been suggested by Orwoll[11] for the evaluation of the χ parameter of polymer–solvent systems.

The polyisobutylene–benzene system may be a suitable candidate for further investigation employing the present experimental technique. The strong dependence of the χ parameter of this system on concentration and temperature has accurately been formulated by previous experiments.[15]

Registry No. (Styrene)·(*p*-divinylbenzene) (copolymer), 9003-70-7; cyclohexane, 110-82-7; toluene, 108-88-3; methanol, 67-56-1.

References and Notes

(1) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(2) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(3) Höcker, H.; Shih, H.; Flory, P. J. *Trans. Faraday Soc.* **1971**, *67*, 2275.
(4) Schick, M. J.; Doty, P.; Zimm, B. H. *J. Am. Chem. Soc.* **1950**, *72*, 530.
(5) Krigbaum, W. R.; Geymer, D. O. *J. Am. Chem. Soc.* **1959**, *81*, 1859.
(6) Scholte, Th. G. *J. Polym. Sci., Part A-2* **1970**, *8*, 841.
(7) Koningsveld, R.; Kleintjens, L. A.; Shultz, A. R. *J. Polym. Sci., Part A-2* **1970**, *8*, 1261.
(8) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook"; Interscience: New York, 1967.
(9) Erman, B.; Flory, P. J. *Macromolecules* **1982**, *15*, 806.
(10) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(11) Orwoll, R. A. *Rubber Chem. Technol.* **1977**, *50*, 451.
(12) Gee, G.; Herbert, J. B. M.; Roberts, R. C. *Polymer* **1965**, *6*, 541.
(13) Yen, L. Y.; Eichinger, B. E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 121.
(14) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(15) Eichinger, B.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2053.

On the Kinetic Theory and Rheology of a Solution of Rigid-Rodlike Macromolecules

Andrzej R. Altenberger and John S. Dahler*

Departments of Chemistry and Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455.

Received December 3, 1984

ABSTRACT: A new model is proposed to describe the dynamics of a solution of rigid-rodlike particles. A new expression is obtained for the stress tensor of the solution. The kinetic equation for the problem is solved by using the projection operator method. The loss and storage moduli, non-Newtonian viscosity, and normal stresses are calculated.

1. Introduction

In recent years there has been an increased interest in the study of dynamical and transport properties of nonspherical molecules. In particular, molecules having cylindrical symmetry have been studied extensively due to their importance in the theories of liquid crystals and of linear, rigid polymer particles. The rigid dumbbell and rigid, multibead rod frequently are used as models for these particles. In these models two or more spherical particles or "beads" are spaced at equal intervals along a straight line. The "free space" between the beads is assumed to be penetrable by the molecules of the solvent in which the rodlike particle is suspended. The diffusional (longitudinal transverse) anisotropy of the rod is then a consequence of hydrodynamic interactions among the beads. This "porous rod" model is obviously both inadequate and oversimplified. The large rodlike particles (for example, long polymer chains or cylindrical viruses, like tobacco mosaic virus) more closely resemble continuous impenetrable bodies. Even if some penetration of the "inside" of the polymer particle by solvent is possible, it is unlikely that macroscopic hydrodynamics can be used to analyze the consequences.

In the present paper a new model is proposed for the particle–solvent interaction which we hope will provide a more convenient and realistic tool for the study of rheological properties of such solutions. The mechanical model which we advocate here is that of a continuous, thin fiber, impenetrable to the solvent and characterized by a uniform distribution of the mass along its length (slender body). The spatial configuration of such a particle is described by the location of its center of mass and by a vector directed along the particle axis. The length of this vector is proportional to the length of the particle. For a strictly rigid particle (which we shall consider in this paper) it is only necessary to introduce a unit vector parallel to the long axis of the molecule, since the particle has but five degrees of freedom.

The anisotropic mobility of the particle can be taken into account by assigning to it a cylindrically symmetric friction tensor. The two friction coefficients associated with this tensor can be identified with the familiar expressions of slender-body hydrodynamics[1]

$$\xi_{\parallel} = \eta_0 L \frac{2\pi}{\ln (L/a) - 3/2 + \ln 2} \tag{1.1}$$

and

$$\xi_{\perp} = \eta_0 L \frac{4\pi}{\ln (L/a) - 1/2 + \ln 2} \tag{1.2}$$

Here $\xi_{\parallel}$ and $\xi_{\perp}$ are the friction coefficients for motions in the longitudinal and transverse directions, η_0 is the solvent viscosity, L is the particle length, and a is the cylinder radius. However, we think it is more reasonable to determine the value of these coefficients from experimental data such as, for example, the translational and rotational diffusion constants at infinite dilution. The reason for this is that the macroscopic hydrodynamic theory from which the formulas (1.1) and (1.2) are derived may not adequately account for the drag on an individual molecule and even if it did we do not know what type of boundary conditions should be used. For example, for the tobacco mosaic virus (TMV), which is a very good example of a rigid-rodlike particle, the ratio $\kappa = \xi_{\parallel}/\xi_{\perp}$ of the friction coefficients calculated from the above expressions is about 0.7, while the same ratio calculated from existing experimental data (on translational and rotational diffusion) is about 0.3. The same ratio has been computed by Kirkwood and Auer[2] for

0024-9297/85/2218-1700$01.50/0

an infinitely long array of beads. They obtained a value of 0.5, in agreement with the limiting value predicted by the slender-body equations (1.1) and (1.2).

In the next section we discuss in detail the equations of motion for the linear particle, taking into account the presence of flow and the action of an external force. In section 3 a new general expression for the stress tensor is derived and in section 4 we derive the kinetic equation appropriate to our model. Model rheological calculations for a dilute solution are presented in section 5. Details concerning the solution of the kinetic equation are relegated to Appendices. In the last section a general discussion of results is given.

2. Equation of Motion

Let us consider the dynamics of a single rodlike particle suspended in a continuous medium. We shall assume that the gradients in the systems are small on the scale of the particle length. The particle will be modeled as an element of a straight line with mass distributed uniformly along its length. By $\mathbf{r}_1$ and $\mathbf{r}_2$ we denote the locations of the centers of mass of the parts gotten by cleaving the entire particle into two at its center of mass

$$\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2 \tag{2.1}$$

We assume that the equations of motion for both "parts" of the rod can be expressed in the form

$$m\ddot{\mathbf{r}}_1 = \mathbf{K}(\dot{\mathbf{r}}_1,\mathbf{r}_1) + \mathbf{F}(\mathbf{r}_1 - \mathbf{r}_2) + \Phi(\mathbf{r}_1) \tag{2.2a}$$

$$m\ddot{\mathbf{r}}_2 = \mathbf{K}(\dot{\mathbf{r}}_2,\mathbf{r}_2) - \mathbf{F}(\mathbf{r}_1 - \mathbf{r}_2) + \Phi(\mathbf{r}_2) \tag{2.2b}$$

$\mathbf{K}(\dot{\mathbf{r}},\mathbf{r})$ is the friction force acting on the half of the rod with its center of mass at $\mathbf{r}$

$$\mathbf{K}(\dot{\mathbf{r}},\mathbf{r}) = -\xi\cdot[\dot{\mathbf{r}} - \mathbf{w}(\mathbf{r})] \tag{2.3}$$

and the friction tensor ξ is given by

$$\xi = \xi_{\parallel}\mathbf{ee} + \xi_{\perp}(\mathbf{I} - \mathbf{ee}) \tag{2.4}$$

where $\mathbf{e}$ is the unit vector directed along the axis

$$\mathbf{e} = (\mathbf{r}_1 - \mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2| \tag{2.5}$$

By $\mathbf{F}(\mathbf{r})$ we denote an effective binding force which is responsible for keeping the two parts of the rod bound together. Thus

$$\mathbf{F}(\mathbf{r}) = -\mathbf{e}U'(r) \tag{2.6}$$

where $U(r)$ is the binding potential energy. $\Phi(\mathbf{r})$ is an external force acting on the rod at the point $\mathbf{r}$. Although $\Phi(\mathbf{r})$ could include forces of interaction with other rods present in the solution, it is assumed here that the solution is sufficiently dilute that these particle interactions can be neglected. We also shall assume that forces due to sources located outside the system do not distinguish between the two parts of the particle. The case of a "dipolar" particle, with one end positive and the other negative, is treated in Appendix A.

By $\mathbf{w}(\mathbf{r})$ in the expression (2.3) we denote the mean velocity field of *solvent* calculated at the point $\mathbf{r}$. It is now more convenient to replace the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ by the coordinates of the total center of mass $\mathbf{R}$ and the vector $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ connecting the two "subcenters". The equations of motion for these coordinates are respectively

$$2m\ddot{\mathbf{R}}(t) = -2\xi\cdot[\dot{\mathbf{R}} - \cosh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_{\mathbf{R}})\mathbf{w}(\mathbf{R})] + 2\cosh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_{\mathbf{R}})\Phi(\mathbf{R}) \tag{2.7}$$

and

$$m\ddot{\mathbf{r}}(t) = -\xi\cdot[\dot{\mathbf{r}} - 2\sinh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_{\mathbf{R}})\mathbf{w}(\mathbf{R})] + 2\mathbf{F}(\mathbf{r}) + 2\sinh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_{\mathbf{R}})\Phi(\mathbf{R}) \tag{2.8}$$

If the gradients are small on the scale of the particle length, we can approximate (2.7) and (2.8) by

$$m\ddot{\mathbf{R}}(t) = -\xi[\dot{\mathbf{R}} - \mathbf{w}(\mathbf{R})] + \Phi(\mathbf{R}) \tag{2.9}$$

$$m\ddot{\mathbf{r}}(t) = -\xi\cdot[\dot{\mathbf{r}} - \mathbf{r}\cdot\nabla_{\mathbf{R}}\mathbf{w}(\mathbf{R})] + 2\mathbf{F}(\mathbf{r}) + \mathbf{r}\cdot\nabla_{\mathbf{R}}\Phi(\mathbf{R}) \tag{2.10}$$

Except for the anisotropic friction tensor these equations of motion are very similar to those for the simple dumbbell model.

For a rigid rod we have an additional constraint

$$\mathbf{r}^2(t) = l^2 \tag{2.11}$$

from which it follows that

$$\dot{\mathbf{r}}\cdot\mathbf{r} = 0 \tag{2.12}$$

and

$$\ddot{\mathbf{r}}\cdot\mathbf{r} = -\dot{\mathbf{r}}\cdot\dot{\mathbf{r}} \tag{2.13}$$

(The length of the rod is $L = 2l$.) These relations imply that the tension force inside the rigid particle is given by

$$|\mathbf{F}(\mathbf{r})| = U'(r) = \tfrac{1}{2}l\{\xi_{\parallel}(\mathbf{e}\cdot\nabla_{\mathbf{R}})\mathbf{e}\cdot\mathbf{w}(\mathbf{R}) + (\mathbf{e}\cdot\nabla_{\mathbf{R}})\mathbf{e}\cdot\Phi(\mathbf{R}) + m\dot{\mathbf{e}}\cdot\dot{\mathbf{e}}\} \tag{2.14}$$

The equation of motion for the (unit) orientation vector $\mathbf{e}$ is

$$m\ddot{\mathbf{e}}_{\perp} = -\xi_{\perp}[\dot{\mathbf{e}}_{\perp} - \mathbf{e}\cdot\nabla_{\mathbf{R}}\mathbf{w}_{\perp}(\mathbf{R})] + (\mathbf{e}\cdot\nabla_{\mathbf{R}})\Phi_{\perp}(\mathbf{R}) \tag{2.15}$$

wherein $\ddot{\mathbf{e}}_{\perp}$ and $\dot{\mathbf{e}}_{\perp}$ are the components of $\ddot{\mathbf{e}}$ and $\dot{\mathbf{e}}$ perpendicular to the direction of $\mathbf{e}$. In general we use the symbol

$$\mathbf{a}_{\perp} = (\mathbf{I} - \mathbf{ee})\cdot\mathbf{a}$$

to denote the transverse component of a vector $\mathbf{a}$.

3. Stress Tensor

The increase of stress due to a dilute suspension of macromolecules can be represented as a sum of independent contributions due to the separate rodlike particles. In order to take account of the internal stress generated inside a particle at the location of its total center of mass $\mathbf{R}$, we define the microscopic mass density of the rod by

$$\hat{\rho}(\mathbf{R}_0,t) = m\{\delta[\mathbf{R}_0 - \mathbf{r}_1(t)] + \delta[\mathbf{R}_0 - \mathbf{r}_2(t)]\} = 2m\cosh[\tfrac{1}{2}\mathbf{r}\cdot\nabla_{\mathbf{R}_0}]\delta[\mathbf{R}_0 - \mathbf{R}(t)] \tag{3.1}$$

Here $2m$ is the total mass of the rod. The equation of evolution for this mass density can be expressed in the form

$$\partial_t\hat{\rho}(\mathbf{R}_0,t) = -\nabla_{\mathbf{R}_0}\cdot\hat{\mathbf{p}}(\mathbf{R}_0,t) \tag{3.2}$$

where $\hat{\mathbf{p}}(\mathbf{R}_0,t)$ is the macroscopic momentum density of the particle

$$\hat{\mathbf{p}}(\mathbf{R}_0,t) = \{\dot{\mathbf{R}}(t) - \tfrac{1}{2}\dot{\mathbf{r}}(t)\tanh[\tfrac{1}{2}\mathbf{r}(t)\cdot\nabla_{\mathbf{R}_0}]\}\hat{\rho}(\mathbf{R}_0,t) \tag{3.3}$$

The equation of motion for the momentum density is, in turn, given by

$$\partial_t\hat{\mathbf{p}}(\mathbf{R}_0,t) = -\nabla_{\mathbf{R}_0}\cdot\{\dot{\mathbf{R}}(t)\dot{\mathbf{R}}(t) + \tfrac{1}{4}\dot{\mathbf{r}}(t)\dot{\mathbf{r}}(t) - \tfrac{1}{2}[\dot{\mathbf{R}}(t)\dot{\mathbf{r}}(t) + \dot{\mathbf{r}}(t)\dot{\mathbf{R}}(t)]\tanh[\tfrac{1}{2}\mathbf{r}(t)\cdot\nabla_{\mathbf{R}_0}]\}\hat{\rho}(\mathbf{R}_0,t) + [\ddot{\mathbf{R}}(t) - \tfrac{1}{2}\ddot{\mathbf{r}}(t)\tanh(\tfrac{1}{2}\mathbf{r}(t)\cdot\nabla_{\mathbf{R}_0})]\hat{\rho}(\mathbf{R}_0,t) \tag{3.4}$$

By neglecting nonlinear terms in the gradients, this can be reduced to the simpler form

$$\partial_t\hat{\mathbf{p}}(\mathbf{R}_0,t) + \nabla_{\mathbf{R}_0}\cdot\mathbf{w}(\mathbf{R}_0)\mathbf{w}(\mathbf{R}_0)\hat{\rho} = \ddot{\mathbf{R}}(t)\hat{\rho}(\mathbf{R}_0,t) + \nabla_{\mathbf{R}_0}\cdot\hat{\sigma}(\mathbf{R}_0,t) \tag{3.5}$$

where the microscopic stress tensor contribution due to the rod is

$$\hat{\sigma}(\mathbf{R}_0,t) = -[\dot{\mathbf{R}}(t)\dot{\mathbf{R}}(t) - \mathbf{w}(\mathbf{R}_0)\mathbf{w}(\mathbf{R}_0)]\hat{\rho}(\mathbf{R}_0,t) - \tfrac{1}{4}\dot{\mathbf{r}}(t)\dot{\mathbf{r}}(t)\hat{\rho}(\mathbf{R}_0,t) - \tfrac{1}{4}\mathbf{r}(t)\ddot{\mathbf{r}}(t)\hat{\rho}(\mathbf{R}_0,t) \quad (3.6)$$

Explicit expression for the accelerations $\ddot{\mathbf{R}}(t)$ and $\ddot{\mathbf{r}}(t)$ are provided by eq 2.9 and 2.10.

The average stress due to the linear particle can be obtained provided that the probability distributions of the center-of-mass velocity $\dot{\mathbf{R}}$ and the internal motion velocity $\dot{\mathbf{r}}$ are known. We also shall need appropriate distribution functions for the relative and center-of-mass coordinates $\mathbf{r}$ and $\mathbf{R}$. Following a standard type of approach, we assume that the velocity distribution of the "partial" centers of mass located at $\mathbf{r}_1$ and $\mathbf{r}_2$ can be approximated at any time by the product of two local Maxwellian distributions ($\beta = 1/(kT)$)

$$f_{eq}(\dot{\mathbf{r}}_1,\dot{\mathbf{r}}_2) \propto \exp\left\{-\beta\frac{m}{2}[\dot{\mathbf{r}}_1 - \mathbf{w}(\mathbf{r}_1)]^2 - \beta\frac{m}{2}[\dot{\mathbf{r}}_2 - \mathbf{w}(\mathbf{r}_2)]^2\right\} \quad (3.7)$$

In terms of the total center-of-mass velocity and the relative velocity of the two subcenters, this distribution becomes

$$f_{eq}(\dot{\mathbf{R}},\dot{\mathbf{r}}) \propto \exp\{-\beta m[\dot{\mathbf{R}} - \mathbf{w}(\mathbf{R})]^2\} \exp\left\{-\frac{\beta m}{4}[\dot{\mathbf{r}} - \mathbf{r}\cdot\nabla_{\mathbf{R}}\mathbf{w}(\mathbf{R})]^2\right\} \quad (3.8)$$

Calculations must be performed differently for elastic and rigid rods since in the latter case there is an additional constraint in the form of the factor $\delta(\dot{\mathbf{r}}\cdot\mathbf{r})$ which must be introduced into the distribution function (3.8).

For the elastic rod we obtain the formula

$$\sigma_{el}(\mathbf{R}_0,t) = \langle\hat{\sigma}(\mathbf{R}_0,t)\rangle = -\mathbf{I}\left(\frac{1}{m\beta}\right)\rho(\mathbf{R}_0,t) - \frac{1}{4}\langle\mathbf{r}\cdot\alpha(\mathbf{R})\mathbf{r}\cdot\alpha(\mathbf{R})\rangle\rho(\mathbf{R}_0,t) - \frac{1}{2m}\langle\mathbf{r}\mathbf{F}(\mathbf{r})\rangle\rho(\mathbf{R}_0,t) - \frac{1}{4m}\langle\mathbf{r}\mathbf{r}\rangle\cdot\gamma(\mathbf{R}_0)\rho(\mathbf{R}_0,t) \quad (3.9)$$

Here $\rho(\mathbf{R}_0,t)$, the mean local mass density of the rodlike particle, is related to the particle number density $c(\mathbf{R}_0,t)$ by the formula

$$\rho(\mathbf{R}_0,t) = 2mc(\mathbf{R}_0,t) \quad (3.10)$$

The quantity $\alpha(\mathbf{R})$ appearing in (3.9) is the velocity field gradient

$$\alpha(\mathbf{R}) = \nabla_{\mathbf{R}}\mathbf{w}(\mathbf{R}) \quad (3.11)$$

and $\gamma(\mathbf{R})$ is the second-rank tensor defined as the gradient of the external force

$$\gamma(\mathbf{R}) = \nabla_{\mathbf{R}}\Phi(\mathbf{R}) = -\nabla_{\mathbf{R}}\nabla_{\mathbf{R}}U^{ext}(\mathbf{R}) \quad (3.12)$$

The averaging indicated by the symbol $\langle\cdots\rangle$ is with respect to the unknown time-dependent distribution of the internal coordinate $\mathbf{r}$. Our expression (3.9) differs from the already known[3] formula for the stress tensor contribution of elastic dumbbells (to which it is closely related) by the presence of the terms involving the tensors (3.11) and (3.12).[4]

Similar calculations can be performed for a rigid-rod particle. We must take into account the constraint (2.12) and remember that the tension inside the particle is determined by eq 2.14. The average of the relative velocity tensor (over the velocity distribution) is then given by the expression

$$\langle\dot{\mathbf{r}}\dot{\mathbf{r}}\rangle = (\mathbf{I} - \mathbf{e}\mathbf{e})\frac{2}{m\beta} + (\mathbf{e}\cdot\alpha(\mathbf{R}))(\mathbf{e}\cdot\alpha(\mathbf{R}))l^2 \quad (3.13)$$

and correspondingly, the stress tensor due to the rigid rod is

$$\sigma_{rigid}(\mathbf{R}_0,t) = -\mathbf{I}(2kT)c(\mathbf{R}_0,t) + 3kTc(\mathbf{R}_0,t)\langle\mathbf{e}\mathbf{e}\rangle + \tfrac{1}{2}c(\mathbf{R}_0,t)\xi_{\parallel}l^2\langle\mathbf{e}\mathbf{e}\mathbf{e}\cdot\alpha(\mathbf{R}_0,t)\cdot\mathbf{e}\rangle - \tfrac{1}{2}mc(\mathbf{R}_0,t)l^2\langle[\mathbf{e}\cdot\alpha(\mathbf{R}_0,t)\mathbf{e}\cdot\alpha(\mathbf{R}_0,t) - \mathbf{e}\mathbf{e}(\mathbf{e}\cdot\alpha)^2]\rangle + \tfrac{1}{2}c(\mathbf{R}_0,t)l^2\langle\mathbf{e}\mathbf{e}\mathbf{e}\cdot\gamma(\mathbf{R}_0)\cdot\mathbf{e}\rangle - \tfrac{1}{2}l^2c(\mathbf{R}_0,t)\langle\mathbf{e}\mathbf{e}\rangle\cdot\gamma(\mathbf{R}_0) \quad (3.14)$$

The averaging in (3.14) is performed with respect to the time-independent distribution of the particle orientation vector $\mathbf{e}$. As before, our expression (3.14) differs from the known formula for the stress tensor of the rigid rod[3,5-7] by the presence of the term which is quadratic in the velocity field gradient α and by all the terms involving the tensor γ. The derivation of the stress tensor presented here also differs from those of other authors. Furthermore, there are differences between the stress tensor (3.14) of our theory and the analogous expressions recently used by Doi and Edwards[6] and Jain and Cohen.[8] The first and second terms of (3.14) are the same as those in ref 6 and 8 but there is a nontrivial difference in the third term regarding the factor accompanying the average $\langle\mathbf{e}\mathbf{e}\mathbf{e}\mathbf{e}\rangle$. According to our theory this term originates from the longitudinal tension condition (2.14) and so is multiplied by the longitudinal component of the friction tensor. In the theories of Doi and Edwards and Jain and Cohen it is multiplied by the inverse of the rod's rotational diffusion coefficient, which is (see (5.3) below) proportional to the inverse of the *transverse* component of the friction tensor.

4. Probability Distribution

The microscopic density in the single-particle configuration space is defined by

$$\hat{f}(\mathbf{R}_0,\mathbf{r}_0,t) = \delta[\mathbf{R}(t) - \mathbf{R}_0]\delta[\mathbf{r}(t) - \mathbf{r}_0] \quad (4.1)$$

and satisfies the continuity equation

$$\partial_t\hat{f} + \nabla_{\mathbf{R}_0}\cdot\hat{\mathbf{J}}_{\mathbf{R}_0}(\mathbf{R}_0,\mathbf{r}_0,t) + \nabla_{\mathbf{r}_0}\cdot\hat{\mathbf{J}}_{\mathbf{r}_0}(\mathbf{R}_0,\mathbf{r}_0,t) = 0 \quad (4.2)$$

The corresponding currents related to the total center-of-mass and internal variable flows are

$$\hat{\mathbf{J}}_{\mathbf{R}_0}(\mathbf{R}_0,\mathbf{r}_0,t) = \dot{\mathbf{R}}(t)\hat{f}(\mathbf{R}_0,\mathbf{r}_0,t) \quad (4.3)$$

and

$$\hat{\mathbf{J}}_{\mathbf{r}_0}(\mathbf{R}_0,\mathbf{r}_0,t) = \dot{\mathbf{r}}(t)\hat{f}(\mathbf{R}_0,\mathbf{r}_0,t) \quad (4.4)$$

The equations of evolution for the currents can be written as

$$\partial_t\hat{\mathbf{J}}_{\mathbf{R}_0} + \nabla_{\mathbf{R}_0}\cdot[\mathbf{w}(\mathbf{R}_0)\mathbf{w}(\mathbf{R}_0)]\hat{f} = -\nabla_{\mathbf{R}_0}\cdot[\dot{\mathbf{R}}\dot{\mathbf{R}} - \mathbf{w}(\mathbf{R}_0)\mathbf{w}(\mathbf{R}_0)]\hat{f} - \nabla_{\mathbf{r}_0}\cdot[\dot{\mathbf{r}}\dot{\mathbf{R}}]\hat{f} - m^{-1}\xi\cdot[\hat{\mathbf{J}}_{\mathbf{R}_0} - \mathbf{w}(\mathbf{R}_0)\hat{f}] + m^{-1}\Phi(\mathbf{R}_0)\hat{f} \quad (4.5)$$

and

$$\partial_t\hat{\mathbf{J}}_{\mathbf{r}_0} + \nabla_{\mathbf{r}_0}\cdot[\mathbf{r}_0\cdot\alpha(\mathbf{R}_0)\mathbf{r}_0\cdot\alpha(\mathbf{R}_0)]\hat{f} = -\nabla_{\mathbf{r}_0}\cdot[\dot{\mathbf{r}}\dot{\mathbf{r}} - \mathbf{r}_0\cdot\alpha(\mathbf{R}_0)\mathbf{r}_0\cdot\alpha(\mathbf{R}_0)]\hat{f} - \nabla_{\mathbf{R}_0}\cdot[\dot{\mathbf{R}}\dot{\mathbf{r}}]\hat{f} - m^{-1}\xi\cdot[\hat{\mathbf{J}}_{\mathbf{r}_0} - \mathbf{r}_0\cdot\alpha(\mathbf{R}_0)\hat{f}] + 2m^{-1}\mathbf{F}(\mathbf{r}_0)\hat{f} + m^{-1}\mathbf{r}_0\cdot\gamma(\mathbf{R}_0)\hat{f} \quad (4.6)$$

To obtain these results the equations of motion (2.9) and (2.10) have been used to eliminate the accelerations. The tensors α and γ are defined by (3.11) and (3.12).

The so-called inertial terms appearing on the left-hand sides of eq 4.5 and 4.6 are the only ones that would occur if the flows in configuration space were to occur without dispersion about the appropriate average velocities. Consequently, it is reasonable to expect that the deviations represented by the right-hand sides of these equations will be small. By setting these deviations equal to zero we

obtain equations which can be solved for the quasi-steady-state values of the currents. Since our configuration space formalism makes no provision for computing the distributions in momentum or velocity space, some ansatz must be introduced to deal with the terms of (4.5) and (4.6) which are quadratic functions of $\dot{\mathbf{R}}$ and $\dot{\mathbf{r}}$. What we do here is replace these terms with their local equilibrium averages calculated with the help of the velocity distribution function (3.8). This procedure apparently is equivalent to the use of the "entropic" or "Brownian" force in other formulations. Using these approximations we obtain the following expressions for the currents:

$$\hat{\mathbf{J}}_{\mathbf{R}_0}(\mathbf{R}_0,\mathbf{r}_0,t) = \mathbf{w}(\mathbf{R}_0)\hat{f} - \tfrac{1}{2}kT\xi^{-1}\cdot\nabla_{\mathbf{R}_0}\hat{f} - m\xi^{-1}\cdot\mathbf{w}(\mathbf{R}_0)\nabla_{\mathbf{r}_0}\cdot(\mathbf{r}_0\cdot\alpha(\mathbf{R}_0))\hat{f} + \xi^{-1}\cdot\Phi(\mathbf{R}_0)\hat{f} \quad (4.7)$$

and

$$\hat{\mathbf{J}}_{\mathbf{r}_0}(\mathbf{R}_0,\mathbf{r}_0,t) = \mathbf{r}_0\cdot\alpha(\mathbf{R}_0)\hat{f} - 2kT\xi^{-1}\cdot\nabla_{\mathbf{r}_0}\hat{f} - m\xi^{-1}\cdot\nabla_{\mathbf{R}_0}\cdot\mathbf{w}(\mathbf{R}_0)(\mathbf{r}_0\cdot\alpha(\mathbf{R}_0))\hat{f} + 2\xi^{-1}\cdot\mathbf{F}(\mathbf{r}_0)\hat{f} + \xi^{-1}\cdot(\mathbf{r}_0\cdot\gamma(\mathbf{R}_0))\hat{f} \quad (4.8)$$

The result of substituting these expressions into the continuity equation (4.2) is the following equation of evolution for the microscopic density in the particle configuration space:

$$\partial_t\hat{f} + \nabla_{\mathbf{R}_0}\cdot\mathbf{w}(\mathbf{R}_0)\hat{f} + \nabla_{\mathbf{r}_0}\cdot(\mathbf{r}_0\cdot\alpha(\mathbf{R}_0))\hat{f} = \nabla_{\mathbf{R}_0}\cdot\left(\frac{kT}{2}\xi^{-1}\right)\cdot\left[\nabla_{\mathbf{R}_0} + 2m\frac{1}{kT}\mathbf{w}(\mathbf{R}_0)\nabla_{\mathbf{r}_0}\cdot(\mathbf{r}_0\cdot\alpha) - 2\frac{1}{kT}\Phi(\mathbf{R}_0)\right]\hat{f} + \nabla_{\mathbf{r}_0}\cdot(2kT\xi^{-1})\cdot\left[\nabla_{\mathbf{r}_0} + \frac{m}{2kT}\nabla_{\mathbf{R}_0}\cdot\mathbf{w}(\mathbf{R}_0)\mathbf{r}_0\cdot\alpha(\mathbf{R}_0) - \frac{1}{kT}\mathbf{F}(\mathbf{r}_0) - \frac{1}{2kT}\mathbf{r}_0\cdot\gamma(\mathbf{R}_0)\right]\hat{f} \quad (4.9)$$

The same equation is satisfied by the time-dependent probability density of the configuration space variables.

The derivation must be slightly modified in order to obtain the analogous evolution equation for the rigid-rod particle. Since one degree of freedom (the motion along the axis) is permanently frozen, it must be that

$$\hat{\mathbf{J}}_{\mathbf{r}_0}(\mathbf{r}_0,\mathbf{R}_0,t)\cdot\hat{\mathbf{r}}_0 = 0 \quad (4.10)$$

Therefore, only the transverse component of the current (4.8) remains and it is given by the expression

$$\hat{\mathbf{J}}_{\mathbf{r}_0}{}^{\perp}(\mathbf{e}_0,\mathbf{R}_0,t) = l\mathbf{e}_0\cdot\alpha(\mathbf{R}_0)\cdot(\mathbf{I}-\mathbf{e}_0\mathbf{e}_0)\hat{f} - 2kTl^{-1}\xi_{\perp}{}^{-1}(\mathbf{I}-\mathbf{e}_0\mathbf{e}_0)\cdot\nabla_{\mathbf{e}_0}\hat{f} - ml\xi_{\perp}{}^{-1}\nabla_{\mathbf{R}_0}\cdot\mathbf{w}(\mathbf{R}_0)\mathbf{e}_0\cdot\alpha(\mathbf{R}_0)\cdot(\mathbf{I}-\mathbf{e}_0\mathbf{e}_0)\hat{f} + \xi_{\perp}{}^{-1}l\mathbf{e}_0\cdot\gamma(\mathbf{R}_0)\cdot(\mathbf{I}-\mathbf{e}_0\mathbf{e}_0)\hat{f} \quad (4.11)$$

The microscopic density in the five-dimensional space is defined by the formula

$$\hat{g}(\mathbf{R}_0,\mathbf{e}_0,t) = \delta[\mathbf{R}_0 - \mathbf{R}(t)]\delta[\mathbf{e}_0 - \mathbf{e}(t)] \quad (4.12)$$

and satisfies the equation of evolution

$$\partial_t\hat{g} + \nabla_{\mathbf{R}_0}\cdot\mathbf{w}(\mathbf{R}_0)\hat{g} + \nabla_{\mathbf{e}_0}\cdot(\mathbf{e}_0\cdot\alpha(\mathbf{R}_0))\hat{g} = [S_{\mathrm{cms}} + S_{\mathrm{or}} + S_{\mathrm{mx}}]\hat{g} \quad (4.13)$$

Here

$$S_{\mathrm{cms}} = \nabla_{\mathbf{R}_0}\cdot\left(\frac{kT}{2}\xi^{-1}\right)\cdot\left[\nabla_{\mathbf{R}_0} - \frac{4}{kT}\Phi(\mathbf{R}_0)\right] \quad (4.14)$$

is the Smoluchowski operator for the center-of-mass diffusion and

$$S_{\mathrm{or}} = \frac{2kT}{l^2\xi_{\perp}}\nabla_{\mathbf{e}_0}{}^2 + \nabla_{\mathbf{e}_0}\cdot\mathbf{e}_0\mathbf{e}_0\cdot\alpha(\mathbf{R}_0)\cdot\mathbf{e}_0 - \xi_{\perp}{}^{-1}\nabla_{\mathbf{e}_0}\cdot(\mathbf{I}-\mathbf{e}_0\mathbf{e}_0)\cdot\gamma(\mathbf{R}_0)\cdot\mathbf{e}_0 \quad (4.15)$$

is the orientational diffusion operator. Finally

$$S_{\mathrm{mx}} = \nabla_{\mathbf{R}_0}\cdot(m\xi^{-1})\cdot\mathbf{w}(\mathbf{R}_0)\nabla_{\mathbf{e}_0}\cdot(\mathbf{e}_0\cdot\alpha(\mathbf{R}_0)) + m\xi_{\perp}{}^{-1}\nabla_{\mathbf{e}_0}\cdot[\nabla_{\mathbf{R}_0}\cdot\mathbf{w}(\mathbf{R}_0)\mathbf{e}_0\cdot\alpha(\mathbf{R}_0)\cdot(\mathbf{I}-\mathbf{e}_0\mathbf{e}_0)] \quad (4.16)$$

is a mixture of derivative operators pertaining both to the center-of-mass and to the orientation coordinates.

When the velocity gradient α is independent of position [so-called "homogeneous flow"] and the gradient of the external force γ is spatially uniform, the orientational distribution function $\Phi(\mathbf{e},t)$ needed to compute the stress tensor (3.14) satisfies the partial differential equation

$$\partial_t\phi(\mathbf{e}_0,t) + \nabla_{\mathbf{e}_0}\cdot(\mathbf{e}_0\cdot\alpha)\phi = S_{\mathrm{or}}\phi(\mathbf{e}_0,t) \quad (4.17)$$

which, apart from the term involving the external force, is identical with the equation used by Kirkwood and Auer.[2]

5. Rheology of a Dilute Solution

The external force gradient and the enforced flow of the mixture both tend to orientate the rodlike particles. The transport properties of the anisotropic "oriented" fluid are different from those of the corresponding isotropic fluid. There are two interesting limiting cases of the rheology of "orientable" fluids. In the first we apply a small-amplitude, oscillatory shear to the initially disoriented solution, probing the dynamics of an equilibrium, isotropic solution. In the second, we determine the transport coefficients of a fluid which is in a stationary flow with a constant rate of shear. The transport coefficients associated with the second case are characteristic of the "oriented" fluid. In the case of a small-amplitude, spatially uniform oscillatory rate of shear the velocity gradient has the form

$$\alpha(t) = \alpha_0(\omega)e^{i\omega t} \quad (5.1)$$

Linear response theory leads to the following expression for the stress tensor contribution due to the rigid-rod particles:

$$\sigma_{\mathrm{rod}}{}^{\mathrm{lr}}(\omega) = -\mathbf{I}(2\pi)\delta(\omega)ckT + \tfrac{1}{18}c\xi_{\parallel}l^2\mathbf{I}\ \mathrm{Tr}\ \alpha_0(\omega) + \left[\tfrac{1}{30}c\xi_{\parallel}l^2 + \tfrac{3}{5}ckT\frac{1}{i\omega + 6D_{\mathrm{rot}}}\right][\alpha_0(\omega) + \alpha_0{}^{\mathrm{T}}(\omega) - \tfrac{2}{3}\mathbf{I}\ \mathrm{Tr}\ \alpha_0(\omega)] \quad (5.2)$$

where

$$D_{\mathrm{rot}} = 2kT/l^2\xi_{\perp} \quad (5.3)$$

is the rotational diffusion coefficient of a rod.

From the expression (5.2) it follows immediately that the shear viscosity increase due to the presence of rods is

$$\delta\eta(\omega) = \tfrac{1}{30}c\xi_{\parallel}l^2 + \tfrac{3}{5}ckT\frac{1}{i\omega + 6D_{\mathrm{rot}}} \quad (5.4)$$

and

$$\delta\eta(\omega = 0) = \frac{cl^2}{30}[\xi_{\parallel} + 1.5\xi_{\perp}] \quad (5.5)$$

The bulk viscosity increase is

$$\delta\zeta = \tfrac{1}{18}c\xi_{\parallel}l^2 \quad (5.6)$$

and for the Trouton viscosity we obtain the simple relationship

$$\eta_{\mathrm{T}}(\omega) = 3\delta\eta(\omega) \quad (5.7)$$

The two intrinsic moduli of rigidity are given by the expressions

$$[G'(\omega)] = \lim_{c\to 0}\frac{\mathrm{Re}\ G(\omega)}{2mc} = \frac{3}{5}\left(\frac{kT}{2m}\right)\frac{[\omega/6D_{\mathrm{rot}}]^2}{1 + [\omega/6D_{\mathrm{rot}}]^2} \quad (5.8)$$

and

$$[G''(\omega)] = \lim_{c\to 0} \frac{\text{Im } G(\omega) - \omega\eta_0}{2mc} = \frac{2}{5}\left(\frac{kT}{2m}\right)\left(\frac{\omega}{6D_{\text{rot}}}\right)\left[\frac{\xi_\parallel}{\xi_\perp} + \frac{3}{2}\frac{1}{1+(\omega/6D_{\text{rot}})^2}\right] \quad (5.9)$$

For large frequencies ($\omega \gg 6D_{\text{rot}}$) our theory predicts the following asymptotic behavior for these moduli:

$$[G'(\omega)]_{\omega\to\infty} \sim \frac{3}{5}kT/(2m) \quad (5.10)$$

$$[G''(\omega)]_{\omega\to\infty} \sim \frac{2}{5}\left(\frac{\xi_\parallel}{\xi_\perp}\right)\left(\frac{kT}{2m}\right)\left(\frac{\omega}{6D_{\text{rot}}}\right) \quad (5.11)$$

Expression 5.11 reduces to the well-known result obtained by Auer and Kirkwood[2] provided that the ratio of the longitudinal and transverse mobilities for the infinitely long rod is calculated using eq 1.1 and 1.2 for the two friction coefficients. However, it should be noted that the value of this ratio obtained from the experimentally determined rotational and translational diffusion coefficients often differs quite significantly from the asymptotic ($l/a \to \infty$) limit of $\xi_\parallel/\xi_\perp = 0.5$. The relation between the rotational diffusion coefficient and the transverse friction is given by eq 5.3. The translational diffusion coefficient can be expressed in terms of both friction coefficients as

$$D_{\text{transl}} = \frac{kT}{6}\left[\frac{1}{\xi_\parallel} + \frac{2}{\xi_\perp}\right] \quad (5.12)$$

For the tobacco mosaic virus (TMV), which is a good example of the rigid-rodlike particle, with a length $2l = 3000$ Å and diameter $d = 180$ Å, we have[3] $D_{\text{rot}} = 350 \pm 30$ s^{-1} and $D_{\text{transl}} = (3.4 \pm 0.1) \times 10^8$ Å^2/s. These values are for a water solution at 20 °C in the presence of a sodium phosphate buffer (pH 7.5). The friction coefficients corresponding to these data are $\xi_\perp = 1.03 \times 10^{-6}$ and $\xi_\parallel = 3.22 \times 10^{-7}$ g/s: their ratio is $\kappa = \xi_\parallel/\xi_\perp = 0.313$. Let us now use these friction coefficients to compute the intrisic viscosity

$$[\eta] = \frac{kT}{30mD_{\text{rot}}\eta_0}(1.5 + \kappa) \quad (5.13)$$

of the TMV solution. Using the value $2m = 6.48 \times 10^{-12}$ g/molecule for the mass of the TMV particle,[10] we obtain an estimate of $[\eta] = 22$ cm^3 g^{-1}. This is approximately 25% less than the observed experimental value 27.28 g^{-1} cm^3. The discrepancy between these two values may be due, at least in part, to the fact that we used the viscosity of pure water at 20 °C because data for the sodium phosphate buffer were not available.

We have calculated the rigidity moduli (5.8) and (5.9) as functions of the reduced frequency $\omega^* = \omega/6D_{\text{rot}}$ for different values of the friction coefficient ratio $\kappa = \xi_\parallel/\xi_\perp$. Figure 1 displays the results. Pertinent experiments were performed by Nemoto et al.,[11] who measured the storage and loss moduli of dilute solutions of TMV in glycerol–water mixtures. Unfortunately, despite the claims made by these and other[3] authors, the agreement between theory and experiment is at best only qualitative. For the asymptotic, high-frequency limit of the storage modulus we obtain (in agreement with the Kirkwood–Auer result)

$$\lim_{\omega\to\infty} [G'(\omega)]\frac{2\mu}{kT} = 0.6$$

while the experimental value is 0.99.

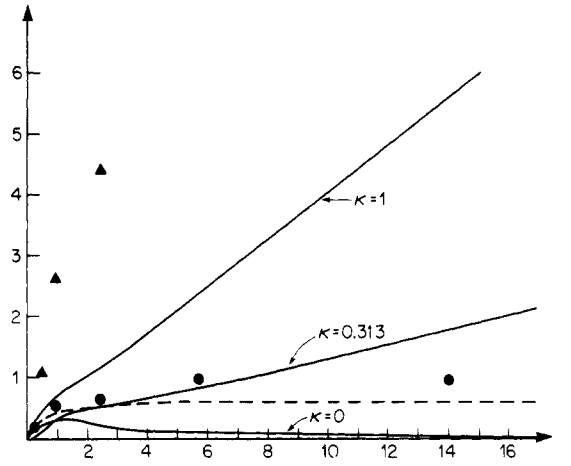

Figure 1. Loss and storage moduli vs. the reduced frequency, $\omega^* = \omega/6D_{\text{rot}}$. The dashed curve and circles, respectively, indicate the theoretical predictions and experimental[11] values of $[G'(\omega)](2m/kT)$. The solid curves and the triangles indicate the κ-dependent theoretical predictions and the experimental[11] values of $[G''(\omega)](2m/kT)$: $\kappa \equiv \epsilon_\parallel/\epsilon_\perp$.

The asymptotic value of the loss moduli is given by the expression

$$\lim_{\omega\to\infty} [G''(\omega)]\frac{2m}{kT}\frac{1}{\omega^*} = \frac{2}{5}\kappa$$

The numerical value is 0.2 for the Kirkwood–Auer theory and 0.13 for the present theory, using the experimental value of $\kappa = 0.313$. The experimental value of about 3 is far greater than any of the theoretical predictions.

The large discrepancies between the experimental results and linear response theory are rather disquieting. They may indicate that the simple diffusion-type theory is incapable of producing predictions of the transport properties. However, more precise measurements of the moduli are needed before a final conclusion can be reached.

A convenient feature of the present theory is the fact that we can recover results obtained previously for the rigid dumbbell model by assigning to κ the value of unity. Since the parameter κ is a measure of the anisotropy of the transport properties of the rod, we may conclude that results obtained for this particular value pertain to particles with no anisotropic translational properties. The value of $\kappa = 0$ corresponds to the opposite extreme of particles which only can move along their symmetry axis.

The non-Newtonian effects in the "oriented" fluid can be studied by considering a steady-state, nonlinear response of the stress to a constant (time independent) rate of strain turned on abruptly at time $t = 0$. To account for this response we must solve the kinetic equation (4.17) for an arbitrary, constant shear rate

$$\alpha = \dot{\alpha}\mathbf{n}_x\mathbf{n}_z$$

and subject to the initial condition $\phi(t = 0) = 1/(4\pi)$. Details are provided in Appendices B–D. For a homogeneous flow without external forces and particle interactions, it is convenient to use the Giesekus form of the stress tensor. This involves eliminating the fourth-rank tensor $\langle\mathbf{eeee}\rangle$ from (3.14) by using the equation of change for $\langle\mathbf{ee}\rangle$ obtained from the kinetic equation (B.1). The resulting Giesekus form of the stress is given by the expression

$$\sigma_{\text{rigid}}(t^*) = -\mathbf{I}kTc(2-\kappa) + 3kTc(1-\kappa)\langle\mathbf{ee}\rangle + \tfrac{1}{2}kTc\kappa[\alpha^{*\text{T}}\cdot\langle\mathbf{ee}\rangle + \langle\mathbf{ee}\rangle\cdot\alpha^*] - \tfrac{1}{2}kTc\kappa\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathbf{ee}\rangle - kTc\nu\langle\mathbf{e}\cdot\alpha^*\mathbf{e}\cdot\alpha^* - \mathbf{ee}(\mathbf{e}\cdot\alpha^*)^2\rangle \quad (5.14)$$

Here α^{*T} is the tensor transpose of the dimensionless shear rate $\alpha^* = \alpha/D_{rot}$ and $t^* = D_{rot}t$ is a dimensionless time variable.

The shear viscosity increase caused by the (noninteracting) rods then can be written in the form

$$\delta\eta(\omega^*,\dot\alpha^*) = \frac{kTc}{D_{rot}}\Big\{(1-\kappa)\times \left(\frac{12\pi}{5}\right)^{1/2}\frac{1}{\dot\alpha^*}\phi_{2,1}(\omega^*) - \kappa\left(\frac{i\omega^*}{\dot\alpha^*}\right)\left(\frac{\pi}{15}\right)^{1/2}\phi_{2,1}(\omega^*) + \frac{1}{3}\kappa\pi^{1/2}\left[\phi_{0,0}(\omega^*) + \frac{1}{5^{1/2}}\phi_{2,0}(\omega^*) - \left(\frac{3}{5}\right)^{1/2}\phi_{2,2}(\omega^*)\right] + \nu\dot\alpha^*\pi^{1/2}\left[\frac{2}{7}\left(\frac{3}{5}\right)^{1/2}\phi_{2,1}(\omega^*) + \frac{1}{7}\left(\frac{2}{5}\right)^{1/2}\phi_{4,1}(\omega^*) - \frac{1}{3}\left(\frac{2}{35}\right)^{1/2}\phi^*_{4,3}(\omega^*)\right]\Big\} \quad (5.15)$$

where $\dot\alpha^*$ is the dimensionless rate of strain

$$\dot\alpha^* = \dot\alpha/D_{rot} \quad (5.16)$$

and the dimensionless parameter ν is defined by

$$\nu = D_{rot}{}^2\left(\frac{ml^2}{2kT}\right) = \frac{m}{\xi_\perp}D_{rot} \quad (5.17)$$

The objects $\phi_{L,M}(\omega^*)$ are the projections on symmetry-adapted spherical harmonics of the Fourier time transform of $\phi(\mathbf{e},t)$

$$\phi_{L,M}(\omega^*) = \langle L,\pm M|\phi(\mathbf{e},\omega)\rangle \quad (5.18)$$

By $\omega^* = \omega/D_{rot}$ we denote the dimensionless frequency. The bracket notation of (5.18) is explained in Appendix A.

The steady-state viscosity increase is given by

$$\delta\eta(\dot\alpha^*) = \lim_{\omega^*\to 0}[i\omega^*\delta\eta(\omega^*,\dot\alpha^*)] \quad (5.19)$$

It is interesting to note that the viscosity of the present theory is a two-parameter function of the shear rate. For the TMV solution in water at 20 °C the value of the parameter ν is 2.21×10^{-8}. Since ν is so very small its contribution can be safely neglected.

This dependence of the viscosity on characteristic molecular parameters is a new feature introduced by our theory. All previous theories[6,8,12-14] led to universal expressions for the viscosity increase, common to all rodlike particle solutes. We recover the previous results for the stress tensor and viscosity obtained by Bird et al.[3] for the rigid dumbbell model (as well as the results of Jain and Cohen[8] and Dahler et al.[13,16] in the low-concentration limit) if we assign to the parameters the values $\kappa = 1$ and $\nu = 0$. Kuzuu and Doi[12] and Doi and Edwards[6] completely neglected the terms involving these parameters.

For the normal stress coefficients defined by

$$\Psi_1(\omega^*,\dot\alpha^*) = \dot\alpha^{-2}[\sigma_{zz}(\omega^*,\dot\alpha^*) - \sigma_{xx}(\omega^*,\dot\alpha^*)] \quad (5.20)$$

and

$$\Psi_2(\omega^*,\dot\alpha^*) = \dot\alpha^{-2}[\sigma_{xx}(\omega^*,\dot\alpha^*) - \sigma_{yy}(\omega^*,\dot\alpha^*)] \quad (5.21)$$

we obtain the following expressions:

$$\Psi_1(\omega^*,\dot\alpha^*) = -\left(\frac{kTc}{D_{rot}{}^2}\right)\Big\{\left(\frac{1}{\dot\alpha^*}\right)^2(1-\kappa)(6)\times \left(\frac{\pi}{5}\right)^{1/2}\left[\phi_{2,0}(\omega^*) - \frac{1}{3^{1/2}}\phi_{2,2}(\omega^*)\right] - \left(\frac{\kappa}{\dot\alpha^*}\right)\left(\frac{4\pi}{5}\right)^{1/2}\phi_{2,1}(\omega^*) - \left(\frac{\kappa i\omega^*}{\dot\alpha^{*2}}\right)\left(\frac{\pi}{5}\right)^{1/2}\left[\phi_{2,0}(\omega^*) - \frac{1}{3^{1/2}}\phi_{2,2}(\omega^*)\right] + \nu\Big[\frac{2}{105}(35\pi)^{1/2}\phi_{4,4}(\omega^*) - \frac{8}{7}\left(\frac{3\pi}{5}\right)^{1/2}\phi_{2,2}(\omega^*) - \frac{8}{105}(5\pi)^{1/2}\phi_{4,2}(\omega^*) + \frac{14}{15}\pi^{1/2}\phi_{0,0}(\omega^*) + \frac{4}{3}\left(\frac{\pi}{5}\right)^{1/2}\phi_{2,0}(\omega^*) + \frac{2}{15}\pi^{1/2}\phi_{4,0}(\omega^*)\Big]\Big\} \quad (5.22)$$

$$\Psi_2(\omega^*,\dot\alpha^*) = -\left(\frac{kTc}{D_{rot}{}^2}\right)\Big\{\left(\frac{1}{\dot\alpha^*}\right)^2(1-\kappa)(12)\times \left(\frac{\pi}{15}\right)^{1/2}\phi_{2,2}(\omega^*) - \left(\frac{\kappa i\omega^*}{\dot\alpha^{*2}}\right)(2)\left(\frac{\pi}{15}\right)^{1/2}\phi_{2,2}(\omega^*) - \nu\pi^{1/2}\Big[\frac{4}{15}\phi_{0,0}(\omega^*) + \frac{8}{21(5^{1/2})}\phi_{2,0}(\omega^*) + \frac{4}{105}\phi_{4,0}(\omega^*) - \frac{4}{7}\left(\frac{3}{5}\right)^{1/2}\phi_{2,2}(\omega^*) - \frac{4}{105}(5^{1/2})\phi_{4,2}(\omega^*) + \frac{4}{105}(35^{1/2})\phi_{4,4}(\omega^*)\Big]\Big\} \quad (5.23)$$

For small values of the shear rate $\dot\alpha^*$ the solution of the kinetic equation (4.17) can be written as a power series in $\dot\alpha^*$. Details of this series solution are reported in Appendix C. For a stationary flow we obtain the following approximations to the viscosity and normal stress coefficients:

$$\delta\eta(\dot\alpha^*) = \frac{kTc}{15D_{rot}}(1.5+\kappa)\left\{1 - \frac{\dot\alpha^{*2}}{1.5+\kappa}\left(\frac{1}{7}\right)\left(\frac{19}{60} - \frac{1}{15}\kappa + \frac{3}{2}\nu\right)\right\} \quad (5.24)$$

$$\Psi_1(\dot\alpha^*) = \frac{kTc}{30D_{rot}{}^2}\left\{1 - 14\nu - \dot\alpha^{*2}\left(\frac{1}{105}\right)\left[\frac{841555}{223608} - \frac{1103}{1848}\kappa - 31\nu\right]\right\} \quad (5.25)$$

$$\Psi_2(\dot\alpha^*) = -\frac{kTc}{105D_{rot}{}^2}\left\{(1-\kappa) - 14\nu - \dot\alpha^{*2}\left(\frac{1}{30}\right)\left(\frac{1891}{1617}(1-\kappa) - 11\nu\right)\right\} \quad (5.26)$$

For higher values of the reduced rate of strain we have solved the kinetic equation using the well-known projection operator technique. Details of this solution technique and of the approximations it entails are given in Appendix D. Results obtained with various values of the parameter κ for the viscosity increase and the two normal stress coefficients are presented in Figures 2–4. Our calculations of the viscosity are compared with Wada's[15] experimental measurements on TMV solutions. The agreement between the theoretical predictions and experiments is very good for $\dot\alpha^* < 3$. For higher values of $\dot\alpha^*$ the experimental viscosity decreases more rapidly with the rate of shear than the theoretical predictions for $\kappa = 0.313$. In fact, the two experimental points for $\dot\alpha^* > 3$ lie outside the range of theoretical predictions for any admissible value (0–1) of

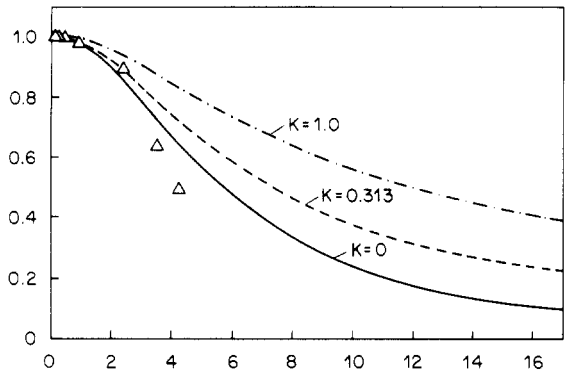

Figure 2. Variation $\delta\eta(\dot{\alpha}^*)/\delta\eta(0)$ of the shear viscosity with the dimensionless rate of strain $\dot{\alpha}^* = \dot{\alpha}/D_{rot}$. The triangles indicate the experimental values reported in ref 15.

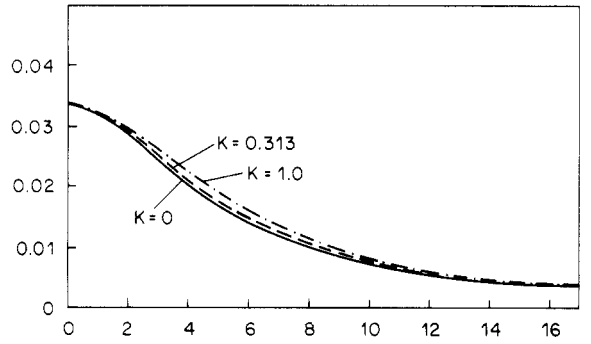

Figure 3. First normal stress coefficient $\Psi_1(\dot{\alpha}^*)(D_{rot}^2/kTc)$ vs. $\dot{\alpha}^*$.

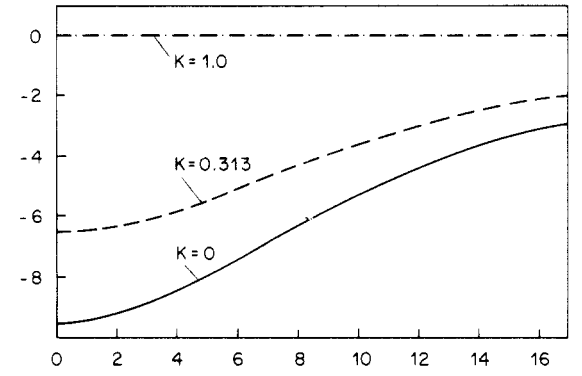

Figure 4. Second normal stress coefficient $\Psi_2(\dot{\alpha}^*)(D_{rot}^2/kTc) \times 10^3$ vs. $\dot{\alpha}^*$.

κ. In all cases the terms involving ν, here equal to 2.21×10^{-8}, were found to be totally negligible.

The discrepancies between theory and experiment for large values of $\dot{\alpha}^*$ may be due to interactions among the TMV particles, since Wada made no attempt to extrapolate his results to the limit of infinite dilution. However, it also is possible that our approximate solution of eq 4.17 is inadequate at high rates of shear.

It should be noted that the same experiments with which we have made our comparisons also have been discussed by Bird et al.[3] in connection with their studies of the rigid dumbbell model. The locations of the experimental points in their Figure 11.4.1 are incorrect and the agreement which they obtain between theory and experiment is for a rotational diffusion coefficient with the unacceptable value of $^1/_6$ s^{-1} instead of the experimental value of 400.3 s^{-1}.

6. Final Remarks

We have proposed a new, comprehensive theory of the dynamics of solutions containing rodlike particles. This theory has been formulated so that after the values of a few essential parameters (like D_{rot}, κ, and ν) have been established by experimental measurements on an infinitely dilute solutions, all of the remaining rheological observables can be computed as functions of time (or frequency), rate of strain, and concentration. The theory presented here is restricted to very dilute solutions.

The calculations which we have performed show that the theory is useful and provides a unified view of various rheological properties. However, two things have prevented us from thoroughly testing the theory. The first of these is the incompleteness of the experimental data and the diversity of its sources—properties have not been measured for one and the same solution. Furthermore, the presentation of results in overcrowded graphs and the all-too-frequent use of logarithmic scales makes it difficult to recover the experimental results from the research papers. There is an obvious need for a comprehensive experimental study of the flow properties of solutions of well-characterized rodlike particles! The second problem is that the accuracy of our theoretical predictions depends upon the accuracy with which we can solve the kinetic equation for the orientational distribution function, especially for large values of the dimensionless rate of shear $\dot{\alpha}^*$. Besides simple perturbation-like expansions in powers of $\dot{\alpha}^*$ which cannot be expected to work well for $\dot{\alpha}^* > 1$, most previous investigators have used truncated spherical harmonic expansions, retaining the terms in (B.13) with $L \leq 10$ or 12 and solving by numerical means the resulting (finite) set of coupled equations for the moments $\phi_{L,M}(t)$. In contrast to this, we have used the projection operator method to generate an approximate analytic solution which should be valid for all values of $\dot{\alpha}^*$. Neither method is exact and so a truly satisfactory solution to the numerical problem is still missing. However, the two methods produce nearly indistinguishable predictions of the viscosity $\delta\eta(\dot{\alpha}^*)$ provided that $\dot{\alpha}^* \leq 10$. At higher values of $\dot{\alpha}^*$ our method predicts that $\delta\eta(\dot{\alpha}^*)$ will approach a finite limit whereas the truncated moment method shows a monotone decay, presumably to zero. This comparison was conducted with the parameter values $\kappa = 1$ and $\nu = 0$, which should cause our results to agree with those of Jain and Cohen.

The referee has drawn our attention to several interesting papers on the dynamics of axisymmetric particles which treat the solute Brownian particle as a rigid macroscopic body with tensorial translational and rotational mobilities. An extensive presentation of this approach, as well as some additional pertinent references, can be found in the papers by Brenner et al.[19] This approach is evidently more general (but also much more involved) than the simple "one-dimensional rod" model proposed in the present paper. Whether the added complexity is a necessary price to pay for an adequate description of rheological properties of macroparticle suspensions is unknown because the theory has not been tested against experimental data. When the mobilities of this more complicated theory are adapted to the rigid dumbbell model, the previously mentioned results of Bird and his co-workers[3,5] are recovered. For suspensions formed from cylindrical particles of macroscopic dimensions the use of the Brenner description with the material friction tensors calculated on the basis of hydrodynamics is very likely to be useful. It is less certain that those formulas will be reliable for particles of molecular dimensions. Only comprehensive tests involving a number of different experimental observables can settle this matter.

Acknowledgment. This research has been supported

by a grant from the National Science Foundation.

Appendix A. External Fields

By replacing the external forces $\Phi(\mathbf{r}_1)$ and $\Phi(\mathbf{r}_2)$ which appear in eq 2.2 with $q_1\phi(\mathbf{r}_1)$ and $q_2\phi(\mathbf{r}_2)$, respectively, we obtain in place of (2.7) and (2.8) the two equations

$$2m\ddot{\mathbf{R}} = -2\xi\cdot[\dot{\mathbf{R}} - \cosh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_{\mathbf{R}})\mathbf{w}(\mathbf{R})] + \Phi_{cm} \quad (A.1)$$

$$m\ddot{\mathbf{r}} = -\xi\cdot[\dot{\mathbf{r}} - 2\sinh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_{\mathbf{R}})\mathbf{w}(\mathbf{R})] + 2\mathbf{F}(\mathbf{r}) + \Phi_{rel} \quad (A.2)$$

The external forces associated with the center-of-mass and relative, internal motions are defined by the formulas

$$\Phi_{cm} = q_1\phi(\mathbf{R} + \tfrac{1}{2}\mathbf{r}) + q_2\phi(\mathbf{R} - \tfrac{1}{2}\mathbf{r})$$

$$= 2\cosh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_R)\phi(\mathbf{R}); \qquad q_1 = q_2 = 1 \quad (A.3a)$$

$$= 2\sinh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_R)\phi(\mathbf{R}); \qquad q_1 = -q_2 = 1 \quad (A.3b)$$

and

$$\Phi_{rel} = q_1\phi(\mathbf{R} + \tfrac{1}{2}\mathbf{r}) + q_2\phi(\mathbf{R} - \tfrac{1}{2}\mathbf{r})$$

$$= 2\sinh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_R)\phi(\mathbf{r}); \qquad q_1 = q_2 = 1 \quad (A.4a)$$

$$= 2\cosh(\tfrac{1}{2}\mathbf{r}\cdot\nabla_R)\phi(\mathbf{R}); \qquad q_1 = -q_2 = 1 \quad (A.4b)$$

The choice of $q_1 = q_2 = 1$ is the same as that made in the text and corresponds to gravitational or wall forces which do not distinguish between the two elements (ends) of the rod. The second choice of $q_1 = -q_2 = 1$ is appropriate to the interaction of a dipolar rod with an external electric field $\phi = \mathbf{E}$.

The analogues of the text equations (2.9) and (2.10) are

$$m\ddot{\mathbf{R}} = -\xi\cdot[\dot{\mathbf{R}} - \mathbf{w}(\mathbf{R})] + \begin{Bmatrix}\Phi(\mathbf{R})\\ {}^1/_2\,\mathbf{r}\cdot\nabla_{\mathbf{R}}\phi(\mathbf{R})\end{Bmatrix} \quad (A.5)$$

and

$$m\ddot{\mathbf{r}} = -\xi\cdot[\dot{\mathbf{r}} - \mathbf{r}\cdot\nabla_{\mathbf{R}}\mathbf{w}(\mathbf{R})] + 2\mathbf{F}(\mathbf{r}) + \begin{Bmatrix}\mathbf{r}\cdot\nabla_{\mathbf{R}}\Phi(\mathbf{R})\\ 2\Phi(\mathbf{R})\end{Bmatrix} \quad (A.6)$$

respectively. From these we conclude that results appropriate to the "polar" case can be gotten from those of the "nonpolar" theory by performing the interchange $\Phi \leftrightarrow {}^1/_2\mathbf{r}\cdot\gamma$. The corresponding interchange for rigid rods is $\Phi \leftrightarrow {}^1/_2 l\mathbf{e}\cdot\gamma$. To transform the theory from one model to the other, these interchanges should be made wherever the quantities Φ and γ occur in eq 2.9, 2.10, 2.14, 2.15, 3.9, 3.14, 4.5–4.9, 4.11, and 4.15.

Appendix B. Orientational Distribution Function for Simple Shear

In the special case of the steady simple shear defined by (5.14), eq 4.17 for the orientational distribution function becomes

$$D_{rot}^{-1}[\partial_t\phi(\mathbf{e},t)] = (S_0 + \delta S)\phi(\mathbf{e},t) \quad (B.1)$$

with

$$S_0 = \nabla_e^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \quad (B.2)$$

and

$$\delta S = 3\dot{\alpha}^*(\mathbf{e}\cdot\mathbf{n}_x)(\mathbf{e}\cdot\mathbf{n}_z) - \dot{\alpha}^*(\mathbf{e}\cdot\mathbf{n}_x)(\mathbf{n}_z\cdot\nabla_e) =$$
$$\frac{\dot{\alpha}^*}{2}(e^{i\phi} + e^{-i\phi})\left[3\sin\theta\cos\theta - \sin^3\theta\frac{\partial}{\partial\cos\theta}\right] \quad (B.3)$$

The spherical harmonics defined in the manner[16]

$$Y_L^M(\mathbf{e}) = \langle\mathbf{e}|L,M\rangle =$$
$$(-1)^M i^L\left[\frac{2L+1}{4\pi}\frac{(L-M)!}{(L+M)!}\right]^{1/2} e^{iM\phi}P_L^M(\cos\theta) \quad (B.4)$$

are eigenfunctions of S_0 with eigenvalues equal to $-L(L+1)$. These functions satisfy the orthonormality conditions

$$\langle L,M|L',M'\rangle = \delta_{L,L'}\delta_{M,M'} \quad (B.5)$$

wherein

$$\langle L,M|\mathbf{e}\rangle = Y_L^M(\mathbf{e})^* = (-1)^{L+M}Y_L^{-M}(\mathbf{e}) \quad (B.6)$$

In this spherical harmonic basis the matrix elements of the operator δS conform to the relationship

$$\langle L',M'|\delta S|L,M\rangle =$$
$$\delta S(L,M+1|L,M)\delta_{L',L}\delta_{M',M+1} - \delta S(L,-M+1|L,-M)\delta_{L',L}\delta_{M',M-1} + \delta S(L+2,M+1|L,M)\delta_{L',L+2}\delta_{M',M+1} - \delta S(L+2,-M+1|L,-M)\delta_{L',L+2}\delta_{M',M-1} + \delta S(L-2,M+1|L,M)\delta_{L',L-2}\delta_{M',M+1} - \delta S(L-2,-M+1|L,-M)\delta_{L',L-2}\delta_{M',M-1} \quad (B.7)$$

and satisfy the conditions

$$\delta S(L,M-1|L,M) = -\delta S(L,-M+1|L,-M)$$
$$\delta S(L+2,M-1|L,M) = -\delta S(L+2,-M+1|L,-M) \quad (B.8)$$
$$\delta S(L-2,M-1|L,M) = -\delta S(L-2,-M+1|L,-M)$$

The nonvanishing matrix elements of δS are given explicitly by the expressions

$$\delta S(L,M+1|L,M) = \frac{1}{2}\dot{\alpha}^*\left[\frac{(L-M+1)(L+3)}{(2L+1)(2L+3)} + \frac{(L-2)(L+M)}{(2L+1)(2L-1)}\right][(L-M)(L+M+1)]^{1/2}$$

$$\delta S(L+2,M+1|L;M) = \frac{1}{2}\dot{\alpha}^*\left[\frac{L+3}{2L+3}\right]\times$$
$$\left[\frac{(L+M+1)(L+M+2)(L+M+3)(L-M+1)}{(2L+1)(2L+5)}\right]$$

$$\delta S(L-2,M+1|L,M) = \frac{1}{2}\dot{\alpha}^*\left[\frac{L-2}{2L-1}\right]\times$$
$$\left[\frac{(L+M)(L-M)(L-M-1)(L-M-2)}{(2L+1)(2L-3)}\right]^{1/2} \quad (B.9)$$

The two ends of a particle are indistinguishable. This implies that $\phi(\mathbf{e},t) = \phi(-\mathbf{e},t)$ and that the only terms which contribute to the expansion

$$\phi(\mathbf{e},t) = \langle\mathbf{e}|\phi(t)\rangle = \sum_{L=0}^{\infty}\sum_{M=-L}^{L}\langle\mathbf{e}|L,M\rangle\langle L,M|\phi(t)\rangle \quad (B.10)$$

are those with even values of L. Furthermore, because of the symmetry of the flow

$$\phi(\mathbf{e},t) = \phi(\theta,\phi;t) = \phi(\theta,-\phi;t) \quad (B.11)$$

This leads to the conclusion that

$$\langle L,M|\phi(t)\rangle = (-1)^M\langle L,-M|\phi(t)\rangle \quad (B.12)$$

which, in turn, permits us to rewrite (B.10) as an expansion

$$\phi(\mathbf{e},t) = \sum_{\substack{L=0\\(L\text{ even})}}^{\infty}\sum_{M=0}^{L}\langle\mathbf{e}|L,\pm M\rangle\langle L,\pm M|\phi(t)\rangle \quad (B.13)$$

in terms of the symmetry-adapted orthonormal basis ele-

ments (restricted to even values of L and $M \geq 0$)

$$|L,\pm M\rangle \equiv 2^{-1/2}[|L,M\rangle + (-1)^M|L,-M\rangle]; \qquad M > 0 \quad \text{(B.14)}$$

$$|L,\pm 0\rangle \equiv |L,0\rangle; \qquad M = 0$$

The matrix elements of δS specific to this new basis are related to those of the old as follows:

$$\langle L',\pm M'|\delta S|L,\pm M\rangle = \langle L',M'|\delta S|L,M\rangle; \qquad \text{for } M,M' \geq 1 \text{ and } M = M' = 0$$

$$\langle L',\pm 0|\delta S|L,\pm M\rangle = 2^{1/2}\langle L',0|\delta S|L,M\rangle; \qquad \text{for } M \geq 1 \text{ and } M' = 0 \quad \text{(B.15)}$$

$$\langle L',\pm M'|\delta S|L,\pm 0\rangle = 2^{1/2}\langle L',M'|\delta S|L,0\rangle; \qquad \text{for } M' \geq 1 \text{ and } M = 0$$

Appendix C. Perturbative Series for $\phi(\mathbf{e},t)$

The solution of eq B.1 can be expressed in the form

$$|\phi(t)\rangle = \frac{1}{2\pi^{1/2}}|0,0\rangle + |\delta\phi(t)\rangle \qquad \text{(C.1)}$$

Introducing the Fourier–Laplace transform

$$|\delta\phi(\omega)\rangle = \int_0^\infty dt\ e^{-i\omega t}|\delta\phi(t)\rangle \qquad \text{(C.2)}$$

we obtain the integral form of eq B.1

$$|\delta\phi(\omega)\rangle = \gamma(\omega)|2,\pm 1\rangle + \frac{1}{i\omega^* - S_0}\delta S|\delta\phi(\omega)\rangle \qquad \text{(C.3)}$$

with $\omega^* = \omega/D_{\text{rot}}$ and where

$$\gamma(\omega) = \left(\frac{3}{20\pi}\right)^{1/2}\frac{\dot\alpha^*}{i\omega^*(i\omega^* + 6)} \qquad \text{(C.4)}$$

The perturbation $|\delta\phi(\omega)\rangle$ can be represented in the form of the series

$$|\delta\phi(\omega)\rangle = \sum_{n=1}^{\infty}|\delta\phi^{(n)}(\omega)\rangle \qquad \text{(C.5)}$$

with consecutive terms proportional to increasingly higher powers of $\dot\alpha^*$. In particular, we find that

$$|\delta\phi^{(1)}(\omega)\rangle = \gamma(\omega)|2,\pm 1\rangle \qquad \text{(C.6)}$$

$$|\delta\phi^{(2)}(\omega)\rangle = \dot\alpha^*\gamma(\omega)\left(\frac{2}{7}\right)\left\{\frac{1}{i\omega^* + 6}[|2,\pm 2\rangle - 2(3^{1/2}) \times |2,0\rangle] + \frac{1}{i\omega^* + 20}\left[\frac{5}{3^{1/2}}|4,\pm 2\rangle - 2\left(\frac{5}{3}\right)^{1/2}|4,0\rangle\right]\right\} \qquad \text{(C.7)}$$

and

$$|\delta\phi^{(3)}(\omega)\rangle = -\dot\alpha^{*2}\gamma(\omega)\left\{\frac{1}{i\omega^* + 6}\left[\frac{1}{i\omega^* + 6}\left(\frac{46}{49}\right) + \frac{1}{i\omega^* + 20}\left(\frac{24}{49}\right)\right]|2,\pm 1\rangle + \frac{1}{i\omega + 20}\left[\frac{1}{i\omega^* + 6}\left(\frac{65}{49}\right) + \frac{1}{i\omega^* + 20}\left(\frac{955}{539}\right)\right]\left(\frac{2}{3}\right)^{1/2}|4,\pm 1\rangle - \frac{1}{i\omega^* + 20}\left[\frac{1}{i\omega^* + 6} + \left(\frac{31}{11}\right)\frac{1}{i\omega^* + 20}\right]\left(\frac{5}{49}\right) \times \left(\frac{14}{3}\right)^{1/2}|4,\pm 3\rangle - \frac{1}{i\omega^* + 42}\ \frac{1}{i\omega^* + 20}\left(\frac{10}{11}\right)\left(\frac{14}{13}\right)^{1/2}|6,\pm 3\rangle + \frac{1}{i\omega^* + 42}\ \frac{1}{i\omega^* + 20}\left(\frac{10}{11}\right)\left(\frac{35}{13}\right)^{1/2}|6,\pm 1\rangle\right\} \qquad \text{(C.8)}$$

The stationary distribution function in the presence of the shear flow can be obtained from the expression

$$|\phi^{\text{stat}}\rangle = \lim_{t\to\infty}|\phi(t)\rangle = \frac{1}{2\pi^{1/2}}|0,0\rangle + |\delta\phi^{\text{stat}}\rangle \qquad \text{(C.9)}$$

with

$$|\delta\phi^{\text{stat}}\rangle = \lim_{\omega\to 0}[i\omega|\delta\phi(\omega)\rangle] = |\delta\phi^{(1)}_{\text{stat}}\rangle + |\delta\phi^{(2)}_{\text{stat}}\rangle + \ldots \qquad \text{(C.10)}$$

and where

$$|\delta\phi^{(1)}_{\text{stat}}\rangle = \dot\alpha^*\left(\frac{1}{12}\right)\left(\frac{3}{5\pi}\right)^{1/2}|2,\pm 1\rangle \qquad \text{(C.11)}$$

$$|\delta\phi^{(2)}_{\text{stat}}\rangle = \dot\alpha^{*2}\left(\frac{1}{42(5\pi)}^{1/2}\right)\left[\frac{1}{2(3^{1/2})}|2,\pm 2\rangle + \frac{1}{4}|4,\pm 2\rangle - |2,0\rangle - \frac{1}{2(5^{1/2})}|4,0\rangle\right] \qquad \text{(C.12)}$$

$$|\delta\phi^{(3)}_{\text{stat}}\rangle = -\dot\alpha^{*3}\left(\frac{1}{12}\right)\left(\frac{3}{5\pi}\right)^{1/2}\left[\frac{19}{630}|2,\pm 1\rangle + \frac{2003}{129360}\left(\frac{2}{3}\right)^{1/2}|4,\pm 1\rangle - \frac{29}{18480}\left(\frac{14}{3}\right)^{1/2}|4,\pm 3\rangle - \frac{1}{924}\left(\frac{14}{13}\right)^{1/2}|6,\pm 3\rangle + \frac{1}{924}\left(\frac{35}{13}\right)^{1/2}|6,\pm 1\rangle\right] \qquad \text{(C.13)}$$

Appendix D. Approximate Solution of Kinetic Equation Using the Projection Operator Method

The simple series expansion can be expected to give an adequate approximation of the solution only for small values of the reduced rate of strain ($\dot\alpha^* \ll 1$). In order to extend the range of $\dot\alpha^*$ we apply the well-known projection operator technique[17,18] to the equation

$$\partial_{t^*}|\delta\phi(t)\rangle = (S_0 + \delta S)|\delta\phi(t)\rangle + \delta S|\phi^{\text{eq}}\rangle \qquad \text{(D.1)}$$

with the initial condition $|\delta\phi(0)\rangle = 0$. The operators in (D.1) are defined according to (B.2) and (B.3). We use the dimensionless time $t^* = D_{\text{rot}}t$.

In the Fourier–Laplace representation the equation of motion for the projection $P|\delta\phi(\omega)\rangle$ can be written as

$$i\omega^*P|\delta\phi(\omega^*)\rangle = PS_0P|\delta\phi(\omega^*)\rangle + \Omega(\omega^*)P|\delta\phi(\omega^*)\rangle + |\Xi(\omega^*)\rangle \qquad \text{(D.2)}$$

where the "scattering" operator $\Omega(\omega^*)$ is given by the expression

$$\Omega(\omega^*) = P\delta SQ\frac{1}{i\omega^* - Q(S_0 + \delta S)Q}Q\delta SP \qquad \text{(D.3)}$$

and the vector $|\Xi(\omega^*)\rangle$ by

$$i\omega^*|\Xi(\omega^*)\rangle = P\delta S|\phi^{\text{eq}}\rangle + \Omega(\omega^*)|\phi^{\text{eq}}\rangle + P\delta S\frac{1}{i\omega - Q(S_0 + \delta S)Q}Q\delta SQ|\phi^{\text{eq}}\rangle \qquad \text{(D.4)}$$

P is the projection operator onto the space spanned by the basis element $|L,\pm M\rangle$ and $Q = 1 - P$ is the complementary projector.

Because $P\delta SP = 0$ and S_0 is diagonal in this representation, we can rewrite the operator $\Omega(\omega^*)$ in the form

$$\Omega(\omega^*) = P\delta S\frac{1}{i\omega^* - Q(S_0 + \delta S)}\delta SP \qquad \text{(D.5)}$$

Using now the operator equality

$$\frac{1}{i\omega^* - Q(S_0 + \delta S)} = \frac{1}{i\omega^* - S_0 - \delta S} - \frac{1}{i\omega^* - S_0 - \delta S} P(S_0 + \delta S) \frac{1}{i\omega^* - Q(S_0 + \delta S)} \quad \text{(D.6)}$$

we obtain the following expression for the "scattering" operator:

$$\Omega(\omega^*) = V(\omega^*) - V(\omega^*) \frac{1}{i\omega^* - PS_0P + V(\omega^*)} V(\omega^*) \quad \text{(D.7)}$$

where the "elementary interaction" operator $V(\omega^*)$ is defined by

$$V(\omega^*) = P\delta S \frac{1}{i\omega^* - S_0 - \delta S} \delta SP \quad \text{(D.8)}$$

Equation D.2 is exact. The approximations we use to proceed further are the following:

(1) We approximate the operator $\Omega(\omega^*)$ by

$$\Pi^0(\omega^*) = P\delta S \frac{1}{i\omega^* - S_0} \delta SP \quad \text{(D.9)}$$

(2) We approximate the vector $|\Xi(\omega^*)\rangle$ by its perturbation expansion through terms of third order in $\dot{\alpha}^*$

$$|\Xi(\omega^*)\rangle = [i\omega^* - PS_0P][P|\delta\phi^{(1)}(\omega^*)\rangle + P|\delta\phi^{(2)}(\omega^*)\rangle + P|\delta\phi^{(3)}(\omega^*)\rangle] - \Omega^0(\omega^*)|\delta\phi^{(1)}(\omega^*)\rangle \quad \text{(D.10)}$$

where the vectors $|\delta\phi^{(i)}(\omega^*)\rangle$ are given in Appendix C. The final expression for the projection of the distribution function is

$$\delta\phi_{LM}(\omega^*) = \langle L,\pm M|\delta\phi(\omega)\rangle = \frac{1}{i\omega^* + L(L+1) - \Omega_{LM}(\omega^*)} \Xi_{LM}(\omega^*) \quad \text{(D.11)}$$

where

$$\Omega_{LM}(\omega^*) = \langle L,\pm M|\Omega^0(\omega^*)|L,\pm M\rangle \quad \text{(D.12)}$$

and

$$\Xi_{LM}(\omega^*) = \langle L,\pm M|\Xi(\omega^*)\rangle \quad \text{(D.13)}$$

The diagonal matrix element $\Omega^0_{LM}(\omega^*)$ can be expressed in terms of the matrix elements of the perturbation operator as

$$\Omega^0_{LM}(\omega^*) = \frac{1}{i\omega^* + L(L+1)}[\langle L,\pm M|\delta S|L,\pm(M+1)\rangle \times \langle L,\pm(M+1)|\delta S|L,\pm M\rangle + \langle L,\pm M|\delta S|L,\pm(M-1)\rangle\langle L,\pm(M-1)|\delta S|L,\pm M\rangle] + \frac{1}{i\omega^* + (L+2)(L+3)}[\langle L,\pm M|\delta S|L+2,\pm(M+1)\rangle \times \langle L+2,\pm(M+1)|\delta S|L,\pm M\rangle + \langle L,\pm M|\delta S|L+,\pm(M-1)\rangle\langle L+2,\pm(M-1)|\delta S|L,\pm M\rangle] + \frac{1}{i\omega^* + (L-2)(L-1)}[\langle L,\pm M|\delta S|L-2,\pm(M+1)\rangle\langle L-2,\pm(M+1)|\delta S|L,\pm M\rangle + \langle L,\pm M|\delta S|L-2,\pm(M-1)\rangle\langle L-2,\pm(M-1)|\delta S|L,\pm M\rangle] \quad \text{(D.14)}$$

where we have used the selection rules (D.7).

In the calculations performed in this paper we deal only with the stationary-flow viscometric functions.

For the stationary perturbation of the orientation distribution function we have

$$\delta\phi^{\text{stat}}_{LM} = \frac{1}{L(L+1) - \Omega^0_{LM}(0)} \Xi^{\text{stat}}_{LM} \quad \text{(D.15)}$$

where

$$\Xi^{\text{stat}}_{LM} = \lim_{\omega\to 0}[i\omega^* \Xi_{LM}(\omega^*)] \quad \text{(D.16)}$$

The appropriate coefficients are

$$\Xi^{\text{stat}}_{LM} = \Xi^{(1)\text{stat}}_{LM} + \Xi^{(2)\text{stat}}_{LM} + \Xi^{(3)\text{stat}}_{LM} \quad \text{(D.17)}$$

with

$$\Xi^{(1)\text{stat}}_{LM} = \dot{\alpha}^* \left(\frac{1}{2}\right)\left(\frac{3}{5\pi}\right)^{1/2} \delta_{L,2}\delta_{M,1}$$

$$\Xi^{(2)\text{stat}}_{LM} = \dot{\alpha}^{*2} \left(\frac{1}{42(5\pi)^{1/2}}\right) \times [3^{1/2}\delta_{L,2}\delta_{M,2} + 5\delta_{L,4}\delta_{M,2} - 6\delta_{L,2}\delta_{M,0} - 2(5^{1/2})\delta_{L,4}\delta_{M,0}]$$

$$\Xi^{(3)\text{stat}}_{LM} = -\dot{\alpha}^{*3}\left(\frac{1}{12}\right)\left(\frac{3}{5\pi}\right)^{1/2}\left[\frac{19}{105}\delta_{L,2}\delta_{M,1} + \frac{2003}{6468}\left(\frac{2}{3}\right)^{1/2}\delta_{L,4}\delta_{M,1} - \frac{29}{924}\left(\frac{14}{3}\right)^{1/2}\delta_{L,4}\delta_{M,3} - \frac{1}{22}\left(\frac{14}{13}\right)^{1/2}\delta_{L,6}\delta_{M,3} + \frac{1}{22}\left(\frac{35}{13}\right)^{1/2}\delta_{L,6}\delta_{M,1}\right] - \Omega^0_{LM}(0)\dot{\alpha}^*\left(\frac{1}{12}\right)\left(\frac{3}{5\pi}\right)^{1/2}\delta_{L,2}\delta_{M,1} \quad \text{(D.18)}$$

The functions $\Omega^0_{LM}(\omega^*)$ involved in the calculation of the non-Newtonian viscometric coefficients are given by the expressions

$$\Omega^0_{2,0}(\omega^*) = -\left(\frac{\dot{\alpha}^*}{7}\right)^2\left[\frac{72}{i\omega^* + 6} + \frac{40}{i\omega^* + 20}\right]$$

$$\Omega^0_{2,1}(\omega^*) = -\left(\frac{\dot{\alpha}^*}{7}\right)^2\left[\frac{46}{i\omega^* + 6} + \frac{24}{i\omega^* + 20}\right]$$

$$\Omega^0_{2,2}(\omega^*) = -\left(\frac{\dot{\alpha}^*}{7}\right)^2\left[\frac{10}{i\omega^* + 6} + \frac{40}{3}\frac{1}{i\omega^* + 20}\right]$$

$$\Omega^0_{4,0}(\omega^*) = -\left(\frac{\dot{\alpha}^*}{7}\right)^2\left[\frac{29600}{121}\frac{1}{i\omega^* + 20} + \frac{480200}{4719}\frac{1}{i\omega^* + 42} + \frac{64}{3}\frac{1}{i\omega^* + 6}\right] \quad \text{(D.19)}$$

$$\Omega^0_{4,1}(\omega^*) = -\left(\frac{\dot{\alpha}^*}{7}\right)^2\left[\frac{16993}{121}\frac{1}{i\omega^* + 20} + \frac{318304}{4719}\frac{1}{i\omega^* + 42} + \frac{65}{3}\frac{1}{i\omega^* + 6}\right]$$

$$\Omega^0_{4,2}(\omega^*) = -\left(\frac{\dot{\alpha}^*}{7}\right)^2\left[\frac{7184}{121}\frac{1}{i\omega^* + 20} + \frac{220892}{4719}\frac{1}{i\omega^* + 42} + \frac{40}{3}\frac{1}{i\omega^* + 6}\right]$$

$$\Omega^0_{4,3}(\omega^*) = -\left(\frac{\dot{\alpha}^*}{7}\right)^2\left[\frac{7735}{121}\frac{1}{i\omega^* + 20} + \frac{186592}{4719}\frac{1}{i\omega^* + 42} + \frac{35}{3}\frac{1}{i\omega^* + 6}\right]$$

References and Notes

(1) R. G. Cox, *J. Fluid Mech.*, **44** 791 (1970).
(2) J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951).
(3) R. B. Bird, O. Hassager, R. C. Armstrong, and C. F. Curtiss, "Dynamics of Polymeric Liquids", Vol. 2, Wiley, New York, 1977.
(4) In a recent paper, Bird et al. (R. B. Bird, X. J. Fan, and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, *15*, 85 (1984)) also obtained the term involving the velocity gradient tensor.
(5) R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **14**, 85 (1984).

(6) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, **74**, 918 (1978).
(7) G. Marrucci and N. Grizzuti, *J. Non-Newtonian Fluid Mech.*, **14**, 103 (1984).
(8) S. Jain and C. Cohen, *Macromolecules*, **14**, 759 (1981).
(9) T. A. King, A. Knox, and J. D. G. McAdam, *Biopolymers*, **12**, 1917 (1973).
(10) V. Bloomfield, K. E. Van Holde, and W. O. Dalton, *Biopolymers*, **5**, 149, (1967).
(11) N. Nemoto, J. L. Schrag, J. D. Ferry, and R. W. Fulton, *Biopolymers*, **14**, 409, (1975).
(12) N. Y. Kuzuu and M. Doi, *Polym. J.*, **12**, 883 (1980).
(13) S. Fesciyan and J. S. Dahler, *Macromolecules*, **15**, 517 (1982).
(14) J. S. Dahler, S. Fesciyan, and N. Xystris, *Macromolecules*, **16**, 1673 (1983).
(15) E. Wada, *J. Sci. Res. Inst.*, **47** 159 (1953); *J. Polym. Sci.*, **14**, 305 (1954).
(16) R. G. Newton, "Scattering Theory of Waves and Particles", Springer, New York, Heidelberg, Berlin, 1982, Chapter 2.
(17) W. Krolikowski and J. Rzewuski, *Nuovo Cimento*, **3**, 260 (1956).
(18) R. Zwanzig, in "*Boulder Lect. Theor. Phys.*, **3**, 106 (1960).
(19) H. Brenner, *Int. J. Multiphase Flow*, 1, 195 (1974); H. Brenner and D. W. Condiff, *J. Colloid Interface Sci.*, **47**, 199 (1974).

Microstructure and Dynamic Behavior of Terpolymers of SO_2, But-1-ene, and But-2-ene

Stephen A. Chambers and Allan H. Fawcett*

Department of Pure and Applied Chemistry, The Queen's University of Belfast, Belfast, Northern Ireland. *Received October 19, 1984*

ABSTRACT: Terpolymers of but-1-ene and but-2-ene with sulfur dioxide have been prepared with a range of compositions and with meso and racemic but-2-ene units so that the microstructure might be characterized by ^{13}C NMR spectroscopy. A model for high-frequency motion of a 1-olefin sulfone and a terpolymer with a high 1-olefin content is proposed; the model views the chain as a series of helices whose rotation is controlled by viscous drag at their surface and by the kinetics of the link articulation. Though a polymer consisting entirely of r_c but-2-ene sulfone units is 50 times as free as the but-1-ene polysulfone, according to T_1 measurements, no extra flexibility results from the inclusion of a small proportion of such but-2-ene units at randomly distributed fixed points in a mainly but-1-ene sulfone chain.

Introduction

In poly(1-olefin sulfone) chains electrostatic interactions between adjacent sulfone groups are sufficiently strong to create order in solution, which in the simplest accounts results in a helical segment model.[1-4] The points of disorder, or kinks, between helical units are randomly created in a poly(1-olefin sulfone) chain when a C–C bond is thermally promoted to the trans conformation so that its flanking sulfone groups are separated and their relative orientations are decoupled. Kinks may also be introduced chemically by the inclusion within the chain of a small proportion of cyclic olefin or 2-olefin structures, according to a simply theory that was supported by some measurements of the equilibrium longitudical dipole moment.[1,5] The dynamic behavior of but-1-ene and of but-2-ene polysulfone has been probed by T_1 and nuclear Overhauser measurements upon the main-chain ^{13}C NMR signals.[6-8] It has been suggested that the consequence of the electrorestrictions present in the former chain is a relatively long correlation time for high-frequency segmental motion (τ_c = 26 ns at 303 K)[6] and that their absence in the latter polymer, where the C–C bonds are trans, permits a much shorter correlation time (τ_c = 0.47 ns at 303 K).[9]

Here we offer a development of some of these ideas. For the poly(1-olefin sulfone) chain a simple hydrodynamic model is proposed for high-frequency rotations of the helical segments about their long axis and is examined by means of T_1 measurements upon the methylene carbon atoms of but-1-ene units in a terpolymer of SO_2, but-1-ene, and but-2-ene. Before that test is performed and assessed, the ^{13}C spectrum of these copolymers is related to the chain microstructure, which has three chief features: olefin sequence effects, the meso/racemic relationship of two chiral centers linked by a sulfone group (m_s/r_s), and the meso/racemic relationship of the two chiral centers within a but-2-ene structure (m_c/r_c). In order to ensure that this latter feature has been properly characterized, a copolymer has been prepared from but-1-ene and *trans*-but-2-ene at such a sufficiently low tempertaure that a large proportion of the 2-olefin units retained the configuration of the active centers to form an m_c unit.[7,10] The substitution parameters, γ_s = −2.7 ppm and δ_s = 1.0 ppm have been used when making assignments.[7,11]

Model of High-Frequency Motions of the Helices

The terpolymer of SO_2, but-1-ene, and but-2-ene is viewed as a system of linked cylinders, with one residue at a link (or kink) and $m - 1$ but-1-ene sulfone residues within a cylinder. For a cylinder of length l_m and radius a rotating in a medium of viscosity η about its axis defined by the positions of the kinks at each end,[12]

$$\tau_c = \zeta/kT$$

where

$$\zeta = \frac{\text{frictional torque at surface + torque at kinks}}{\text{angular velocity}} = 4\pi\eta a^2 l_m + \zeta_k$$

As $l_m = (m - 1)l_o$, we may write

$$\tau_{c,m} = (m - 1)\tau_o + \tau_k$$

where τ_o is the contribution to the relaxation time of a helical section made by a but-1-ene sulfone unit of length l_o and τ_k is the characteristic relaxation time of the link or kink process. If as before,[1] p is the probability that the 1-olefin unit is part of a helix and x is the mole fraction of those units in the chain, the number of helices containing m units is

$$N_m = z(1 - px)^2(px)^{m-1}$$

0024-9297/85/2218-1710$01.50/0