(12) A. Isihara, "Statistical Physics", Academic Press, New York, N.Y. 1971, Chapter 3.
(13) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **234**, 60 (1956).
(14) C. Robinson, J. Ward, and R. Beevers, *Discuss. Faraday Soc.*, **25**, 29 (1958).
(15) A. M. Elyashevich and A. M. Skvortsov, *Mol. Biol.*, **5**, 204 (1971).
(16) W. H. Stockmayer, *Rev. Mod. Phys.*, **31**, No. 1 (1959).
(17) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(18) T. M. Birshtein, A. A. Sariban, and A. M. Skvortsov, *Vysokomol. Soedin., Ser. A*, **17**, 1962 (1975).
(19) T. M. Birshtein, A. M. Skvortsov, and A. A. Sariban, *Vysokomol. Soedin., Ser. A*, **17**, 1700, (1975).
(20) Ch. Tanford, "Physical Chemistry Of Macromolecules", Wiley, New York, N.Y., 1961.
(21) For the cylinder of doubled diameter the effective excluded volume is $4dA^2$ in accordance with eq 5. As can be seen, the distinction is connected with the shape of a segment in the lattice model if there is a repulsive layer. The segment cross section has the form of a four-petal rosette.

Normal Stresses in Dilute Polymer Solutions. The Effects of Preaveraging the Hydrodynamic Interaction Tensor

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ABSTRACT: The two normal stress differences, σ_1 and σ_2, are calculated for a dilute solution of random coil polymers without preaveraging the Oseen tensor used to describe the intramolecular hydrodynamic interaction. ($\sigma_1 = \sigma_{xx} - \sigma_{zz}$ and $\sigma_2 = \sigma_{zz} - \sigma_{yy}$ where σ_{xx}, etc., are elements of the stress tensor and the unperturbed solvent velocity filed is $V_x{}^0 = Kz$, $V_y{}^0 = V_z{}^0 = 0$.) The perturbation theory developed by Fixman is carried out to second order and the results show that σ_1 decreases by 15% from the nondraining result of the Rouse–Zimm theory. Previous calculations of σ_2 in dilute solutions of random coil macromolecules yield $\sigma_2 = 0$. In this calculation, due to avoidance of preaveraging the Oseen tensor, σ_2 is non-zero and has the value $\sigma_2 = -0.01\sigma_1$.

In order to completely characterize the rheological properties of a non-Newtonian fluid, three quantities must be determined: the viscosity and the two normal stress differences. A great deal of theoretical work has been done on the viscosity of dilute polymer solutions, but relatively little work has been done on normal stresses. Although normal stress differences are more difficult to measure, they are more sensitive to details of molecular structure than are viscosities. Normal stresses play an important role in stability and secondary flow phenomena and have recently been considered as being responsible for the observation of drag reduction in dilute polymer solutions.[1]

Tanner and Stehrenberger[1] and Curtiss, Bird, and Hassager[2] have recently reviewed previous calculations of normal stresses in dilute polymer solutions from a molecular approach. We simply note here that all calculations on random coil or stiff chain models of polymer statistics have either neglected hydrodynamic interaction completely or have preaveraged the Oseen tensor that describes the hydrodynamic interaction. Consequently, while these calculations result in non-zero values for the first normal stress difference, σ_1, the second normal stress difference, σ_2, is zero (see below for definitions of σ_1 and σ_2). One exception to this is the calculation of Segawa and Ishida,[19] based on the boson formulation of Fixman.[20,21] This formulation, while applicable to nonideal conditions, uses a hydrodynamic interaction tensor averaged over some steady state. Thus fluctuations in the hydrodynamic interaction are neglected. They obtained a nonvanishing result for σ_2/κ^2, where κ is the shear rate, for finite κ, but no numerical results were presented. For the rigid rod macromolecule, Kotaka[3] has calculated non-zero values for both σ_1 and σ_2 by not preaveraging the Oseen tensor.

The purpose of this paper is to calculate the normal stress differences in a dilute solution of random coil macromolecules without preaveraging the hydrodynamic interaction tensor. Our approach is to employ the perturbation theory developed by Fixman[4] and applied to intrinsic viscosity calculations by Fixman and Pyun.[5,6] This method is based on the general theory of irreversible processes in solutions of macromolecules developed by Kirkwood.[7,8]

Method of Calculation

We begin by briefly recapitulating the perturbation theory developed by Fixman[4] and Fixman and Pyun.[5,6] The reader is referred to the original articles for the detailed presentation of the theory. Unless otherwise specified, the notation of ref 5 and 6 will be adhered to in what follows. The model considers a dilute solution of linear, flexible polymer chains, each consisting of N equal segments. The equation of motion of each segment is determined by balancing the thermal, Brownian motion force, the intersegmental forces, and the force arising from hydrodynamic resistance of segment motion relative to solvent, including hydrodynamic interaction between segments on one molecule. The segments are assumed to interact through a spring, or Hooke's law, potential, S, which at equilibrium determines a Gaussian, random coil distribution function. In addition, the hydrodynamic interaction between segments is described by the Oseen interaction tensor in the nonpreaveraged form (see below). The equation of motion of each segment along with the equation of continuity determines the diffusion equation for the distribution function, ψ, for the polymer segments in coordinate space.

Let ψ be written as

$$\psi = \psi_0\rho \tag{1}$$

where ψ_0 is the equilibrium distribution function. The equation for ρ is written as

$$\frac{\partial\rho}{\partial t} + L\rho = 0 \tag{2}$$

The operator L can be split into the sum of a self-adjoint operator, A, with a scalar product defined with ψ_0 as a weighting function and an external perturbation operator B. These operators are defined by the equations

$$A\rho = -kT\nabla^{\mathrm{T}}(D\nabla\rho) + (\nabla^{\mathrm{T}}S)D(\nabla\rho) \tag{3}$$

$$B\rho = \nabla^{\mathrm{T}}(V^0\rho) - (1/kT)(\nabla^{\mathrm{T}}S)V^0\rho \tag{4}$$

Here ∇ is an $N \times 1$ matrix whose ith element is the column matrix operator

$$\nabla_i = (\partial/\partial x_i,\ \partial/\partial y_i,\ \partial/\partial z_i) \tag{5}$$

and ∇^{T} is the transpose of ∇. D is an $N \times N$ matrix whose ij element is given by

$$\mathbf{D}_{ij} = (1/\beta)1 + \mathbf{T}_{ij} \tag{6}$$

with $\mathbf{T}_{ij}$, the Oseen tensor, written as

$$\mathbf{T}_{ij} = (1/8\pi\eta_0 r_{ij})\left(1 + \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2}\right) \tag{7}$$

β is the segment frictional coefficient, η_0 the solvent viscosity, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ where $\mathbf{r}_i$ is the position of the ith segment. Finally, V^0 is an $N \times 1$ matrix whose ith element is the column vector $\mathbf{V}_i{}^0 = (V_{xi}{}^0, V_{yi}{}^0, V_{zi}{}^0)$ describing the solvent velocity at the position of the ith segment in the absence of the polymer.

Since the exact eigenfunctions of the operator A are not known, we chose a basis set consisting of the eigenfunctions of the self-adjoint operator A^α obtained from A by neglecting hydrodynamic interaction between segments. Thus A^α is obtained from eq 3 by setting $\mathbf{T}_{ij} = 0$ for all i, j. The free-draining eigenfunctions ϕ_n and eigenvalues $\lambda_n{}^0$ are then determined by the equation

$$A^\alpha\phi_n = \lambda_n{}^0\phi_n \tag{8}$$

The eigenfunctions ϕ_n are given in terms of normal coordinates $\mathbf{q}_i = (\xi_i, \eta_i, \zeta_i)$ which diagonalize A^α by

$$\phi_n = \prod_{i=1}^{N} \phi_{n(i)}(\mathbf{q}_i) \tag{9}$$

$$\phi_{n(i)}(\mathbf{q}_i) = \phi_{n(i\xi)}(\xi_i)\phi_{n(i\eta)}(\eta_i)\phi_{n(i\zeta)}(\zeta_i) \tag{10}$$

where

$$\phi_{n(i\xi)}(\xi_i) = A_{n(i\xi)}H_{n(i\xi)}(\alpha_i\xi_i) \tag{11}$$

with similar solutions for $\phi_{n(i\eta)}$ and $\phi_{n(i\zeta)}$. Here $Hn(x)$ is the nth Hermite polynomial of argument x, $\alpha_i = (6/b^2)^{1/2} \sin(\pi i/2N)$ and $A_{n(i\xi)} = (2^{n(i\xi)}n(i\xi)!)^{-1/2}$. The index n in eq 9 refers to the set of N triplets, $\{n(i\xi), n(i\eta), n(i\zeta), i = 1, 2, \ldots, N\}$ where, for example, $n(i\xi)$ describes the state of excitation of the ξ component of the ith normal mode. The eigenvalues, $\lambda_n{}^0$, are given by the expression

$$\lambda_n{}^0 = \sum_i \lambda_{n(i)}{}^0;\ \lambda_{n(i)}{}^0 = \lambda_{n(i\xi)}{}^0 + \lambda_{n(i\eta)}{}^0 + \lambda_{n(i\zeta)}{}^0 \tag{12}$$

$$\lambda_{n(i\xi)}{}^0 = (12kT/\beta b^2)n(i\xi)\sin^2(\mathrm{i}\pi/2N) \tag{13}$$

and similarly for $\lambda_{n(i\eta)}{}^0$, $\lambda_{n(i\zeta)}{}^0$. Note that $\phi_0 = 1$ corresponds to the equilibrium solution.

In order to specify the form of the operator B in eq 4 the following unperturbed solvent flow field is assumed,

$$V_x{}^0 = \kappa z,\ \mathrm{V}_y{}^0 = 0,\ \mathrm{V}_z{}^0 = 0 \tag{14}$$

where κ is the time-independent shear rate. We now proceed to obtain the time-independent steady-state solution to eq 2 required for the calculation of normal stresses. To do so, we form matrix representations of all operators and functions in the basis set of free-draining eigenfunctions, $\{\phi_n\}$. Denoting the matrix representation of the operator B by L^{b}, we get

$$L^{\mathrm{b}}{}_{nm} = \int \psi_0\phi_n B\phi_m\,\mathrm{d}\mathbf{q}_1 \ldots d\mathbf{q}_N$$

$$\begin{aligned} L^{\mathrm{b}}{}_{nm} = -\kappa \sum_{i=1}^{N} \Bigg\{ \Bigg(\prod_{j\neq i} \delta_{m(j),n(j)} \Bigg) \delta_{m(i\eta),n(i\eta)}[n(i\xi)]^{1/2} \\ \times\, \delta_{m(i\xi),n(i\xi)-1}([n(i\zeta)]^{1/2}\delta_{m(i\zeta),n(i\zeta)-1} \\ + [n(i\zeta)+1]^{1/2}\delta_{m(i\zeta),n(i\zeta)+1}) \Bigg\} \end{aligned} \tag{15}$$

where $\delta_{m(i),n(i)} = \delta_{m(i\xi),n(i\xi)}\delta_{m(i\eta),n(i\eta)}\delta_{m(i\zeta),n(i\zeta)}$. Let L^{a} denote the matrix representation of A and separate L^{a} into a diagonal part, Λ, and off-diagonal part P:

$$L^{\mathrm{a}} = \Lambda + P \tag{16}$$

where $L^{\mathrm{a}}{}_{nn} = \Lambda_{nn} = \lambda_n$, $P_{nn} = 0$, $L^{\mathrm{a}}{}_{nm} = P_{nm}$, $n \neq m$. Finally, let f_n denote the components of ρ in the basis $\{\phi_n\}$,

$$\rho = \sum_{n=0}^{N} f_n\phi_n = 1 + \sum_{n=1}^{N} f_n\phi_n \tag{17}$$

where $\phi = 1 = f_0$. Then for $n \neq 0$, the f_n are given by

$$\begin{aligned} f_n = -\frac{L^{\mathrm{b}}{}_{n0}}{\lambda_n} + \sum_{\substack{m \\ m\neq n}} \left(\frac{P_{nm}L^{\mathrm{b}}{}_{m0}}{\lambda_n\lambda_m} + \frac{L^{\mathrm{b}}{}_{nm}L^{\mathrm{b}}{}_{m0}}{\lambda_n\lambda_m} \right) \\ - \sum_m \sum_{\substack{l \\ l\neq n \\ l\neq m}} \frac{1}{\lambda_n\lambda_l\lambda_m} (P_{nl}P_{lm}L^{\mathrm{b}}{}_{m0} + P_{nl}L^{\mathrm{b}}{}_{lm}L^{\mathrm{b}}{}_{m0} \\ + L^{\mathrm{b}}{}_{nl}P_{lm}L^{\mathrm{b}}{}_{m0} + L^{\mathrm{b}}{}_{nl}L^{\mathrm{b}}{}_{lm}L^{\mathrm{b}}{}_{m0}) + \ldots \end{aligned} \tag{18}$$

Application to Normal Stresses

As in the calculation of intrinsic viscosity, all the f_n need not be determined for the calculation of normal stresses. In order to determine which f_n are necessary, we turn to the expression for the stress tensor, σ,[5,9]

$$\sigma - \sigma^0 = -p \sum_{j=1}^{N} \langle \mathbf{F}_j\mathbf{r}_j \rangle \tag{19}$$

where $\mathbf{F}_j$ is the force exerted by the jth segment on the fluid, p is the number density of polymer molecules, and σ^0 is the stress due to the solvent alone, which is assumed to be a Newtonian fluid. The angular brackets denote averaging with respect to the distribution function ψ, $\langle g \rangle = \int \psi_0\rho g\,\mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N$. The xx component of σ, σ_{xx}, will be considered explicitly with similar results holding for σ_{yy} and σ_{zz}. Thus

$$\sigma_{xx} - \sigma_{xx}{}^0 = -p \sum_{j=1}^{N} \langle F_{xj}X_j \rangle \tag{20}$$

where

$$F_{xj} = -(3kT/b^2)(\mathbf{C}\mathbf{x})_j - kT\left(\frac{\partial}{\partial x_j}\ln\psi\right) \tag{21}$$

Here, the matrix $\mathbf{C}$ describes the transformation to normal coordinates.[5] In normal coordinates, eq 21 becomes[6]

$$\sigma_{xx} - \sigma_{xx}{}^0 = kTp \sum_{n=1}^{N} (-1 + 2\langle \alpha_n{}^2\xi_n{}^2 \rangle) \tag{22}$$

Using eq 17 in eq 22 and the orthogonality of the Hermite polynomials, the following equation for $\langle \alpha_n{}^2\xi_n{}^2 \rangle$ is obtained,

$$\langle \alpha_n{}^2\xi_n{}^2 \rangle = \tfrac{1}{2}(1 + 2^{1/2}f_{200}{}^n) \tag{23}$$

Here we have introduced a new notation. The superscript on f indicates the normal mode and the triplet of numbers in the subscript represent the state of excitation of the ξ, η, and ζ components, respectively, of the indicated normal mode. All other modes are in the ground state. Thus, for σ_{xx}, σ_{yy}, and σ_{zz} we must calculate, respectively, $f_{200}{}^n$, $f_{020}{}^n$, $f_{002}{}^n$, $n = 1, 2, \ldots, N$.

Returning to eq 18, and using the selection rules embodied in eq 15, we note that all terms in eq 15 containing only products of three or more matrix elements of L^{b} vanish for the required f_n. Now consider first the diagonal representation, in which P is suppressed, i.e., L^{a} has diagonal matrix elements only. In this case, $f_{020}{}^{\mathrm{n}}$, $f_{002}{}^{\mathrm{n}}$ both vanish and $f_{200}{}^n$ is given by

$$f_{200}{}^n = \frac{2^{1/2}\kappa^2}{\lambda_{200}{}^n\lambda_{101}{}^n} \tag{24}$$

$\lambda_{101}{}^n$ is evaluated in ref 5 where it is written as $\lambda_{(n)}$. $\lambda_{200}{}^n$ can be similarly evaluated, using eq 3, as[6]

$$\lambda_{200}{}^n = \lambda_2{}^0 + kT\int \psi^0(\nabla^{\mathrm{T}}\phi_{200}{}^n)\mathrm{T}(\nabla\phi_{200}{}^n)\mathrm{d}\mathbf{q}_1 \ldots \mathrm{d}\mathbf{q}_N \tag{25}$$

where $\lambda_2{}^0$ is given by eq 12 and $\mathrm{T} = D - (1/\beta)1$. The evaluation of the integral in eq 25 requires integration over a bivariate Gaussian distribution function. This type of calculation is presented in detail in ref 5. The result for $\lambda_{200}{}^n$ is

$$\lambda_{200}{}^n = \frac{6kT\pi^2}{\beta b^2N^2}\{n^2 + (4h/\pi^2)[I_1(n) + \tfrac{2}{3}I_2(n)]\} \tag{26}$$

where $h = N^{1/2}\beta/(12\pi^3)^{1/2}b\eta_0$ is the draining parameter and $I_1(n), I_2(n)$ are given in ref 5. In all such calculations, sums are converted to integrals and $\sin(n\pi/2N)$ is replaced by $n\pi/2N$, i.e., results are valid for small n.

These considerations lead to the following results for the normal stresses and normal stress differences:

$$\sigma_{xx} - \sigma_{xx}{}^0 = 2kTp\sum_{n=1}^{N}(\lambda_{200}{}^n\lambda_{101}{}^n)^{-1} \tag{27}$$

$$\sigma_{yy} - \sigma_{yy}{}^0 = \sigma_{zz} - \sigma_{zz}{}^0 = 0 \tag{28}$$

$$\sigma_1 = \sigma_{xx} - \sigma_{zz} = 2kTp\sum_{n=1}^{N}(\lambda_{200}{}^n\lambda_{101}{}^n)^{-1} \tag{29}$$

$$\sigma_2 = \sigma_{zz} - \sigma_{yy} = 0 \tag{30}$$

In the free-draining limit $h = 0$ and $\lambda_{200}{}^n = \lambda_{101}{}^n = 6kTn^2\pi^2/\beta b^2N^2$ and we obtain

$$\sigma_{xx} - \sigma_{xx}{}^0 = p\beta^2b^4N^4\kappa^2/1620kT \tag{31}$$

This is identical with the free-draining limit of the Rouse–Zimm theory for the normal stresses.[10,11] In the nondraining limit, the result is

$$\sigma_{xx} - \sigma_{xx}{}^0 = \frac{p\eta_0{}^2L^6\kappa^2}{kT} \times \left(\frac{\pi^3}{24}\sum_n[(I_1(n) + I_2(n))(I_1(n) + \tfrac{2}{3}I_2(n))]^{-1}\right) \tag{32}$$

or

$$\sigma_{xx} - \sigma_{xx}{}^0 = 7.87 \times 10^{-2}\,p\eta_0{}^2L^6\kappa^2/kT \tag{33}$$

where $L = bN^{1/2}$. The nondraining result of the Zimm theory[11] gives

$$\sigma_{xx} - \sigma_{xx}{}^0 = 9.12 \times 10^{-2}\,p\eta_0{}^2L^6\kappa^2/kT \tag{34}$$

Comparison of eq 33 and eq 34 shows a 13% decrease in $\sigma_{xx} - \sigma_{xx}{}^0$ from the preaveraged Oseen tensor result to the diagonal approximation.

By taking account of the terms in eq 18 involving matrix elements of P, the calculation can be extended beyond the diagonal approximation. We carry out here the perturbation expansion to include all the terms explicitly written out in eq 18, with the restriction that only matrix elements of P involving excitations of the same normal mode be calculated. The only nonzero term in eq 18 for the required f_n in this approximation is that containing the product $P_{nl}L^{\mathrm{b}}{}_{lm}L^{\mathrm{b}}{}_{m0}$. This can be seen from the selection rules for matrix elements of P and L^{b}. There is only one such term that contributes to $f_{200}{}^n$: $2\kappa^2P_{200,202}{}^n/\lambda_{200}{}^n\lambda_{202}{}^n\lambda_{101}{}^n$.

There are two such terms that contribute to $f_{020}{}^n$: $2\kappa^2P_{020,202}{}^n/\lambda_{020}{}^n\lambda_{202}{}^n\lambda_{101}{}^n$ and $2^{1/2}\kappa^2P_{020,200}{}^n/\lambda_{020}{}^n\lambda_{200}{}^n\lambda_{101}{}^n$. Similarly, the two terms contributing to $f_{002}{}^n$ are $2\kappa^2P_{002,202}{}^n/\lambda_{002}{}^n\lambda_{202}{}^n\lambda_{101}{}^n$ and $2^{1/2}\kappa^2P_{002,200}{}^n/\lambda_{002}{}^n\lambda_{200}{}^n\lambda_{101}{}^n$. It remains to compute the indicated diagonal and off-diagonal elements of L^{a} to complete the calculation. Again, as this type of matrix element has been calculated in detail before,[5] we present only the results. For $f_{200}{}^n$, we obtain

$$f_{200}{}^n = \frac{2^{1/2}\kappa^2}{\lambda_{200}{}^n\lambda_{101}{}^n}\left\{1 - \left(\frac{3\cdot2^{1/2}}{70}I_3(n) + \tfrac{1}{3}I_2(n)\right)\Big/(I_1(n) + I_2(n))\right\} \tag{35}$$

where

$$I_3(n) = \frac{2}{(n\pi)^{3/2}}\int_0^{n\pi}\mathrm{d}s\int_s^{n\pi}\mathrm{d}t \times \frac{\cos t\cos(t-s)[\cos t - \cos(t-s)]^4}{s^{5/2}} \tag{36}$$

$$I_3(n) = \frac{64}{3n^2\pi^2}[(-1)^n - 1] + \frac{2^{1/2}}{72n^{3/2}\pi}[1040\,S(n\pi) - 1120\cdot2^{1/2}\,S(2n\pi) + 711\cdot3^{1/2}\,S(3n\pi) - 448S(4n\pi) + 25\cdot5^{1/2}\,S(5n\pi) - n\pi(204C(n\pi) - 384\cdot2^{1/2}\,C(2n\pi) + 108\cdot3^{1/2}\,C(3n\pi))] \tag{37}$$

$C(x)$ and $S(x)$ are the Fresnel integrals defined by

$$C(x) = \frac{1}{(2\pi)^{1/2}}\int_0^x\frac{\cos t}{t^{1/2}}\mathrm{d}t \qquad S(x) = \frac{1}{(2\pi)^{1/2}}\int_0^x\frac{\sin t}{t^{1/2}}\mathrm{d}t \tag{38}$$

To obtain eq 35, we have used the approximation $\lambda_{202}{}^n = 2\lambda_{101}{}^n$ which was shown valid previously.[5] Using these results, we obtain the following expression for σ_{xx} in the nondraining limit,

$$\sigma_{xx} - \sigma_{xx}{}^0 = 7.72 \times 10^{-2}\,p\eta_0{}^2L^6\kappa^2/kT \tag{39}$$

This represents only a 2% decrease from the result for σ_{xx} in the diagonal approximation.

The results for σ_{yy} and σ_{zz} are found to be

$$\sigma_{yy} - \sigma_{yy}{}^0 = 1.19 \times 10^{-3}\,p\eta_0{}^2L^6\kappa^2/kT \tag{40}$$

$$\sigma_{zz} - \sigma_{zz}{}^0 = 4.14 \times 10^{-4}\,p\eta_0{}^2L^6\kappa^2/kT \tag{41}$$

Using eq 39, 40, and 41, σ_1 and σ_2 are given by

$$\sigma_1 = 7.68 \times 10^{-2}\,p\eta_0{}^2L^6\kappa^2/kT \tag{42}$$

$$\sigma_2 = -7.72 \times 10^{-4}\,p\eta_0{}^2L^6\kappa^2/kT \tag{43}$$

Discussion of Results

Calculation of the first and second normal stress differences, σ_1 and σ_2 respectively, has been carried out to second order in the off-diagonal matrix elements of L^{a} with the restriction that matrix elements of L^{a} be evaluated between excited states of the same normal mode. Removal of this restriction leads to a large increase in complexity. While it is difficult to evaluate the extent of convergence of the results, we note that $\sigma_{xx} - \sigma_{xx}{}^0$ changes by only 2% on going from the diagonal approximation to the second-order nondiagonal calculation. As discussed below, it is difficult to obtain reliable measurements of the second normal stress differences, σ_2, in moderately concentrated solutions and no measurements have been done on dilute solutions. Thus, more refined calculation of σ_2 in dilute solution is not warranted at this time.

The numerical results show that σ_1 decreases by 15% from the value obtained using the equilibrium preaveraged form of the Oseen tensor. This will also affect calculation of the extinction angle in flow birefringence, which depends on normal as well as shear stresses. More significant, however, is that, although small, σ_2 does not vanish. This result is due to the retention of the anisotropic terms of the Oseen tensor. All previous calculations have rejected these terms, or the hydrodynamic interaction, entirely, resulting in zero values for σ_2. The sign of σ_2 agrees with that calculated by Kotaka[3] for rigid rod macromolecules ($\sigma_2 = \sigma_{yy} - \sigma_{zz}$ in Kotaka's work since his choice of unperturbed solvent flow field is $V^0 = (\kappa y, 0, 0)$). The magnitude of σ_2, however, is considerably smaller than that obtained by Kotaka. The nonzero value for σ_2 demonstrates that the Weissenberg hypothesis ($\sigma_2 = 0$) does not hold for the random coil model of polymers.

Comparison with experiment is not possible at present because all measurements of normal stresses have been made in concentrated or moderately concentrated solutions rather than in dilute solutions. Those measurements that have been made have generated much controversy concerning the sign of σ_2,[12,13] and there have been many reports on errors in pressure determinations.[14-16] Tanner[12] has surveyed measurements of σ_1 and σ_2 on solutions of polyisobutylene and concludes that $\sigma_2 \cong -0.15\sigma_1$ throughout a wide range of shear rates. Recent experiments on other systems also have found σ_2/σ_1 to be negative.[13,16]

Clearly, measurement of σ_1 and σ_2 would be extremely difficult in dilute solution. Even for a polymer of molecular weight 10^9, such as a bacterial chromosome, σ_1 would be of the order of 10^{-6} atm. Nonetheless, an interesting manifestation of normal stress effects in dilute solutions of large DNA-radial migration of molecules in concentric cylinder flow toward the inner cylinder has been observed and studied theoretically.[17,18]

Acknowledgments. The author would like to thank one of the referees for pointing out the work of Segawa and Ishida.

References and Notes

(1) R. I. Tanner and W. Stehrenberger, *J. Chem. Phys.*, **55**, 1958 (1971).
(2) C. F. Curtiss, R. B. Bird, and O. Hassager, Rheology Research Center, University of Wisconsin, Report No. 24, 1974.
(3) T. Kotaka, *J. Chem. Phys.*, **30**, 1566 (1959).
(4) M. Fixman, *J. Chem. Phys.*, **42**, 3831 (1965).
(5) C. W. Pyun and M. Fixman, *J. Chem. Phys.*, **42**, 3838 (1965).
(6) C. W. Pyun and M. Fixman, *J. Chem. Phys.*, **44**, 2107 (1966).
(7) J. G. Kirkwood, *Recl. Trav. Chim. Pays-Bas*, **68**, 649 (1949).
(8) J. G. Kirkwood, *J. Polym. Sci.*, **12**, 1 (1954).
(9) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.
(10) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
(11) M. C. Williams, *J. Chem. Phys.*, **42**, 2988 (1964).
(12) R. I. Tanner, *Trans. Soc. Rheol.*, **17**, 365 (1973).
(13) E. B. Christiansan and W. R. Leppard, *Trans. Soc. Rheol.*, **18**, 65 (1974).
(14) J. M. Broadbent, A. Kaye, A. S. Lodge, and D. G. Vale, *Nature (London)*, 55 (1968).
(15) E. J. Novotny, Jr., and R. E. Eckart, *Trans. Soc. Rheol.*, **17**, 227 (1973).
(16) O. Olabisi and M. C. Williams, *Trans. Soc. Rheol.*, **16**, 727 (1972).
(17) R. H. Shafer, N. Laiken, and B. H. Zimm, *Biophys. Chem.*, **2**, 180 (1974).
(18) R. H. Shafer, *Biophys. Chem.*, **2**, 185 (1974).
(19) W. Segawa and K. Ishida, *J. Phys. Soc. Jpn.*, **32**, 792 (1972).
(20) M. Fixman, *J. Chem. Phys.*, **45**, 785 (1966).
(21) M. Fixman, *J. Chem. Phys.*, **45**, 791 (1966).

An Approximation for Nonrandomness in Polymer-Solution Thermodynamics

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ABSTRACT: In concentrated polymer solutions, residual thermodynamic functions arise from the variation of free volume with composition. These functions are traditionally calculated from an equation of state using a one-fluid theory, coupled with the assumption of random mixing. This article suggests that one limitation of Flory's equation for liquid mixtures may, in part, be due to the random-mixing assumption. To account for nonrandomness, a phenomenological equation is used to relate the potential energy of a mixture to its composition. This equation, while not rigorous, is based on the intuitive notion of a "local composition" which, in concept, is related to Guggenheim's quasichemical theory. Since the local compositions are temperature dependent, the residual entropy is also affected by nonrandomness. When applied to experimental data for a few binary polymer-solvent systems, the local-composition equation can represent both enthalpy-of-mixing and activity data using only two adjustable parameters.

It is now well known that the lattice model for polymer solutions is inadequate and that free-volume (or equation-of-state) contributions cannot be neglected when calculating thermodynamic excess functions.[1]

For the last ten years it has become common practice to use for this purpose an equation of state proposed by Flory;[2] this equation follows from a partition function that is fundamentally of the van der Waals type (hard spheres located in a uniform field of attractive energy), modified to take into account all external degrees of freedom through the parameter $3c$, as suggested by Prigogine.[3] When this partition function is extended to binary mixtures, it is necessary to make some assumption concerning the effect of composition on potential energy. The common assumption made by Flory and all subsequent workers assumes complete randomness: the polymer segments and the solvent molecules arrange themselves in a state of maximum disorder, that is, a state where a polymer segment (or a solvent molecule) chooses its closest neighbors blindly, without preference for one or the other. This assumption is attractive because it is simple and because no rigorous method is known for introducing nonrandomness, even in solutions of equisized molecules. In this work we propose an approximation for introducing nonrandomness. The approximation is not based on any clearly defined statistical-mechanical procedure but is fundamentally intuitive or phenomenological. It retains simplicity and, judging from a preliminary comparison, appears to be consistent with experimental data.

The limitations of Flory's equation of state have been pointed out previously[4-6] but in these earlier papers, primary attention was given to the failure of this equation at very low densities and to its inadequacy at very high pressures. Here we are concerned with the extension of Flory's equation of state to mixtures. For a binary mixture containing N_1 molecules of component 1 and N_2 molecules of component 2, the key relation used by Flory for the energy E_0 is

$$-E_0 = (A_{11}\eta_{11} + A_{22}\eta_{22} + A_{12}\eta_{12})/v \tag{1}$$

where

$$2A_{11} + A_{12} = s_1 r_1 N_1$$

$$2A_{22} + A_{12} = s_2 r_2 N_2$$

where s_2 is the external area of interaction of a polymer segment and s_1 is the external area of interaction of a solvent molecule. As indicated by the single subscript, these are properties of the pure components, independent of the nature of the other component.