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Intrinsic Viscosity and Friction Coefficient of Flexible Polymers

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ABSTRACT: Padê approximants, assuming Flory's limiting exponent and utilizing the first-order perturbation results for the intrinsic viscosity $[\eta]$ and the friction coefficient f of a flexible polymer, are shown to agree well with experimental data over a wide range of the interaction parameter z. Based on these approximants, it is shown that the unperturbed dimension $\langle R^2\rangle_0$ and the polymer–solvent interaction parameter B can be estimated from viscosity or friction coefficient data in good solvents by a linear extrapolation of a plot of $([\eta]/M^{1/2})^{5/3}$ or $(f/\eta_0 M^{1/2})^5$ against $M^{1/2}$, where M is the polymer molecular weight and η_0 is the solvent viscosity coefficient. Values of $\langle R^2\rangle_0$ and B determined from viscosity plots are in good agreement with that of experiment and that from mean-square radii, respectively.

Introduction

In the previous paper,[1] we derived a new exact formula for the intrinsic viscosity of a chain polymer in steady-state Newtonian flow, and it was shown that in general an exact theory of the intrinsic viscosity requires the solution of a model-specific diffusion equation. However, practical methods to solve the diffusion equation are not yet available and in these circumstances some kind of approximation is necessary. We observed that for flexible polymers the preaveraging approximation[2] to the hydrodynamic interaction tensor is better than the approximation of rigid-body rotation around axes through the center of mass (which is exact for some symmetrical rigid bodies). In this paper we study the effect of excluded volume on the frictional properties of polymer chains with the use of the preaveraged hydrodynamic interaction tensor. In particular, our attention is directed to flexible polymers in good solvents, where the effect is large.

With the preaveraged hydrodynamic interaction tensor, the steady-flow intrinsic viscosity and the friction coefficient involve only equilibrium moments of the interaction tensor,[1-5] and the Kirkwood–Riseman theory[6] is exact for unperturbed chains without excluded volume. Thus, on the basis of this theory it is possible to develop perturbation calculations for excluded volume effects. But such series are useful only in a limited range, and it is difficult to evaluate higher terms. On the other hand, this difficulty can be sidestepped by assuming[7-12] that the mean-square distance $\langle R_{ij}^2\rangle$ between two segments, i and j, in a chain of N segments is the same as for a chain consisting of just $|j-i|$ segments, i.e., only a function of $|j-i|$. However, this assumption is in disagreement with perturbation calculations[13,14] and also with Monte Carlo data,[15,16] which show that $\langle R_{ij}^2\rangle$ depends on the positions of two segments in the chain contour. Therefore, for example, this assumption yields a value of 7.04 for a ratio of the mean-square end-to-end distance $\langle R^2\rangle$ to the mean-square radius $\langle S^2\rangle$ in the limit of long chains, which is considerably larger than the figure 6.4 estimated from lattice chain data;[15,17] further, it also predicts that near the Θ temperature the intrinsic viscosity of a flexible-ring polymer increases with excluded volume less rapidly than that of a linear chain with the same molecular weight[8] and contradicts the perturbation theory.[18-20] Ullman[21] recently modified this assumption by forcing $\langle R_{ij}^2\rangle$ to fit the first-order perturbation result. However, his procedure leads to a positive second-order correction and is thus inconsistent with second-order perturbation theory.[22] Agreement[9,10,21,23] between theory and experiment therefore does not necessarily mean that these assumptions are correct.

The perturbation series is asymptotic[24-27] but predicts[13,14] that $\langle R_{ij}^2\rangle$ is a function of i and j as well as $|j-i|$. In the limit of large excluded volume, the expansion factor α_R, defined by $\alpha_R^2 = \langle R^2\rangle/\langle R^2\rangle_0$, the ratio of the mean-square end-to-end distance of the chain to its unperturbed value $\langle R^2\rangle_0$, has the asymptotic form[2]

$$\lim_{z\to\infty} z^{-1}\alpha_R^{\nu} = \text{const} \tag{1}$$

where the excluded volume parameter z is defined by

$$z = \left(\frac{3}{2\pi\langle R^2\rangle_0}\right)^{3/2} N^2\beta \tag{2}$$

with β the binary cluster integral for a pair of segments. The exact value of the exponent is still somewhat uncertain,[28-30] but it is clear that the original Flory value,[31] $\nu = 5$, is quite accurate. Since the average segment density about the molecular center of mass reaches a limiting form for very long chains in very good solvents,[32] it is almost certain that any expansion factor retains the same limiting functional form as α_R.[33]

We desire an expansion factor for all positive values of z. For this purpose, therefore, we can construct a closed formula by applying the Padê approximant method,[34] utilizing the first few perturbation coefficients for the expansion factor α and assuming that $\nu = 5$. Stockmayer first proposed[35] this procedure for α_R, and subsequently the present author[36,37] studied it more extensively, including the expansion factor α_S for the radius of gyration and the second virial coefficient and comparing various approximants with experiment. The results showed that simple Padê approximants give good values over the entire range of positive z.

In this paper, it is shown that 5(1,1) approximants[36]

$$\alpha^5 = 1 + Cz \tag{3}$$

for expansion factors for viscosity and friction coefficient (Stokes) radii fit experimental data surprisingly well. On the basis of these results, new viscosity and friction coefficient plots are suggested for estimation of unperturbed dimensions and binary cluster integrals.

Expansion Factors

The intrinsic viscosity may be expressed in the form[2]

$$[\eta] = 6^{3/2}\Phi\frac{\langle S^2\rangle^{3/2}}{M} \tag{4}$$

where M is the polymer molecular weight and Φ is the Flory–Fox viscosity constant that in general depends on

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chain stiffness, excluded volume, and hydrodynamic draining. If $[\eta]_\Theta$ is the intrinsic viscosity of unperturbed chains, the cubed viscosity radius expansion factor α_η^3 is defined by

$$\alpha_\eta^3 \equiv [\eta]/[\eta]_\Theta = \Phi\alpha_S^3/\Phi_0 \tag{5}$$

The viscosity constant Φ_0 for unperturbed chains with hydrodynamic preaveraging is 2.862×10^{23} in the nondraining limit.[38] Experimentally, it is well-known that there is no draining effect on long unperturbed chains. For simplicity, therefore, we hereafter ignore possible draining effects also in perturbed chains with excluded volume. Then for flexible chains α_η^3 is a function only of z, and for small z

$$\alpha_\eta^3 = 1 + C_{1\eta}z - ... \qquad \text{(small } z\text{)} \tag{6}$$

where the coefficient $C_{1\eta}$ is a numerical constant.

Evaluation of $C_{1\eta}$ is not trivial, and earlier results have been only approximate. For example, Kurata and Yamakawa[14] obtained $C_{1\eta} = 1.55$ on the basis of the Kirkwood–Riseman theory. Fixman[39] applied boson-operator techniques to the Zimm–Hearst theory[40,41] but his predicted value of 1.80 is appreciably greater than the observed values;[42] subsequently, Yamakawa and Tanaka[43] attempted to introduce the excluded volume effect exactly into the Zimm–Hearst theory and obtained $C_{1\eta} = 1.06$, which is close to the experimental value. Finally, Fujita et al.[44] have shown that $C_{1\eta}$ can be rigorously calculated by the procedure of Auer and Gardner.[38] The result, after being corrected by Shimada and Yamakawa,[20] is $C_{1\eta} = 1.14$. Thus our Padé approximant for α_η is taken to be

$$\alpha_\eta^5 = 1 + 1.90z \tag{7}$$

By analogy with eq 4, the translational friction coefficient may be written as[2]

$$f/\eta_0 = 6^{1/2}P\langle S^2\rangle^{1/2} \tag{8}$$

and the corresponding expansion factor is defined as

$$\alpha_f \equiv (f/\eta_0)/(f/\eta_0)_\Theta = \alpha_S P/P_0 \tag{9}$$

$$= 1 + C_{1f}z - ... \qquad \text{for small } z \tag{10}$$

where η_0 is the solvent viscosity coefficient, P is the Flory–Mandelkern constant corresponding to Φ in the intrinsic viscosity, and the subscript Θ indicates the value for unperturbed chains. The Kirkwood–Riseman theory gives $P_0 = (3\pi/2)^{3/2}/2$ in the nondraining limit.

Approximate values of C_{1f} corresponding to the Kurata–Yamakawa[14] and Fixman[45] theories of the intrinsic viscosity are 0.416 and 0.415, respectively. The exact value of C_{1f} is known[46] to be 0.609. Therefore, we try the closed formula

$$\alpha_f^5 = 1 + 3.045z \tag{11}$$

Comparison with Experiment

We now compare eq 7 and 11 with experimental data. The expansion factors α_η^3 and α_f are evaluated as the ratios of observed values for perturbed chains to their values for unperturbed chains. On the other hand, the parameter β, or z, cannot be determined directly from solution experiments, and some device is necessary. Here we estimate z by one of the following three methods, depending on the experimental situation. The first method[37] is to evaluate z from observed values of α_S for real polymers in solution and the relation between α_S and z for self-avoiding lattice chains without short-range interactions. For lattice chains of this class the quantity β can be identified[47] as the volume per lattice point. The second method is to use empirical relations[42] between α_η^3 and z:

$$\alpha_\eta^3 = 1 + 1.05z \qquad \text{for } 0 < \alpha_\eta^3 < 1.6 \tag{12}$$

$$\alpha_\eta^3 = 1.05 + 0.87z \qquad \text{for } 0 < \alpha_\eta^3 < 2.5 \tag{13}$$

This method is applicable for relatively mild excluded volume conditions as indicated in eq 12 and 13. Finally, the parameter z can also be estimated from the temperature dependence of the second virial coefficient near the Θ temperature.[2] This method is strictly limited to the close neighborhood of the Θ point. It should be noted that eq 7 and 11 contain no adjustable parameters, once a value of z has been independently selected by one of the above three methods.

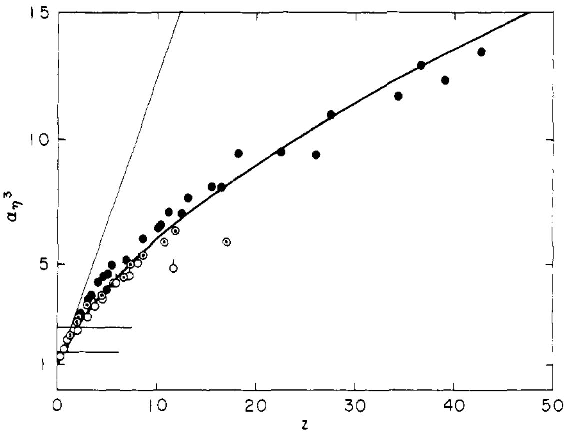

Figure 1. Plots of α_η^3 against z for poly(D-β-hydroxybutyrate) and poly(D-β-methyl-β-propiolactone-co-L-β-methyl-β-propiolactone) in trifluoroethanol at 25 °C (●), chloroform at 30 °C (⊙), ethylene dichloride at 30 °C (ȯ), and α-chloronaphthalene at 40 °C (○).[48-50] The solid curve and thin straight line are eq 7 and 6, respectively. The two thin horizontal lines indicate the upper bound below which eq 12 and 13 are valid.

In Figure 1 are plotted values of α_η^3 against values of z thus determined for poly(D-β-hydroxybutyrate) and poly(D-β-methyl-β-propiolactone-*co*-L-β-methyl-β-propiolactone) in various solvents at several temperatures, as reported by Fujita et al.[48-50] The solid curve and thin straight line represent eq 7 and the initial slope at $z = 0$, eq 6, respectively. Two horizontal thin lines indicate the upper bound below which eq 12 and 13 are valid, corresponding to $\alpha_\eta^3 = 1.6$ and 2.5, respectively. Agreement between theory and experiment is automatic in the region for $\alpha_\eta^3 < 2.5$ because here z was determined from eq 12 and 13. Even excluding this region from consideration, we can conclude that eq 7 fits the data surprisingly well over a wide range of z. Our treatment here neglects a possible draining effect. Very recently, Miyaki and Fujita[51] suggested the possibility of partial draining and chain stiffness effects on the intrinsic viscosity of these polymers. However, such effects are too small to be detected in Figure 1 and we do not comment further on this point.

Now the empirical eq 12 and 13 support a linear relationship between $[\eta]/M^{1/2}$ and $M^{1/2}$ for small values of z as first proposed by Burchard[52] and by Stockmayer and Fixman[33] to estimate the unperturbed dimensions and the binary cluster integral, or the polymer–solvent interaction parameter B, defined by

$$B = (N/M)^2\beta \tag{14}$$

But it is well-known[2] that the Burchard–Stockmayer–Fixman plot shows concave-downward curvature, particularly for good solvent systems, i.e., for large values of z. The weak curvature seen in Figure 1 corresponds to this fact, since the plot of α_η^3 against z is essentially equivalent

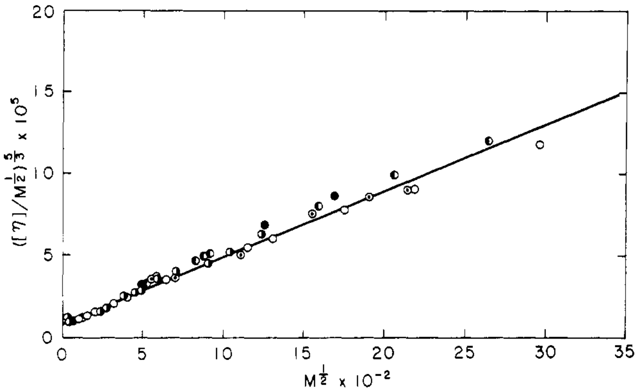

Figure 2. Plots of $([\eta]/M^{1/2})^{5/3}$ against $M^{1/2}$ for polystyrene in benzene at 25 and 30 °C. The symbols are as follows: (●) data of Yamamoto et al;[53] (○) data of Einaga et al.;[54] (◎) data of Fukuda et al.;[55] (◐) data of Krigbaum and Flory;[56] (◑) data of Altares et al.[57] The straight line is the best fit to the data.

to the Burchard–Stockmayer–Fixman plot. Such curvature will cause errors in the extrapolation to $M = 0$, even if nonlinear extrapolation is used, and unperturbed dimensions and binary cluster integrals obtained in this way are often unreliable. Equation 7, on the other hand, predicts that $([\eta]/M^{1/2})^{5/3}$, rather than $[\eta]/M^{1/2}$, should be linear in $M^{1/2}$:

$$([\eta]/M^{1/2})^{5/3} = K^{5/3} + 0.627\Phi_0^{5/3}(\langle R^2\rangle_0/M)BM^{1/2} \qquad (15)$$

with

$$K = \Phi_0(\langle R^2\rangle_0/M)^{3/2} \qquad (16)$$

Thus, graphically one can plot $([\eta]/M^{1/2})^{5/3}$ against $M^{1/2}$. As in the case of the Burchard–Stockmayer–Fixman plot, the intercept at $M = 0$ here yields the unperturbed dimensions and the slope is proportional to the interaction parameter B. This linearity is demonstrated in Figure 2 for data on polystyrene in benzene at 25 and 30 °C, published by various groups.[53-57] The straight line in the figure is the best linear fit to the data. We find $K = 8.75 \times 10^{-3}$ dL g$^{-3/2}$ mol$^{1/2}$ and $B = 2.94 \times 10^{-27}$ cm^3 g^{-2} mol^2. This estimated value of K is very close to the observed[53,55,58] one, $K = [\eta]_\Theta/M^{1/2} = 8.8 \times 10^{-3}$ dL g$^{-3/2}$ mol$^{1/2}$. Also the value of B is in good agreement with that calculated from mean-square radii.[53,58]

An extrapolation of $[\eta]/M^{1/2}$ against $M^{1/2}$ leads to erroneous values of unperturbed dimensions if the Mark–Houwink–Sakurada exponent $a = \mathrm{d}\log[\eta]/\mathrm{d}\log M$ is larger than 0.8 due to partial draining or chain stiffness or both.[35] An interesting feature of the present plot is that for most stiff chains, a plot of $([\eta]/M^{1/2})^{5/3}$ against $M^{1/2}$ gives a good straight line but the linear extrapolation to $M = 0$ yields a negative intercept, indicating inapplicability of the treatment to these polymers. In any case, it is highly advisable to supplement the viscosity data by other measurements, e.g., by measurements of radii of gyration.

We now proceed to test eq 11. In Figure 3, observed values of α_f are plotted against z for poly(α-methylstyrene) in toluene at 25 °C,[59-61] and in *trans*-decalin at 20 and 40 °C.[61] The solid curve represents the values calculated from eq 11. The thin line is the tangent $C_{1f} = 0.609$ to the curve at $z = 0$. Equation 11 may be regarded as fairly good, though it seems that eq 11 slightly overestimates α_f for $z > 4$.

Similar to eq 15, we have

$$(f/\eta_0 M^{1/2})^5 = K_f^5 + 1.00P_0^5(\langle R^2\rangle_0/M)^{7/2}BM^{1/2} \qquad (17)$$

with

$$K_f = P_0(\langle R^2\rangle_0/M)^{1/2} \qquad (18)$$

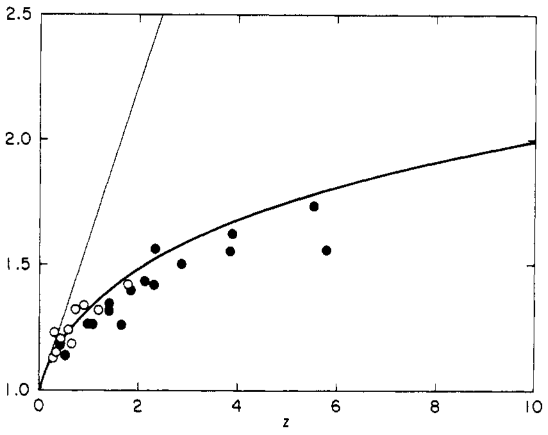

Figure 3. Plots of α_f against z for poly(α-methylstyrene) in toluene at 25 °C (●)[59-61] and *trans*-decalin at 20 and 40 °C (○).[61] The solid curve is eq 11 and the thin straight line is eq 10.

Thus, according to eq 17, the unperturbed dimensions and the polymer–solvent interaction parameter can also be obtained from the intercept and the slope for a plot of $(f/\eta_0 M^{1/2})^5$ against $M^{1/2}$. Since the intrinsic viscosity can in general be measured more accurately than the friction coefficient, eq 15 seems to be more useful than eq 17.

If eq 7 and 11 are combined with a Padé approximant[36] for α_S, the ratio $P/P_0 = \alpha_f/\alpha_S$ is very close to unity for all values of positive z, while the ratio $\Phi/\Phi_0 = \alpha_\eta^3/\alpha_S^3$ decreases sharply from unity for small values of z and then gradually reaches a nonzero asymptotic value. Such behavior of P/P_0 and Φ/Φ_0 is in good agreement with experimental results.[2,61] The relation $\alpha_\eta^3 = \alpha_S^2\alpha_f$ suggested by Weill and des Cloizeaux[62] leads to $P/P_0 = \Phi/\Phi_0$ and thus clearly conflicts with experiment.

Within the binary cluster approximation, the interaction free energy is represented by a pseudopotential proportional to β. When the parameter β is negative, the segments tend to attract each other to lower the free energy, and if β is much less than zero the polymer chain collapses.[47,63-66] It is necessary to introduce higher than pairwise short-range interaction terms[63-66] to prevent a prediction of collapse to a point. The binary cluster approximation is meaningful if the interaction energy is bounded[67] by

$$N^2\beta \geq -AN \qquad (19)$$

where A is a positive constant. Equation 19 leads to

$$z \geq z_{\min} = -\left(\frac{3}{2\pi a^2}\right)^{3/2} AN^{-1/2} \qquad (20)$$

Then $z_{\min}$ is inversely proportional to the square-root of the molecular weight, and, as the molecular weight increases, $z_{\min}$ approaches zero. When N is finite, $z_{\min}$ remains negative and thus the binary cluster approximation can be extended to small negative values of z. Experimentally, finite chains can be observed and their data may be compared with eq 7 and 11. At present, however, data for negative z are limited and we can compare only eq 11 with experiment. In Figure 4, observed values of α_f are plotted against $-(1 - \Theta/T)M^{1/2}$ for polystyrene in cyclohexane below Θ. These data were reported by Bauer and Ullman[68] and by Sun, Nishio, Swislow, and Tanaka.[69] Numerical values of eq 10 and 11 are shown by the thin straight line and the solid curve, respectively. In this calculation the temperature dependence of z is assumed to be

$$z = 6.25 \times 10^{-3}(1 - \Theta/T)M^{1/2} \qquad (21)$$

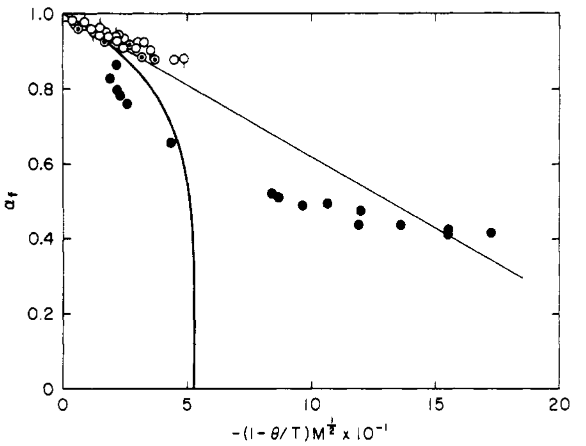

Figure 4. Plots of α_f against $(1 - \Theta/T)M^{1/2}$ for polystyrene in cyclohexane below Θ: all points except the solid circles (○, ϙ, ⊙, ȯ, -○) are from Bauer and Ullman[68] with $10^{-4}M = 4400$, 720, 220, 39, and 24, respectively; the solid circles (●) are from Sun et al.[69] with $10^{-4}M = 2600$. The solid curve is eq 11 and the thin straight line is eq 10.

based on the recent work by Miyaki and Fujita.[51] For $(1 - \Theta/T)M^{1/2} \le -25$, i.e., $z \le -0.15$, eq 10 and 11 compare favorably with experiment. Beyond this region, the data obtained by the two groups split into different directions, reflecting experimental difficulties. Further experimental studies are needed to settle this problem. In any case, it is clear that the binary cluster approximation can be extended to small values of negative z and that it predicts reasonably the observed initial behavior of a polymer chain before it collapses.

In summary, we see that simple 5(1,1) Padé approximants can usefully imitate the observed behavior of α_η and α_f for flexible polymers in good solvents. It should, however, be remembered that the present treatment implicitly assumes agreement between theory and experiment for unperturbed chains. Actually, there are some discrepancies. Observed values of Φ_0 are at least 10% smaller than the theoretical preaveraged one, and the experimental P_0 is about 15% larger[70] than the KR value (one exception is Nose and Chu's value of $P_0 = 4.64$,[23] which is nearly 10% smaller than the KR value; we note, however, that their value of $\langle S^2\rangle_0/M = 13.6 \times 10^{-18}$ (cm² mol)/g is about 50% larger than the best established figure). There is no consistent interpretation to solve these disagreements. Further studies are necessary.

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References and Notes

(1) Wilemski, G.; Tanaka, G. *Macromolecules* **1981**, *14*, 1531.
(2) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(3) Gotlib, Yu. Ya.; Svetlov, Yu. Ye. *Polym. Sci. USSR (Engl. Transl.)* **1966**, *8*, 1670.
(4) Stockmayer, W. H. *J. Phys. (Paris), Colloq.* **1971**, *5*, 255.
(5) Zimm, B. H. *Makromol. Chem., Suppl.* **1975**, *1*, 441.
(6) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(7) Peterlin, A. *J. Chem. Phys.* **1955**, *23*, 2464.
(8) Bloomfield, V. A.; Zimm, B. H. *J. Chem. Phys.* **1966**, *44*, 315.
(9) Benmouna, M.; Akcasu, A. Z. *Macromolecules* **1978**, *11*, 1187. *Ibid.* **1980**, *13*, 409.
(10) François, J.; Schwartz, T.; Weill, G. *Macromolecules* **1980**, *13*, 564.
(11) Akcasu, A. Z.; Benmouna, M.; Alkhafaji, S. *Macromolecules* **1981**, *14*, 147.
(12) Fujita, H.; Norisuye, T. *Macromolecules* **1981**, *14*, 1130.
(13) Kurata, M.; Yamakawa, H.; Teramoto, E. *J. Chem. Phys.* **1958**, *28*, 785.
(14) Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958**, *29*, 311.
(15) Wall, F. T.; Erpenbeck, E. J. *J. Chem. Phys.* **1959**, *30*, 634, 637.
(16) Alexandrowicz, Z.; Accad, Y. *J. Chem. Phys.* **1971**, *54*, 5338.
(17) Domb, C.; Barrett, A. J. *Polymer* **1976**, *17*, 179.
(18) Fukatsu, M.; Kurata, M. *J. Chem. Phys.* **1966**, *44*, 4539.
(19) Tanaka, G.; Yamakawa, H. *Polym. J.* **1973**, *4*, 446.
(20) Shimada, J.; Yamakawa, H. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1927.
(21) Ullman, R. *Macromolecules* **1981**, *14*, 746.
(22) Tanaka, G.; Šolc, K., unpublished results.
(23) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 1122.
(24) Edwards, S. F. *J. Phys. A.: Math., Nucl. Gen.* **1975**, *8*, 1171.
(25) Oono, Y. *J. Phys. Soc. Jpn.* **1975**, *39*, 25. *Ibid.* **1976**, *41*, 787.
(26) Gordon, M.; Ross-Murphy, S. B.; Suzuki, H. *Eur. Polym. J.* **1976**, *12*, 733.
(27) Aronowitz, S.; Eichinger, B. E. *Macromolecules* **1976**, *9*, 377.
(28) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1974**, *25*, 179.
(29) de Gennes, P.-G. *Phys. Lett. A* **1972**, *38*, 339.
(30) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(31) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(32) Fixman, M. *J. Chem. Phys.* **1962**, *36*, 3123.
(33) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.
(34) Baker, G. A., Jr. *Adv. Theor. Phys.* **1965**, *1*, 1.
(35) Stockmayer, W. H. *Br. Polym. J.* **1977**, *9*, 89.
(36) Tanaka, G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 305.
(37) Tanaka, G. *Macromolecules* **1980**, *13*, 1513.
(38) Auer, P. L.; Gardner, C. S. *J. Chem. Phys.* **1955**, *23*, 1545, 1546.
(39) Fixman, M. *J. Chem. Phys.* **1966**, *45*, 786, 793.
(40) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(41) Hearst, J. E. *J. Chem. Phys.* **1962**, *37*, 2547.
(42) Tanaka, G.; Imai, S.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2639.
(43) Yamakawa, H.; Tanaka, G. *J. Chem. Phys.* **1971**, *55*, 3188.
(44) Fujita, H.; Taki, N.; Norisuye, T.; Sotobayashi, H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2255.
(45) Horta, A.; Fixman, M. *J. Am. Chem. Soc.* **1968**, *90*, 3048.
(46) Stockmayer, W. H.; Albrecht, A. C. *J. Polym. Sci.* **1958**, *32*, 215.
(47) Stockmayer, W. H. *Makromol. Chem.* **1960**, *35*, 54.
(48) Akita, S.; Einaga, Y.; Miyaki, Y.; Fujita, H. *Macromolecules* **1976**, *9*, 774.
(49) Miyaki, Y.; Einaga, Y.; Hirosye, T.; Fujita, H. *Macromolecules* **1977**, *10*, 1356.
(50) Hirosye, T.; Einaga, Y.; Fujita, H. *Polym. J.* **1979**, *11*, 819.
(51) Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.
(52) Burchard, W. *Makromol. Chem.* **1961**, *50*, 20.
(53) Yamamoto, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971**, *2*, 799.
(54) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2103.
(55) Fukuda, M.; Fukutomi, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 871.
(56) Krigbaum, W. R.; Flory, P. J. *J. Polym. Sci.* **1953**, *11*, 37.
(57) Altares, T., Jr.; Wyman, D. P.; Allen, V. R. *J. Polym. Sci., Part A* **1964**, *2*, 4533.
(58) Miyaki, Y.; Einaga, Y.; Fujita, H.; Fukuda, M. *Macromolecules* **1980**, *13*, 588.
(59) Noda, I.; Saito, S.; Fujimoto, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 4048.
(60) Ooms, G.; Mijnlieff, P. F.; Beckers, H. L. *J. Chem. Phys.* **1970**, *53*, 4123.
(61) Noda, I.; Mizutani, K.; Kato, T. *Macromolecules* **1977**, *10*, 618.
(62) Weill, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.
(63) Lifshitz, I. M.; Grosberg, A.; Khakholov, A. *Rev. Mod. Phys.* **1978**, *50*, 685.
(64) Post, C. B.; Zimm, B. H. *Biopolymers* **1979**, *18*, 1487.
(65) Sanchez, I. C. *Macromolecules* **1979**, *12*, 980.
(66) Williams, C.; Brochard, F.; Frisch, H. L. *Annu. Rev. Phys. Chem.* **1981**, *32*, 433.
(67) Toda, M. In "Statistical Physics" (in Japanese); Toda, M., Kubo, R., Eds.; Iwanami: Tokyo, 1972.
(68) Bauer, D. R.; Ullman, R. *Macromolecules* **1980**, *13*, 392.
(69) Sun, S.-T.; Nishio, I.; Swislo, G.; Tanaka, T. *J. Chem. Phys.* **1980**, *73*, 5971.
(70) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 210.