

CONSTITUTIVE EQUATIONS FOR POLYMERIC LIQUIDS

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INTRODUCTION

This review addresses the origins, uses, and evaluation of constitutive equations for the stress tensor of polymeric liquids. The continuum aspects of the subject up to about 1986 were summarized by Bird et al (1987a), and the molecular aspects by Bird et al (1987b); these two textbooks will be referred to as DPL-1 and DPL-2. Bird & Öttinger (1992) review advances in molecular theory from 1986 to 1991. Here we put into perspective those aspects of the subject that are of primary concern in fluid dynamics, with extra emphasis on noteworthy advances of the past decade. A comparison of this review with one prepared by Bird (1976) nearly two decades ago will show that much progress has been made in this field and that there has been a considerable shift in emphasis, largely because of increased computational capability and the influence of developments in kinetic theory.

To solve fluid dynamics problems we use the equations of continuity, motion, and energy:

$$\frac{\partial}{\partial t} \rho = -(\nabla \cdot \rho \mathbf{v}) \quad (1)$$

$$\frac{\partial}{\partial t} \rho \mathbf{v} = -[\nabla \cdot \rho \mathbf{v} \mathbf{v}] - \nabla p - [\nabla \cdot \boldsymbol{\tau}] + \rho \mathbf{g} \quad (2)$$

$$\frac{\partial}{\partial t} \rho \hat{U} = -(\nabla \cdot \rho \hat{U} \mathbf{v}) - (\nabla \cdot \mathbf{q}) - (\boldsymbol{\tau} : \nabla \mathbf{v}) - p(\nabla \cdot \mathbf{v}), \quad (3)$$

in which ρ is the density, t is time, \mathbf{v} is the velocity, p is the pressure, $\boldsymbol{\tau}$ is the stress tensor (assumed to be symmetric), \mathbf{g} is the gravitational acceleration, \hat{U} is the internal energy per unit mass, and \mathbf{q} is the heat flux. For isothermal problems we do not need the energy equation; for multi-component systems we also need equations of continuity for each of the chemical species. We use the same conventions for vector/tensor notation as in DPL: Results from vector-tensor multiplication that are scalars are enclosed in (), results that are vectors are enclosed in [], and results that are second order tensors are enclosed in { }.

The fundamental problem facing the polymer fluid dynamicist is that in the equation of motion and the energy equation an expression is needed for the stress tensor in terms of various kinematic tensors. That is, a "constitutive equation" for the stress is required.

The problem is similar to that arising in turbulence, where an expression is needed for the Reynolds stress tensor. In both fields empirical expressions have been suggested, and in both fields mathematical expansions have been proposed; also in both areas, certain benchmark experiments are used to test the stress tensor expressions. However, in the polymer field we have an extra advantage in that we can gain considerable important information by using molecular theories. From molecular models and kinetic theory (i.e. nonequilibrium statistical mechanics and Brownian dynamics) we can get not only suggestions about the form of the stress tensor, but also additional information about the stretching and orientation of the molecules making up the fluid.

The importance of the molecular viewpoint cannot be overlooked, and the fluid dynamicist who fails to take cognizance of the advances in kinetic theory limits his ability to solve problems. Why do we need the molecular approach? First, the rheological properties of polymer solutions and undiluted polymers are dependent on the molecular architecture of the constituent molecules: molecular weight, chain stiffness, chain branching, electrical charge distribution. Second, solute-solvent interactions can play a role in the motions of the polymers and affect the macroscopic behavior. Third, most polymeric liquids are composed of polymer molecules of different lengths; that is, they have a distribution of molecular weights,

and this “polydispersity” strongly affects the rheological properties and therefore the flow behavior. Fourth, in the neighborhood of fluid-solid interfaces, the polymer molecules are restricted in their motions, with the result that wall effects arise, including solute segregation effects and slip effects. And finally, through the molecular theories, one can obtain useful relationships between the rheological properties and other physico-chemical properties, such as diffusional, optical, electrical, and thermodynamic properties. The Bird & Öttinger (1992) review cites some of the key references for these topics.

The assumption that the stress tensor in Equation (2) is symmetric implies that there is no interchange between macroscopic and molecular angular momenta. No experiments have been performed on polymeric liquids to measure asymmetry of the stress tensor. Almost all kinetic theories for polymeric liquids give a symmetrical stress tensor; in those few instances where an asymmetric contribution appears, it is found to be negligibly small. Anyone wishing to pursue this point further is advised to examine the review by Dahler (1965), where key references are cited.

Several books have appeared in the past decade that deal with constitutive equations, rheology, and solution of polymer fluid dynamics problems. Tanner's (1985) textbook shows how to use constitutive equations to solve problems of engineering interest. Larson (1988) published a monograph dealing solely with constitutive equations. The small monograph of Barnes et al (1989) provides a sensible and well-balanced overview of non-Newtonian fluid mechanics, with minimal use of mathematics and careful attention to experimental facts. A nice companion volume to this is the collection of photographs of rheological phenomena by Boger & Walters (1993). Joseph's (1990) book addresses the mathematical techniques of solving flow problems with various types of constitutive equations. The proceedings of the XIth International Congress on Rheology (Moldenaers & Keunings 1992) give a good presentation of the problems of current interest. The book by Dealy & Wissbrun (1990) discusses the use of rheology in industry. A new treatise by Beris & Edwards (1994) is concerned with the relation between rheology and thermodynamics. The subject of Brownian dynamics simulations of polymers is described in the new book by Öttinger (1995).

The publications of H. Giesekus dealing with constitutive equations have often been overlooked because many were written in German. In a *Festschrift* prepared in his honor, a bibliography of Giesekus's publications was given by Winter (1989). Similar bibliographies for J. G. Oldroyd and J. G. Kirkwood have been given by Bird (1988). Continuum and molecular constitutive equations have been reviewed by Jongschaap (1990) with particular reference to the thermodynamics of irreversible processes. Tanner

(1988) has given an overview of constitutive equations of the integral type.

TESTING CONSTITUTIVE EQUATIONS BY COMPARISON WITH EXPERIMENT

All constitutive equations ultimately have to be tested against experimental data. There are two kinds of experiments that are currently being used: rheometric experiments (carefully designed experiments from which "material functions" can be extracted), and benchmark experiments (non-trivial flows suitable for testing both numerical methods and constitutive equations).

Rheometric Experiments

Many experiments of this type are used, as explained in DPL-1 (Chapters 3 and 10) and in other books dealing with rheology. Examples of books dealing specifically with the science of rheometry are those by Walters (1975) and Dealy (1982). Meissner (1985) provided a review of rheometric experiments for polymer melts. Here we list just three rheometric experiments as examples.

STEADY SHEAR FLOW In steady shear flow between two parallel planes, $v_x = \dot{\gamma}y$, one can measure a shear stress τ_{yx} and two normal stress differences $\tau_{xx} - \tau_{yy}$ and $\tau_{yy} - \tau_{zz}$; three material functions are then defined by

$$\tau_{yx} = -\eta\dot{\gamma} \quad (4)$$

$$\tau_{xx} - \tau_{yy} = -\Psi_1\dot{\gamma}^2 \quad (5)$$

$$\tau_{yy} - \tau_{zz} = -\Psi_2\dot{\gamma}^2. \quad (6)$$

The (non-Newtonian) viscosity η is positive for all fluids, and it is usually found to be a monotonically decreasing function of the shear rate $\dot{\gamma}$. The first normal-stress coefficient, Ψ_1 , has been found to be positive for nearly all polymeric liquids, and it decreases very rapidly with increasing shear rate; fragmentary data on liquid crystals suggest that they may have negative Ψ_1 . The second normal-stress coefficient, Ψ_2 , has been found to be negative and much smaller in magnitude than Ψ_1 . Measurements of Ψ_2 are quite sparse; the current state of the measurement techniques for Ψ_2 has been described by Ohl & Gleissle (1992). Measurement of Ψ_2 for liquid crystalline systems has been discussed by Magda et al (1991).

SMALL-AMPLITUDE OSCILLATORY SHEARING MOTION In this type of experiment a fluid is placed between two closely spaced parallel plates, and one of the plates is made to oscillate unidirectionally in its own plane with a

very small amplitude at frequency ω ; the velocity gradient is then time-dependent and given by $\dot{\gamma}(t) = \dot{\gamma}^0 \cos \omega t$, where $\dot{\gamma}^0$ is the amplitude of the velocity gradient. The shear stress τ_{yx} required to produce the motion is measured. One can define two material functions η' and η'' , both functions of the frequency, by

$$\tau_{yx} = -\eta' \dot{\gamma}^0 \cos \omega t - \eta'' \dot{\gamma}^0 \sin \omega t. \quad (7)$$

The functions η' and η'' are called the components of the complex viscosity, $\eta^* = \eta' - i\eta''$.

STEADY-STATE ELONGATIONAL FLOW In this rheometric experiment a fluid sample is stretched with a constant elongational rate $\dot{\epsilon} = dv_z/dz$, and the force required to perform the stretching is measured. From this, one can obtain a normal-stress difference. The elongational viscosity, $\bar{\eta}$, a function of the elongational rate, is then defined by

$$\tau_{zz} - \tau_{xx} = -\bar{\eta} \dot{\epsilon}. \quad (8)$$

For some fluids it may not be possible to attain a steady-state flow of this type. Meissner & Hostettler (1994) discuss a new measuring technique for unsteady elongational flows.

Many other rheometric measurements may be made, including responses to step functions in strain, step functions of rate of strain, and large amplitude, sinusoidal oscillations. Recoil and creep measurements are also made. In addition, it is possible to superpose some of these motions and measure still more material functions.

Nontrivial Flows

The community of researchers dealing with the development of numerical methods for viscoelastic flows agreed on a few "benchmark experiments" for concerted attack. These are (see Hassager 1988 for a summary):

1. Flows with a 4:1 sudden contraction.

One computes the pressure drop and the vortex size and shape in the flow from a large tube into a small one, or from a large slit to a small one, in each case with a sudden contraction of 4:1 in the cross-sectional area. For an example of this kind of calculation see Debbaut et al (1988).

2. Motion of a sphere in a cylinder.

One computes the drag on the sphere as a function of the Deborah number as the sphere moves along the axis of the cylinder. The ratio of the radius of the sphere to that of the cylinder is 0.5. A recent study of this system (using single and multimode Oldroyd models) is by Becker

et al (1994). See also Zheng et al (1991) for a study using the Phan-Thien-Tanner model.

3. Flow in a tube of sinusoidally varying cross-section.

One computes the pressure drop required to cause the fluid to flow through the "wiggly-wall tube" as a function of the Deborah number. The ratio of the amplitude of the sinusoid to the average radius of the tube is 0.1 or 0.4; the ratio of the wavelength to the average tube radius is 2. For an example of this flow problem, see Pilitsis & Beris (1989).

4. Tangential flow between two eccentric rotating cylinders.

One computes the load and phase angle for specified dimensions and ratios of angular velocities (see e.g. King et al 1988).

These and other flows have been the object of considerable study, and the reader is referred to various workshop proceedings in the *Journal of Non-Newtonian Fluid Mechanics*. Considerable progress has been made in the past decade in the development of numerical techniques for solving the flow problems for nonlinear viscoelastic constitutive equations (see Keunings 1990). The bulk of experiments used to compare with numerical flow studies have involved polymer solutions; more work needs to be done with polymer melts.

METHODS FOR DEVELOPING CONSTITUTIVE EQUATIONS

Clearly there is an infinite number of possible relations that one could propose linking the stress tensor with kinematic tensors, and there is a bewildering number of kinematic tensors (strain tensors, rate-of-strain tensors, etc) that can be used. Initially, then, one has to narrow the field of possible relations by arbitrarily imposing some "admissibility conditions"; one such set of conditions was proposed by Oldroyd (1950) and refined in a later paper published posthumously (Oldroyd 1964) (see also DPL-1, Section 9.1). Briefly, for incompressible fluids Oldroyd proposed to restrict consideration to models that are (a) form invariant under a change of coordinate systems, (b) value invariant under a change of translational or rotational rigid body motion of a fluid element as it moves through space, and (c) value invariant under a change of rheological history of neighboring fluid elements. Oldroyd's admissibility conditions have provided the guidelines for constructing constitutive equations since 1950, and most of the molecular theories have given constitutive equations that are in agreement with Oldroyd's conditions; an example of one kinetic theory that does not agree with Oldroyd's criteria is provided by Schieber & Öttinger (1988). For further perspectives on admissibility criteria see Lodge (1974), in particular Chapter 11.

Some constitutive equations are purely *empirical*. An equation satisfying Oldroyd's admissibility criteria is proposed and then tested against experimental data. It is then improved by including additional terms until reasonable agreement with experiment is obtained. There was much activity of this sort between 1950 and 1980, and it still continues. Many of these empirical equations are summarized in Chapters 4–8 of DPL-1 and in Larson's (1988) book.

A second approach for developing constitutive equations is to use *mathematical expansions*. One can, for example, expand the stress tensor in something like a Taylor series in order to display small departures from Newtonian behavior. This leads to the "retarded motion expansion," which finds use in describing very slow flows such as those encountered in flow around particles and droplets. However, it is of no value for computing flows in pipes and industrial equipment, because the series converges too slowly. Siddiqui & Schwartz (1993) recently used a third-order fluid model for studying peristaltic motion in a planar channel. Another possibility is to perform a Frechet expansion, which describes the deviations from linear viscoelastic behavior. This "memory integral expansion" gives for the first term a single time integral over the strain history, for the second term a double integral, and for higher terms integrals of increasing multiplicity. This expansion has not been popular, although Siginer (1991) has recently used it for analyzing the pulsatile flow in a tube. (See Chapters 6 and 9 of DPL-1 for additional information.)

A third approach is to develop equations of a rather general nature that apply only within certain *well-defined classes of flows*. For example, for flows with small displacement gradients the general linear viscoelastic fluid is quite important (Chapter 5, DPL-1); linear viscoelastic experiments are widely used for polymer characterization. For steady-state unidirectional shear flows, the Criminale-Ericksen-Filbey (CEF) equation is applicable (Chapter 9, DPL-1). For further information, see Tanner (1985) and Goddard (1979). The CEF equation includes as a special case the "generalized Newtonian fluid" model, which has been widely used—and is still being used—for industrial calculations because of its simplicity (Chapter 4, DPL-1).

A fourth approach is to use *molecular theory*. Here one represents the polymer molecules by some kind of mechanical model, usually "beads" and "springs" (or "rods") joined together in such a way as to reflect the architecture of the molecules. In this way one can mimic the orientation and stretching of the polymers and also provide for the large number of configurations that the molecule can assume. See DPL-2 and Doi & Edwards (1986) for in-depth discussions. Except for some very simple models, mathematical approximations have to be made to obtain consti-

tutive equations from molecular theories. Much progress has been made in developing our ability to go from a molecular model to the constitutive equation to the solution of flow problems, as described by Wedgewood & Bird (1988).

A fifth approach is to make use of various extensions of the *thermodynamics of irreversible processes*. Basically this involves establishing a new framework, with new sets of postulates, such that the known experimental, continuum mechanics, and statistical mechanical results are incorporated. By doing this one hopes to establish some rather general constitutive equations capable of describing a wide range of materials. For summaries of current activities in this area, see Beris & Edwards (1990a,b; 1994), Jongschaap et al (1994), and Grmela (1991).

USES OF CONSTITUTIVE EQUATIONS

The choice of constitutive equation depends to a considerable extent on the use to which it is to be put. For making order-of-magnitude estimates in industrial problems in which the flow is a steady-state shear flow (or approximately so), the “generalized Newtonian model”—just Newton’s law of viscosity with a shear-rate-dependent viscosity—is simple, useful, and effective in many instances (DPL-1, Chapter 4); if normal-stress effects are important, then the Criminale-Filbey-Ericksen equation is a good choice (DPL-1, pp. 503–4). For the characterization of polymeric liquids, linear viscoelastic experiments, such as sinusoidal shear flow, are widely used, and the “general linear viscoelastic model” is exactly what one needs (DPL-1, Chapter 5). For describing the very slow flows around particles in suspensions, the “retarded-motion expansion” may be helpful (DPL-1, Chapter 6). For flows that are time dependent, for converging-diverging flows, and for general three-dimensional flows, nonlinear viscoelastic models are needed. In the next section we consider these kinds of models.

The main driving force for developing constitutive equations is the need for solving polymer-processing problems in the plastics industry, for describing the functioning of polymer-containing lubricants, and for developing an understanding of the behavior of various body fluids in human physiology. There are also other uses for constitutive equations, such as the study of the interrelations of material functions measured in rheometric experiments (e.g. Chan Man Fong & De Kee 1992), analysis of rheometric devices (e.g. McClelland & Finlayson 1988a), study of instabilities (Larson 1992; Leonov 1987, Saasen & Hassager 1991), and the analysis of molecular motions in flow problems. For this last purpose one clearly needs a constitutive equation that is based on a molecular theory.

SOME NONLINEAR VISCOELASTIC CONSTITUTIVE EQUATIONS

In the past five decades many constitutive equations have been proposed for polymeric fluids, and many have been discarded. Here we summarize a few that have survived and are currently receiving attention; we consider only nonlinear viscoelastic models that have been proposed for arbitrary, time-dependent flows. Slightly different lists of key constitutive equations have been given by Zdilar & Tanner (1992) and by Larson (1992).

The Oldroyd 8-Constant Model

Despite the fact that it is over 35 years old, this model proposed by Oldroyd (1958) is still being used. It is an empirical expression that is linear in the stress tensor, but contains all allowable terms quadratic in velocity gradients and all allowable products of stresses and velocity gradients. Since it can give qualitatively correct results in a wide variety of flow situations, it has been popular for developing the numerical techniques for non-Newtonian fluid dynamics. (For further details, see DPL-1, Chapter 7.) The constitutive equation is

$$\begin{aligned} \tau + \lambda_1 \tau_{(1)} + \frac{1}{2} \lambda_3 \{\dot{\gamma} \cdot \tau + \tau \cdot \dot{\gamma}\} + \frac{1}{2} \lambda_5 (\text{tr } \tau) \dot{\gamma} + \frac{1}{2} \lambda_6 (\tau : \dot{\gamma}) \delta \\ = -\eta_0 [\dot{\gamma} + \lambda_2 \dot{\gamma}_{(1)} + \lambda_4 \{\dot{\gamma} \cdot \dot{\gamma}\} + \frac{1}{2} \lambda_7 (\dot{\gamma} : \dot{\gamma}) \delta], \end{aligned} \quad (9)$$

in which $\dot{\gamma} = \nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger$ is the rate of deformation tensor, and δ is the unit tensor. The subscript (1) indicates the first contravariant convected time derivative, defined for a second-order tensor α as follows:

$$\alpha_{(1)} = \frac{D}{Dt} \alpha - \{(\nabla \mathbf{v})^\dagger \cdot \alpha + \alpha \cdot (\nabla \mathbf{v})\}, \quad (10)$$

where the dagger indicates the transpose, and D/Dt is the substantial derivative. The eight constants are the zero-shear-rate viscosity (η_0) and the time constants ($\lambda_1, \dots, \lambda_7$). Equation (9) includes as special cases:

- (a) the Newtonian model (λ_1 to λ_7 all zero),
- (b) the upper convected Maxwell model (λ_2 to λ_7 all zero),
- (c) the Oldroyd-B model (λ_3 to λ_7 all zero),
- (d) the second-order fluid model ($\lambda_1 = \lambda_3 = \lambda_5 = \lambda_6 = \lambda_7 = 0$),
- (e) the Gordon-Schowalter or Johnson-Segalman model [$\lambda_2 = (\eta_s/\eta_0)\lambda_1$, $\lambda_3 = \xi\lambda_1$, $\lambda_4 = \xi\lambda_2$, $\lambda_5 = \lambda_6 = \lambda_7 = 0$].

The Oldroyd-B model has been popular lately for numerical calculations because of "Boger fluids." Boger (1977) synthesized some fluids that were presumed to have a constant viscosity and a constant first normal-stress

coefficient (which are also properties of the Oldroyd-B model). Very careful rheological measurements by Quinzani et al (1990) have revealed that the Boger fluids are in fact more complicated than the Oldroyd-B model. The Oldroyd-B model should now be deemphasized, and attention should be focused on constitutive equations that can describe the polymers that are of interest to industry—namely, those that have viscosities that decrease dramatically with increasing shear rate.

The Johnson-Segalman model has been used in studies of “spurt phenomena” by Kolkka et al (1988), who believe that some of the instabilities observed in tube flow are a result of the fact that the shear stress is not monotonically increasing with the shear rate. Malkus et al (1990, 1991, 1993) and Kolkka et al (1991) have also used this model.

The Giesekus Model

Giesekus (1982), using molecular ideas, developed a three-constant ($\eta_0, \lambda_1, \alpha$) model that is nonlinear in the stresses (see DPL-1, p. 353). This model has gained prominence because it describes the power-law regions for viscosity and normal-stress coefficients; it also gives a reasonable description of the elongational viscosity and the complex viscosity. The constitutive equation for this model is

$$\tau + \lambda_1 \tau_{(1)} - (\alpha \lambda_1 / \eta_0) \{ \tau \cdot \tau \} = -\eta_0 \dot{\gamma}. \quad (11)$$

Bird & Wiest (1985) have given an alternative interpretation of the Giesekus model, and Wiest & Bird (1986) have studied the model further; they obtained the constitutive equation as the result of a mean-field theory that uses Hookean dumbbells as a model for the constituent polymers.

Wiest (1989a) has developed an extension of the model by using non-Hookean springs; his model has been used by Iyengar & Co (1993) for studying film casting. Another extension of the model is to use a superposition of equations of the form of Equation (5), the so-called “multi-mode Giesekus model.” This allows for a large number of time constants and viscosity constants, thus providing much more flexibility for fitting data.

The Phan-Thien-Tanner Model

The four-constant model of Phan-Thien & Tanner (1977) and Phan-Thien (1978) was derived from a network theory for polymer melts and is also nonlinear in the stresses:

$$Y\tau + \lambda \tau_{(1)} + \frac{1}{2} \xi \lambda \{ \dot{\gamma} \cdot \tau + \tau \cdot \dot{\gamma} \} = -\eta_0 \dot{\gamma} \quad (12)$$

(see DPL-2, Chapter 20). Here, Y is a function of the trace of the stress tensor:

$$Y = \exp[-\varepsilon(\lambda/\eta_0) \operatorname{tr} \tau] \approx 1 - \varepsilon(\lambda/\eta_0) \operatorname{tr} \tau. \quad (13)$$

The second relation in Equation (13) is valid for small $\operatorname{tr} \tau$ and makes the constitutive equation somewhat easier to use. Equation (11) gives a monotonically increasing elongational viscosity, whereas Equation (12) gives a maximum in the elongational viscosity vs elongation rate curve when the exponential relation in Equation (13) is used. This model has also been used in a multimode form by superposition of equations of the form of Equation (12) in order to do a better job of fitting data.

The FENE (Finitely-Extensible-Nonlinear-Elastic) Dumbbell Model

This constitutive equation results from a kinetic theory derivation using a nonlinear elastic dumbbell model to represent the polymer molecules in a dilute solution, where the solvent is a Newtonian fluid with viscosity η_s , and where the number of dumbbells per unit volume is n . This leads, after making the Peterlin approximation (in the expression for the stress tensor, the average of a ratio is replaced by the ratio of the averages), to

$$\tau = -\eta_s \dot{\gamma} + \tau_p, \quad (14)$$

in which the polymer contribution, τ_p , is given by the differential equation

$$Z \tau_p + \lambda_H \tau_{p(1)} - \lambda_H \left(\tau_p - \frac{b}{b+2} nkT \delta \right) \frac{D \ln Z}{Dt} = - \left(\frac{b}{b+2} \right) nkT \lambda_H \dot{\gamma}, \quad (15)$$

where λ_H is a time constant and Z is a function of the trace of the polymer contribution to the stress tensor:

$$Z = 1 + \frac{3}{b} \left(\frac{b}{b+2} - \frac{\operatorname{tr} \tau_p}{3nkT} \right). \quad (16)$$

The parameter b is a measure of the potential energy in the spring relative to the thermal energy. When b is infinite, the Hookean dumbbell result is obtained; in this limit, the polymer contribution to the stress tensor is described by the upper convected Maxwell model. The FENE dumbbell model is useful because it allows for the possibility of describing the polymer stretching and orientation in various flow systems (Wedgewood & Bird 1988). (Further discussion of this model can be found in DPL-2, Chapter 13.)

There are many extensions of the FENE dumbbell constitutive equation. Armstrong & Ishikawa (1980) developed a simplified equation for the

“nearly Hookean” dumbbell solution. Bird & DeAguiar (1983) and Wiest (1989a) developed modifications appropriate for describing polymer melts. Ng & Leal (1993) included dumbbell-dumbbell interactions (according to Hess 1984) in order to describe concentration dependence in semi-dilute polymer solutions. Chilcott & Rallison (1988) altered the FENE dumbbell equation in an empirical way to eliminate the shear-rate dependence of the viscosity, in order to describe Boger fluids; the resulting model is devoid of any molecular significance.

A constitutive equation was also obtained for a multibead flexible chain model, with nonlinear connecting springs, using the Peterlin approximation (Öttinger 1987, Wedgewood & Öttinger 1988, Wiest & Tanner 1989). Using this model, Wiest et al (1989) studied the mechanism of uncoiling of macromolecules in extensional flows. A much simpler constitutive equation was obtained by Wedgewood et al (1991) using a modification of the Peterlin approximation; this results in a “multimode” version of Equation (15), but with some coupling between the modes included. The modified Peterlin approximation has been evaluated and criticized by van den Brule (1993a). Kobe & Wiest (1993) examined the validity of the Peterlin approximation for chains in steady elongational flows.

Recently there has been a revived interest in including “internal viscosity” in bead-spring models; this involves including, in addition to the spring force, an additional resistive force proportional to the rate of the spring extension (i.e. a dashpot). The publications of Manke & Williams (1991, 1993), Wedgewood (1993), and Schieber (1993) provide an excellent introduction to the literature on this subject. Another modification of bead-spring models involves including the “excluded volume” effect, as discussed in a recent paper by Ahn et al (1993).

The Kaye-BKZ Model

The Kaye-BKZ model is a nonlinear generalization of the general linear viscoelastic model, and contains two unspecified functions:

$$\tau = + \int_{-\infty}^t M(t-t') \left[\frac{\partial W}{\partial I_1} \gamma_{[0]} + \frac{\partial W}{\partial I_2} \gamma^{[0]} \right] dt'. \quad (17)$$

Here, $M(t-t')$ is a “memory function” (a property of the material), and $W(I_1, I_2)$ is a “potential function” that depends on the two scalar invariants of the Finger strain tensor \mathbf{B} . The two relative finite strain tensors are defined by: $\gamma_{[0]} = \delta - \mathbf{B}$ and $\gamma^{[0]} = \mathbf{B}^{-1} - \delta$. It is necessary to require that the potential function obeys the relation $(\partial W / \partial I_1) + (\partial W / \partial I_2) = 1$ at $I_1 = 3$, $I_2 = 3$ to guarantee that the model simplifies correctly in the linear limit.

An evaluation of this model has been given by Tanner (1988), and a variational principle for it has been developed by Hassager (1981).

The Kaye-BKZ model includes the Rouse-Zimm model for dilute solutions, the Lodge elastic liquid derived from a network theory, the Tanner-Simmons network rupture model, and the Doi-Edwards model for polymer melts derived from a "tube theory" for a melt made up of freely jointed bead-rod chains. A slightly more general model is the factorized Rivlin-Sawyers model, in which the coefficients of the relative finite strain tensors are arbitrary functions of the two invariants, but not necessarily derivatives of a potential function W . A model proposed by Wagner of this type has attracted much attention [see DPL-2, Section 8.3 for additional references and an example using special choices for M and W ; see also Wagner (1990) and Wagner & Demarmels (1990)].

Kaye (1992) recently proposed a modification of the Kaye-BKZ model in which the potential function is given in terms of the principal stretches. Specifically, he considers that W is the sum of the n th powers of the principal stresses. All the nonlinear rheological properties can then be computed from the relaxation spectrum of linear viscoelasticity and the power n .

The Curtiss-Bird Model

The Curtiss-Bird constitutive equation was derived for a melt made up of a monodisperse set of freely jointed, interacting bead-rod chains, using a phase-space kinetic theory. The resulting equation is:

$$\tau = NnkT \left\{ \frac{1}{3} \delta - \int_{-\infty}^t \mu(t-t') \mathbf{A}^{(2)} dt' - \frac{1}{2} \varepsilon \dot{\gamma} : \int_{-\infty}^t v(t-t') \mathbf{A}^{(4)} dt' \right\}. \quad (18)$$

Here, N is the number of beads in the bead-rod chain, n is the number density of chains, μ and v are memory functions containing a time constant λ , $\mathbf{A}^{(2)}$ is a second-order tensor function of the nonlinear strain tensor $\gamma^{[0]}$, and $\mathbf{A}^{(4)}$ is a fourth-order tensor function of $\gamma^{[0]}$. The parameter ε is called the link-tension coefficient; when ε is set equal to zero, the Doi-Edwards constitutive equation is obtained. The Curtiss-Bird theory has been extended to polydisperse melts by Schieber et al (1986) and Schieber (1987a,b). The Doi-Edwards theory has been extended to a bead-spring model by Mead et al (1992).

The Curtiss-Bird equation gives realistic shapes for the viscometric functions and the elongational viscosity. It has been used in its polydisperse generalization to describe the Weissenberg rod-climbing experiment by Lodge et al (1988) and recoil of polymer melts after cessation of shear and elongational flows by Borgbjerg & de Pablo (1994). In both of these

problems the term containing the link-tension coefficient is needed to describe the experimental data. Geurts (1988, 1989) extended the Curtiss-Bird theory to a "reptating rope model"; his results lead to a constitutive equation containing an extra term related to correlations between segments.

SOME OTHER CONSTITUTIVE EQUATIONS

In recent years a few new constitutive relations have been proposed. We content ourselves here with a brief mention of equations that have come to our attention, recognizing that some have not yet been sufficiently tested.

Schunk & Scriven (1990) developed a simple empirical model that describes shear thinning and extension thickening in order to model coating and related flows in the polymer industry. This model is not, however, capable of describing the viscoelastic phenomena that arise in time-dependent flows. A minor generalization of the Schunk-Scriven model was put forth by Astarita (1991).

For the general linear viscoelastic fluid model, Scanlan & Janzen (1992) have proposed a stretched-exponential-power-law empiricism for the relaxation modulus; this function contains four parameters.

Several papers have incorporated the idea of polymer diffusion across streamlines into dilute-solution molecular theories. El-Kareh & Leal (1989) first developed this idea, and later Bhawe et al (1991) produced a more extensive phase-space kinetic theory that showed, in addition, how to account for the development of spatial inhomogeneities in the concentration. Öttinger (1991, 1992) has discussed this problem from a continuum mechanical and stochastic point of view, using Lodge's body-tensor formalism. For a comparison of several theories of spatial inhomogeneities, see Mavrantzas & Beris (1994) and Agarwal et al (1994). For more on wall effects, see de Pablo et al (1992).

A new network model for polymer melts was proposed by Hermann & Petruccione (1992), based on Lodge's notion of a network containing different types of strands and Yamamoto's idea of configuration-dependent creation and loss rates. A Gaussian temporary slip-link network theory has been formulated by Wagner & Schaeffer (1992) that in special limits reduces to earlier constitutive equations of Lodge, Wagner, Doi-Edwards, and Marrucci. Doremus & Piau (1991) have developed a two-network theory capable of describing a yield-stress in a viscoelastic fluid. A completely different approach to viscoelastic-plastic fluid modeling was offered by Isayev & Fan (1990) based on a modification of the Leonov model (1987).

The classic Rouse-Zimm model has been modified by Wu & Schümmer (1990), who incorporated the Johnson-Segalman idea that “macroscopic and microscopic strain fields do not conform to each other” and that “non-affineness is described by a slippage factor.”

Using a phase-space kinetic theory, Bhave et al (1993) obtained a constitutive equation for liquid-crystalline polymer solutions; see also Ramalingam & Armstrong (1993) for an application of the constitutive equation.

CONSTITUTIVE EQUATIONS FOR NONISOTHERMAL SYSTEMS

Although most of the work that has been done on the solution of polymer flow problems has been for isothermal systems, it must be recognized that flows of interest in polymer processing operations are decidedly non-isothermal, i.e. the temperature of the fluid is a function of position and time. Most polymer processing operations are designed to cause temperature changes in the material to produce phase changes. In addition, the very high viscosities of polymeric liquids result in the conversion of large amounts of mechanical energy into heat through the third term on the right-hand side of Equation (3), and this heat causes the temperature of the material to change. Because the stress in the material can depend upon both the temperature and the temperature history, it is necessary to develop constitutive equations that include the temperature as an independent variable.

The traditional engineering approach to solving nonisothermal polymer flow problems mirrors the approach used in the solution of nonisothermal Newtonian flow problems. That is, one simply allows the density and non-Newtonian viscosity of the fluid to be functions of temperature. Furthermore, because the density of a fluid is a relatively weak function of temperature when compared with the viscosity, the temperature dependence of the density is frequently neglected, except in problems where natural convection is judged to be important. This strategy has been used extensively in the study of problems where the fluid is modeled as a generalized Newtonian fluid (Metzner 1965, Pearson 1984, McClelland & Finlayson 1988b, Ding et al 1993). The major problem with this traditional approach is that it does not include the effect of temperature variations on the viscoelasticity of the fluid.

The temperature dependence of the linear viscoelastic properties of polymeric liquids has been described by the principle of time-temperature superposition (Ferry 1980). In essence, this principle states that all of the time scales characterizing the memory of the fluid have the same depen-

dence on temperature. Therefore, they can all be characterized by a single function of temperature known as the shift function, a_T . Many empirical and semi-empirical expressions have been proposed for this function; the one most widely used is the Williams-Landel-Ferry function (Williams et al 1955).

Although time-temperature superposition works well for a wide variety of polymers, it is not designed to describe nonisothermal flow. The principle describes the relation between rheological properties at different constant temperatures; it does not describe rheological consequences of temperature changes that occur with time or in space. A continuum mechanical postulate proposed by Morland & Lee (1960) and expanded upon by Crochet & Naghdi (1969) attempts to address this problem. The postulate proposes the existence of a *pseudo-time* that accounts for the rheological consequences of temperature variations. This pseudo-time, ξ , is defined by

$$d\xi = \frac{dt}{a_T[T(t)]} \quad (19)$$

or, as a difference, by

$$\xi - \xi' = \int_{t'}^t \frac{dt''}{a_T[T(t'')]}. \quad (20)$$

The rationale behind the pseudo-time idea is that the molecular motions responsible for mechanical relaxations of the material occur more rapidly at higher temperatures and more slowly at lower temperatures; this temperature dependence is described by the shift function, a_T . From the point of view of the material, time appears to move faster (or slower) relative to laboratory time as the temperature increases (or decreases). Therefore, the prescription of the pseudo-time approach is to replace the time variable in an isothermal constitutive equation by the pseudo-time, which includes this "stretching" and "shrinking" of time caused by temperature variations. The relation given in Equation (19) is used for transforming differential constitutive equations, and the relation given in Equation (20) is used for transforming integral constitutive equations. The validity of the pseudo-time postulate is still open to experimental confirmation, but it has been used recently to describe nonisothermal flows (Luo & Tanner 1987).

Molecular theories have also been used to obtain constitutive equations for nonisothermal flows. Marrucci (1972) (see also Bird 1979) modified the kinetic theory for dilute solutions of Hookean dumbbells to include the temperature history, and Wiess (1989b) extended this to bead-spring

(Rouse) chains. Wiest & Phan-Thien (1989) have extended the Curtiss-Bird theory to describe nonisothermal flows, and Wiest (1994) has examined the nonisothermal form of the Giesekus equation and its variants. Each of these molecular theories gives a constitutive equation that differs from that predicted by application of the pseudo-time approach, but the significance of the differences has not been fully explored.

Other difficulties that arise in the solution of nonisothermal flow problems are not directly associated with the constitutive equation for the material but are associated with the energy equation (3). It has been traditional to assume that the internal energy of the fluid is independent of its kinematic state, so that \hat{U} can be expressed in terms of a heat capacity and the temperature. However, this may not be an appropriate assumption for polymeric materials (Astarita et al 1974), and the question requires further investigation. Because of the large viscosities of polymeric liquids, the third term on the right-hand side of Equation (3), which describes the conversion of mechanical energy into thermal energy, is often important. This issue has been addressed in a viscometric flow by Ko & Lodge (1989, 1991). It has been traditional to assume that heat transfer in polymeric materials is adequately described by Fourier's law, but there is also evidence that this may not be appropriate. van den Brule (1989, 1990, 1993b) has studied this question and has proposed alternatives to Fourier's law for polymers wherein the thermal conductivity tensor is related to kinematic quantities. It is apparent that a great deal of work remains to be done in the field of nonisothermal rheology.

AVOIDANCE OF USE OF CONSTITUTIVE EQUATIONS

Description of Rheometric Experiments

Brownian dynamics has been used for getting the material functions for various kinds of molecular models; in such calculations the flow pattern is specified and the molecular motions are computed. For example, Liu (1989) obtained the viscometric functions for Kramers chains in shear flows and studied the coil-stretch transition. This work was extended by Slot (1992), who included hydrodynamic interaction and excluded volume. The bead-spring chain model with nonlinear springs has been studied with Brownian dynamics simulations by van den Brule (1993).

Molecular dynamics, a still more detailed description for rheometric flows, is just beginning to appear in the literature. Kröger et al (1993) have used nonequilibrium molecular dynamics to compute the steady-state shear flows of polymer melts modeled as long bead-spring chains (up to 100 beads) connected by finitely-extensible-nonlinear-elastic (FENE)

springs; the forces between beads on different chains are described by a modified Lennard-Jones potential.

Description of Nontrivial Flows

Because of the increased power of computers, emphasis is now shifting to the use of molecular models to solve nontrivial flow problems without developing explicit constitutive equations. Instead, one solves the kinetic theory equations at each point in the system, either by nonequilibrium statistical mechanics or by nonequilibrium Brownian dynamics, and in this way computes the local stresses. These are then combined with the equations of motion and continuity to calculate the velocity field, streamlines, and pressure distribution.

The first example of this was the calculation by Fan (1989a,b), who used multibead dumbbell models; he solved the kinetic theory equations at each point in the flow field and then obtained the streamlines and dumbbell orientations everywhere in the flow field. Ramalingam & Armstrong (1993) used a similar method to study the spinning of liquid crystals. A somewhat related method was described by Szeri & Leal (1992). Laso & Öttinger (1993a,b) (see also Öttinger & Laso 1994) used nonequilibrium Brownian dynamics to obtain the local stresses for elastic dumbbells, and then solved the unsteady Couette-flow problem; this model predicted the “velocity-overshoot phenomenon” that had been observed experimentally by Burdette (1989).

FUTURE DIRECTIONS

Constitutive Equations

We expect that there will be increased reliance on molecular theory to suggest the *form* for constitutive equations. By using a greater diversity of molecular models, it should be possible to start developing intuition about how molecular architecture influences the constitutive equation and the rheological responses. It should not be expected that one constitutive equation can be found that will describe all polymeric liquids, but rather that there will be a variety of constitutive equations reflecting the internal structure of the fluids.

In the future it is expected that more complex constitutive equations will be used for fluid dynamics calculations, because of improved numerical methods and more powerful computers. Therefore, it will be possible to use constitutive equations that contain a full spectrum of time constants. To date most of the emphasis in numerical solution of flow problems has been on differential constitutive equations, but more activity can be expected soon in the area of integral constitutive equations.

Nonisothermal Problems

Much more needs to be done on the development of constitutive equations for nonisothermal flows. There is an urgent need for experimental data on nonisothermal flows, including the mapping of temperature profiles in space and time for well-defined flows and the measurement of the dependence of the stress in the material on these temperature profiles. Data are also needed on the thermal conductivity of polymeric liquids—particularly on the anisotropy of thermal conductivity in flowing liquids. In addition, further studies on the coupling between heat flux and velocity gradient are necessary. More nonisothermal flow problems in which solidification (crystallization or glass formation) takes place need to be solved, because these kinds of problems are of considerable industrial importance. This will require the formulation of constitutive equations that are valid through the solidification process and, therefore, greater understanding of the solidification process itself.

Kinetic Theory

The assumptions made in kinetic theory require further investigation. For example, the “equilibration in momentum space” assumption has almost universally been made, but little is known about the appropriateness of the assumption. More knowledge of the pair distribution function could possibly be very revealing about the mechanisms behind rheological behavior; in particular, this could be helpful in advancing kinetic theories for polymer melts. Much more can be done about getting optical, electrical, diffusional, and thermal properties for the same molecular models used in rheological work. Finally, there is the hope that totally new techniques may be found for kinetic theory studies; for example, virial and hypervirial theorems could prove a useful starting point.

Molecular Simulations

Only a small beginning has been made in using molecular and Brownian dynamics simulations for nonequilibrium systems involving polymeric liquids. These simulation techniques can allow us to improve kinetic theories, or possibly supplant them. These techniques also permit the study of much more complex systems and much more realistic molecular models. Most of all, they are enormously helpful in visualizing the molecular motions occurring in flows, including wall effects and interfacial phenomena. Current research on solution of flow problems by use of simulation techniques suggests that this part of polymer fluid dynamics will expand rapidly in the coming decade (Öttinger 1995).

Experimental Data

Despite the perception in funding agencies that making basic rheological measurements is “routine” and therefore unworthy of financial support, these measurements are essential for the testing of constitutive equations and kinetic theories. What is needed is a fluid dynamical “rheonome project” in which extensive data-taking can be done on very carefully characterized fluids in a very wide range of rheometric experiments. These measurements should be made on a wide variety of polymeric liquids, including solutions and melts and monodisperse and polydisperse systems. Some outstanding experimentalists have been and are still active in this area (J. D. Ferry, J. Meissner, A. S. Lodge, K. Osaki, J. L. Schrag, H. Janeschitz-Kriegl, W. W. Graessley, and others), but they have each tended to specialize in one or two types of experiments and have generally not all worked on the same polymeric liquids. Those who want to test constitutive equations and kinetic theories have therefore not had complete sets of data for many rheometric experiments for one single fluid.

In connection with the testing of numerical methods (as well as constitutive equations), data are needed on velocity and stress fields in nontrivial flows of increasing complexity. For maximum effectiveness the experiments should be performed on fluids for which the rheometric data are available.

One can adopt two views of the field: One can be very pessimistic and concentrate on the inadequacy of present knowledge to solve industrial problems and on the inherent difficulties in this highly nonlinear subject; or one can be optimistic and acknowledge the considerable advances that have been made in the past few decades and extrapolate these advances to continuing successes in the future. The field remains a challenging, fascinating, and important subject with a wide range of potential applications; it requires considerable background in continuum physics, statistical mechanics, polymer chemistry, fluid dynamics, and experimental techniques.

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