

## FLEXIBLE AND RIGID MACROMOLECULES IN SHEAR AND ELECTRIC FIELDS

O Ok PARK

Department of Chemical Engineering, Korea Advanced Institute of Science & Technology,  
P.O. Box 131, Cheongryang, Seoul, Korea

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**Abstract**—Models for rigid and flexible polymers dissolved at low concentration in a dielectric Newtonian fluid and subjected to shear and electric (or magnetic) fields are developed. The rigid polymers are taken to be a rigid spheroid with high aspect ratio and the flexible chains are considered as an elastic dumbbell with a nonlinear spring constant. Specific calculation schemes are developed for transient shear and/or electric fields. Rheo-optical properties such as birefringence and extinction angle are calculated and also interesting components for stress tensor are predicted.

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### INTRODUCTION

The coupling of electric (or magnetic) and hydrodynamic fields can be found in a number of fields involving colloidal dispersions and polymeric liquids. The most current examples are processes involving ink jet printing, and the coating of record media with magnetic particles. Although the cross-discipline of electrohydrodynamics [1,2] has a relatively long history, it has not enjoyed a great deal of fundamental research. For polymeric liquids, although electric and hydrodynamic effects have been extensively studied separately in the past [3,4], there is a scarcity of reported research on the electrohydrodynamic response of these materials [5].

Dynamics of both rigid and flexible macromolecules dissolved in a dielectric, Newtonian fluid and subjected to electric and hydrodynamic fields is considered in this paper. Mason and coworkers [6] have considered most questions pertaining to large, non-Brownian particles at infinite dilution. Ikeda and coworkers [7,8] studied the steady state response of rod-like polymer chains with an assumed permanent dipole moment subjected to electrohydrodynamic fields. As pointed out by Okagawa et al. [6], however, the assumption employed by Ikeda in [7] that the force on the macromolecule arises from the electric field within the molecule is not as realistic as utilizing the electric field existing outside the macromolecule. This paper focuses on questions involving the role of Brownian motion. In addition, transient flow phenomena are considered and induced dipole moments are assumed.

The transient behaviors are considered here, which can be compared with the steady state dynamics in the previous paper [5]. In addition, both flexible and rigid macromolecules are considered. There are practical advantages in considering the induced dipole moment due to the fact that it is convenient to utilize oscillating electric fields in many experiments and such fields are not sensitive to the permanent dipole moment if the frequency of oscillation is large enough. Oscillating fields minimize the effects of Joule heating and electrophoretic migration. In section 2, the convective diffusion equation for rigid macromolecules of high aspect ratio is developed. The solution to this equation is presented in section 3 and applied to the calculation of birefringence, extinction angle and rheological material properties.

In section 4 a theory for flexible polymer chains is presented. Stockmayer and Baur [9] were among the first to consider the application of an electric field on flexible chains with parallel dipole moments and employed the multibead and spring model of Rouse [10] and Zimm [11]. For the purposes of this paper, however, the simple elastic dumbbell model with both linear and nonlinear spring functions was used (see reference [4] for a discussion on various mechanical models for flexible chains).

### FOKKER-PLANCK DIFFUSION EQUATION FOR SLENDER, RIGID SPHEROIDS

Mason and coworkers [2,6] have worked out the motion of non-Brownian, spheroidal particles sub-

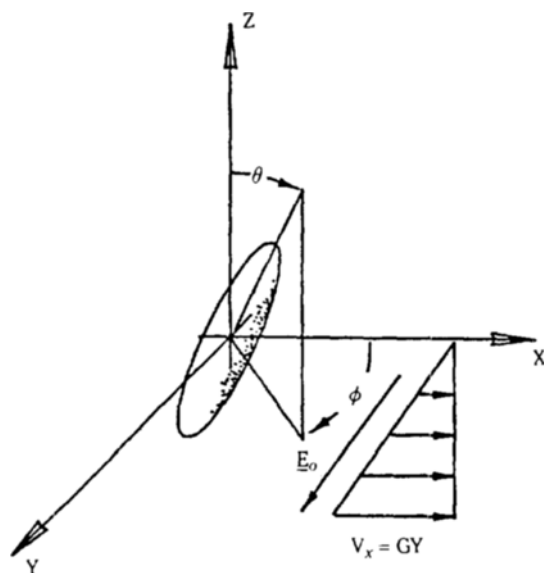


Fig. 1. Coordinate system and axis of revolution of an axisymmetric rigid spheroid for the specific combination of shear and electric fields considered.

jected to a simple shear flow and simultaneously acted upon by an electric field of an arbitrary orientation with respect to the flow axis. In this paper the specific problem of an electric field,  $E_0$ , aligned parallel to the direction of the velocity gradient is considered as pictured in Figure 1. In that case, the equations of motion of the symmetry axis of a spheroid would be [6]:

$$\dot{\theta} = \frac{G(r^2 - 1)}{4(r^2 + 1)} \sin 2\varphi \sin 2\theta + \frac{Gf'r}{r^2 + 1} \sin^2 \varphi \sin 2\theta \quad (1)$$

$$\dot{\varphi} = -\frac{G}{r^2 + 1} (r^2 \sin^2 \varphi + \cos^2 \varphi) + \frac{Gf'r}{r^2 + 1} \sin 2\varphi \quad (2)$$

Where  $\theta$ ,  $\varphi$  are two Euler angles which determine the orientation of the spheroid as shown in Figure 1.  $G$  is the shear rate and  $r$  is the aspect ratio of a spheroidal macromolecule. The electrohydrodynamic field parameter  $f'$  is the ratio of electric torque to hydrodynamic torque as defined in reference [6]. When  $r > 1$ , this parameter is the following [6]:

$$f' = \frac{4\pi\epsilon_0 K_2 E_0^2 P(q, r)}{G\eta_2} \left(r + \frac{1}{r}\right) \quad (3)$$

$$P(q, r) = \frac{(3A - 2)(q - 1)^2 Q(r)}{8\pi[2 + (q - 1)A][(q - 1)A - q]} \quad (4)$$

$$Q(r) = \frac{2r^2 + (1 - 2r^2)A}{4(r^2 + 1)} \quad (5)$$

and

$$A = \frac{r^2}{r^2 - 1} - \frac{r \operatorname{arccosh}(r)}{(r^2 - 1)^{3/2}} \quad (6)$$

Here  $\epsilon_0$  is the permittivity of free space,  $\eta_2$  is the viscosity of suspending Newtonian fluid, and  $K_2$  is the dielectric constant of suspending fluid.  $q$  is defined as the ratio of dielectric constant of a macromolecule to that of the fluid. We shall focus our attention on the problem of rodlike chains of high aspect ratio. As  $r$  tend to infinity,  $f'$  can be shown to have the following asymptotic form:

$$f' = \frac{\epsilon_0 K_2 E_0^2 (q - 1)^2}{4r(q + 1)G\eta_2} \left[ \frac{\ln(2r)}{r^2} + O\left(\frac{1}{r^2}\right) \right] \quad (7)$$

Thus equations (1) and (2) become

$$\dot{\theta} = \frac{1}{4} G \sin 2\varphi \sin 2\theta + \frac{f'}{r} G \sin^2 \varphi \sin 2\theta + O\left(\frac{1}{r^2}\right) \quad (8)$$

$$\dot{\varphi} = -G \sin^2 \varphi + \frac{f'}{r} G \sin 2\varphi + O\left(\frac{1}{r^2}\right) \quad (9)$$

When the Brownian motion is present, it is necessary to introduce an orientation distribution function  $\Psi(\theta, \varphi; t)$  which prescribes the probability that a chain has a particular orientation. The normalized diffusion equation describing the evolution of  $\Psi$  is:

$$6 \frac{\partial \Psi}{\partial \tau} + \beta \Omega_1 \Psi + f \Omega_2 \Psi - \Lambda \Psi = 0 \quad (10)$$

Where  $f = f'/r$ ,  $\beta = G/D$ , is the dimensionless velocity gradient and  $\tau = Dt$  is a dimensionless time. Here  $D_r$  is the rotational diffusivity of the macromolecule [4]. The normalization condition for  $\Psi$  is the following:

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\varphi \Psi = 1 \quad (11)$$

The operators  $\Omega_1$ ,  $\Omega_2$  and  $\Lambda$  in (10) are:

$$\Omega_1 = \frac{1}{\sin \theta} \sin \varphi \cos \varphi \frac{\partial}{\partial \theta} (\sin^2 \theta \cos \theta) - \frac{\partial}{\partial \varphi} (\sin^2 \varphi) \quad (12)$$

$$\Omega_2 = \frac{2}{\sin \theta} \sin^2 \varphi \frac{\partial}{\partial \theta} (\sin^2 \theta \cos \theta) + 2 \frac{\partial}{\partial \varphi} (\sin \varphi \cos \varphi) \quad (13)$$

$$\Lambda = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \quad (14)$$

The operators  $\Omega_1$  is due to the shear flow and its properties are tabulated in reference [4]. The operator  $\Lambda$  is the spherical Laplacian which is also discussed in [4].  $\Omega_2$  is due to the electric field and its properties with respect to spherical harmonic functions are tabulated in Appendix A.

## 1. Solution procedure

We shall seek a solution to equation (10) for time dependent electric and hydrodynamic fields of the following form:

$$\beta = \beta_0 g_1(\tau) \quad (15)$$

$$f = f_0 g_2(\tau) \quad (16)$$

Where  $g_1$  and  $g_2$  are arbitrary, dimensionless functions of  $\tau$ . Furthermore, perturbation solution will be obtained assuming both  $\beta_0$  and  $f_0$  are less than 1. As Kim and Fan [12] have shown recently, this manner of solution has a finite radius of convergence with respect to  $\beta_0$ , and it is expected that this is also true for  $f_0$ . Expanding  $\Psi$  in a series in powers of  $f_0$  leads to:

$$\Psi = \sum_{k=0}^{\infty} f_0^k \Psi_k \quad (17)$$

Substituting equation (17) into (10) leads to:

$$\frac{\partial \Psi_0}{\partial \tau} + \beta_0 g_1(\tau) \Omega_1 \Psi_0 - \Lambda \Psi_0 = 0 \quad (18)$$

$$\frac{\partial \Psi_k}{\partial \tau} + \beta_0 g_1(\tau) \Omega_1 \Psi_k - \Lambda \Psi_k = -g_2(\tau) \Omega_2 \Psi_{k-1} \quad (19)$$

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\varphi \Psi_k = \delta_{k,0} \quad (20)$$

The zero order solution  $\Psi_0$  is simply the solution obtained in reference [13] and [14] for the case of no electric field. Following the procedure in reference [13], the distribution function is expanded in terms of the velocity gradient  $\beta_0$  and the following solution is obtained.

$$\Psi_0 = \frac{1}{4\pi} \sum_{j=0}^{\infty} \beta_0^j \phi_{0j} \quad (21)$$

$$\phi_{00} = P_0^0 \quad (22a)$$

$$\phi_{01} = \frac{1}{12} (1; \tau) P_2^2 S_2 \quad (22b)$$

$$\phi_{02} = -\frac{1}{84} (0, 1; \tau) P_2^0 + \frac{1}{72} (0, 1; \tau) P_2^2 C_2 + \dots \quad (22c)$$

$$\phi_{03} = -\frac{1}{10584} [23 (0, 0, 1; \tau) + 12 (-\frac{7}{3}, \frac{7}{3}, 1; \tau)] P_2^2 S_2 + \dots \quad (22d)$$

Here  $P_n^m$  are the associated Legendre functions and  $C_m$  and  $S_m$  denote  $\cos m\varphi$  and  $\sin m\varphi$  respectively. The functions  $(a, b; \tau)$  in equation (22) are defined as:

$$(a, b; \tau) = \int_{-\infty}^{\tau} dt' e^{-a(t'-\tau)} g_1(t') \int_{-\infty}^{\tau} dt'' e^{-b(t''-\tau)} g_2(t'') \quad (23a)$$

In order to solve the combined hydrodynamic and electric field problem it is also necessary to define the

following time-dependent functions:

$$[(a), b; \tau] = \int_{-\infty}^{\tau} dt' e^{-a(t'-\tau)} g_2(t') \int_{-\infty}^{\tau} dt'' e^{-b(t''-\tau)} g_1(t'') \quad (23b)$$

Where terms enclosed by  $( )$  signify integration over  $g_2(t)$  instead of  $g_1(t)$ .

## 2. First order solution

Substituting equation (21) into (19) and (20), the following equations are obtained:

$$\Psi_1 = \frac{1}{4\pi} \sum_{j=0}^{\infty} \beta_0^j \phi_{1j} \quad (24)$$

$$\frac{\partial \phi_{10}}{\partial \tau} - \Lambda \phi_{10} = -g_2 \Omega_2 \phi_{00} \quad (25a)$$

$$\frac{\partial \phi_{1j}}{\partial \tau} - \Lambda \phi_{1j} = -g_1 \Omega_1 \phi_{1,j-1} - g_2 \Omega_2 \phi_{0j} \quad (25b)$$

The results are:

$$\phi_{10} = -\frac{1}{3} [(1); \tau] P_2^0 - \frac{1}{6} [(1); \tau] P_2^2 C_2 \quad (26a)$$

$$\phi_{11} = \frac{1}{252} \{8 [0, (1); \tau] + [(0), 1; \tau]\} P_2^2 S_2 + \dots \quad (26b)$$

$$\begin{aligned} \phi_{12} = & \frac{1}{1323} P_2^0 \{ -6 [(0), 0, 1; \tau] + 6 [0, 0, (1); \tau] \\ & - \frac{3}{4} [0, (0), 1; \tau] + \frac{5}{2} [-\frac{7}{3}, \frac{7}{3}, (1); \tau] \\ & + \frac{5}{2} [-\frac{7}{3}, (\frac{7}{3}), 1; \tau] + [(-\frac{7}{3}), \frac{7}{3}, 1; \tau] \} \\ & + \frac{1}{31752} P_2^2 C_2 \{ 84 [0, 0, (1); \tau] + 6 [(0), 0, 1; \tau] \\ & + \frac{21}{2} [0, (0), 1; \tau] + 35 [-\frac{7}{3}, \frac{7}{3}, (1); \tau] \\ & + 35 [-\frac{7}{3}, (\frac{7}{3}), 1; \tau] - 34 [(-\frac{7}{3}), \frac{7}{3}, 1; \tau] \} \\ & + \dots \end{aligned} \quad (26c)$$

## 3. Higher order solution

Second and higher order terms can be obtained successively, but for simplicity, only pertinent terms to third order in  $\beta_0$  and  $f_0$  are listed here.

$$\phi_{20} = -\frac{2}{63} [(0), (1); \tau] P_2^0 - \frac{1}{63} [(0), (1); \tau] P_2^2 C_2 + \dots \quad (27a)$$

$$\begin{aligned} \phi_{21} = & \frac{1}{15876} P_2^2 S_2 \{ 48 [0, (0), (1); \tau] \\ & + 24 [(0), 0, (1); \tau] + 3 [(0), (0), 1; \tau] \\ & + 64 [-\frac{7}{3}, (\frac{7}{3}), (1); \tau] - 80 [(-\frac{7}{3}), \frac{7}{3}, (1); \tau] \} \end{aligned}$$

$$-80\left\{\left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), 1; \tau\right\} + \dots \quad (27b)$$

$$\begin{aligned} \phi_{30} = & \frac{4}{1323} P_2^0 \left\{ 8\left\{\left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (1); \tau\right\} \right. \\ & - \left\{(0), (0), (1); \tau\right\} + \frac{2}{3969} P_2^2 C_2 \left\{ 24\left\{\left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), \right. \right. \\ & \left. \left. (1); \tau\right\} - 3\left\{(0), (0), (1); \tau\right\} + \dots \right\} \quad (27c) \end{aligned}$$

Terms up to fourth order can be found in APPENDIX B.

### PROPERTIES OF THE STRESS AND REFRACTIVE INDEX TENSORS

Once the distribution function is known, the stress tensor can be constructed through the Giesekus expression given in Bird [12]. Rheo-optical properties such as flow birefringence (or dichroism) and extinction angle can be evaluated through expressions discussed in reference [15] and [16]. Birefringence  $\Delta n$  is defined as the difference in the principal values by the real part of the refractive index tensor in the plane orthogonal to the propagation axis of the light in a given experiment. The extinction angle  $\chi$  defines the orientation of the principal axis of the refractive index tensor with respect to a laboratory frame. If the light is propagating along the  $z$  axis the birefringence and extinction angle are:

$$\Delta n = M \left[ \langle P_2^2 C_2 \rangle^2 + \langle P_2^2 S_2 \rangle^2 \right]^{1/2} \quad (28a)$$

$$\tan(2\chi) = \langle P_2^2 S_2 \rangle / \langle P_2^2 C_2 \rangle \quad (28b)$$

The shear and normal stress components of interest can be shown to be the following [4]:

$$\begin{aligned} \tau_{xy} - G\eta_s = & \frac{1}{6} n_0 kT \left\{ \frac{1}{2} \frac{\partial}{\partial \tau} \langle P_2^2 S_2 \rangle - \beta_0 g_1(\tau) \right. \\ & \left. \left[ 1 - \langle P_2^0 \rangle - \frac{1}{2} \langle P_2^2 C_2 \rangle \right] \right\} \quad (29a) \end{aligned}$$

$$\begin{aligned} \tau_{xx} - \tau_{yy} = & \frac{1}{6} n_0 kT \left\{ \frac{\partial}{\partial \tau} \langle P_2^2 C_2 \rangle \right. \\ & \left. - \beta_0 g_1(\tau) \langle P_2^2 S_2 \rangle \right\} \quad (29b) \end{aligned}$$

$$\begin{aligned} \tau_{yy} - \tau_{zz} = & -\frac{1}{2} n_0 kT \left\{ \frac{\partial}{\partial \tau} \left[ \langle P_2^0 \rangle \right. \right. \\ & \left. \left. + \frac{1}{6} \langle P_2^2 C_2 \rangle \right] \right\} \quad (29c) \end{aligned}$$

As indicated above, the bulk solution properties are all functions of averages over the distribution function (as indicated by the angular brackets  $\langle \rangle$ ) of various spherical harmonic functions. Using the orthogonality properties of these functions it is straightforward to evaluate these averages. The following sections consider a number of specific cases.

### 1. Steady state ( $g_1 = g_2 = 1$ )

At steady state, three integrals are required to calculate the material functions and optical properties. The results are listed below to fourth order in  $\beta_0$  and  $f_0$ .

$$\begin{aligned} \langle P_2^2 C_2 \rangle = & \frac{1}{30} \beta_0^2 - \frac{23}{18900} \beta_0^4 - \frac{2}{5} f_0 + \frac{53}{3150} f_0 \beta_0^2 \\ & - \frac{4}{105} f_0^2 + \frac{1}{770} f_0^2 \beta_0^2 + \frac{3}{1575} f_0^3 + \frac{16}{10395} f_0^4 \quad (30a) \end{aligned}$$

$$\begin{aligned} \langle P_2^2 S_2 \rangle = & \frac{1}{5} \beta_0 - \frac{19}{3150} \beta_0^3 + \frac{3}{35} f_0 \beta_0 - \frac{127}{34650} f_0 \beta_0^3 \\ & + \frac{11}{1575} f_0^2 \beta_0 - \frac{31}{24255} f_0^3 \beta_0 \quad (30b) \end{aligned}$$

$$\begin{aligned} \langle P_2^0 \rangle = & -\frac{1}{420} \beta_0^2 + \frac{4}{51975} \beta_0^4 - \frac{1}{15} f_0 + \frac{1}{6300} f_0 \beta_0^2 \\ & - \frac{2}{315} f_0^2 + \frac{79}{207900} f_0^2 \beta_0^2 + \frac{4}{4725} f_0^3 + \frac{8}{31185} f_0^4 \quad (30c) \end{aligned}$$

The steady shear viscosity can be obtained by (29a) and it is plotted against the dimensionless shear rate  $\beta_0$  after normalization by its zero field value (the viscosity in the limit of zero shear and electric fields) in Figure 2a. The viscosity is shear thinning for all values of the parameter  $f_0$  which were explored with the rate of shear thinning increasing with  $f_0$ . As is apparent from this figure, the zero-shear-rate viscosity (the intercept in Fig. 2a) increases with increasing  $f_0$ . This is easily understood by recognizing that the effect of the electric field is to align the rods normal to the flow direction thereby causing a greater energy dissipation. The upper bound on  $f_0$  for each plot was determined by evaluating the radius of convergence for the expansion of equation (17) (typically 4). This was accomplished through examination of the coefficients for the zero-shear-rate viscosity up to the fourth order in  $f_0$ . This is the same procedure as followed in reference [12] although they evaluated many more terms for their particular case.

The first normal stress coefficient was also calculated and found to follow trends similar to the shear viscosity. Plots of this function under steady shear are found in Fig. 2b. The steady second normal stress coefficient is always zero for all values of  $f_0$ .

The extinction angle is plotted in Figure 3a. At zero electric field, the zero shear intercept is at  $45^\circ$  with respect to the flow direction and parallel to the principal axis of strain in the shear flow. Any finite value of  $f_0$ , however, causes the zero shear intercept to equal  $90^\circ$ . Further application of the flow leads to a decrease in

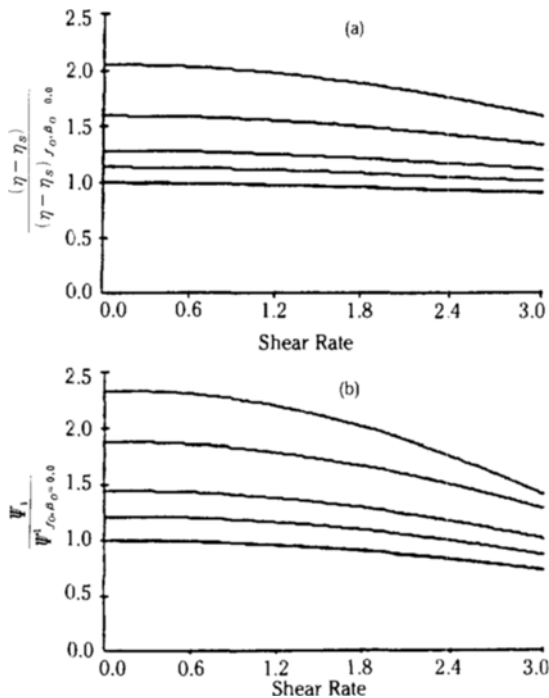


Fig. 2. (a) Dimensionless steady viscosity, (b) first normal stress coefficient as function of shear rate  $\beta_0$  (from the top,  $f_0 = 4, 2, 1, 0.5, 0$ ).

the angle towards a zero value. The birefringence is plotted in Figure 3b and shows an expected trend as the electric and hydrodynamic fields are simultaneously applied. For weak fields, the birefringence increases as either  $\beta_0$  or  $f_0$  is increased. For large electric fields, however, increasing the flow strength decreases the birefringence due to the fact that the two fields tend to orient the rods in orthogonal directions.

## 2. Transient electro-hydrodynamic field ( $g_1 = g_2$ )

When  $g_1 = g_2$ , the time dependent coefficients in equations (28) and (29) can be simplified due to the fact that there is now no difference between  $[0, (0), 1; \tau]$  and  $[(0), 0, 1; \tau]$ . In the following section, the case of the simultaneous inception of the electric and flow fields is examined.

### 2-1. Simultaneous inception of both fields

The birefringence resulting from the simultaneous application of electric and hydrodynamic fields is shown in Figure 4 for  $\beta_0 = 4$ . A large overshoot occurs for sufficiently high flow strength and this overshoot is enhanced upon the application of an electric field. The extinction angle for the same value of  $\beta_0$  is plotted in Figure 5a. At zero time the angle has a value between the limit of  $90^\circ$  ( $f_0 \neq 0$ ) and  $45^\circ$  ( $f_0 = 0$ ). Figure 5b summarizes this initial value of the extinction angle as

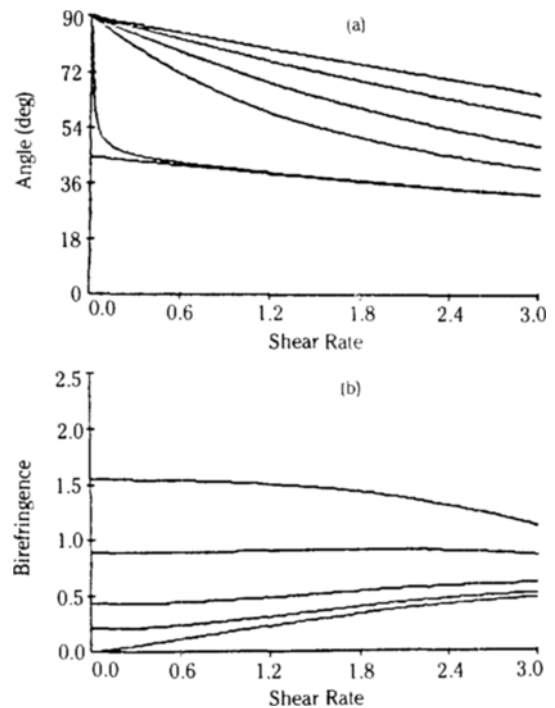


Fig. 3. (a) Steady extinction angle, (b) birefringence of rigid spheroid solution as function of shear rate  $\beta_0$  (from the top,  $f_0 = 4, 2, 1, 0.5, 0$ ).

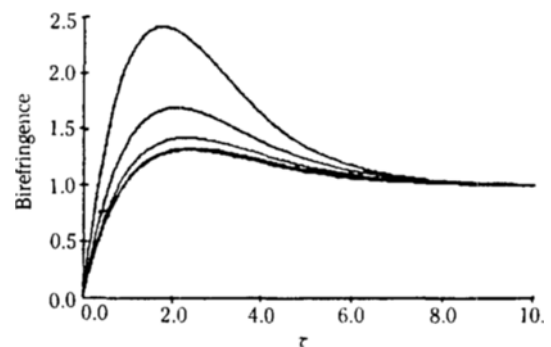


Fig. 4. Unsteady birefringence build-up of rigid spheroid solution during simultaneous sudden inception of both shear and electric fields ( $\beta_0 = 4$ , and from the top,  $f_0 = 4, 2, 1, 0.5, 0$ ).

a function of both  $\beta_0$  and  $f_0$ .

The development of stresses following the inception of flow is also of interest. Enhancement of overshoot in the shear viscosity is predicted as  $f_0$  is increased as shown in Figure 6. However, the superposition of an electric field onto a shear field will not induce overshoot if overshoot does not exist when  $f_0 = 0$ . Figure 6 also indicates that there is a finite jump in the shear

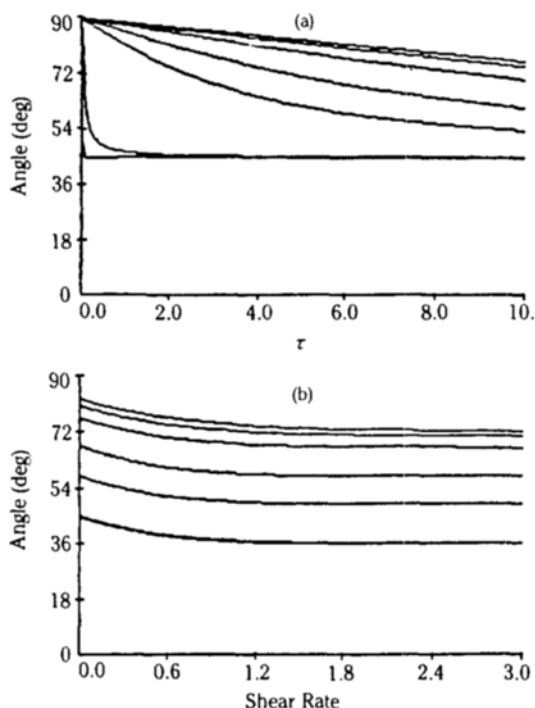


Fig. 5. (a) Unsteady extinction angle change of rigid spheroid solution during simultaneous sudden inception of both shear and electric fields at  $\beta_0 = 4$  (from the top,  $f_0 = 4, 3, 2, 1, 0.5, 0.01, 0$ ), (b) Initial extinction angle of same experiment as function of shear rate  $\beta_0$  (same order off).

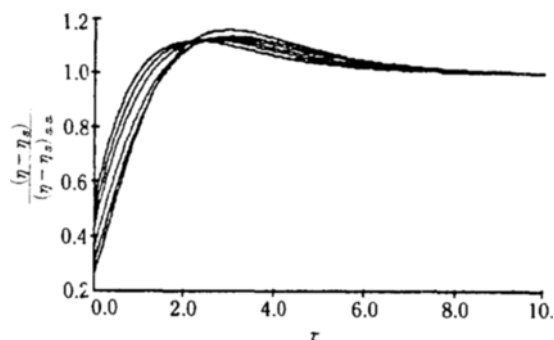


Fig. 6. Unsteady viscosity development during simultaneous sudden inception of both shear and electric fields ( $\beta_0 = 4$ , from the top,  $f_0 = 0, 0.5, 1, 2, 3, 4$ ).

stress at zero time following the inception of flow. The magnitude of this jump is independent of the value of  $f_0$ . The first normal stress coefficient following the inception of flow is plotted in Figure 7. Unlike the shear stress, the first normal stress differences shows no

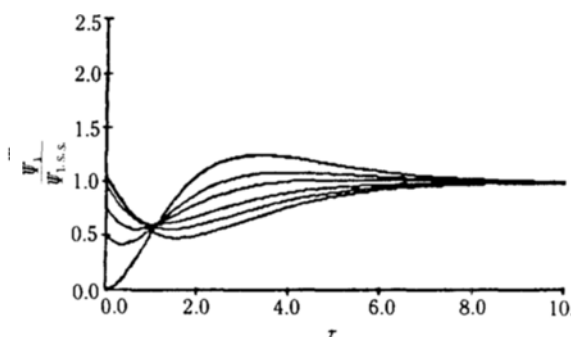


Fig. 7. Unsteady first normal stress coefficient development during simultaneous sudden inception of both shear and electric fields at  $\beta_0 = 4$  (from the top,  $f_0 = 4, 3, 2, 1, 0.5, 0$ ).

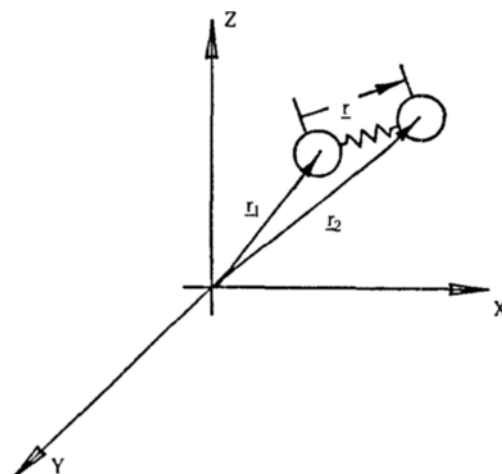


Fig. 8. The elastic dumbbell model and its coordinates.

finite jump at zero time in the absence of an electric field. Application of such a field, however, leads to a substantial instantaneous jump as shown in Figure 7. Although it is not shown here, the second normal stress difference also undergoes a finite jump when an electric field is applied but the steady state value is unaffected and remains at a value of zero.

### KINETIC THEORY FOR FLEXIBLE CHAINS

In this section the elastic dumbbell model [4] pictured in Figure 8 is used to describe flexible polymer chains subjected to electro-hydrodynamic fields. The development of this model proceeds from a force balance on the two beads making up the dumbbell. The contribution to the force balance equations include the hydrodynamic friction, an entropic spring force, a Brownian

force arising from the solvent and a force due to the electric field. Following Stockmayer and Baur [9], we shall assume that the electric field induces a polarization of the chain segments which leads to a force on the beads. Furthermore, we shall make the simplification that the induced dipoles are oriented parallel to the chain axis so that the net induced dipole for the chain is parallel to the end to end vector  $\underline{r}$ . The electrical force acting on the ends of the dumbbell is then

$$\underline{F} = 2g\underline{e} \cdot \underline{r}. \quad (31)$$

Where the dimensionless tensor  $\underline{g}$  defines the orientation of the applied electric field. The constant  $g$  is defined as

$$g = \frac{3}{5} (\alpha_1 - \alpha_2) E_0^2 \quad (32)$$

where  $\alpha_1$  and  $\alpha_2$  are the induced polarizabilities in excess of displaced solvent parallel and perpendicular to the chain axis respectively.

From the force balance equations the following diffusion equation for the probability distribution function  $\Psi(\underline{r}, t)$  can be obtained.

$$\frac{\partial \Psi}{\partial t} + \nabla \cdot \underline{M} \cdot \underline{r} \Psi - \frac{2}{\xi} \nabla \cdot [K(\underline{r}) \underline{r} \Psi] - \frac{2kT}{\xi} \nabla^2 \Psi = 0 \quad (33)$$

$$\underline{M} = G\underline{\Gamma} + \frac{2g}{\xi} \underline{e} \quad (34)$$

Here  $\xi$  is the friction factor of each bead and  $K(\underline{r})$  is the spring constant.  $G\underline{\Gamma}$  is the velocity gradient tensor and it is apparent from equation (33) that the superposition of an electric field onto a flow field merely causes this tensor to be replaced with the tensor  $\underline{M}$ . The solution of equation (33) and the evaluation of bulk solution properties can therefore proceed in the same manner as used for purely hydrodynamic problems.

It is useful to make the diffusion equation dimensionless by introducing a length scale  $L = Na$  (the contour length of the chain) and a time scale  $\lambda = \xi L^2 / 12kTN$ . Here  $N$  is the number of submolecules of length  $a$  making up the chain. The spring constant is then taken to be  $3kTN/L^2 E(r)$ . For the linear elastic dumbbell model  $E(r)$  is 1, and one commonly used nonlinear model is the Warner spring,  $E(r) = 1/(1-r^2)$ , which was used here for calculations. The diffusion equation is then:

$$\frac{\partial \Psi}{\partial t} + \nabla \cdot \left( \alpha \underline{\Gamma} + \frac{f}{2} \underline{e} \right) \cdot \underline{r} \Psi - \frac{1}{2} \nabla \cdot [E(\underline{r}) \underline{r} \Psi] - \frac{1}{6N} \nabla^2 \Psi = 0 \quad (35)$$

The hydrodynamic and electric fields are then characterized by the dimensionless parameters  $\alpha = \lambda G$  and  $f = 4g\lambda/\xi$ . One immediate consequence of applying an electric field is that the "strong flow/weak flow" criterion discussed by Tanner [17] and Olbricht et al. [18] is altered. This condition defines the state at which a dramatic extension from the coiled to the stretched state occurs. The criterion for the present model is given by the following inequality:

$k^+ < 1/2$ : weak field, coiled configuration

$k^+ \geq 1/2$ : strong field, stretched configuration

where  $k^+$  is the largest, positive eigenvalue of  $(\alpha \underline{\Gamma} + f/2 \underline{e})$ . One would anticipate that for strong fields, it will be necessary to utilize nonlinear spring functions,  $E(r)$  which preserve the finite extensibility of the dumbbell.

Although calculation were carried out for this model, the results are all qualitatively similar to those found for the rigid dumbbell model and are not reproduced here. There is, however, a much weaker dependence by the electric field on the overshoot phenomena in material functions for the elastic dumbbell.

## CONCLUSIONS

The simple rigid and elastic dumbbell models can be used to provide predictions for the response of polymeric liquids to simultaneous hydrodynamic and electric fields. Although this problem has been considered to a limited extent in the past, the use of electrohydrodynamic field is becoming increasingly important in applications (e.g. fabrication of flexible mass storage disks and ink-jet printing). Alternatively, combined hydrodynamic and electric fields can often be used to offer greater insights into the structure of the polymer chains themselves (the recent article by van de Ven [19] considers this point for spheroidal particles), or to alter the rheology of these materials.

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## APPENDIX A. Properties of Operator $\mathcal{Q}_2$

The operator  $\mathcal{Q}_2$  has the following properties.

$$\mathcal{Q}_2 \{P_n^m C_m\} = \sum_{p=1}^3 \sum_{q=1}^3 b_{n,n+2p-4}^{m,m+2p-4} P_{n,n+2q-4}^{m,m+2q-4} C_{m+2p-4} \quad (A1)$$

This relationship is true for  $S_m$  if we switch every  $C_m$

with  $S_m$ .

The coefficients  $b$ 's are:

$m \neq 1$

$$b_{n,n-2}^{m,m} = \frac{(n-m+1)(n-m+2)(n+3)}{(2n+1)(2n+3)} \quad (A2)$$

$$b_{n,n}^{m,m} = \frac{(n^2+n-3m^2)}{(2n-1)(2n+1)} \quad (A3)$$

$$b_{n,n-2}^{m,m} = \frac{(2-n)(n+m)(n+m-1)}{(2n-1)(2n+1)} \quad (A4)$$

$$b_{n,n+2}^{m,m} = \frac{(n+3)}{2(2n+1)(2n+3)} [1+\delta_{m,o}] \quad (A5)$$

$$b_{n,n}^{m,m+2} = \frac{-3}{2(2n-1)(2n+3)} [1+\delta_{m,o}] \quad (A6)$$

$$b_{n,n-2}^{m,m+2} = \frac{(2-n)}{2(2n-1)(2n+1)} [1+\delta_{m,o}] \quad (A7)$$

$$b_{n,n-2}^{m,m-2} = \frac{(n+3)(n-m+1)(n-m+2)(n-m+3)(n-m+4)(1-\delta_{m,o})}{2(2n+1)(2n+3)} \quad (A8)$$

$$b_{n,n}^{m,m-2} = \frac{-3(n+m)(n+m-1)(n-m+1)(n-m+2)(1-\delta_{m,o})}{2(2n-1)(2n+3)} \quad (A9)$$

$$b_{n,n-2}^{m,m-2} = \frac{(2-n)(n+m)(n+m-1)(n+m-2)(n+m-3)(1-\delta_{m,o})}{2(2n-1)(2n+1)} \quad (A10)$$

If  $m = 1$ , we have different formulars.

$$b_{n,n+2}^{1,1} = \frac{n(n+1)(n+3)}{2(2n+1)(2n+3)} \text{ or } \frac{3n(n+1)(n+3)}{2(2n+1)(2n+3)} \quad (A11)$$

$$b_{n,n}^{1,1} = \frac{5n^2+5n-6}{2(2n-1)(2n+3)} \text{ or } \frac{-(n^2+n+6)}{4(2n-1)(2n+3)} \quad (A12)$$

$$b_{n,n-2}^{1,1} = \frac{(2-n)n(n+1)}{2(2n-1)(2n+1)} \text{ or } \frac{3(2-n)n(n+1)}{2(2n-1)(2n+1)} \quad (A13)$$

$$b_{n,n+2}^{1,3} = \frac{(n+3)}{2(2n+1)(2n+3)} \quad (A14)$$

$$b_{n,n}^{1,3} = \frac{-3}{2(2n-1)(2n+3)} \quad (A15)$$

$$b_{n,n-2}^{1,3} = \frac{(2-n)}{2(2n-1)(2n+1)} \quad (A16)$$

First columns are for  $C_m$  and 2nd columns for  $S_m$ , respectively. All indices should be positive or zero, and the lower one should be greater than or equal to the upper one.

## APPENDIX B. Details of Base Functions

$$\phi_{00} = P_0^0 \quad (B1)$$

$$\phi_{01} = \frac{1}{12} [1; t] P_2^2 S_2 \quad (B2)$$

$$\phi_{02} = -\frac{1}{2^2 \cdot 3 \cdot 7} [0, 1; t] P_2^0 + \frac{1}{2^2 \cdot 3 \cdot 7} \left\{ \frac{7}{3}, 1; t \right\} P_4^0 + \frac{1}{2^3 \cdot 3^2} [0, 1; t] P_2^2 C_2 - \frac{1}{2^5 \cdot 3^2 \cdot 7} \left\{ \frac{7}{3}, 1; t \right\} P_4^2 C_4 \quad (B3)$$

$$\begin{aligned} \phi_{03} = & \left\{ -\frac{23}{2^3 \cdot 3^3 \cdot 7^2} [0, 0, 1; t] - \frac{1}{2 \cdot 3^2 \cdot 7^2} \left\{ -\frac{7}{3}, \frac{7}{3}, 1; t \right\} \right\} P_2^2 S_2 + \left\{ -\frac{1}{2^4 \cdot 3^2 \cdot 7^2} \left\{ \frac{7}{3}, 0, 1; t \right\} - \frac{5}{2^3 \cdot 3^2 \cdot 7^2 \cdot 11} \right. \\ & \left. \left\{ 0, \frac{7}{3}, 1; t \right\} \right\} P_4^2 S_2 + \frac{1}{2^5 \cdot 3^3 \cdot 11} \left\{ \frac{11}{3}, \frac{7}{3}, 1; t \right\} P_6^2 S_2 + \left\{ \frac{1}{2^6 \cdot 3^3 \cdot 7} \left\{ \frac{7}{3}, 0, 1; t \right\} + \frac{1}{2^5 \cdot 3^3 \cdot 7} \left\{ 0, \frac{7}{3}, 1; t \right\} \right\} \\ & P_4^2 S_4 - \frac{1}{2^8 \cdot 3^5 \cdot 11} \left\{ \frac{11}{3}, \frac{7}{3}, 1; t \right\} P_6^2 S_6 \end{aligned} \quad (B4)$$

$$\begin{aligned} \phi_{04} = & \left\{ \frac{23}{2^3 \cdot 3^3 \cdot 7^2} [0, 0, 0, 1; t] + \frac{1}{2 \cdot 3^2 \cdot 7^2} \left[ 0, -\frac{7}{3}, \frac{7}{3}, 1; t \right] + \frac{5}{2^3 \cdot 3^2 \cdot 7^2} \left[ -\frac{7}{3}, \frac{7}{3}, 0, 1; t \right] + \frac{5^2}{2^2 \cdot 3^3 \cdot 7^3 \cdot 11} \right. \\ & \left. \left[ -\frac{7}{3}, 0, \frac{7}{3}, 1; t \right] \right\} P_2^0 - \left\{ \frac{23}{2^4 \cdot 3^4 \cdot 7^2} [0, 0, 0, 1; t] + \frac{1}{2^2 \cdot 3^2 \cdot 7^2} \left[ 0, -\frac{7}{3}, \frac{7}{3}, 1; t \right] \right. \\ & \left. + \frac{5}{2^3 \cdot 3^3 \cdot 7} \left[ -\frac{7}{3}, \frac{7}{3}, 0, 1; t \right] + \frac{5}{2^2 \cdot 3^5 \cdot 7} \left[ -\frac{7}{3}, 0, \frac{7}{3}, 1; t \right] \right\} P_2^2 C_2 + \text{extra terms} \end{aligned} \quad (B5)$$



$$\phi_{10} = -\frac{1}{3} [(1); t] P_2^0 - \frac{1}{6} [(1); t] P_2^1 S_2 \quad (B6)$$

$$\begin{aligned} \phi_{11} = & \left\{ \frac{2}{3^2 \cdot 7} [0, (1); t] + \frac{1}{2^2 \cdot 3^2 \cdot 7} [(0), 1; t] \right\} P_2^2 S_2 + \left\{ -\frac{1}{2^2 \cdot 3^2 \cdot 7} \left[ \frac{7}{3}, (1); t \right] - \frac{1}{2^2 \cdot 3^2 \cdot 7} \left[ \left( \frac{7}{3} \right), 1; t \right] \right\} P_2^1 S_2 \\ & + \left\{ -\frac{1}{2^4 \cdot 3^2 \cdot 7} \left[ \frac{7}{3}, (1); t \right] - \frac{1}{2^4 \cdot 3^2 \cdot 7} \left[ \left( \frac{7}{3} \right), 1; t \right] \right\} P_4^1 S_4 \end{aligned} \quad (B7)$$

$$\begin{aligned} \phi_{12} = & \left\{ -\frac{2}{3^2 \cdot 7^2} [0, 0, (1); t] - \frac{1}{2^2 \cdot 3^2 \cdot 7^2} [0, (0), 1; t] + \frac{5}{2 \cdot 3^2 \cdot 7^2} \left[ \left[ -\frac{7}{3}, \frac{7}{3}, (1); t \right] + \left[ -\frac{7}{3}, \left( \frac{7}{3} \right), 1; t \right] \right] \right. \\ & + \frac{2}{3^2 \cdot 7^2} [(0), 0, 1; t] + \frac{1}{3^3 \cdot 7^2} \left[ \left( -\frac{7}{3} \right), \frac{7}{3}, 1; t \right] \Big\} P_2^0 + \left\{ \frac{2}{3^2 \cdot 7^2} \left[ \frac{7}{3}, 0, (1); t \right] + \frac{1}{2^2 \cdot 3^2 \cdot 7^2} \left[ \frac{7}{3}, (0), 1; t \right] \right. \\ & + \frac{5}{2^2 \cdot 7^2 \cdot 11} \left[ [0, \frac{7}{3}, (1); t] + [0, \left( \frac{7}{3} \right), 1; t] \right] - \frac{1}{2^2 \cdot 3^2 \cdot 7^2} \left[ \left( \frac{7}{3} \right), 0, 1; t \right] - \frac{5}{2 \cdot 3^2 \cdot 7^2 \cdot 11} [(0), \frac{7}{3}, 1; t] \Big\} P_2^1 \\ & - \frac{5}{2^2 \cdot 3^3 \cdot 11} \left\{ \left[ \frac{11}{3}, \frac{7}{3}, (1); t \right] + \left[ \frac{11}{3}, \left( \frac{7}{3} \right), 1; t \right] + \left[ \left( \frac{11}{3} \right), \frac{7}{3}, 1; t \right] \right\} P_2^0 + \left\{ \frac{1}{2^2 \cdot 3^3 \cdot 7} [8[0, 0, (1); t] \right. \\ & + [0, (0), 1; t] + \frac{4}{7} [(0), 0, 1; t]] + \frac{5}{2^2 \cdot 3^4 \cdot 7} \left[ \left[ -\frac{7}{3}, \frac{7}{3}, (1); t \right] + \left[ -\frac{7}{3}, \left( \frac{7}{3} \right), 1; t \right] \right] \\ & - \frac{17}{2 \cdot 3^4 \cdot 7^2} \left[ \left( -\frac{7}{3} \right), \frac{7}{3}, 1; t \right] \Big\} P_2^2 C_2 - \left\{ \frac{1}{3^3 \cdot 7 \cdot 11} \left[ [0, \frac{7}{3}, (1); t] + [0, \left( \frac{7}{3} \right), 1; t] \right] \right. \\ & + \frac{1}{2 \cdot 3^3 \cdot 7^2} \left[ \left( \frac{7}{3} \right), 0, 1; t \right] + \frac{1}{2 \cdot 3^2 \cdot 7^2 \cdot 11} [(0), \frac{7}{3}, 1; t] \Big\} P_2^1 C_2 - \frac{1}{2^4 \cdot 3^4 \cdot 11} \left\{ \left[ \frac{11}{3}, \frac{7}{3}, (1); t \right] \right. \\ & + \left[ \frac{11}{3}, \left( \frac{7}{3} \right), 1; t \right] - \left[ \left( \frac{11}{3} \right), \frac{7}{3}, 1; t \right] \Big\} P_2^1 C_2 - \left\{ \frac{1}{2^2 \cdot 3^3 \cdot 7^2} [8 \left[ \frac{7}{3}, 0, (1); t \right] + \left[ \frac{7}{3}, (0), 1; t \right]] \right. \\ & + \frac{157}{2^5 \cdot 3^3 \cdot 7^2 \cdot 11} \left[ [0, \frac{7}{3}, (1); t] + [0, \left( \frac{7}{3} \right), 1; t] \right] + \left[ \frac{1}{2^5 \cdot 3^3 \cdot 7 \cdot 11} [11 \left[ \left( \frac{7}{3} \right), 0, 1; t \right] + 2[(0), \frac{7}{3}, 1; t]] \right] \Big\} P_2^1 C_4 \\ & + \frac{1}{2^5 \cdot 3^5 \cdot 11} \left\{ \left[ \frac{11}{3}, \frac{7}{3}, (1); t \right] + \left[ \frac{11}{3}, \left( \frac{7}{3} \right), 1; t \right] + \left[ \left( \frac{11}{3} \right), \frac{7}{3}, 1; t \right] \right\} P_2^0 C_4 + \frac{1}{2^2 \cdot 3^5 \cdot 11} \left\{ \left[ \frac{11}{3}, \frac{7}{3}, (1); t \right] \right. \\ & + \left[ \frac{11}{3}, \left( \frac{7}{3} \right), 1; t \right] + \left[ \left( \frac{11}{3} \right), \frac{7}{3}, 1; t \right] \Big\} P_2^1 C_4 \end{aligned} \quad (B8)$$

$$\begin{aligned} \phi_{13} = & -\left\{ \frac{23}{2^2 \cdot 3^4 \cdot 7^3} [12[0, 0, 0, (1); t] + [0, 0, (0), 1; t]] + \frac{1}{2^2 \cdot 3^4 \cdot 7^3} [26[0, (0), 0, 1; t] + 23[(0), 0, 0, 1; t]] \right. \\ & + \frac{65}{2 \cdot 3^5 \cdot 7^3} \left[ [0, -\frac{7}{3}, \frac{7}{3}, (1); t] + [0, -\frac{7}{3}, \left( \frac{7}{3} \right), 1; t] \right] + \frac{1}{2 \cdot 3^5 \cdot 7^3} [-58[0, \left( -\frac{7}{3} \right), \frac{7}{3}, 1; t] + 9[(0), \\ & -\frac{7}{3}, \frac{7}{3}, 1; t]] + \frac{1}{2 \cdot 3^3 \cdot 7^3} [8[-\frac{7}{3}, \frac{7}{3}, 0, (1); t] + [-\frac{7}{3}, \frac{7}{3}, (0), 1; t]] + \frac{1}{2^2 \cdot 3^5 \cdot 7^3} [122[-\frac{7}{3}, \left( \frac{7}{3} \right), 0, 1; t] \\ & - 105[( -\frac{7}{3} ), \frac{7}{3}, 0, 1; t]] + \frac{5 \cdot 277}{2 \cdot 3^5 \cdot 7^3 \cdot 11} \left[ [-\frac{7}{3}, 0, \frac{7}{3}, (1); t] + [-\frac{7}{3}, 0, \left( \frac{7}{3} \right), 1; t] \right] \\ & + \frac{5}{3^5 \cdot 7^3 \cdot 11} [12[-\frac{7}{3}, (0), \frac{7}{3}, 1; t] - 131[( -\frac{7}{3} ), 0, \frac{7}{3}, 1; t]] \Big\} P_2^2 S_2 + \text{extra terms} \end{aligned} \quad (B9)$$

$$\begin{aligned} \phi_{20} = & -\frac{2}{3^2 \cdot 7} [(0), (1); t] P_2^0 + \frac{1}{7} \left[ \left( \frac{7}{3} \right), (1); t \right] P_4^0 - \frac{1}{3^2 \cdot 7} [(0), (1); t] P_2^1 C_2 + \frac{1}{3^2 \cdot 7} \left[ \left( \frac{7}{3} \right), (1); t \right] P_4^1 C_2 \\ & + \frac{1}{2^3 \cdot 3^2 \cdot 7} \left[ \left( \frac{7}{3} \right), (1); t \right] P_4^1 C_4 \end{aligned} \quad (B10)$$

$$\begin{aligned}
\phi_{21} = & \frac{1}{2^2 \cdot 3^3 \cdot 7^2} [16(0, (0), (1); t) + 8((0)0, (1); t) + [(0), (0), 1; t] + \frac{1}{3^4 \cdot 7^2} [16(-\frac{7}{3}, (\frac{7}{3}), (1); t) \\
& - 20((-\frac{7}{3}), \frac{7}{3}, (1); t) - 20((-\frac{7}{3}), (\frac{7}{3}), 1; t)] \{P_2^* S_2 - \frac{1}{2 \cdot 3^3 \cdot 7^2} [( \frac{7}{3}, (0), (1); t) + 4((\frac{7}{3}), 0, (1); t)] \\
& - \frac{1}{2^2 \cdot 3^3 \cdot 7^2 \cdot 11} [11((\frac{7}{3}), (0), 1; t) + 160(0, (\frac{7}{3}), (1); t) + \frac{17}{2^2 \cdot 3^3 \cdot 7^2 \cdot 11} ((0), \frac{7}{3}, (1); t) \\
& + [(0), (\frac{7}{3}), 1; t)] \} P_2^* S_2 + \frac{5}{2^3 \cdot 3^4 \cdot 11} \{(\frac{11}{3}, (\frac{7}{3}), (1); t) + ((\frac{11}{3}), \frac{7}{3}, (1); t) + ((\frac{11}{3}), (\frac{7}{3}), 1; t)\} P_2^* S_2 \\
& - \frac{1}{2^3 \cdot 3^3 \cdot 7^2} [( \frac{7}{3}, (0), (1); t) + 4((\frac{7}{3}), 0, (1); t)] + \frac{1}{2^4 \cdot 3^3 \cdot 7^2 \cdot 11} [11((\frac{7}{3}), (0), 1; t) + 2^5 \cdot 5(0, (\frac{7}{3}), (1); t)] \\
& + \frac{17}{2^4 \cdot 3^3 \cdot 7^2 \cdot 11} [( (0), \frac{7}{3}, (1); t) + ((0), (\frac{7}{3}), 1; t)] \{P_2^* S_4 + \frac{1}{2^3 \cdot 3^3 \cdot 11} \{(\frac{11}{3}, (\frac{7}{3}), (1); t) + ((\frac{11}{3}), \frac{7}{3}, (1); t) \\
& + ((\frac{11}{3}), (\frac{7}{3}), 1; t)\} \cdot P_2^* S_4 + \frac{1}{8} P_2^* S_4 \} \quad (B11)
\end{aligned}$$

$$\begin{aligned}
\phi_{22} = & \{-\frac{4}{3^3 \cdot 7^3} [0, 0, (0), 1; t] - \frac{2}{3^3 \cdot 7^3} [0, (0), 0, (1); t] - \frac{1}{2^2 \cdot 3^3 \cdot 7^3} [0, (0), (0), 1; t] - \frac{16}{3^4 \cdot 7^3} [0, -\frac{7}{3}, (\frac{7}{3}), \\
& (1); t] + \frac{2^2 \cdot 5}{3^4 \cdot 7^3} [0, (-\frac{7}{3}), \frac{7}{3}, (1); t] + \frac{2^2 \cdot 5}{3^4 \cdot 7^3} [0, (-\frac{7}{3}), (\frac{7}{3}), 1; t] + \frac{5}{3^4 \cdot 7^3} [-\frac{7}{3}, \frac{7}{3}, (0), (1); t] \\
& + \frac{2^2 \cdot 5}{3^4 \cdot 7^3} [-\frac{7}{3}, (\frac{7}{3}), 0, (1); t] + \frac{5}{2 \cdot 3^4 \cdot 7^3} [-\frac{7}{3}, (\frac{7}{3}), (0), 1; t] \\
& + \frac{5 \cdot 80}{3^4 \cdot 7^3 \cdot 11} [-\frac{7}{3}, 0, (\frac{7}{3}), (1); t] + \frac{5 \cdot 17}{2 \cdot 3^4 \cdot 7^3 \cdot 11} \{[-\frac{7}{3}, (0), \frac{7}{3}, (1); t] + [-\frac{7}{3}, (0), (\frac{7}{3}), 1; t] \\
& + \frac{2^4}{3^3 \cdot 7^3} [(0), 0, 0, (1); t] + \frac{2}{3^3 \cdot 7^3} [(0), 0, (0), 1; t] - \frac{1}{3^3 \cdot 7^3} [(0), (0), 0, 1; t] + \frac{5}{3^3 \cdot 7^3} [(0), -\frac{7}{3}, \frac{7}{3}, \\
& (1); t] + \frac{5}{3^3 \cdot 7^3} [(0), -\frac{7}{3}, (\frac{7}{3}), 1; t] - \frac{2}{3^3 \cdot 7^3} [(0), (-\frac{7}{3}), \frac{7}{3}, 1; t] + \frac{2^3}{3^4 \cdot 7^3} [(-\frac{7}{3}), \frac{7}{3}, 0, (1); t] \\
& + \frac{1}{3^4 \cdot 7^3} [(-\frac{7}{3}), \frac{7}{3}, (0), 1; t] - \frac{11}{3^4 \cdot 7^3} [(-\frac{7}{3}), (\frac{7}{3}), 0, 1; t] - \frac{5 \cdot 19}{3^4 \cdot 7^3 \cdot 11} [(-\frac{7}{3}), 0, \frac{7}{3}, (1); t] \\
& - \frac{5 \cdot 19}{3^4 \cdot 7^3 \cdot 11} [(-\frac{7}{3}), 0, (\frac{7}{3}), 1; t] - \frac{2^3 \cdot 5}{3^4 \cdot 7^3 \cdot 11} [(-\frac{7}{3}), (0), \frac{7}{3}, 1; t] \} P_2^* + \frac{2}{3^4 \cdot 7^2} [0, 0, (0), (1); t] \\
& + \frac{1}{3^4 \cdot 7^2} [0, (0), 0, (1); t] + \frac{1}{2^3 \cdot 3^4 \cdot 7^2} [0, (0), (0), 1; t] + \frac{2^2}{3^4 \cdot 7^3} [(0), 0, 0, (1); t] + \frac{1}{2 \cdot 3^4 \cdot 7^3} [(0), 0, (0), 1; t] \\
& + \frac{1}{2 \cdot 3^4 \cdot 7^2} [(0), (0), 0, 1; t] + \frac{16}{2 \cdot 3^4 \cdot 7^2} [0, -\frac{7}{3}, (\frac{7}{3}), (1); t] - \frac{2 \cdot 5}{3^5 \cdot 7^2} [0, (-\frac{7}{3}), \frac{7}{3}, (1); t] \\
& - \frac{2 \cdot 5}{3^5 \cdot 7^2} [0, (-\frac{7}{3}), (\frac{7}{3}), 1; t] + \frac{5^2}{2 \cdot 3^5 \cdot 7^3} [(0), -\frac{7}{3}, \frac{7}{3}, (1); t] + \frac{5^2}{2 \cdot 3^5 \cdot 7^3} [(0), -\frac{7}{3}, (\frac{7}{3}), 1; t] \\
& - \frac{1}{3^5 \cdot 7^2} [(0), (-\frac{7}{3}), \frac{7}{3}, 1; t] + \frac{5}{2 \cdot 3^5 \cdot 7^2} [-\frac{7}{3}, \frac{7}{3}, (0), (1); t] + \frac{2 \cdot 5}{3^5 \cdot 7^2} [-\frac{7}{3}, (\frac{7}{3}), 0, (1); t] \\
& + \frac{5}{2^2 \cdot 3^5 \cdot 7^2} [-\frac{7}{3}, (\frac{7}{3}), (0), 1; t] - \frac{2^2 \cdot 17}{3^5 \cdot 7^2} [(-\frac{7}{3}), \frac{7}{3}, 0, (1); t] - \frac{17}{2 \cdot 3^5 \cdot 7^2} [(-\frac{7}{3}), \frac{7}{3}, (0), 1; t] \\
& - \frac{19}{2 \cdot 3^5 \cdot 7^2} [(-\frac{7}{3}), (\frac{7}{3}), 0, 1; t] + \frac{2^3 \cdot 5^2}{3^5 \cdot 7^2 \cdot 11} [-\frac{7}{3}, 0, (\frac{7}{3}), (1); t] + \frac{5 \cdot 17}{2^2 \cdot 3^5 \cdot 7^2 \cdot 11} [-\frac{7}{3}, (0), \frac{7}{3}, (1); t]
\end{aligned}$$

$$\begin{aligned}
& + \frac{5 \cdot 17}{2^2 \cdot 3^5 \cdot 7^2 \cdot 11} \left[ -\frac{7}{3}, (0), \left(\frac{7}{3}\right), 1; t \right] - \frac{5 \cdot 191}{2 \cdot 3^4 \cdot 7^3 \cdot 11} \left[ \left(-\frac{7}{3}\right) 0, \frac{7}{3}, (1); t \right] - \frac{5 \cdot 191}{2 \cdot 3^4 \cdot 7^3 \cdot 11} \left[ \left(-\frac{7}{3}\right), 0, \left(\frac{7}{3}\right), 1; t \right] \\
& - \frac{2^2 \cdot 5}{3^4 \cdot 7^2 \cdot 11} \left[ \left(-\frac{7}{3}\right), (0), \frac{7}{3}, 1; t \right] \} P_2^2 C_2 + \text{extra terms} \quad (B12)
\end{aligned}$$

$$\begin{aligned}
\phi_{10} = & \left\{ -\frac{4}{3^3 \cdot 7^2} [(0), (0), (1); t] + \frac{2^5}{3^3 \cdot 7^2} \left[ \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (1); t \right] \right\} P_2^0 + \left\{ \frac{2 \cdot 3}{3^2 \cdot 7^2} \left[ \left(\frac{7}{3}\right), (0), (1); t \right] \right. \\
& + \frac{2^4 \cdot 5}{3 \cdot 7^2 \cdot 11} [(0), \left(\frac{7}{3}\right), (1); t] \} P_4^0 - \frac{5^2}{3^3 \cdot 11} \left[ \left(\frac{7}{3}\right), \left(\frac{7}{3}\right), (1); t \right] P_6^0 + \left\{ -\frac{2}{3^3 \cdot 7^2} [(0), (0), (1); t] \right. \\
& + \frac{2^4}{3^3 \cdot 7^2} \left[ \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (1); t \right] \} P_2^2 C_2 + \left\{ \frac{2}{3^3 \cdot 7^2} \left[ \left(\frac{7}{2}\right), (0), (1); t \right] + \frac{2^2 \cdot 5}{3^3 \cdot 7^2 \cdot 11} \left[ (0), \left(\frac{7}{3}\right), (1); t \right] \right\} P_4^2 C_2 \\
& - \frac{5}{2^2 \cdot 3^3 \cdot 11} \left[ \left(\frac{11}{3}\right), \left(\frac{7}{3}\right), (1); t \right] P_6^2 C_2 + \frac{1}{2^2 \cdot 3^3 \cdot 7^2 \cdot 11} \{ 11 \left[ \left(\frac{7}{3}\right), (0), (1); t \right] + 10 \left[ (0), \left(\frac{7}{3}\right), (1); t \right] \} P_4^2 C_4 \\
& - \frac{1}{2^3 \cdot 3^4 \cdot 11} \left[ \left(\frac{11}{3}\right), \left(\frac{7}{3}\right), (1); t \right] \} P_6^4 C_4 + \frac{1}{12} P_6^6 C_6 \} \quad (B13)
\end{aligned}$$

$$\begin{aligned}
\phi_{11} = & \left\{ \frac{8}{3^4 \cdot 7^3} [(0), (0), (0), (1); t] + \frac{4}{3^4 \cdot 7^3} [(0), 0, (0), (1); t] + \frac{2}{3^4 \cdot 7^3} [(0), (0), 0, (1); t] \right. \\
& + \frac{1}{2^2 \cdot 3^4 \cdot 7^3} [(0), (0), (0), 1; t] - \frac{2^4}{3^4 \cdot 7^3} \left[ 0, \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (1); t \right] + \frac{16}{3^5 \cdot 7^3} \left[ (0), -\frac{7}{3}, \left(\frac{7}{3}\right), (1); t \right] \\
& - \frac{2^2 \cdot 5}{3^5 \cdot 7^3} \left[ (0), \left(-\frac{7}{3}\right), \frac{7}{3}, (1); t \right] - \frac{2^2 \cdot 5}{3^5 \cdot 7^3} \left[ (0), \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), 1; t \right] + \frac{2 \cdot 16}{3^5 \cdot 7^3} \left[ -\frac{7}{3}, \left(\frac{7}{3}\right), (0), (1); t \right] \\
& - \frac{2^3 \cdot 5}{3^5 \cdot 7^3} \left[ \left(-\frac{7}{3}\right), \frac{7}{3}, (0), (1); t \right] - \frac{2^3 \cdot 5}{3^5 \cdot 7^3} \left[ \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), 0, (1); t \right] - \frac{2^2 \cdot 5}{3^5 \cdot 7^3} \left[ \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (0), 1; t \right] \\
& + \frac{2 \cdot 5 \cdot 32}{3^5 \cdot 7^3 \cdot 11} \left[ -\frac{7}{3}, (0), \left(\frac{7}{3}\right), (1); t \right] - \frac{2^7 \cdot 5^2}{3^5 \cdot 7^3 \cdot 11} \left[ \left(-\frac{7}{3}\right), 0, \left(\frac{7}{3}\right), (1); t \right] \\
& - \frac{2^2 \cdot 5 \cdot 17}{3^5 \cdot 7^3 \cdot 11} \left[ \left[ \left(-\frac{7}{3}\right), (0), \frac{7}{3}, (1); t \right] + \left[ \left(-\frac{7}{3}\right), (0), \left(\frac{7}{3}\right), 1; t \right] \right] \} P_2^2 S_2 + \text{extra terms} \quad (B14)
\end{aligned}$$

$$\begin{aligned}
\phi_{10} = & \left\{ \frac{4}{3^4 \cdot 7^3} \left[ -2 \left[ (0), (0), (0), (1); t \right] + 16 \left[ (0), \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (1); t \right] \right] + \frac{2^6}{3^4 \cdot 7^3 \cdot 11} \{ 11 \left[ \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (0), (1); t \right] \right. \right. \\
& + 10 \left[ \left(-\frac{7}{3}\right), (0), \left(\frac{7}{3}\right), (1); t \right] \} \} P_2^0 + \left\{ \frac{2^2}{3^4 \cdot 7^3} \left[ - \left[ (0), (0), (0), (1); t \right] + 8 \left[ (0), \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (1); t \right] \right] \right. \\
& + \frac{2^5}{3^4 \cdot 7^3} \left[ \left(-\frac{7}{3}\right), \left(\frac{7}{3}\right), (0), (1); t \right] + \frac{2^4 \cdot 5}{3^4 \cdot 7^3 \cdot 11} \left[ \left(-\frac{7}{3}\right), (0), \left(\frac{7}{3}\right), (1); t \right] \} \} P_4^2 C_2 + \text{extra terms} \quad (B15)
\end{aligned}$$

## NOMENCLATURE

- $D_r$  : rotational diffusivity  
 $f$  : electrohydrodynamic field parameter  
 $G$  : shear rate  
 $K_2$  : dielectric constant of suspending fluid  
 $K(r)$  : spring constant  
 $q$  : ratio of dielectric constant of macromolecule to that of the suspending fluid  
 $r$  : aspect ratio of spheroidal molecule  
 $\mathbf{r}$  : end to end vector

- $\beta$  : dimensionless velocity gradient  
 $\Delta n$  : birefringence  
 $\epsilon_0$  : permittivity of free space  
 $\zeta$  : friction factor  
 $\eta_2$  : viscosity of suspending Newtonian fluid  
 $\chi$  : extinction angle  
 $\Psi(\theta, \varphi; t)$  : orientation distribution function

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