International Journal of Thermophysics, Vol. 10, No. 1, 1989

Theoretical Rheology of Suspensions of Ferromagnetic Rod-like Particles[1]

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We extend the linear response-like derivation of the generalized Navier–Stokes equation to non-Newtonian flows with rate of strain-dependent transport coefficients. We derive a time correlation function expression for the viscosity tensor and point out possible ambiguities in the operational definitions of viscosity coefficients. Our analysis is specific to a suspension of polar, rod-like ferromagnetic particles. A commentary is included about the approximations that lead from the time correlation function and the molecular definition of the viscosity tensor to the standard, Brownian dynamics model used in the theoretical rheology of suspensions. Some theoretical difficulties and logical inconsistencies are pointed out. Preliminary results for the transport coefficients of dilute suspension of magnetic rod-like particles are presented.

KEY WORDS: ferromagnetic suspensions; non-Newtonian fluids; rheology; time correlation functions.

1. INTRODUCTION

During recent years an increased interest can be detected in the study of the rheological properties of nonsimple fluid mixtures. In particular, solutions of rod-like macroparticles or polymers are often investigated due to their common occurrence in nature and important practical applications. There are numerous, unanswered theoretical questions related to proper statistical mechanical and hydrodynamical descriptions of such

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[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

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systems. Particularly important are questions pertaining to their non-Newtonian and viscoelastic behavior and to the ordering produced by externally applied electric or magnetic fields.

In the present paper we report results of our theoretical research on the rheology of dilute solutions of rod-like particles having permanent magnetic (or electric) dipoles along the particle axes. Solutions of ferromagnetic inorganic crystals (iron oxide, chromium dioxide) or rigid organic macromolecules (*p*-azoxyanisole, TMV virus) belong to this class. Our model of dipolar rod-like particles is similar to that we have used previously [1–4]. The ferro- or paramagnetic particle is represented by a rigid dumbbell whose two interaction sites have identical masses but opposite, formal magnetic charges. The solvent consists of spherical, non-polarizable molecules with diameters much smaller than the lengths of the rods. We assume that the mixture is placed in a uniform, constant magnetic field which orients the dipoles. This ordering is disturbed by the flow of the solution.

The model of a solution that is most often used in polymer rheology treats solute components as sets of Brownian particles moving randomly in a structureless continuum described by a linearized Navier–Stokes equation [5, 6]. This model greatly oversimplifies the mechanical description of the system and, although useful, poses some conceptual problems that are not likely to be solved without reference to a more complete statistical mechanical description. Some of these difficulties are discussed here in connection with the definition of the viscosity tensor in terms of the microscopic stress, the equilibrium time correlation function, and a proposed extension of this formalism to the region of non-Newtonian flows. In our opinion, it is advisable to retain a detailed micromechanical formulation of the problem as long as possible, thus postponing the introduction of the Brownian approximation to the dynamics to a very late stage in the calculation. A premature introduction of the Langevin-like, Rouse–Zimm equations of motion with a semiphenomenological friction force (and "random" force) can lead to serious difficulties and even to erroneous conclusions.

2. THE DYNAMICS OF SOLUTIONS OF POLAR ROD-LIKE PARTICLES

The momentum conservation equation for the mixture can be written in the form

$$\partial_t \mathbf{g}(\mathbf{r}, t) = \nabla_{\mathbf{r}} \cdot \boldsymbol{\sigma}(\mathbf{r}, t) \tag{1}$$

where $\mathbf{g}(\mathbf{r}, t)$ is the momentum density and $\boldsymbol{\sigma}(\mathbf{r}, t)$ the stress tensor of the solution. The latter can be expressed as the ensemble average

$$\boldsymbol{\sigma}(\mathbf{r}, t) = \int d\Gamma\, F(\Gamma, t)\, \hat{\boldsymbol{\sigma}}(r, 0) = \int d\Gamma\, F(\Gamma, 0)\, \hat{\boldsymbol{\sigma}}(r, t) \tag{2}$$

of the corresponding microscopic stress, $\hat{\boldsymbol{\sigma}}(\mathbf{r}, t)$. The symbol Γ appearing here denotes a complete set of phase space variables and $F(\Gamma, t)$ is the ensemble distribution function at time t.

The microscopic stress is a sum of contributions due to the two components of the mixture (solvent S and Brownian solute B) taken separately and a term due to their mutual interactions, *viz.*,

$$\hat{\boldsymbol{\sigma}} = \hat{\boldsymbol{\sigma}}_{\mathrm{S}} + \hat{\boldsymbol{\sigma}}_{\mathrm{B}} + \hat{\boldsymbol{\sigma}}_{\mathrm{BS}} \tag{3}$$

Detailed formulas for these quantities are not necessary here.

Using the Zwanzig–Mori projection operator technique [7] with the set of projection operators appropriate to generating the equations of fluid mechanics [8], we obtain the following form of the generalized Navier–Stokes equation:

$$\begin{aligned}\partial_t\, \delta\mathbf{g}(\mathbf{r}, t) = {}& -\nabla_{\mathbf{r}}\, \delta P(\mathbf{r}, t) + \int_0^t dt'\, \nabla_{\mathbf{r}} \cdot \mathbf{H}(\mathbf{r} - \mathbf{r}', t - t') \colon \nabla_{\mathbf{r}'}\, \delta\mathbf{g}(\mathbf{r}', t') \\ & + \nabla_{\mathbf{r}} \cdot \delta\boldsymbol{\sigma}_{\mathrm{R}}(\mathbf{r}, t)\end{aligned} \tag{4}$$

Here

$$\delta\mathbf{g}(\mathbf{r}, t) = \mathbf{g}(\mathbf{r}, t) - \langle \hat{\mathbf{g}}(\mathbf{r}, 0) \rangle \tag{5}$$

is the deviation of the momentum density field from its average value in the stationary reference state and $\delta P(\mathbf{r}, t)$ is the deviation of the generalized pressure. Finally, $\delta\boldsymbol{\sigma}_{\mathrm{R}}(\mathbf{r}, t)$ is the part of the stress tensor that cannot be expressed as a functional of the deviations of the momentum density, temperature, and mass density fields from the average values appropriate to the reference steady state.

The fourth-rank viscosity tensor $\mathbf{H}(\mathbf{r}, t)$ is the time–autocorrelation function

$$\mathbf{H}(\mathbf{r}, t) = \frac{1}{kTV} \int d\mathbf{r}' \langle \delta\hat{\boldsymbol{\sigma}}_{\mathrm{R}}(\mathbf{r} + \mathbf{r}', t)\, \delta\hat{\boldsymbol{\sigma}}(\mathbf{r}', 0) \rangle \tag{6}$$

of the random microscopic stress fluctuation, $\delta\hat{\boldsymbol{\sigma}} = \hat{\boldsymbol{\sigma}} - \langle \hat{\boldsymbol{\sigma}} \rangle$, and

$$\hat{\boldsymbol{\sigma}}_{\mathrm{R}}(\mathbf{r}, t) = \exp[iQL]\, Q\hat{\boldsymbol{\sigma}}(\mathbf{r}, 0) \tag{7}$$

Here L is the Liouville operator of the system and Q is the projection operator complementary to the projection onto the fluctuations of the hydrodynamic fields mentioned above. The angle bracket denote averaging over a stationary distribution function $F_0(\Gamma)$ such that $LF_0(\Gamma) = 0$.

If one choses the equilibrium state of the system as the reference state, then Eq. (6) becomes the familiar equilibrium time–correlation function from which the Green–Kubo molecular definitions of various viscosity coefficients can be extracted. However, the equilibrium time–correlation functions cannot describe a non-Newtonian effect like shear thinning since the latter reflects the ordering of the nonspherical solute particles by an imposed nonuniform flow. In order to describe properties of the mixture that depend on certain types of imposed flows we must consider transport coefficients defined with respect to reference steady states different from states of equilibrium. Naturally, the stationary distribution function of the phase space variables, $F_0(\Gamma)$, must depend on the parameters that characterize the stationary state. In other words, the non-Newtonian effects are, in the present formulation, connected with propagation of small perturbations superimposed upon the reference stationary flow. In general, exact analytic expressions for the nonequilibrium stationary distributions $F_0(\Gamma)$ for particular flows are not known. Besides, as is the case for the Green–Kubo formulas, calculations of the transport coefficients directly from their definitions are impractical. The problem must first be reduced to a manageable level of complexity. Nevertheless, the general formulas are important and convenient in analysis. In particular, some conclusions about reciprocal relations can be obtained much more easily in this formulation than from the formulas of the standard theoretical rheology [6]. With this point of view in mind we write the following expression for the stress generated in the mixture by a small perturbation of the stationary flow:

$$\begin{aligned}\boldsymbol{\sigma}[\mathbf{r}, t; \boldsymbol{\alpha}_0 + \delta\boldsymbol{\alpha}(\mathbf{r}, t)] &\\ = \boldsymbol{\sigma}_0(\boldsymbol{\alpha}_0) - \mathbf{I}\,\delta P(\mathbf{r}, t; \boldsymbol{\alpha}_0) &\\ + \int_0^t dt' \int d\mathbf{r}' \left(\frac{\delta\boldsymbol{\sigma}(\mathbf{r}, t)}{\delta\boldsymbol{\alpha}(\mathbf{r}', t')}\right)_{\boldsymbol{\alpha} = \boldsymbol{\alpha}_0} &: \delta\boldsymbol{\alpha}(\mathbf{r}', t') + \delta\boldsymbol{\sigma}_{\mathrm{R}}(\mathbf{r}, t; \boldsymbol{\alpha}_0) \qquad (8)\end{aligned}$$

where, in the component notation,

$$\left(\frac{\delta\sigma_{ij}(\mathbf{r}, t)}{\delta\alpha_{kl}(\mathbf{r}', t')}\right)_{\boldsymbol{\alpha}_0} = H_{ijkl}(\mathbf{r} - \mathbf{r}', t - t') \qquad (9)$$

Equation (8) is specific to translationally invariant systems but easily can be generalized. The quantity denoted by $\boldsymbol{\sigma}_0$ is the stress of the reference steady flow. The stationarity of this flow implies that the divergence of $\boldsymbol{\sigma}_0$ is zero. By $\boldsymbol{\alpha}(\mathbf{r}, t)$ in Eq. (8) we denote the velocity gradient tensor, $\boldsymbol{\alpha}(\mathbf{r}, t) = \nabla_{\mathbf{r}}\mathbf{g}(\mathbf{r}, t)/\bar{\rho}$, with $\bar{\rho}$ the stoichiometric mass density of the mixture and $\boldsymbol{\alpha}_0$ the velocity gradient of the reference state (we consider only homogenous flows). Finally, $\delta\boldsymbol{\alpha}(\mathbf{r}, t)$ is the perturbation $\delta\boldsymbol{\alpha}(\mathbf{r}, t) = \boldsymbol{\alpha}(\mathbf{r}, t) - \boldsymbol{\alpha}_0$. From Eq. (8) it seems that there is a possible ambiguity in defining the viscosity tensor for a system in a nonequilibrium stationary state. Thus, one may define a stationary or hydrodynamic viscosity tensor through the connection

$$H^0_{ijkl}(\boldsymbol{\alpha}_0) = \frac{\partial\sigma_{0_{ij}}(\boldsymbol{\alpha}_0)}{\partial\alpha_{0_{kl}}} \tag{10}$$

between the stationary stress $\boldsymbol{\sigma}_0$ and the corresponding velocity gradient $\boldsymbol{\alpha}_0$. Alternatively, one can define the viscosity through the role it plays in the generalized Navier–Stokes equation (4), which governs the propagation of the perturbations upon the reference state. The second of these viscosity tensors is defined by the fluctuation–correlation formula, Eq. (6). The two sets of viscosities are likely to be related but not to be identical.

3. SINGLE-ROD CONTRIBUTIONS TO THE STRESS

One of the standard assumptions of rod-like particle suspension rheology is that the main contribution to the stress of the mixture comes from the internal stresses of single particles (due to the bonds that keep segments of the particle together) and, at higher concentrations, from interactions between different rods. The part of the stress due to the solvent–solute interaction is commonly neglected ($\boldsymbol{\sigma}_{\mathrm{BS}} = 0$) and the contribution of the solvent is assumed to be the same in the mixture as it is in a pure solvent. Possible cross-correlations between microscopic stresses of solvent–solute and solute–solute particles also are neglected (at least in dilute solutions). Neither of these simplifications has ever been critically evaluated. By adopting these approximations we obtain the following expression for the Brownian particle contribution to the viscosity tensor (6):

$$\begin{aligned}\mathbf{H}_{\mathrm{B}}(\mathbf{r}, t) &= \frac{1}{kTV}\int d\mathbf{r}'\langle \delta\hat{\boldsymbol{\sigma}}_{\mathrm{RB}}(\mathbf{r}+\mathbf{r}', t)\,\delta\hat{\boldsymbol{\sigma}}_{\mathrm{B}}(\mathbf{r}', 0)\rangle \\ &\simeq \frac{c}{kT}\int d\mathbf{r}'\langle \delta\hat{\boldsymbol{\sigma}}^{\mathrm{I}}_{\mathrm{RB}}(\mathbf{r}+\mathbf{r}', t)\,\delta\hat{\boldsymbol{\sigma}}^{\mathrm{I}}_{\mathrm{B}}(\mathbf{r}', 0)\rangle\end{aligned} \tag{11}$$

The symbol $\hat{\boldsymbol{\sigma}}_{\mathrm{B}}^{\mathrm{I}}$ appearing in the last of these expressions denotes the single-particle microscopic stress tensor

$$\hat{\boldsymbol{\sigma}}_{\mathrm{B}}^{\mathrm{I}}(\mathbf{r}, 0) = [-M\dot{\mathbf{R}}\dot{\mathbf{R}} - m\dot{\mathbf{q}}\dot{\mathbf{q}} + \mathbf{q}\mathbf{q}\,|q|^{-1}\,U'_{\mathrm{B}}(|\mathbf{q}|) - z\mathbf{q}\mathbf{B}]\,\delta(\mathbf{r}-\mathbf{R}) \quad (12)$$

Here c is the number concentration of rods, M is the total mass of a rod, and $m = M/4$ is the reduced mass of the dumbbell. $\mathbf{R}$ and $\dot{\mathbf{R}}$, respectively, are the location and velocity of the center of mass and $\mathbf{q}$ and $\dot{\mathbf{q}}$ are the relative distance vector and corresponding velocity. $U_{\mathrm{B}}(|\mathbf{q}|)$ is the binding potential, $\mathbf{B}$ is the (uniform) magnetic field, and z is the magnetic charge ($\boldsymbol{\mu} = z\mathbf{q}$ is the magnetic dipole moment). For a rigid dumbbell we must take into account the additional constraint $\mathbf{q}\cdot\dot{\mathbf{q}} = 0$, which may be used to eliminate the binding force with the help of the equation of motion,

$$m\ddot{\mathbf{q}} = -\mathbf{q}\,|\mathbf{q}|^{-1}\,U'_{\mathrm{B}}(|\mathbf{q}|) + z\mathbf{B} + \tfrac{1}{2}\mathbf{q}\cdot\nabla_{\mathbf{R}}\boldsymbol{\Phi}(\mathbf{R}) \quad (13)$$

for the relative distance vector. Here $\boldsymbol{\Phi}(\mathbf{R})$ is the force of interaction of the dumbbell site with the surrounding solvent molecules.

Consequently, for a rigid dumbbell Eq. (12) becomes

$$\begin{aligned}\hat{\boldsymbol{\sigma}}_{\mathrm{B}}^{\mathrm{I}}(\mathbf{r}, 0) = \{&-M\dot{\mathbf{R}}\dot{\mathbf{R}} - J\mathbf{e}\times(\dot{\mathbf{e}}\times\mathbf{e})\,\mathbf{e}\times(\dot{\mathbf{e}}\times\mathbf{e})\\ &+\mathbf{e}\mathbf{e}(\tfrac{1}{2}l^2(\mathbf{e}\cdot\nabla_{\mathbf{R}})\boldsymbol{\Phi}\cdot\mathbf{e} + \mu\mathbf{e}\cdot\mathbf{B} + J\dot{\mathbf{e}}^2] - \mu\mathbf{e}\mathbf{B}\}\,\delta(\mathbf{r}-\mathbf{R}) \quad (14)\end{aligned}$$

with $l = |\mathbf{q}|$ denoting the distance between the sites and $J = (M/4)1^2$ the moment of inertia of the rod. Finally, $\mathbf{e} = \mathbf{q}/|\mathbf{q}|$ is the unit vector in the direction of the dumbbell axis.

The expression (14) still differs from the standard formulas for the rigid dumbbell stress [6] by the presence of the kinetic variables $\dot{\mathbf{R}}$ and $\dot{\mathbf{e}}$ and the mechanical force $\boldsymbol{\Phi}$. The kinetic theory used almost exclusively in polymer and macroparticle rheology incorporates the assumption that the kinetic variables in liquids relax to their local equilibrium values on a time scale much shorter than that characteristic of the corresponding configuration variables. In condensed matter the kinetic energy is "thermalized" more rapidly than is the potential energy because the latter process requires relatively slow particle transport. It also is assumed that the response of the smaller solvent particles is much faster than that of the macroparticles. These arguments enable one to simplify the calculation of the viscosities by using instead of the true microscopic stresses, Eq. (14) or (12), their preaveraged forms. Preaveraging (denoted by an over bar) is done over a distribution of the kinetic variables related to the dumbbells and of all other phase-space variables related to the particles that participate in the reference steady state.

If we tentatively adopt the local Maxwellian velocity distributions

$$f_{\mathrm{L.EQ.}}(\dot{\mathbf{R}}) = \left(\frac{M}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{M}{2kT}[\dot{\mathbf{R}} - \mathbf{w}_0(\mathbf{R})]^2\right\} \tag{15}$$

and

$$f_{\mathrm{L.EQ.}}(\dot{\mathbf{e}}) = \delta(\mathbf{e}\cdot\dot{\mathbf{e}})\left(\frac{J}{2\pi kT}\right)\exp\left\{-\frac{J}{2kT}[\dot{\mathbf{e}} - \mathbf{e}\cdot\boldsymbol{\alpha}_0]\cdot(\mathbf{I}-\mathbf{ee})\cdot[\dot{\mathbf{e}} - \mathbf{e}\cdot\boldsymbol{\alpha}_0]\right\} \tag{16}$$

then the substitutions

$$\overline{M\dot{\mathbf{R}}\dot{\mathbf{R}}} \simeq kT\mathbf{I} + M\mathbf{w}_0(\mathbf{R})\,\mathbf{w}_0(\mathbf{R}) \tag{17}$$

$$\overline{J\dot{\mathbf{e}}\dot{\mathbf{e}}} \simeq kT(\mathbf{I}-\mathbf{ee}) + J\mathbf{e}\cdot\boldsymbol{\alpha}_0\cdot(\mathbf{I}-\mathbf{ee})\mathbf{e}\cdot\boldsymbol{\alpha}_0\cdot(\mathbf{I}-\mathbf{ee}) \tag{18}$$

can be used in Eqs. (12) and (14). It is less clear what one should substitute for an average force of the site–solvent particle interaction when the reference state is a steady flow. Obviously, if the reference state is a state of equilibrium, then the average force should vanish, i.e., $\overline{\boldsymbol{\Phi}^{\mathrm{EQ}}(\mathbf{R})} = 0$. In the case of a stationary flow most rheological treatises suggest the choice

$$\overline{\boldsymbol{\Phi}(\mathbf{R})} = -\tfrac{1}{2}\boldsymbol{\xi}\cdot[\dot{\mathbf{R}} - \mathbf{w}_0(\mathbf{R})] \tag{19}$$

Here $\boldsymbol{\xi} = \xi_{\|}\mathbf{ee} + \xi_{\perp}(\mathbf{I}-\mathbf{ee})$ is the friction tensor [3] and $\mathbf{w}_0(\mathbf{R})$ the velocity of the reference steady flow. With this choice for the average force the preaveraged stress takes the form

$$\overline{\boldsymbol{\sigma}^{\mathrm{I}}_{\mathrm{B}}(\mathbf{r}, 0)} = kT\left[-\mathbf{I} + \boldsymbol{\Omega}(\mathbf{e}, \boldsymbol{\alpha}_0) - \frac{M}{kT}\mathbf{w}_0(\mathbf{R})\,\mathbf{w}_0(\mathbf{R})\right]\delta(\mathbf{r}-\mathbf{R}) \tag{20}$$

The tensor $\boldsymbol{\Omega}$ appearing here is defined by

$$\begin{aligned}\boldsymbol{\Omega} &= 3\mathbf{ee} - \mathbf{I} + \lambda(\mathbf{eee}\cdot\mathbf{b} - \mathbf{eb}) + \frac{\kappa}{D}\mathbf{eee}\cdot\boldsymbol{\alpha}_0\cdot\mathbf{e} \\ &\quad - \frac{J}{kT}[\mathbf{e}\cdot\boldsymbol{\alpha}_0\cdot(\mathbf{I}-\mathbf{ee})\mathbf{e}\cdot\boldsymbol{\alpha}_0\cdot(\mathbf{I}-\mathbf{ee}) - \mathbf{eee}\cdot\boldsymbol{\alpha}_0\cdot(\mathbf{I}-\mathbf{ee})\cdot\boldsymbol{\alpha}_0^{\mathrm{T}}\cdot\mathbf{e}]\end{aligned} \tag{21}$$

$\boldsymbol{\alpha}_0^{\mathrm{T}}$ is the transpose of $\boldsymbol{\alpha}_0$, $\kappa = \xi_{\|}/\xi_{\perp}$ is an anisotropy factor [3], $D = MkT/J\xi_{\perp}$ is the rotational diffusivity of the rod, and $\lambda = \mu B/kT$ is the magnetic field coupling coefficient. Except for the numerical factor multiplying the unit tensor and "centrifugal" terms related to the kinetic part of the stress, Eq. (20) agrees with that given in the Bird et al. monograph [9] and attributed to Prager [10]. One should note here that the authors just cited do not distinguish between the reference flow and the perturbation. The velocity gradient in Ref. 9 can, in principle, be time dependent [10, 11] but this is not correct according to the present formulation. It also is not certain that Eq. (19) is truly correct even though the resulting Kramers–Prager formula for the stress and the related Giesekus expression [9] are now well established in the rheological literature. In Eq. (21) the third term (proportional to κ) is a direct consequence of the assumption given by Eq. (19). It means physically that the solvent molecules in a stationary flow exert a stretching force along the rod axis due to the difference of the velocities of the flow at the two interaction sites. This seems plausible, but in contrast to the case of an equilibrium reference state, we are unable in this instance to check directly if the force $\bar{\mathbf{\Phi}}(\bar{\mathbf{R}})$ really is different from zero and given by the standard friction force Eq. (19). The necessary conditional probabilities for a system in a stationary flow are unknown. However, if the Kramers–Prager expression is correct, then its direct consequence for the problem studied here is that the hydrodynamic viscosity $\mathbf{H}^0$ defined by Eq. (10) differs from that given by the fluctuation–correlation formula, Eq. (11), even for those terms which are linear with respect to $\boldsymbol{\alpha}_0$. This would produce a discontinuity between the linear response theory expressions obtained by perturbation of the equilibrium state and the "linear response" transport coefficients obtained for a stationary non-equilibrium flow. This problem does not arise if the Prager term is neglected as has been done by some theoreticians interested in the dynamics of rod-like particles [12–14]. The terms linear with respect to the tensor $\boldsymbol{\alpha}_0$ are then identical (in the low-frequency or long-time limit). However, differences still are to be expected in the nonlinear terms.

4. DIFFUSION IN THE SMOLUCHOWSKI–DEBYE SPACE

Since the microscopic stress given by Eq. (20) is expressed solely in terms of the dumbbell coordinates, one can perform in Eq. (11) a partial preaveraging (over a conditional, stationary probability distribution of all remaining phase space variables) of the evolution operator. Assuming that the standard Brownian dynamics theory is appropriate, the resulting propagator in the dumbbell configuration sphere is

$$\Xi^{+}(t, \boldsymbol{\alpha}_0) = \exp[tS^{+}(\boldsymbol{\alpha}_0)] \tag{22}$$

The object S^{+} appearing here is the adjoint Smoluchowski–Debye operator defined by

$$S^{+}(\boldsymbol{\alpha}_0) = D[\mathbf{\nabla}_{\mathbf{e}} + \lambda \mathbf{b} + \mathbf{e} \cdot \boldsymbol{\alpha}_0^{*}] \cdot \mathbf{\nabla}_{\mathbf{e}} \tag{23}$$

and $\boldsymbol{\alpha}_0^* = \boldsymbol{\alpha}_0/D$. We also shall use the adjoint propagator

$$\Xi(t, \boldsymbol{\alpha}_0) = \exp[tS(\boldsymbol{\alpha}_0)] \tag{24}$$

with

$$S(\boldsymbol{\alpha}_0) = D\boldsymbol{\nabla}_{\mathbf{e}} \cdot [\boldsymbol{\nabla}_{\mathbf{e}} - \lambda \mathbf{b} \cdot (\mathbf{I} - \mathbf{ee}) - e \cdot \boldsymbol{\alpha}_0^* \cdot (\mathbf{I} - \mathbf{ee})] \tag{25}$$

denoting the Smoluchowski–Debye operator for rotational diffusion in the presence of the magnetic field and a homogeneous stationary flow.

The operator given by Eq. (23) implies the following Rouse-like equation of motion for normal component $[\dot{\mathbf{e}}_\perp = \dot{\mathbf{e}} \cdot (\mathbf{I} - \mathbf{ee})]$ of the orientation vector:

$$\dot{\mathbf{e}}_\perp = D[\lambda b \cdot (\mathbf{I} - \mathbf{ee}) + \mathbf{e} \cdot \boldsymbol{\alpha}_0^* \cdot (\mathbf{I} - \mathbf{ee})] \tag{26}$$

The operators given by Eqs. (22)–(25) have the following properties.

(1) For an arbitrary function of orientation $\psi(\mathbf{e})$

$$\psi(\mathbf{e}, t) = \Xi^+(t, \boldsymbol{\alpha}_0)\, \psi(\mathbf{e}) \tag{27}$$

(2) For any distribution function $\phi(\mathbf{e}, t \neq 0)$

$$\phi(\mathbf{e}, t) = \Xi(t, \boldsymbol{\alpha}_0)\, \phi(\mathbf{e}, t = 0) \tag{28}$$

(3) For a stationary distribution function such that $S(\boldsymbol{\alpha}_0)\, \phi_0(\mathbf{e}) = 0$, it can be shown that $\Xi(t, \boldsymbol{\alpha}_0)\phi_0 = \phi_0$ and $S\phi_0 = \phi_0 \mathrm{S}^+$.

As a consequence of these relations the autocorrelation function expression for the viscosity tensor can be written in several alternative forms,

$$\begin{aligned} H_{ijkl}^{\mathrm{vol}}(t, \boldsymbol{\alpha}_0) &= kTc \int d\mathbf{e}\, \phi_0(\mathbf{e}, \boldsymbol{\alpha}_0)\, \delta\Omega_{kl} \Xi^+(t, \boldsymbol{\alpha}_0)\, \delta\Omega_{ij} \\ &= kTc \int d\mathbf{e}\, \delta\Omega_{ij} \Xi(t; \boldsymbol{\alpha}_0)\, \delta\Omega_{kl} \phi_0(e, \boldsymbol{\alpha}_0) \\ &= kTc\, \tfrac{1}{2} \int d\mathbf{e} [\phi_0\, \delta\Omega_{kl} \Xi^+(t)\, \delta\Omega_{ij} + \delta\Omega_{ij} \Xi(t)\, \delta\Omega_{kl} \phi_0] \end{aligned} \tag{29}$$

the last of which [15] is manifestly invariant with respect to an interchange of the first and last index pairs, (ij) and (kl).

5. LINEAR VISCOELASTIC EFFECTS

In the linear response approximation ($\boldsymbol{\alpha}_0 = 0$) the viscosity tensor given by Eq. (29) can be written in the form

$$H^{\text{vol}}_{ijkl}(t) = \frac{kTc}{D}\,[a_0(t)\delta_{ij}\delta_{kl} + a_1(t)(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl}) + a_2(t)(\delta_{ij}b_k b_l + \delta_{kl}b_i b_j)$$
$$+ a_3(t)\,\delta_{ik}b_j b_l + a_4(t)\delta_{jl}b_i b_k + a_5(t)(\delta_{jk}b_i b_l + \delta_{il}b_j b_k) + a_6(t)\,b_i b_j b_k b_l] \tag{30}$$

where the a_n's are time-dependent, scalar viscosity coefficients. In this approximation the tensor $\delta\boldsymbol{\Omega}$ is traceless and so the coefficients satisfy the two relations

$$3a_0 + 2a_1 + a_2 = 0; \qquad 3a_2 + a_3 + a_4 + 2a_5 + a_6 = 0 \tag{31}$$

Thus, there are only five linearly independent viscosity coefficients a_n associated with an incompressible flow.

Since the equilibrium distribution of the permanent dipole orientation in a constant magnetic field is known to be

$$\phi_{\text{EQ}}(\mathbf{e}\cdot\mathbf{b}) = [4\pi\lambda^{-1} sh\lambda]^{-1}\exp[\lambda\mathbf{e}\cdot\mathbf{b}] \tag{32}$$

a calculation of the coefficients a_n from Eq. (29) is, in principle, possible. Once the viscosities are known as functions of time and the coupling constant λ, we then can calculate all relevant rheological quantities (such as the Leslie coefficients, Mięsowicz viscosities, and elongational viscosity) which are linear combinations of the a_n's. In particular, we obtain the following formulas for the Mięsowicz viscosities corresponding to flow geometries given below:

$$\tilde{\eta}_1 = \frac{kTc}{D}(\tilde{a}_1 + \tilde{a}_3) \tag{33}$$

for $\mathbf{b} \parallel \mathbf{n}_3$, $\mathbf{w}_0 \parallel \mathbf{n}_3$, $\boldsymbol{\alpha}_0 = \alpha^0 \mathbf{n}_1\mathbf{n}_3$,

$$\tilde{\eta}_2 = \frac{kTc}{D}(\tilde{a}_1 + \tilde{a}_4) \tag{34}$$

for $\mathbf{b} \parallel \mathbf{n}_3$, $\mathbf{w}_0 \parallel \mathbf{n}_1$, $\boldsymbol{\alpha}_0 = \alpha^0 \mathbf{n}_3\mathbf{n}_1$, and

$$\tilde{\eta}_3 = \frac{kTc}{D}\tilde{a}_1 \tag{35}$$

for $\mathbf{b} \| \mathbf{n}_3$, $\mathbf{w}_0 \| \mathbf{n}_2$, $\boldsymbol{\alpha}_0 = \alpha^0 \mathbf{n}_1 \mathbf{n}_2$. Here $\mathbf{n}_i$ ($i = 1, 2, 3$) denotes a unit vector in the direction of the ith Cartesian axis.

For a stationary elongational flow the Trouton viscosity is given by

$$\bar{n}_t = \frac{kTc}{D}(3\tilde{a}_1 + \tilde{a}_3 + 2\tilde{a}_5 + \tilde{a}_6) \tag{36}$$

In Eqs. (33)–(36) the symbols $\tilde{a}_n(\omega)$ denote Laplace transforms of the corresponding time-dependent functions $a_n(t)$. Stationary values of the transport coefficients are the zero-frequency values of $\tilde{a}_n$.

The Leslie coefficients occur in the Leslie–Ericksen form of the viscous stress tensor, which can be written as [16]

$$\sigma_{ij}^{\text{visc}} = \mu_1 b_k b_l D_{kl} b_i b_j + \mu_2 b_i N_j + \mu_3 b_j N_i + \mu_4 D_{ij} + \mu_5 b_i b_k D_{kj} + \mu_6 b_j b_k D_{ki} \tag{37}$$

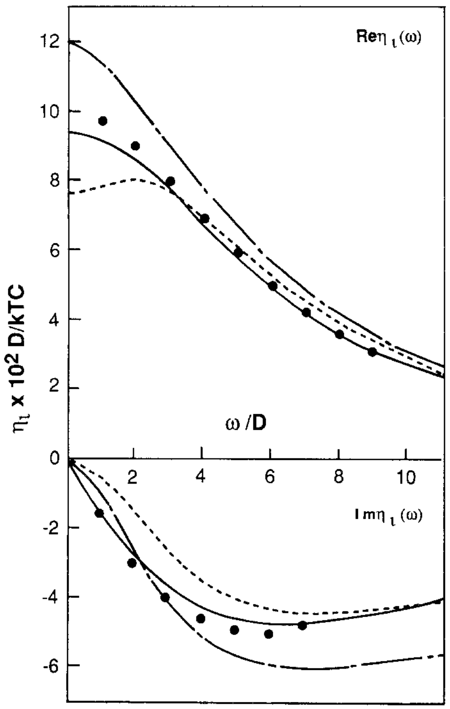

Fig. 1. Mięsowicz viscosities versus reduced frequency ω/D. (●) Viscosity values in the field-free limit of $\lambda = 0$. All of the curves are specific to the value of $\lambda = 1$. (——) η_1; (– – –) η_2; (——) for η_3. The upper set of curves shows the real parts of these complex valued coefficients, whereas the lower set shows the imaginary parts.

with $D_{ij} = \frac{1}{2}(\alpha_{0_{ij}} + \alpha_{0_{ji}})$ and $N_i = -\frac{1}{2}(\alpha_{0_{ik}} - \alpha_{0_{ki}})b_k$. Summations over repeating indexes are implied.

The Leslie coefficients μ_n are related to the coefficients a_n by the expressions

$$\mu_j = [kTc/D]\bar{\mu}_j \tag{38}$$

with $\bar{\mu}_1 = a_6$, $\bar{\mu}_2 = a_4 - a_5$, $\bar{\mu}_3 = a_5 - a_3$, $\bar{\mu}_4 = 2a_1$, $\bar{\mu}_5 = a_4 + a_5$, and $\bar{\mu}_6 = a_3 + a_5$.

Unfortunately, in spite of the apparent simplicity of the evolution operators given by Eqs. (22) and (24), an exact solution of the diffusion

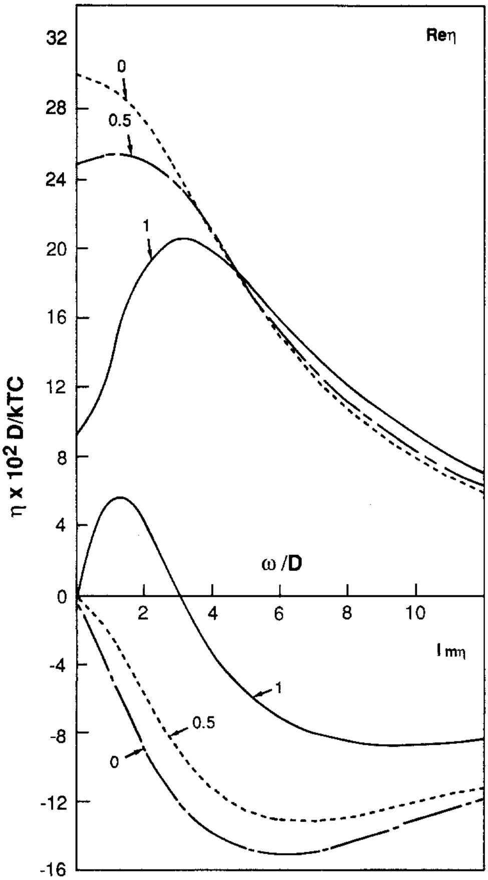

Fig. 2. The elongational viscosity versus reduced frequency. The labels on the curves indicate values of the parameter λ.

problem has not yet been found. We [8] have been able to obtain relatively simple asymptotic formulas only for small values of λ. In the low-frequency limit these are

$$\begin{aligned} &\tilde{a}_0(0) = -\frac{1}{15} - \lambda^2\frac{7}{450}; \quad \tilde{a}_1(0) = \frac{1}{10} - \lambda^2\frac{1}{180}; \quad \tilde{a}_2(0) = \lambda^2\frac{91}{1575}; \\ &\tilde{a}_3(0) = -\lambda^2\frac{11}{600}; \quad \tilde{a}_4(0) = \lambda^2\frac{3}{200}; \quad \tilde{a}_5(0) = -\lambda^2\frac{51}{600} \end{aligned} \tag{39}$$

and $\tilde{a}_6(0) = 0(\lambda^4)$. Examples of Męsowicz and elongational viscosities as functions of frequency are given [8] in Figs. 1 and 2.

6. SHEAR VISCOSITY FOR A STATIONARY FLOW

It is of interest to compare previous results with those obtained from a calculation of the apparent hydrodynamic viscosity of a stationary flow. By retaining only the orientation-dependent part of the stress in Eq. (20), we obtain the formula

$$\boldsymbol{\sigma}_0(\boldsymbol{\alpha}_0) = kTc\int d\mathbf{e}\boldsymbol{\Omega}(\mathbf{e}, \boldsymbol{\alpha}_0)\,\varphi_0(\mathbf{e}, \boldsymbol{\alpha}_0) \tag{40}$$

This contains a stationary distribution function φ_0 which satisfies $S(\boldsymbol{\alpha}_0)\varphi_0 = 0$. Assuming that the stationary distribution is an analytic function of the velocity gradient $\boldsymbol{\alpha}_0^*$ and that the latter is small, we can write φ_0 as a sum, $\varphi_0 = \varphi_{\mathrm{EQ}} + \delta\varphi_0$, where $\delta\varphi_0$ is linear with respect to $\boldsymbol{\alpha}_0^*$. The substitution of this into Eq. (40) leads to the following expression for the rod contribution to the stationary Newtonian stress tensor:

$$\boldsymbol{\sigma}_0(\boldsymbol{\alpha}_0) = \mathbf{H}^0 : \boldsymbol{\alpha}_0 \tag{41}$$

The stationary viscosity tensor $\mathbf{H}^0$ occurring in (41) is given by the formula

$$\mathbf{H}^0 = \frac{kTc}{D}\kappa\int d\mathbf{e}\varphi_{\mathrm{EQ}}(\mathbf{e}\cdot\mathbf{b})\,\mathbf{eeee} + \int_0^\infty dt\,\mathbf{H}^{\mathrm{vol}}(t, \boldsymbol{\alpha}_0 = 0) \tag{42}$$

and $\mathbf{H}^{\mathrm{vol}}$ is defined by Eq. (29). The first term on the right-hand side of Eq. (42) can be calculated exactly. Here we report the corrections $\delta\mathbf{a}_n$ which must be added to the corresponding coefficients a_n of Eq. (39):

$$a_0 = \delta a_1 = \frac{1}{15}\kappa\left[1 - \frac{2}{21}\lambda^2\right]; \qquad \delta a_n = \frac{1}{105}\kappa\lambda^2 \qquad \text{for} \quad n > 1 \tag{43}$$

7. CONCLUSIONS AND SUMMARY

Our results indicate that the present understanding of the rheology of nonsimple fluids is far from complete. More work on the formal structure of the theory is necessary. It apparently is possible to define transport coefficients (in this case the viscosity tensor) with respect to a stationary state different from the equilibrium state. These are given by time-correlation functions similar to the Green–Kubo formulas to which they reduce in case of ordinary linear-response theory. These transport coefficients are functionally defined by a generalized Navier–Stokes equation which determines the time evolution of the perturbation of the flow from the reference steady state. Within the particular rheological model studied here it is somewhat unsettling to find that the two possible methods of defining viscosity (through the time-correlation function formula and relation between stationary stress in the reference state and velocity gradient tensor) may lead to different results for stationary, nonequilibrium flows. This ambiguity is related in part to a particular assumption about the average force of solvent–particle interaction which leads to the Kramers–Prager formula for the stress contribution of the rod-like particles. However, the problem does not disappear even if the contribution of this force is totally neglected (as should be done in the linear response theory for the equilibrium reference state).

Another problem that concerns us is the search for fundamental solutions of the rotational diffusion equation in the presence of an external field and flow. A solution to this problem is essential for the calculation of the transport properties for a field of arbitrary strength and for the determination of non-Newtonian effects.

Finally, it would be interesting to extend the theory to concentrated solutions with particle interactions taken into account. Some progress in this direction has been made in a closely related field of nematic liquid crystals.

ACKNOWLEDGMENT

This research was supported by a grant from the National Science Foundation.

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