dictions for $\alpha(z)$ becomes more marked at large z, and the PS + 2-butanone data are in better agreement with the Fixman-Stockmayer than with the modified Flory-Fox prescription.

We have also calculated α against $zh(z) \equiv \psi\alpha_s^3$ for three other combinations of theories for A_2 and α. These were as given by eq 17-22 of ref 27, and corresponded to the original Flory-Krigbaum-Orofino A_2 expression combined with the original Flory α expression, the combination of the modified expressions, and the Kurata-Fukatsu-Sotobayashi-Yamakawa A_2 combined with the Yamakawa-Tanaka α expressions. The first and third recipes gave curves of α against $zh(z)$ close to curves c and d in Figure 3, while the second gave a lower curve toward e. The experimental points lie slightly above these three curves, but the difference is probably within experimental error.

Effects of Polydispersity. We have used the Yamakawa-Kurata treatment[28] to assess the effect of polydispersity on the value of A_2. Their series expansion for $h(z)$ is

$$h(z) = 1 - 2.865Q_w'z_w \ldots \tag{27}$$

Here z_w is the value of z corresponding to the weight-average molecular weight of the sample and Q_w' is a parameter greater than unity in the case of polydispersity. For the present polydisperse PIB sample, characterized by $h \simeq 2.2$, Figure 1 of ref 26 indicates that $Q_w' \simeq 1.07$. Following eq 27, we have replaced z in the closed expressions for $h(z)$ with the product $Q_w'z_w$. We find that a monodisperse fraction of the same M_w would have values of A_2 approximately 4% higher than those found experimentally with our polydisperse sample. The treatment of Casassa[29] also indicates that the change in A_2 would be very small, and it seems reasonable to ignore it.

In the case of the coil expansion factor α, Kurata and Stockmayer[9] give the series expansion

$$\alpha^2 - 1 = (134/105)q_sz_w + \ldots \tag{28}$$

where the factor introduced by polydispersity, q_s, is 1.257 for $h = 2.2$. Following ref 9, we have assumed that the product q_sz_w may be used in the closed expressions, *i.e.*, eq 25 and 26, in order to correct the values for α for the polydispersity of the PIB sample. We find that the difference between the value of α and unity is decreased by approximately 15%. The points in Figure 3 for the PIB + 2-methylbutane system would be lowered and fall closer to curve c than to b. It seems, however, that the general conclusions of the last section would remain, particularly since the points in Figure 3 for the polystyrene + 2-butanone system would be virtually unchanged, corresponding to the very low polydispersity of this polymer sample.

Acknowledgment. We acknowledge with gratitude the award of the Newell P. Beckwith Fellowship of the Paint Research Institute to D. G. and the support of the National Research Council of Canada.

(28) H. Yamakawa and M. Kurata, *J. Chem. Phys.*, 32, 1852 (1960).

(29) E. F. Casassa, *Polymer*, 3, 625 (1962).

A Revised Version of the Integrodifferential Equation in the Zimm Theory for Polymer Solution Dynamics

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ABSTRACT: Some of the viscoelastic quantities provided by the bead-spring model theory of Zimm have been reevaluated with the use of a new version of the integrodifferential equation, revising the numerical solutions of Tschoegl for intermediate degrees of hydrodynamic interaction. Comparison for low numbers of submolecules (N) with the result of the exact solution of Zimm's eigenvalue problem by Lodge and Wu reveals that the revised version (in contrast with the original) gives almost identical results for dynamic-mechanical properties and intrinsic viscosity. Numerical results showed that the quantities previously regarded as determined solely by the hydrodynamic interaction parameter h depend also on N even if N is not very small. An apparent "non-free-draining" effect is expected for the intrinsic viscosity irrespective of the value of h if $h/N^{1/2}$ is close to 0.25.

The bead-spring model theory of Zimm[1] is extremely important in determining the viscoelastic properties of dilute polymer solutions. Recently, it was pointed out by Lodge and Wu[2] that the use of the approximate integrodifferential equation given by Zimm[1] may cause a serious error for some cases. This led us to a closer examination of the integrodifferential equation. It turned out that the approximate version is good only for the free-draining or non-free-draining limits and not for intermediate degrees of hydrodynamic interaction. A revised equation, with an additional term, gives results in satisfactory agreement with the exact numerical solution (without the use of the integrodifferential equation)[2] for low values of N, the number of submolecules in a molecule. Since the integrodifferential equation is a better approximation for larger values of N, this is expected to give an almost mathematically exact evaluation of the Zimm theory for large values of N. In this paper, we report numerical results for some viscoelastic quantities as evaluated from the revised equation for the Zimm theory.

Theory and Method of Calculation

The problem this paper is concerned with is the solution of the eigenvalue problem

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(1) B. H. Zimm, *J. Chem. Phys.*, 24, 269 (1956).

(2) A. S. Lodge and Y-J. Wu, to be published.

$$\sum_{j=1}^{N} A_{ij}\alpha_j{}^p + (2/N)^{1/2}h\sum_{\substack{j=1\\j\neq i}}^{N}\sum_{k=1}^{N} A_{jk}\alpha_k{}^p/(|i-j|)^{1/2} = \lambda_p\alpha_i{}^p \quad (1)$$

for various values of N and h. Here A_{ij} is an element of the matrix defined by eq 11 of Zimm's paper,[1] h is the hydrodynamic interaction parameter defined by eq 69 of that paper, $\alpha_k{}^p$ is kth component of the pth eigenvector, and λ_p is pth eigenvalue. Relaxation times and viscoelastic quantities are obtained from the set of eigenvalues. In order to solve this problem for large values of N, Zimm introduced an integrodifferential equation[1]

$$\alpha''(r) + h\int_{-1}^{1}\alpha''(s)/(|r-s|)^{1/2}ds = (-N^2/4)\lambda\alpha(r) \quad (2)$$

where $\alpha(r)$ is an eigenfunction. An important feature of this equation is that the set of reduced eigenvalues $(N^2/4)\lambda$ is a unique function of one variable h. This equation has been solved numerically[3] for various values of h.

However, recent numerical evaluations of λ_p for eq 1 with $N \leq 222$ by Lodge and Wu[2] revealed that the solution of eq 2 deviates significantly from that of eq 1. For example, some of the quantities expected to be unique functions of h from eq 2 depend also on N even for $N = 200$, where the approximation included in eq 2 is supposed to be good. This deviation disappears if one properly excludes from eq 2 the contribution corresponding to $j = i$ in the second summation in eq 1. Following the procedure of Zimm,[1] one obtains for this contribution a quantity

$$h\int_{r-1/N}^{r+1/N}\alpha''(s)/(|r-s|)^{1/2}ds$$

Assuming $\alpha''(s)$ is a smooth function, one can expand $\alpha''(s)$ around $s = r$ and perform the integration to obtain $4h^*\alpha''(r)$ for this quantity where $h^* = hN^{-1/2}$. The corrected equation reads

$$\alpha''(r)(1-4h^*) + h\int_{-1}^{1}\alpha''(s)/(|r-s|)^{1/2}ds = (-N^2/4)\lambda\alpha(r) \quad (3)$$

(Professor Zimm kindly informed the author that a factor $35\sqrt{2}/12 = 4.13$ is obtained in the place of 4 in the correction term if the Euler–MacLaurin summation formula is applied.) The quantity h^* may be called a reduced hydrodynamic interaction parameter and does not depend on N. The factor $4h^*$ may not necessarily be small compared to unity. We will make the following points with respect to this equation. It reduces to eq 2 only when $h^* = 0$. For finite values of h, the set of reduced eigenvalues $(N^2/4)\lambda$ is not a unique function of h but also depends on N. If $h^* = 0.25$, this reduces to eq 2 with the first term neglected; $h \rightarrow \infty$ is not a necessary condition for the appearance of the non-free-draining limit.[3a] A treatment physically equivalent to the correction in eq 3 was introduced by Yamakawa[4] in the calculation of the intrinsic viscosity and the friction coefficient in the Pyun–Fixman theory[5] by setting a nonzero minimum for the distance between neighboring segments. His result is in accord with the result of eq 3.

The next problem is to solve eq 3 for eigenvalues for several values of h and N. Fortunately, the numerical result of Tschoegl[3c] for eq 3 can be used for this purpose as shown below. Assuming $h^* \neq 0.25$, one may rewrite eq 3 in the following form

$$\alpha''(r) + h_T\int_{-1}^{1}\alpha''(s)/(|r-s|)^{1/2}ds = (-N^2/4)\lambda_T\alpha(r) \quad (4)$$

where

$$h_T = h/(1-4h^*) \quad (5)$$

$$\lambda_T = \lambda/(1-4h^*) \quad (6)$$

If $h^* < 0.25$, eq 4 is equivalent to eq 2 with a different set of parameters h_T and λ_T, and so the eigenvalue problem is essentially solved by Tschoegl.[3c] Owing to the forms of eq 5 and 6, various viscoelastic quantities that depend on the eigenvalues of eq 3 are obtained very easily from Tschoegl's results. If the quantity is a function of the ratios λ_p/λ_1 and h/λ_p, and does not include λ_p or h in any other form, it can be obtained as the corresponding quantity in Tschoegl's results with the value of h in this result replaced by h_T. Although Tschoegl has calculated several other quantities, only the following are discussed here

$$[G']_R = \sum_{p=1}^{\infty}\omega_R{}^2(\lambda_1/\lambda_p)^2/[1+\omega_R{}^2(\lambda_1/\lambda_p)^2] \quad (7a)$$

$$[G'']_R = \sum_{p=1}^{\infty}\omega_R(\lambda_1/\lambda_p)/[1+\omega_R{}^2(\lambda_1/\lambda_p)^2] \quad (7b)$$

and

$$\Phi = (12\pi^3)^{1/2}N_a\sum_{p=1}^{\infty}(h/\lambda_p)/6N^2 \quad (8)$$

where N_a is Avogadro's number. Here $[G']_R$ and $[G'']_R$ are the real and the imaginary parts of the reduced intrinsic complex modulus and are functions of the reduced angular frequency $\omega_R = \omega\tau_1$, where ω is the angular frequency and τ_1 is the longest relaxation time. These quantities reflect the spacing among the set of eigenvalues (the ratio $\lambda_1:\lambda_2:\lambda_3$, etc.). The quantity Φ is the Flory constant related to the intrinsic viscosity and is directly related to the magnitude of the longest relaxation time and hence the smallest eigenvalue. Other quantities such as

$$\sum_{p=1}^{\infty}(\lambda_1/\lambda_p) \text{ and } \sum_{p=1}^{\infty}(\lambda_1/\lambda_p)^2$$

can be easily evaluated for eq 3 from the table of Tschoegl[3c] with the method described above.

For the case of $h^* = 0.25$, eq 3 reduces to the equation solved by Zimm, Roe, and Epstein.[3a] Thus their result can be used without any modification. When h^* is larger than 0.25, there is no numerical result currently available for use, and the perturbation method used for solving eq 2 does not look like a good approach in this case. Since the range of h^* of physical interest seems to be $h^* \leq 0.25$, no calculations were carried out for $h^* > 0.25$ (see Results and Discussion).

Results and Discussion

Complex Modulus. Examples of the comparison of the results for eq 3 and 1 are given in Figure 1, where $[G']_R$ and $[G'']_R$ are plotted against ω_R on a double logarithmic scale. The results for eq 1 were obtained by Lodge and Wu[2] (solid lines). The value of N is 200, and $h^* = 0.05$ and 0.2 for the

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[3] (a) B. H. Zimm, G. L. Roe, and L. F. Epstein, *J. Chem. Phys.*, 24, 279 (1956); (b) J. E. Hearst, *ibid.*, 37, 2547 (1962); (c) N. W. Tschoegl, *ibid.*, 39, 149 (1963).

[4] H. Yamakawa, *ibid.*, 53, 436 (1970).

[5] C. W. Pyun and M. Fixman, *ibid.*, 42 3838 (1965).

upper and lower set of curves, respectively. The corresponding values of h_T that should be used with eq 3 are 0.884 and 14.14, respectively. The dashed lines are the results from eq 3 with the values of $h_T = 1.0$ and 15.0, respectively, since these values are the closest to 0.884 and 14.14 available in Tschoegl's calculations. Apparently, the results from eq 3 are in good agreement with those from eq 1, except for small deviations in the high-frequency range of $\omega_R > 10^{1.5}$. These deviations are expected because eq 7 used with eq 3 includes an infinite number of terms, while the corresponding equations for eq 1 include only N terms. The deviation in $[G']_R$ for $h^* = 0.2$ is in a direction which is not explained by the difference in the number of terms and may represent the approximate nature of eq 3 compared to eq 1. The deviation in this high-frequency range is insignificant when one compares the theory with the experimental results, because another type of deviation, which is not explained by the Zimm theory, is observed in this frequency range.[6]

If one compares the original result and interpretation of Tschoegl's calculation with the exact eigenvalue calculation for the case of $h^* = 0.2$, one obtains large deviations in $[G']_R$ and $[G'']_R$ over a wide range of frequency, as pointed out by Lodge and Wu.[2] This deviation is explained by the large difference in h and h_T in this case. It should be pointed out that the values of h obtained by comparison of experimental results with Tschoegl's results[7] need to be reinterpreted as $h/(1 - 4h^*)$.

Flory Constant Φ. The result for the Flory constant obtained from eq 3 and 8 is plotted against h in Figure 2. Tschoegl's original result[3c] and the result from eq 1 are also included for comparison. The latter is due to Lodge and Wu.[2] The circles represent the exact numerical result from eq 1 for the values of N = 10, 20, 40, 60, 80, 100, 160, and 200 from left to right for each h^* except for h^* = 0.35 and 0.05, where the points for $N \geq 160$ and $N \leq 20$ are missing, respectively. The agreement between the results of eq 3 and that of exact eigenvalues is good for any value of N but it is better for lower h^* and higher N. For the values of $N \geq 60$, the results for eq 1 and eq 3 are within 3% of each other. This deviation may be due to the approximate nature of eq 3 or to the approximation included in Tschoegl's numerical calculation. This small deviation again shows that eq 3 is a good approximation to eq 1, at least in the range of $h^* \leq 0.25$.

The value of Φ stays constant at 2.84×10^{23} for various values of N when $h^* = 0.25$ and approaches the value of Tschoegl's original result as h^* approaches 0. These two points are expected from a comparison of eq 2 and 3. As N becomes larger, the values of Φ for any value of nonzero h^* approach 2.84×10^{23}. It may be pointed out that the value is rather insensitive to the change of N even if h^* is not exactly 0.25 but is as close to this value as 0.2. Almost the same result as given in this section was reported by Yamakawa,[4] who used the Pyun-Fixman method[5] to calculate the intrinsic viscosity.

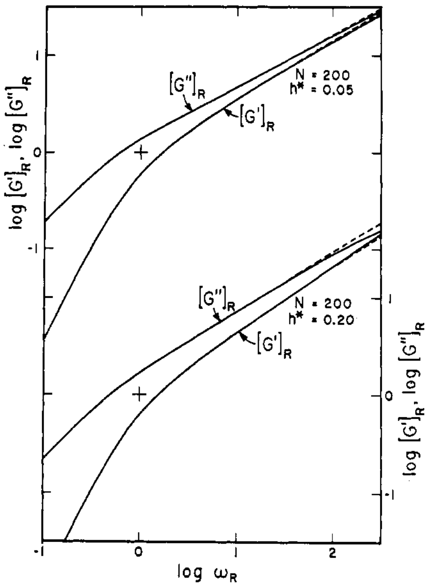

Figure 1. Real part $[G']_R$ and imaginary part $[G'']_R$ of reduced intrinsic complex modulus plotted against reduced angular frequency ω_R from Zimm's theory with N = 200. Solid lines from exact eigenvalues of eq 1; dashed lines from revised approximation equation. Top, $h^* = 0.05$ and $h_T = 1.0$ in the place of the exact value $h_T = 0.884$. Bottom, $h^* = 0.2$ and $h_T = 15$ in the place of the exact value of $h_T = 14.1$.

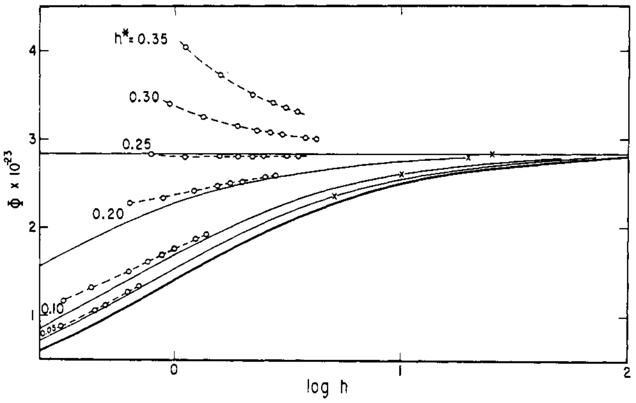

Figure 2. Flory constant Φ from Zimm's theory evaluated by various methods of calculation plotted against the hydrodynamic interaction parameter h: (O) from exact eigenvalues of eq 1; thin lines from eq 3; thick line result of Tschoegl (eq 2). Values of h^* are shown, and cross mark indicates $N = 10^4$ for a given value of $h^* = hN^{-1/2}$.

Remarks on $h^* > 0.25$. The qualitative nature of the eigenvalues in the case of $h^* > 0.25$ may be examined using a zero-order perturbation method for solution of eq 2 as was used by Hearst.[3b] This method uses the eigenfunctions for the free-draining limit and gives fairly good results for any value of h in eq 2, although this may not be the case for eq 3 with $h^* > 0.25$. Following this method, one obtains the approximate eigenvalues of eq 3 for large j as

$$\lambda_j = (\pi^2/N^2)[j^2(1 - 4h^*) + 2h^*N^{1/2}j^{3/2}] \quad (j \gg 1) \qquad (9)$$

This equation shows that eigenvalues for very large j could be negative if $h^* > 0.25$ and that even the Nth eigenvalue could be negative if $h^* > 0.5$. It must be admitted that eq 9 may be a poor approximation for $h^* > 0.25$ because λ_j of eq 9 could be very small for some value of j, violating one of the conditions for applicability of Hearst's method. Probably the perturbation method in which eigenfunctions for the free-draining limit are used may not be appropriate for solving eq 3 when $h^* > 0.25$. However, some negative eigenvalues have been reported as the solution of eq 1.[2]

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(6) D. J. Massa, J. L. Schrag, and J. D. Ferry, *Macromolecules*, 4, 210 (1971).

(7) R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Polym. J.*, 1, 742 (1970).

Concluding Remarks

The comparison of numerical results with those from eq 1 showed that eq 3 is a good limit, for large N, of eq 1. Quantities previously believed to be unique functions of one parameter h can also depend on N unless h is extremely large (impractically large); some of the quantities such as the Flory constant are unique functions of h_T instead of h. The limit $h \rightarrow \infty$ is a sufficient but not a necessary condition for the appearance of the non-free-draining limit: $h^* \rightarrow 0.25$ causes exactly the same effect. Since experimentally the non-free-draining limit seems to apply to infinite-dilution frictional properties of certain real polymer solutions,[8] the appropriate value of h^* in the Zimm theory must correspondingly be near 0.25. However, it should be noted that the hydrodynamic interaction parameter h^* is defined on a simple model of beads and springs which does not represent the detail of the molecular structure. Thus, $h^* \rightarrow 0.25$ could be the result of forcing the Zimm theory to apply to real molecular systems so that its meaning may be obscure.

Since the mathematical structure is almost the same, analogous considerations have to be applied to the integral equations of Kirkwood and Riseman,[9] and almost the same result is expected. Moreover, one may not have to worry about the mathematical difficulty[10] in this type of problem because the h^* value of interest seems to be restricted to a narrow range where this difficulty does not exist.

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(8) See for example H. Yamakawa, "Modern Theory of Polymer Solutions," Harper and Row, New York, N. Y., 1971, Chapter 6.

(9) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

(10) R. Zwanzig, J. Kiefer, and G. H. Weiss, *Proc. Nat. Acad. Sci. U. S.*, **60**, 381 (1968).

Infinite-Dilution Viscoelastic Properties of Poly(α-methylstyrene). Applications of Zimm Theory with Exact Eigenvalues

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ABSTRACT: The storage and loss shear moduli have been measured for solutions of poly(α-methylstyrene) with narrow-distribution molecular weight of 1.43×10^6 in α-chloronaphthalene and decalin. The measurements were performed with the Birnboim–Schrag multiple-lumped resonator at nine frequencies from 100 to 6000 Hz; the data at each frequency were extrapolated to zero concentration to obtain the intrinsic storage and loss moduli. The extrapolated results for poly(α-methylstyrene) as well as previously published results for polystyrene and polybutadiene solutions were compared with the exact numerical result of the bead–spring model theory of Zimm as evaluated by Lodge and Wu for finite numbers of beads and various values of the hydrodynamic interaction parameter h^*. The theory reproduced the experimental data with reasonable values of h^* except for a small deviation at high frequency in the case of poly(α-methylstyrene), which was apparently due to the effect describable by the internal viscosity of the Peterlin theory. Values of h^* obtained from the comparison increased from 0.1 to 0.25 as the solvent power decreased and were not very sensitive to the choice of the polymer and solvent nor to the molecular weight of the polymer. The product $\alpha_\eta h^*$, where α_η is the expansion factor of the excluded volume effect as evaluated from the intrinsic viscosity, had an approximately constant value of 0.21 for most of the systems examined. This result suggested that the assumption of uniform expansion of effective segment length due to the excluded volume effect is sufficient to explain the effect of solvent power on the observed spectrum of viscoelastic relaxation times.

Tanaka and collaborators[1] were the first to succeed in obtaining viscoelastic properties of polymer solutions at infinite dilution. More recently, effort has been devoted to obtaining more extensive data of the same kind over wider ranges of frequency and solvent viscosity. Results for polystyrene solutions in various solvents[2] and polybutadiene in two solvents[3] have been obtained so far with the use of the Birnboim–Schrag multiple-lumped resonator and a computerized data acquisition system.[4] The first purpose of the present publication is to report similar results for poly(α-methylstyrene), which is supposedly stiffer than the polymers studied before and whose molecular weight distribution can be made very narrow.

Recently, extensive numerical calculations for the bead–spring theory of Zimm[5] have been performed by Lodge and Wu,[6] utilizing exact eigenvalues to determine the relaxation spectrum. The eigenvalues, and hence the relaxation spec-

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(1) (a) H. Tanaka, A. Sakanishi, and J. Furuichi, *J. Polym. Sci., Part C*, **No. 15**, 317 (1966); (b) A. Sakanishi and H. Tanaka, *Proc. Int. Congr. Rheol. 5th*, **4**, 251, 259 (1970).

(2) R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Polym. J.*, **1**, 742 (1970).

(3) K. Osaki, Y. Mitsuda, R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 17 (1972).

(4) (a) J. L. Schrag and R. M. Johnson, *Rev. Sci. Instrum.*, **42**, 224 (1971); (b) D. J. Massa and J. L. Schrag, *J. Polym. Sci., Part A-2*, **10**, 71 (1972).

(5) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

(6) A. S. Lodge and Y-J. Wu, *Rheol. Acta*, in press.