	0.4	0.080	1.361
0.02	0.016	1.455	0.5	0.087	1.350
0.04	0.027	1.439	0.6	0.093	1.341
0.06	0.035	1.427	0.7	0.100	1.331
0.08	0.041	1.418	0.8	0.106	1.322
0.1	0.045	1.412	0.9	0.114	1.310
0.2	0.061	1.389	1.0	0.125	1.294
0.3	0.072	1.373			

As discussed previously[17] in some detail, the sum on the right-hand side of eq 3 multiplied by $N^{-1/2}$ converges on a finite value in the limit of $N \to \infty$, so that $\delta_{1,0}$ vanishes for $d/a = 0$. In the second and fifth columns of Table 1 are given the values of $\delta_{1,0}$ evaluated as a function of d/a in the limit of $N \to \infty$. We note that the values of $\delta_{1,0}$ for d/a = 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 have been reproduced from Table IV of ref 17, and the others (except for the trivial case of $d/a = 0$) have been evaluated by the same procedure as before,[17] i.e., by extrapolating the values calculated numerically for N = 99, 249, 499, and 999 (for each value of d/a) to $N^{-1/2} = 0$. In Figure 1, the values of $\delta_{1,0}$ given in Table 1 are plotted against d/a (unfilled circles). For later convenience, we have constructed an approximate interpolation formula for $\delta_{1,0}(d/a)$. The result reads

$$\delta_{1,0}(x) = 0.12x^{0.43} \qquad (0 \le x \le 1) \qquad (6)$$

In the figure, the solid curve represents the (approximate) values of $\delta_{1,0}$ calculated from eq 6. The error in the value of $\delta_{1,0}$ calculated from eq 6 does not exceed 4.2% for $0.06 \le x \le 1.0$. Although the errors for d/a = 0.04 and 0.02 are 11 and 39%, respectively, the approximate formula is good enough for our later use.

Now we consider the transport factor ϱ defined by

$$\varrho = \langle S^2\rangle^{1/2}/R_H \qquad (7)$$

where

$$R_H = k_B T/6\pi\eta_0 D \qquad (8)$$

Note that ϱ may be defined in both the unperturbed and perturbed states.

In the unperturbed state, we have from eqs 1 and 8

$$R_{H,0} = R_{H,0}^{(Z)}(1 - \delta_{1,0})^{-1} \quad (9)$$

where $R_{H,0}^{(Z)}$ is the Zimm hydrodynamic radius of the unperturbed Gaussian chain defined by

$$R_{H,0}^{(Z)} = k_B T/6\pi\eta_0 D_0^{(Z)} \quad (10)$$

with $D_0^{(Z)}$ given by eq 2. From eq 7 with eqs 1 and 8, we then have

$$\varrho_0 = \varrho_0^{(Z)}(1 - \delta_{1,0}) \quad (11)$$

where $\varrho_0^{(Z)}$ is the Zimm value of ϱ_0 and is given by

$$\varrho_0^{(Z)} = \langle S^2\rangle_0^{1/2}/R_{H,0}^{(Z)} = 2\Gamma(5/4)/\Gamma(3/4) = 1.479 \quad \text{(Zimm)} \quad (12)$$

In the third and sixth columns of Table 1 are given the values of ϱ_0 calculated from eq 11 with eq 12 and with the values of $\delta_{1,0}$ given in the second and fifth columns of the table. It is seen that ϱ_0 decreases from the Zimm value 1.479 to 1.294 as d/a is increased from 0 to 1 (corresponding to the touched-bead spring–bead model).

In the perturbed state, both $\langle S^2\rangle^{1/2}$ and R_H appearing in ϱ are generally larger than the respective unperturbed values $\langle S^2\rangle_0^{1/2}$ and $R_{H,0}$ because of the excluded-volume effect, as given by

$$\langle S^2\rangle = \langle S^2\rangle_0 \alpha_S^{\ 2} \quad (13)$$

$$R_H = R_{H,0}\alpha_H \quad (14)$$

so that we have

$$\varrho = \varrho_0 \alpha_S \alpha_H^{\ -1} \quad (15)$$

As in the unperturbed state, R_H may be factored into the Zimm hydrodynamic radius $R_H^{(Z)}$ without fluctuating HI and the correction for it, i.e.,

$$R_H = R_H^{(Z)}(1 - \delta_1)^{-1} \quad (16)$$

This is rather the defining equation for δ_1. From eq 14 with eqs 9 and 16, we have

$$\alpha_H = \alpha_H^{(Z)} f_H \quad (17)$$

where $\alpha_H^{(Z)}$ is the Zimm hydrodynamic-radius expansion factor defined by

$$\alpha_H^{(Z)} = R_H^{(Z)}/R_{H,0}^{(Z)} \quad (18)$$

and f_H is the factor representing the correction for the fluctuating HI and is given by

$$f_H = \frac{1 - \delta_{1,0}}{1 - \delta_1} \quad (19)$$

The factor $\alpha_H^{(Z)}$ may be evaluated following the Kirkwood–Riseman theory[12] without the approximation employed by them in the solution of the integral equation. Its first-order perturbation calculation has already been done with the result[27]

$$\alpha_H^{(Z)} = 1 + 0.593z - ... \quad (20)$$

where z is now defined by[6-8]

$$z = (3/2\pi)^{3/2}(\lambda B)(\lambda L)^{1/2} \quad (21)$$

with λ^{-1} the static stiffness parameter of the HW chain, B the excluded-volume strength (between beads), and L the total contour length of the chain, in the HW language. For later convenience, we also give the Kirkwood hydrodynamic-radius expansion factor $\alpha_H^{(K)}$ evaluated from the Kirkwood general formula for D.[13] Its first-order perturbation calculation has been carried out by Stockmayer and Albrecht[28] with the result

$$\alpha_H^{(K)} = 1 + 0.609z - ... \quad (22)$$

Its asymptotic form in the limit of $z \to \infty$ has also been obtained by Barrett[22] as

$$\lim_{z\to\infty} \alpha_H^{(K)} = 1.13_6 z^{0.2} \quad (23)$$

In the next section, we evaluate f_H.

III. Uniform-Expansion Approximation

It is quite difficult to evaluate f_H, and hence δ_1, even for the Gaussian chain by considering explicitly excluded-volume interactions. For simplicity, therefore, we evaluate it in the uniform-expansion approximation,[29] which consists of scaling a by the factor α_S from the start.

Then, δ_1 may be written in the form

$$\delta_1 = \delta_{1,0}(d/\bar{a}) \quad (24)$$

where $\bar{a}$ is defined by

$$\bar{a} = a\alpha_S \quad (25)$$

It is seen from eq 24 with eq 25 that the effective reduced hydrodynamic thickness $d/\bar{a}$ is decreased by the expansion of the chain due to the excluded-volume effect. From eq 19 with eq 24, the factor f_H, which is eventually a function of α_S and d/a, may be written in the form

$$f_H(\alpha_S, d/a) = \frac{1 - \delta_{1,0}(d/a)}{1 - \delta_{1,0}(d/\bar{a})} \quad (26)$$

$\delta_{1,0}(x)$ is a monotonically increasing function of x (for $0 \le x \le 1$), as shown in section II, and therefore we have

$$f_H(\alpha_S, d/a) \le 1 \qquad \text{for } \alpha_S \ge 1 \quad (27)$$

We note that the (original) error in the value of $\delta_{1,0}$ calculated from eq 6 causes the (final) error in that of f_H which is at most only about one-tenth of the former since $\delta_{1,0}(x)$ varies from 0 to 0.12 at most for $0 \le x \le 1$ (see Table 1), so that the latter error does not exceed 1% over the whole range of x.

In Figure 2, the values of f_H calculated from eq 26 with eqs 6 and 25 for d/a = 0.2, 0.5, and 1.0 are plotted against the logarithm of α_S. For d/a = 1, f_H decreases

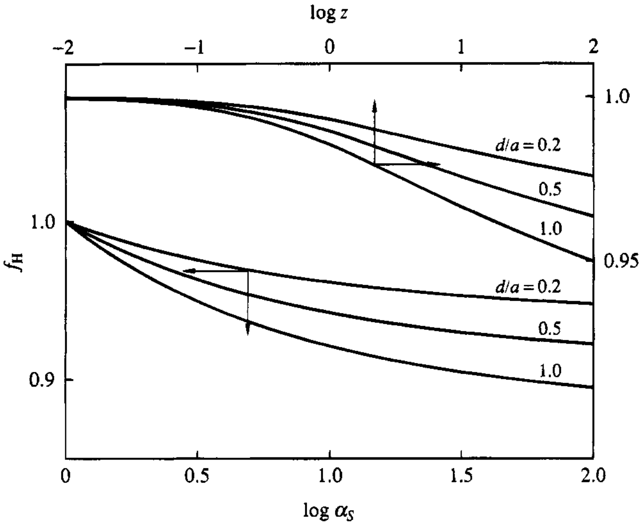

Figure 2. Plots of f_H against log α_S and log z for the values of d/a indicated.

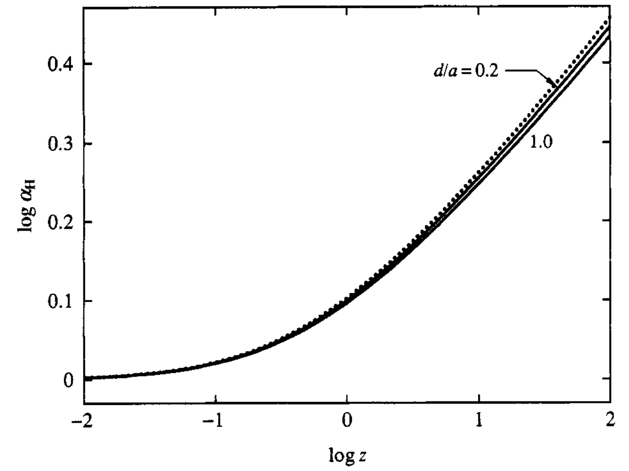

Figure 3. Double-logarithmic plots of α_H against z. The solid curves represent the values calculated from eq 17 for the values of d/a indicated and the dotted curve represents the Barrett values of $\alpha_H^{(Z)}$ calculated from eq 31.

monotonically from 1 to 0.88 as α_S is increased from 0 to infinity. The change in f_H becomes small as d/a is decreased.

IV. Approximate Formula

By the use of the expression for f_H derived in section III, we may calculate α_H as a function of z for the perturbed Gaussian chain, adopting proper expressions for α_S and $\alpha_H^{(Z)}$.

As in the previous studies,[1-5] we use the Domb–Barrett equation for α_S,[30] i.e.,

$$\alpha_S^2 = [1 + 10z + (70\pi/9 + 10/3)z^2 + 8\pi^{3/2}z^3]^{2/15} \times [0.933 + 0.067 \exp(-0.85z - 1.39z^2)] \quad (28)$$

We note that although this equation has been constructed to give the first- and second-order perturbation coefficients, 1.276 and 2.082, and also the asymptotic form[30]

$$\lim_{z\to\infty} \alpha_S^2 = 1.548z^{2/5} \quad (29)$$

it cannot give the exact second-order perturbation coefficient but only its approximate value 2.220. Then f_H as a function of z is given by eq 26 with eqs 6, 25, and 28. For small z, it may be expanded as

$$f_H = 1 - \frac{0.033(d/a)^{0.43}}{1 - 0.12(d/a)^{0.43}}z + \ldots \quad (30)$$

Thus the first-order perturbation coefficient of α_H becomes somewhat smaller than that of $\alpha_H^{(Z)}$. In Figure 2, the values of f_H calculated from eq 26 with eqs 6, 25, and 28 for $d/a = 0.2$, 0.5, and 1.0 are also plotted against the logarithm of z.

As for $\alpha_H^{(Z)}$, we use the Barrett equation,[22]

$$\alpha_H^{(Z)} = (1 + 6.09z + 3.59z^2)^{0.1} \quad (31)$$

Strictly, this α_H does not correspond to the Zimm $\alpha_H^{(Z)}$ but to the Kirkwood $\alpha_H^{(K)}$, since eq 31 has been constructed by interpolation from the first-order perturbation solution given by eq 22 and the asymptotic form given by eq 23. As seen from eqs 20 and 22, however, the difference between the first-order perturbation coefficients for $\alpha_H^{(Z)}$ and $\alpha_H^{(K)}$ is very small, the latter being 2.7% larger than the former. Furthermore, we have calculated numerically the coefficients in the asymptotic forms of $\alpha_H^{(Z)}$ and $\alpha_H^{(K)}$ to be 1.16_4 and 1.16_9, respectively, and have confirmed that the difference between $\alpha_H^{(Z)}$ and $\alpha_H^{(K)}$ in the limit of $z \to \infty$ is also negligibly small. (We note that the minor difference between the original Barrett value 1.13_6 in eq 23 and the above value 1.16_9 may be regarded as arising from that between the numerical-integration procedures used by Barrett[22] and us.) Thus it is not necessary to distinguish between $\alpha_H^{(Z)}$ and $\alpha_H^{(K)}$ in a practical sense. This is the reason why we have adopted the Barrett equation as an expression for $\alpha_H^{(Z)}$.

Then, the desired approximate formula for α_H is given by eq 17, where the factor $\alpha_H^{(Z)}$ is given by eq 31 and the factor f_H is given by eq 26 with eqs 6, 25, and 28. In Figure 3, the values of α_H thus calculated for $d/a = 0.2$ and 1.0 are plotted double-logarithmically against z. In the figure, the dotted curve represents the values calculated from $\alpha_H = \alpha_H^{(Z)}$ (with $f_H = 1$).

Finally, the above formulas are completed by the replacement of z by $\tilde{z}$ in the quasi-two-parameter scheme, as mentioned at the beginning of section II.

V. Discussion

As shown in section II, if the effect of fluctuating HI is taken into account within the framework of our theory previously[17] developed, the hydrodynamic-radius expansion factor α_H for the Gaussian chain may be given by the Zimm hydrodynamic-radius expansion factor $\alpha_H^{(Z)}$ multiplied by the newly introduced factor f_H, which represents the present effect on the excluded-volume interaction. Then, in section III, f_H has been shown to be generally smaller than unity, so that α_H is smaller than $\alpha_H^{(Z)}$. This may be regarded as arising from the fact that the increase in the hydrodynamic radius from the Zimm value due to the fluctuating HI is smaller for the perturbed chain than for the unperturbed chain, since the effective reduced hydrodynamic thickness is smaller for the former than for the latter.

The present result implies that the plot of α_H against $\tilde{z}$ depends on the unperturbed reduced hydrodynamic thickness d/a if z is replaced by $\tilde{z}$ according to the quasi-two-parameter scheme. However, this dependence is too small to detect in the present experimental accuracy. Thus the quasi-two-parameter theory may be considered to be valid also for α_H, which is then actually a function of $\tilde{z}$. In a comparison of the present theory with experiment made in the following paper,[26] we adopt the value 1.0 of d/a, for convenience, since it then gives the value 1.294 of ϱ_0 which is close to the observed values 1.26–1.29.[20] In anticipation of the comparison, however, we here only note that $\delta_{1,0}$, i.e., the decrease in α_H from $\alpha_H^{(Z)}$ may probably be underestimated since the HI tensor has been partially preaveraged.

Finally, it should be noted that the effect of fluctuating HI considered in the present paper is not the draining effect, since for small hydrodynamic thickness the former effect becomes vanishingly small, while the latter becomes significant.

References and Notes

(1) Abe, F.; Einaga, Y.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1993**, *26*, 1884 and succeeding papers.
(2) Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1993**, *26*, 1891.
(3) Horita, K.; Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1993**, *26*, 5067.
(4) Abe, F.; Horita, K.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1994**, *27*, 725.
(5) Kamijo, M.; Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1995**, *28*, 1095.
(6) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972**, *57*, 2843.
(7) Yamakawa, H.; Shimada, J. *J. Chem. Phys.* **1985**, *83*, 2607.
(8) Shimada, J.; Yamakawa, H. *J. Chem. Phys.* **1986**, *85*, 591.
(9) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1984**, *35*, 23.
(10) Yamakawa, H. In *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*; Nagasawa, M., Ed.; Elsevier: Amsterdam, 1988; p 21.
(11) Zimm, B. H. *Macromolecules* **1980**, *24*, 592.
(12) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(13) Kirkwood, J. G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 649; *J. Polym. Sci.* **1954**, *12*, 1.
(14) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(15) Fixman, M. *J. Chem. Phys.* **1984**, *80*, 6324; **1986**, *84*, 4085.
(16) Fixman, M. *Faraday Discuss.* **1987**, *No. 83*, 199; *J. Chem. Phys.* **1988**, *89*, 2442.
(17) Yamakawa, H.; Yoshizaki, T. *J. Chem. Phys.* **1989**, *91*, 7900.
(18) Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3831.
(19) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3838.
(20) Konishi, T.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1991**, *24*, 5614.
(21) Barrett, A. J. *Macromolecules* **1984**, *17*, 1566.
(22) Barrett, A. J. *Macromolecules* **1984**, *17*, 1561.
(23) Varma, B. K.; Fujita, Y.; Takahashi, M.; Nose, T. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1781.
(24) Tsunashima, Y.; Hirata, M.; Nemoto, N.; Kurata, M. *Macromolecules* **1988**, *21*, 1107.
(25) Fetters, L. J.; Hadjichristidis, N.; Lindner, J. S.; Mays, J. W.; Wilson, W. W. *Macromolecules* **1991**, *24*, 3127.
(26) Arai, T.; Abe, F.; Yoshizaki, T.; Einaga, Y.; Yamakawa, H. *Macromolecules*, following paper in this issue.
(27) Shimada, J.; Yamakawa, H. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1927.
(28) Stockmayer, W. H.; Albrecht, A. C. *J. Polym. Sci.* **1958**, *32*, 215.
(29) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(30) Domb, C.; Barrett, A. J. *Polymer* **1976**, *17*, 179.

MA946526J