JOURNAL OF APPLIED POLYMER SCIENCE VOL. 15, PP. 1903–1909 (1971)

Bead-Spring Model of Dilute Polymer Solutions: Continuum Modifications and an Explicit Constitutive Equation

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Synopsis

A continuum modification of the bead-spring (elastic dumbbell) theory of dilute solutions of linear macromolecules, recently introduced by Gordon and Schowalter, is used to obtain explicit constitutive equations for the stress and polarizability tensors. The stress constitutive equation, closely related to a semiempirical result obtained earlier by Spriggs, is superior in predictive capability to the constitutive equation obtained from the elastic dumbbell theory. Results are presented for steady shearing flow, large-amplitude oscillatory shearing, and stress relaxation following cessation of steady shearing and are compared with the results of the elastic and rigid dumbbell theories. In general, predictions are similar to those of the rigid dumbbell and thus are in qualitative agreement with experiment.

INTRODUCTION

The elastic dumbbell theory of dilute solutions of linear macromolecules leads to the following expressions for the stress and polarizability tensors[1–3]

$$\boldsymbol{\tau} = -\left(p + \frac{Nc}{M} kT\right)\boldsymbol{\delta} + 2\eta_s \mathbf{D} + 3\gamma \frac{Nc}{M} \langle \mathbf{rr} \rangle \tag{1}$$

$$\mathbf{P} = p_0 \boldsymbol{\delta} + 3\tilde{\beta} \frac{Nc}{M} \langle \mathbf{rr} \rangle \tag{2}$$

where N = Avogadro's number, c = concentration of polymer (assumed monodisperse), M = polymer molecular weight, η_s = solvent viscosity, k = Boltzmann's constant, T = absolute temperature, $\gamma = 2kTb^2/3$, $\tilde{\beta} = 2(\alpha_1 - \alpha_2)b^2/15$, $b^2 = 3/2nl^2$, l = fixed length of link in (equivalent) random flight chain,[4] n = number of links in random flight chain, (α_1, α_2) = polarizability of link along and normal to link axis, $\mathbf{D} = (1/2)(\nabla\mathbf{v} + \nabla\mathbf{v}\dagger)$, $\mathbf{v}$ = velocity, and $\mathbf{r}$ is the end-to-end vector of the molecule.

A few words are in order on the derivation of eq. (1). This equation is obtained by calculating the contribution to the stress vector on a plane, due to the tension in the polymers cut by that plane. One obtains[1,5]

$$\boldsymbol{\tau}_p = \frac{3\gamma Nc}{M} \langle \mathbf{rr} \rangle. \tag{3}$$

The stress being undetermined up to an arbitrary isotropic pressure, we are free to write eq. (3) as

$$\tau_p = 3\gamma \frac{Nc}{M} \langle \mathbf{rr} \rangle - \frac{Nc}{M} kT\boldsymbol{\delta}, \tag{4}$$

and thus at rest, with $\langle \mathbf{rr} \rangle = (kT/3\gamma)\boldsymbol{\delta}^4$, $\tau_p = 0$ and $\tau = -p\boldsymbol{\delta}$. This is more in keeping with the usual definition of the pressure, p.

Bird and co-workers[1] have pointed out that in the calculation of τ_p (the contribution of the macromolecules to the total stress τ), one must take into account the polymer momentum flux. They thus obtain

$$\tau_p = \frac{3\gamma Nc}{M} \langle \mathbf{rr} \rangle - \frac{Nc}{M} kT\boldsymbol{\delta},$$

which is identical with eq. (4).

To obtain explicit expressions for τ and $\mathbf{P}$, in terms of parameters describing the flow field of interest, one must first evaluate $\langle \mathbf{rr} \rangle$, where

$$\langle \mathbf{rr} \rangle \equiv \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathbf{rr}\psi dr_1 dr_2 dr_3. \tag{5}$$

The distribution function ψ is obtained from the diffusion equation[1,2]

$$\frac{\partial \psi}{\partial t} = -\nabla\psi\dot{\mathbf{r}} + D\nabla^2\psi \tag{6}$$

once an expression for $\dot{\mathbf{r}}$ is given. The development of such an expression forms the central problem in the theory.

EQUATION OF MOTION FOR r

In the elastic dumbbell theory, the rate of change of $\mathbf{r}$ is found to be[1,2]

$$\dot{\mathbf{r}} = \nabla\mathbf{v}\cdot\mathbf{r} - \frac{2b^2kT}{\zeta}\mathbf{r} \tag{7}$$

where ζ is a frictional coefficient (equal to one half the frictional coefficient in reference 1). Equation (7) leads to unrealistic predictions for the viscosity and normal stress differences.[1,6] Gordon and Schowalter (GS)[5,6] have obtained an alternative expression for $\dot{\mathbf{r}}$, using a modification of Ericksen's structured fluid theory[7]:

$$\dot{\mathbf{r}} = \nabla\mathbf{v}\cdot\mathbf{r} - \epsilon\mathbf{D}\cdot\mathbf{r} - \sigma\mathbf{r} \tag{8}$$

where ϵ and σ are phenomenological constants. A detailed discussion of the derivation of eq. (8) has been given previously.[5,6] If desired, one could look upon this result simply as a semiempirical modification of the dumbbell model. Equation (8) yields expressions for the viscosity and normal stress differences in significantly better qualitative agreement with experiment than those of eq. (7) (see below).

AN EXPLICIT CONSTITUTIVE EQUATION

Using techniques clearly laid out by Bird and co-workers,[1] eqs. (1), (5), (6), and (8) may be used to obtain the following expression for $\boldsymbol{\tau}_p = \boldsymbol{\tau} - 2\eta_s\mathbf{D} + p\boldsymbol{\delta}$:

$$\boldsymbol{\tau}_p + \theta \frac{\tilde{\mathfrak{D}}\boldsymbol{\tau}_p}{\mathfrak{D}t} = \frac{2Nc}{M} kT\theta(1 - \epsilon)\mathbf{D} \tag{9}$$

$$\frac{\tilde{\mathfrak{D}}\boldsymbol{\tau}_p}{\mathfrak{D}t} \equiv \frac{\partial\boldsymbol{\tau}_p}{\partial t} + \mathbf{v}\cdot\nabla\boldsymbol{\tau}_p - \nabla\mathbf{v}\cdot\boldsymbol{\tau}_p - \boldsymbol{\tau}_p\cdot\nabla\mathbf{v}\dagger + \epsilon\mathbf{D}\cdot\boldsymbol{\tau}_p + \epsilon\boldsymbol{\tau}_p\cdot\mathbf{D}. \tag{10}$$

In obtaining this result we have used $D = kT/\zeta$[1,2] and have assumed $\sigma = 2kTb^2/\zeta$, as suggested by eqs. (7) and (8); θ is equal to $\zeta/4b^2kT$.

For the elastic dumbbell model one finds[1]

$$\boldsymbol{\tau}_p + \theta \frac{\mathfrak{D}\boldsymbol{\tau}_p}{\mathfrak{D}t} = 2\frac{Nc}{M} kT\theta\mathbf{D} \tag{11}$$

$$\frac{\mathfrak{D}\boldsymbol{\tau}_p}{\mathfrak{D}\tau} \equiv \frac{\partial\boldsymbol{\tau}_p}{\partial t} + \mathbf{v}\cdot\nabla\boldsymbol{\tau}_p - \nabla\mathbf{v}\cdot\boldsymbol{\tau}_p - \boldsymbol{\tau}_p\cdot\nabla\mathbf{v}\dagger. \tag{12}$$

If desired, analogous expressions for $\mathbf{P}$ may easily be obtained by use of the identity

$$\mathbf{P} = \left(\frac{\tilde{\beta}}{\gamma}\frac{Nc}{M}kT + p_0\right)\boldsymbol{\delta} + \frac{\tilde{\beta}\boldsymbol{\tau}_p}{\gamma}. \tag{13}$$

RESULTS

Here we compare the predictions of eqs. (9) and (11) for simple shearing flow, large amplitude oscillatory shearing, and stress relaxation following cessation of steady shearing. Results for an arbitrary steady homogeneous shear field may be found in Gordon and Schowalter[6]; these were obtained by direct evaluation of $\langle\mathbf{rr}\rangle$.

Simple Shearing Flow

The velocity field has the form

$$v_i = (Gx_2, 0, 0). \tag{14}$$

Evaluation of eqs. (9) and (11) leads to the following results:

	Eq. (9)	Elastic DB, eq. (11)
1. Viscosity, $\eta \equiv \tau_{12}/G$	$\eta = \eta_s + \dfrac{n_0kT\theta(1-\epsilon)}{1+\epsilon(2-\epsilon)\beta^2}$	$\eta = \eta_s + n_0kT\theta$
2. Primary normal stress, $N_1 \equiv \tau_{11} - \tau_{22}$	$\dfrac{2n_0kT(1-\epsilon)\beta^2}{1+\epsilon(2-\epsilon)\beta^2}$	$2n_0kT\beta^2$
3. Secondary normal stress, $N_2 \equiv \tau_{22} - \tau_{33}$	$\dfrac{-n_0kT\epsilon(1-\epsilon)\beta^2}{1+\epsilon(2-\epsilon)\beta^2}$	0

β is the generalized shear rate θG^8, and $n_0 = Nc/M$ is the number of macromolecules per unit volume. For the three material functions, the predictions of eq. (9) are in qualitative agreement with experiment[1,6]; those of eq. (11) are not. For η to be a decreasing function of β, we require[6]

$$0 < \epsilon < 1. \tag{15}$$

It is interesting to note that the results of the rigid dumbbell model,[1] viz.,

$$\eta = \eta_s + n_0 kT\theta\left[1 - \frac{18}{35}\beta^2 + \frac{1326}{1925}\beta^4 - \ldots\right]$$

and

$$N_1 = \frac{6}{5} n_0 kT\beta^2\left[1 - \frac{38}{35}\beta^2 + \ldots\right],$$

are much closer to those of eq. (9). Expanding η and N_1 about β^2, we find

$$\eta = \eta_s + n_0 kT\theta(1 - \epsilon)[1 - \epsilon(2 - \epsilon)\beta^2 + \epsilon^2(2 - \epsilon)^2\beta^4 - \ldots]$$

and

$$N_1 = 2n_0 kT(1 - \epsilon)\beta^2[1 - \epsilon(2 - \epsilon)\beta^2 + \ldots].$$

The rigid dumbbell model predicts that $N_2 = 0$; recent experiments on nondilute solutions indicate that N_2 is negative,[9,10] in agreement with the predictions of our model.

Large-Amplitude Oscillatory Shearing[1,11]

For this flow the velocity field is of the form

$$v_i = (Re\{v_0 e^{i\omega t}\},0,0) \tag{16}$$

where v_0 is a complex amplitude. From eq. (9), a set of coupled, ordinary differential equations is obtained (for convenience, the p subscript on τ has been deleted):

$$\tau_{11} + \theta\left[\frac{\partial \tau_{11}}{\partial t} - \tau_{12} Re\{\kappa_0 e^{i\omega t}\}(2 - \epsilon)\right] = 0$$

$$\tau_{22} + \theta\left[\frac{\partial \tau_{22}}{\partial t} + \epsilon\tau_{12} Re\{\kappa_0 e^{i\omega t}\}\right] = 0 \tag{17}$$

$$\tau_{12} + \theta\left[\frac{\partial \tau_{12}}{\partial t} - \tau_{22} Re\{\kappa_0 e^{i\omega t}\} + (\epsilon/2)(\tau_{11} + \tau_{22}) Re\{\kappa_0 e^{i\omega t}\}\right] = \frac{Nc}{M} kT\theta(1 - \epsilon) Re\{\kappa_0 e^{i\omega t}\}$$

and

$$\tau_{33} + \theta\frac{\partial \tau_{33}}{\partial t} = 0$$

where

$$\kappa_0 = \frac{dv_0}{dx_2}.$$

We desire an expression for the complex viscosity, $\eta^* = \eta' - i\eta''$, defined such that

$$\tau_{12} \equiv Re\{\eta^* \kappa_0 e^{i\omega t}\} \tag{18}$$

where τ_{12} is assumed to be of the form $Re\{\tau_{12}^0 e^{i\omega t}\}$, with $\tau_{12}^0 = \tau_{12}^0(\kappa_0,\omega)$ a complex amplitude. Using eqs. (17) and (18), we find

$$\eta' = \eta_s + \frac{n_0 kT\theta(1-\epsilon)[1 + 4(\theta\omega)^2 + C_1|\kappa_0|^2]}{(1 + (\theta\omega)^2)(1 + 4(\theta\omega)^2 + 4C_1|\kappa_0|^2) + 3C_1^2|\kappa_0|^4}$$

and

$$\eta'' = \frac{n_0 kT\theta^2(1-\epsilon)\omega[1 + 4(\theta\omega)^2 - 2C_1|\kappa_0|^2]}{[1 + (\theta\omega)^2][1 + 4(\theta\omega)^2 + 4C_1|\kappa_0|^2] + 3C_1^2|\kappa_0|^4}$$

with

$$C_1 = \frac{\theta^2\epsilon(2-\epsilon)}{4}.$$

Note that η^* depends on $|\kappa_0|$; as $|\kappa_0|$ increases, η'' decreases more rapidly than η'. Both effects have been observed experimentally.[11]

In the limit of small $|\kappa_0|$, η' and η'' reduce to the small-amplitude results obtained previously by Gordon and Schowalter.[6] The elastic dumbbell model does not show a dependence of η^* on $|\kappa_0|$; on the other hand, the rigid dumbbell model does predict such a phenomenon.[1,11]

Stress Relaxation Following Cessation of Steady Shearing[1,12]

For this flow, the fluid undergoes steady shearing up to time $t = 0$. At $t = 0$, the motion is suddenly stopped, and the shear and normal stresses gradually decrease to zero. We find, from eq. (9), for $t \geq 0$ that

$$\tau_{12} = \frac{n_0 kT(1-\epsilon)\beta}{1 + \epsilon(2-\epsilon)\beta^2} e^{-t/\theta}$$

$$N_1 = \frac{2n_0 kT(1-\epsilon)\beta^2}{1 + \epsilon(2-\epsilon)\beta^2} e^{-t/\theta}$$

$$N_2 = \frac{-n_0 kT(1-\epsilon)\beta^2}{1 + \epsilon(2-\epsilon)\beta^2} e^{-t/\theta}.$$

The rate of relaxation is seen to be independent of shear rate, as predicted by the elastic dumbbell model. However, experiments indicate that this rate is, in general, a strong function of G, as is predicted by the rigid dumbbell model.[1] Our feeling is that to predict such an effect within the present framework, one must go to a multispring (Zimm)[13] model, with a

large number of relaxation times. This is suggested by the comparison of eq. (9) with the Spriggs model (see below).

RELATION TO SPRIGGS MODEL

Spriggs proposed a semiempirical constitutive equation which has been quite successful in correlating experimental results for several polymer solutions.[14,15] His equation may be written in the form

$$\tau^{(n)} + \theta_n \frac{\tilde{\mathfrak{D}}\tau^{(n)}}{\mathfrak{D}t} = 2\eta_n \mathbf{D}$$

$$\tau_p = \sum_{n=1}^{\infty} \tau^{(n)} \tag{19}$$

with

$$\frac{\tilde{\mathfrak{D}}\tau^{(n)}}{\mathfrak{D}t} = \frac{\tilde{\mathfrak{D}}\tau^{(n)}}{\mathfrak{D}t} + {}^2/_3(1 - \epsilon)tr(\tau^{(n)} \cdot \mathbf{D})\boldsymbol{\delta}.$$

The derivatives $\tilde{\mathfrak{D}}\tau/\mathfrak{D}t$ and $\tilde{\mathfrak{D}}\tau/\mathfrak{D}t$ only differ by the term ${}^2/_3(1 - \epsilon)tr(\tau \cdot \mathbf{D})\boldsymbol{\delta}$, which appears to have little or no effect on the predictions of the model. Our eq. (9) is thus equivalent to a Spriggs model with a single relaxation time. Note that eq. (19) properly describes stress relaxation phenomena for $n \geq 2$.[15]

CONCLUSIONS

The Gordon-Schowalter modification of the equation of motion of an elastic dumbbell element may be used to obtain explicit constitutive equations for the stress and polarizability tensors. The stress equation is closely related to the semiempirical result of Spriggs and is superior in predictive capability to the equation obtained from the elastic dumbbell model. In many cases results are similar to those of the rigid dumbbell model.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Professor R. B. Bird for helpful comments and for kindly sending us a copy of his paper "Kinetic Theory and Rheology of Dumbbell Suspensions with Brownian Motion"[1] prior to publication.

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Received March 5, 1971.