Viscosity Constant in the Zimm Version

Takenao Yoshizaki and Hiromi Yamakawa*

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

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ABSTRACT: It is shown that for flexible chains without excluded volume in the nondraining limit, the Fixman–Pyun perturbation theory of the intrinsic viscosity with the Oseen tensor preaveraged can provide precisely lower bounds for the viscosity constant Φ_0 in the Zimm version. Evaluation is carried out through the third-order perturbation term with the result $\Phi_0 > 2.856 \times 10^{23}$. The difference between the Φ_0 in the Zimm version and the Auer–Gardner value of 2.862×10^{23} in the Kirkwood–Riseman version is therefore much smaller than expected.

It is well known that for the zero-frequency Newtonian intrinsic viscosity of polymer chains, almost the same predictions are obtained whether the Brownian motion of chain segments is explicitly considered or not. Indeed, for flexible chains without excluded volume in the nondraining limit, the Kirkwood–Riseman theory[1] without explicit consideration of the Brownian motion gives the value of 2.862×10^{23} for the viscosity constant Φ_0, as evaluated by Auer and Gardner,[2] while the Zimm theory[3] with its consideration gives the value of 2.84×10^{23} for the corresponding constant.[4] This difference may be regarded as arising only from the fact that the center of resistance is fixed in the latter instead of the center of mass as in the former, the Oseen hydrodynamic interaction tensor being preaveraged in both cases. However, the Zimm value[4] is not exact within its own framework,[3] though it must be a good approximation. The object of this paper is to reevaluate Φ_0 in the Zimm version.

Recently, Wang and Zimm[5] have reevaluated Zimm's eigenvalues through the first-order perturbation term as in the original evaluation. This leads to $10^{-23}\Phi_0 = 2.843$. However, it is difficult to have an insight into the successive-approximation scheme of this perturbation method.[4] In the present paper, we show that the Fixman–Pyun perturbation theory[6,7] can provide precisely lower bounds for the Φ_0 in the Zimm version and evaluate it through the third-order perturbation term by this alternative method.

Formulation

We formulate the intrinsic viscosity $[\eta]$ of flexible chains without excluded volume in the nondraining limit on the basis of the Fixman–Pyun theory[6,7] with the Oseen tensor preaveraged. Consider the spring-bead model composed of n springs and $n+1$ beads, each spring having root-mean-square length a and each bead having a friction constant ζ in a solvent with viscosity coefficient η_0. Let $\mathbf{R}_i$ be the Cartesian coordinates of the ith bead ($i = 0, 1, 2, \ldots, n$), and let $\{\mathbf{R}_{n+1}\}$ be the set of coordinates $\mathbf{R}_0, \mathbf{R}_1, \ldots, \mathbf{R}_n$. We factor the distribution function $P(\{\mathbf{R}_{n+1}\},t)$ for the entire chain at time t as follows,

$$P(\{\mathbf{R}_{n+1}\},t) = P_0(\{\mathbf{R}_{n+1}\})\rho(\{\mathbf{R}_{n+1}\},t) \tag{1}$$

with P_0 the equilibrium distribution function,

$$P_0 = C\exp(-U/kT) \tag{2}$$

where U is the quadratic spring potential, C is the normalization constant, and kT has the usual meaning.

Now we introduce the nondraining, field-free, time-evolution operator $\mathcal{A}$ on ρ. In matrix notation, it reads

$$\mathcal{A} = -[\nabla^{\mathrm{T}} - (\nabla^{\mathrm{T}}U/kT)]\mathbf{D}\nabla \tag{3}$$

where ∇ is a column vector whose element is the differential operator ∇_i with respect to $\mathbf{R}_i$, ∇^{T} is its transpose, and $\mathbf{D}$ is the nondraining diffusion tensor, an $(n+1) \times (n+1)$ matrix. Its element is

$$\begin{aligned}\mathbf{D}_{ij} &= kT(1-\delta_{ij})\langle\mathbf{T}_{ij}\rangle \\ &= kT(1-\delta_{ij})\mathbf{I}/6^{1/2}\pi^{3/2}\eta_0 a|i-j|^{1/2}\end{aligned} \tag{4}$$

where the Oseen tensor $\mathbf{T}_{ij} \equiv \mathbf{T}(\mathbf{R}_i - \mathbf{R}_j)$ has been preaveraged with P_0 for the present purpose, δ_{ij} is the Kronecker δ, and $\mathbf{I}$ is the unit tensor. We also consider the free-draining operator $\mathcal{A}^0$, i.e., $\mathcal{A}$ with $kT\zeta^{-1}\delta_{ij}\mathbf{I}$ in place of $\mathbf{D}$.

The solutions of the eigenvalue problems for $\mathcal{A}^0$ and $\mathcal{A}$ are formally the same, the former having been solved by Pyun and Fixman.[7] If $\{\mathbf{R}_{n+1}\}$ are transformed to the normal coordinates $\{\xi_{n+1}\}$ with $\xi_i = (X_i, Y_i, Z_i)$, the eigenfunctions ψ_k of $\mathcal{A}^0$ or $\mathcal{A}$ are given by products of the Hermite polynomials (see also eq 17–21 of ref 8) with the eigenvalues λ_k,

$$\lambda_k = (3kT/a^2\zeta)\sum_{p=1}^{n}\lambda_p'[k(pX) + k(pY) + k(pZ)] \tag{5}$$

where $k(pX)$ is the degree of the Hermite polynomial for the X component of the pth mode. The $\{\xi_{n+1}\}$ are the free-draining or nondraining normal coordinates and λ_p' are the Rouse or Zimm eigenvalues, as the case may be.

We choose as the basis set the free-draining eigenfunctions ψ_k of $\mathcal{A}^0$ to expand ρ as

$$\rho = 1 + \sum_{k\neq 0} f_k\psi_k \tag{6}$$

with

$$f_k = \int P_0\rho\psi_k\,\mathrm{d}\{\xi_n\} \tag{7}$$

where the simple translational mode ξ_0 has been excluded. Then, $[\eta]$ may be expressed in terms of f_k as

$$[\eta] = \frac{N_{\mathrm{A}}kT}{M\eta_0 g}\sum_{p=1}^{n} f_{(p)} \tag{8}$$

where N_{A} is the Avogadro number, M is the polymer molecular weight, g is the time-independent rate of shear, assuming that $\mathbf{v}^0 = (gy,0,0)$ for the unperturbed flow field, and the states (p) are those in which the X and Y components of one normal mode p are excited from the zeroth order to the first-order Hermite polynomial, the other component and all other modes being in their ground states. If A_{kl} is the matrix element of $\mathcal{A}$,

$$A_{kl} = \int P_0\psi_k\mathcal{A}\psi_l\,\mathrm{d}\{\xi_n\} \tag{9}$$

then the ratio $f_{(p)}/g$ in eq 8 is given by

$$\begin{aligned}\frac{f_{(p)}}{g} = \frac{1}{A_{(p)(p)}}\Bigg[1 &- \sum_{\substack{(l_1)\\(l_1)\neq(p)}}\frac{A_{(p)(l_1)}}{A_{(l_1)(l_1)}} + \sum_{\substack{l_1\ (l_2)\\(p)\neq l_1\neq(l_2)}}\frac{A_{(p)l_1}A_{l_1(l_2)}}{A_{l_1l_1}A_{(l_2)(l_2)}} - \ldots \\ &+ (-1)^m\sum_{l_1}\sum_{l_2}\cdots\sum_{l_{m-1}}\sum_{(l_m)}{}_{(p)\neq l_1\neq l_2\neq\ \ldots\ \neq(l_m)} \\ &\times\frac{A_{(p)l_1}A_{l_1l_2}A_{l_2l_3}\ldots A_{l_{m-1}(l_m)}}{A_{l_1l_1}A_{l_2l_2}\ldots A_{l_{m-1}l_{m-1}}A_{(l_m)(l_m)}} + \ldots\Bigg]\end{aligned} \tag{10}$$

Table I
Values of $F_1(p)$ for p = 1–30 and $F_2(p)$ and $F_3(p)$ for p = 1–20

p	$F_1(p) \times 10^2$	$F_2(p) \times 10^2$	$F_3(p) \times 10^3$	p	$F_1(p) \times 10^2$	$F_2(p) \times 10^2$	$F_3(p) \times 10^2$
1	1.659	0.289	0.103	16	0.261	0.076	0.034
2	0.902	0.178010.058	17	0.259	0.081	0.036	
3	1.435	0.269	0.093	18	0.233	0.069	0.032
4	0.799	0.168	0.054	19	0.232	0.073	0.034
5	0.877	0.221	0.069	20	0.211	0.063	0.030
6	0.610	0.147	0.050	21	0.210		
7	0.634	0.177	0.058	22	0.193		
8	0.485	0.127	0.048	23	0.191		
9	0.493	0.146	0.049	24	0.177		
10	0.400	0.111	0.042	25	0.176		
11	0.402	0.121	0.044	26	0.164		
12	0.340	0.095	0.039	27	0.163		
13	0.340	0.104	0.039	28	0.153		
14	0.295	0.085	0.036	29	0.151		
15	0.294	0.091	0.037	30	0.143		

If we choose as the basis set the nondraining eigenfunctions of $\mathcal{A}$, we obtain formally the same development as eq 10. In this case, however, the off-diagonal elements A_{kl} vanish, and we have, from eq 5, 9, and 10,

$$f_{(p)}/g = A_{(p)(p)}^{-1} = \lambda_{(p)}^{-1} = (a^2\zeta/6kT)\lambda_p'^{-1} \qquad (11)$$

with λ_p' the Zimm eigenvalues. Equation 8 with eq 11 gives the original Zimm theory result (in the nondraining limit). Since both basis sets give necessarily the same result, the $[\eta]$ in the Zimm version may also be evaluated from eq 8 with 10.

Now, the matrix element A_{kl} in eq 10 is generally found to be

$$\begin{aligned} A_{kl} = {} & (2^{5/2}kT/3n^{3/2}\eta_0)\left(\frac{3}{2\pi a^2}\right)^{3/2} \sum_p \sum_q \{\delta_{k(pX,-1),l(qX,-1)} \\ & \times [k(pX)l(qX)]^{1/2} + \delta_{k(pY,-1),l(qY,-1)}[k(pY)l(qY)]^{1/2} \\ & + \delta_{k(pZ,-1),l(qZ-1)}[k(pZ)l(qZ)]^{1/2}\} \times I(p,q) \qquad (12) \end{aligned}$$

where $k(pX,-1)$ is the abbreviation for the set of $3n$ numbers, $(k(1X), k(1Y), k(1Z), \ldots, k(pX) - 1, k(pY), k(pZ), \ldots)$, representing those states in which the excitation degree of the X component of one normal mode p is smaller than that of k by one, all other degrees being the same as those of k, and $\delta_{k(pX,-1),l(qX,-1)}$ is equal to unity if all the components of the set $k(pX,-1)$ are equal to the corresponding ones of $l(qX,-1)$, and otherwise it vanishes. $I(p,q)$ is defined by

$$\begin{aligned} & I(p,q) \\ & = (\pi/2)^{1/2}pq \int_0^\pi \mathrm{d}x \int_0^\pi \mathrm{d}y|x-y|^{-1/2} \cos(px)\cos(qy) \\ & = [1+(-1)^{p-q}]\pi pq[-p^{1/2}S(p\pi) \\ & \quad + q^{1/2}S(q\pi)]/(p^2-q^2), \quad \text{for } p \neq q \\ & = \pi p^{1/2}[\pi p C(p\pi) - \tfrac{1}{2}S(q\pi)], \quad \text{for } p = q \qquad (13) \end{aligned}$$

with C and S the Fresnel integrals,

$$C(x) = (2\pi)^{-1/2} \int_0^x t^{-1/2} \cos t \, \mathrm{d}t$$

$$S(x) = (2\pi)^{-1/2} \int_0^x t^{-1/2} \sin t \, \mathrm{d}t \qquad (14)$$

Thus we obtain for $[\eta]$

$$[\eta] = \Phi_0(na^2)^{3/2}/M \qquad (15)$$

where

$$\Phi_0 = \sum_{m=0}^{\infty} \Phi_0^{(m)} \qquad (16)$$

$$\Phi_0^{(m)} = (\pi^{3/2}N_A/4(3^{1/2})) \sum_{p=1}^{n} [I(p,p)]^{-1}F_m(p) \qquad (17)$$

$$F_m(p) = (-1)^{m+1} \sum_{\substack{l_1=1 \\ p \neq l_1 \neq l_2 \neq}}^{n} \sum_{l_2=1}^{n} \cdots \sum_{\substack{l_m=1 \\ \ldots \neq l_m \neq p}}^{n} \times \frac{I(p,l_1)I(l_1,l_2)\ldots I(l_{m-1},l_m)I(l_m,p)}{I(p,p)I(l_1,l_1)\ldots I(l_m,l_m)} \qquad (18)$$

with $F_0(p) \equiv 1$. Since we have preaveraged the Oseen tensor, the off-diagonal elements such as $A_{(p)(q)}$ and therefore the second term on the right of eq 10 vanish. Thus, the mth-order perturbation term $\Phi_0^{(m)}$ of Φ_0 results from the $(m+1)$th-order term of $f_{(p)}/g$. Further, we note that $I(p,p) > 0$ and $I(p,q) \leq 0$ for $p \neq q$, and therefore that $F_m(p) > 0$, so that $\Phi_0^{(m)} > 0$ for all m. In other words, the perturbation approximations to Φ_0, i.e., the finite sums of $\Phi_0^{(m)}$, give successively lower bounds for Φ_0. Note that the zeroth-order term $\Phi_0^{(0)}$ is just the Φ_0 in Hearst's version,[9] i.e., $10^{-23}\Phi_0^{(0)} = 2.8182$.

Numerical Results and Discussion

We evaluate Φ_0 numerically through the third-order perturbation term. To do this, we have calculated $F_1(p)$ for p = 1–30 and n = 200, 400, 800, and 1600, and $F_2(p)$ and $F_3(p)$ for p = 1–20 and n = 25, 50, 100, and 200 by the use of a FACOM 230-75 digital computer at this University. The values of $F_m(p)$ obtained for each m and p have been linearly extrapolated to $n = \infty$ by plotting $F_m(p)$ against $n^{-\alpha}$ with proper values of α. The results are summarized in Table I. The errors in $F_1(p)$ are within 1% for p = 1–30, and $F_2(p)$ and $F_3(p)$ are within 5% for p = 1–3 and within 10% for p = 4–20. In order to evaluate the sums over larger p in eq 17, the Euler–Maclaurin summation formula is used with the asymptotic forms of $F_m(p)$, which have been found, from Table I, to be

$$\begin{aligned} F_1(p) &= 0.0420p^{-1}, && \text{for odd } p \\ &= 0.0414p^{-1}, && \text{for even } p \quad (p \geq 31) \\ F_2(p) &= 0.0132p^{-1}, && (p \geq 21) \\ F_3(p) &= 0.00141p^{-1/2}, && (p \geq 21) \end{aligned} \qquad (19)$$

For F_2 and F_3, we have not distinguished between odd and even forms because of their relatively large errors. However, it suffices, since each contribution of the sum over $p \geq 21$ does not exceed 2% of the total sum.

The values of $\Phi_0^{(m)}$ thus obtained are given in Table II, including the Hearst value for $\Phi_0^{(0)}$. We therefore find

$$\Phi_0 > \sum_{m=0}^{3} \Phi_0^{(m)} = 2.856 \times 10^{23} \qquad (20)$$

Table II
Values of the Perturbation Terms of Φ_0

m	$\Phi_0^{(m)} \times 10^{-23}$
0	2.8182
1	0.0298
2	0.0056
3	0.0020

It is seen that the convergence of Φ_0 is rather good and that the difference between the Φ_0 in the Zimm version and the Auer–Gardner value of 2.862×10^{23} in the Kirkwood–Riseman version is much smaller than expected. This is a justification for the approximation that the center of mass is fixed conveniently instead of the center of resistance.[10]

References and Notes

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Rheological Studies on Concentrated Solutions of Poly(α-methylstyrene)

G. C. Berry,* B. L. Hager, and C.-P. Wong

Chemistry Department, Carnegie-Mellon University,
Pittsburgh, Pennsylvania 15213. *Received September 27, 1976*

ABSTRACT: A cone and plate rheometer has been used to study the creep and recovery of solutions of poly(α-methylstyrenes) over a range of shear stresses encompassing both linear and nonlinear viscoelastic response. The steady state viscosity η_κ and the recoverable compliance R_κ determined after steady state flow at shear rate κ are discussed in terms of the reduced rate of shear $\eta_0 R_0 \kappa$ (subscripts zero refer to the limit of small κ). A total strain criterion for the onset of nonlinear behavior in creep is found. It is observed that the recoverable compliance as a function of the time θ of recovery is independent of the shear stress over the range studied for reduced times of recovery $\theta/\eta_0 R_0$ less than 5. For longer times the recoverable compliance decreases with increasing shear stress.

In recent investigations in our laboratory[1,2] the steady state compliance of concentrated solutions of macromolecules has been studied over a range of κ for which the viscosity decreases markedly.[1,2] In those studies, the steady state recovery function R_κ was determined from the recovery $\gamma_{R,\sigma}(S,\theta)$ after creep under a shear stress σ for a time S as the limit

$$R_\kappa = \lim_{S,\theta\to\infty} R_\sigma(S,\theta) = \lim_{S,\theta\to\infty} \frac{\gamma_{R,\sigma}(S,\theta)}{\sigma} \qquad (1)$$

where θ is the time of recovery after cessation of steady state flow at a shear rate $\kappa = \sigma/\eta$ with η_κ the steady state viscosity. We denote the limiting value of R_κ for small σ by R_0; this quantity is often denoted simply as the steady state compliance J_e^{0}.[3] In this study we report similar rheological measurements on solutions of three poly(α-methylstyrene) polymers kindly provided by Professor Nagasawa (Nagoya University). The preparation and characterization of these polymers has been reported elsewhere, along with data on the shear stress and the first normal stress difference N_1 as functions of κ for concentrated solutions of the polymer in α-chloronaphthalene.[4] Of particular interest was a comparison of data on R_κ determined by recoil experiments with a quantity we will designate S_κ determined from the first normal stress difference measured in steady state flow:

$$S_\kappa = \left(\frac{N_1}{2\sigma^2}\right)_\kappa \qquad (2)$$

Of course, for a simple fluid,[5]

$$S_0 \equiv \lim_{\kappa=0} S_\kappa = R_0 \qquad (3)$$

but little is known about the more general relation between S_κ and R_κ for κ large enough, for example, so that η_κ decreases with increasing κ. Thus, it is convenient to maintain separate symbols for the parameters R_κ and S_κ.

Experimental Section

Polymers received from Professor Nagasawa designated as poly(α-methystyrene) samples PαS-9, -12, and -13 were each vacuum dried at room temperature for several days before use. They were then dissolved in methylene chloride at room temperature (about 1 g/dl) and sufficient reagent grade α-chloronaphthalene was added to each solution so that the desired concentration of polymer in α-chloronaphthalene would be obtained on evaporation of the methylene chloride. The methylene chloride solution was filtered and the methylene chloride was evaporated by passing filtered, dry nitrogen over the solution until it reached a constant weight. The concentration of the final solution was checked by a dry weight analysis in which an aliquot was redissolved in methylene chloride. The polymer was then quantitatively precipitated in methanol, washed with methanol, dried, and weighed.

A Waters Gel-Permeation Chromatograph was used to determine the elution profiles of each of the polymers studied here. The chromatograph has previously been calibrated to give $[\eta]M$ as a function of the elution volume V_e using a series of anionically prepared polystyrenes in tetrahydrofuran (THF). The poly(α-methylstyrene) samples were injected onto the column as 0.5 g/dl solutions in THF (0.5 ml injection volume).

Rheological data were obtained with a rotational rheometer described elsewhere.[1] The rheometer, which employs a drag-cup torque transducer and cone and plate platens, can be used to determine the creep, recovery, and steady state flow properties by methods discussed in detail in ref 1. In experiments described here, a cone with an angle of 2° and a radius of 1.89 cm was used throughout.