Co-rotational Rheological Models and the Goddard Expansion

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A survey is given of co-rotational rheological equations suitable for describing the flow of viscoelastic liquids such as polymer solutions and melts. Comparisons are given with experimental data and molecular theories. An introduction to kinematical descriptions in co-rotating reference frames is included.

SCOPE

During the past two decades rheologists have tried to describe the stresses in viscoelastic liquids by using embedded co-deforming coordinate systems. An alternative procedure of using coordinates rotating with the local fluid angular velocity, which is mathematically much simpler, has received far less emphasis. In this review we trace the development of the co-rotating rheological equations beginning with the two-constant co-rotating Maxwell model, or Zaremba (1903)-Fromm (1947, 1948)-DeWitt (1955) model, and concluding with the most general development of this type, namely, the Goddard (1967) memory-integral expansion, the first term of which can describe the shear-rate dependence of the viscosity and most of the important elastic properties as well. Use of the first term alone permits the derivation of a number of relations among rheological properties, several of which seem to be quite good; in particular, a Kramers-Kronig type of relation is found which enables one to estimate the normal stresses rather well from experimental data for the non-Newtonian viscosity. Two methods are suggested whereby one can take the higher terms in the expansion into account in an approximate way.

The relation of the Goddard expansion to molecular theory of polymer solutions is also discussed, using the extensive known results for rigid dumbbell and Hookean dumbbell models for macromolecules. By matching continuum and molecular results the kernel functions in the Goddard expansion can be expressed in terms of the parameters describing the structure of the dissolved macromolecules. The memory-integral expansion thus provides a framework for presenting kinetic theory results and establishes a useful link between the molecular theory and continuum mechanics.

CONCLUSIONS AND SIGNIFICANCE

1. The co-rotational rheological models are attractive because of their mathematical simplicity. Only cartesian tensors are used, the apparatus of general tensor analysis not being required. Although co-rotational models have been known for some time, they have not received as much attention as co-deformational models. It seems to us that research workers should be familiar with both kinds of models and that careful comparison of their relative merits might lead to a better understanding of rheological model building and perhaps to still different approaches to the subject. There may be pedagogical advantages for the co-rotational models, as opposed to the co-deformational models, although the differences here may boil down to matters of personal preference and the needs of the students. As for use in hydrodynamic calculations, it is not yet known which type of model may offer computational advantages; this area needs considerably more research effort.

2. The simplest co-rotational model is the Zaremba (1903)-Fromm (1947, 1948)-DeWitt (1955) model containing two constants: a zero-shear-rate viscosity η_0 and a time constant λ_0. This elementary model plays the same role in rheology as the two-constant van der Waals equation plays in p-V-T work; each equation is based on simple physical ideas and each can represent and interrelate qualitatively a number of observed phenomena in its own field. By superposing an infinite number of ZFD models, the generalized-ZFD model is obtained; this model, with viscosity constants η_k and time constants λ_k, proves to be a useful model for hydrodynamic calculations, since with proper choice of the constants the non-Newtonian viscosity can be fit as accurately as needed, and most of the elastic properties will be described adequately for most engineering purposes. For a few flows, notably sudden inception of shear and elongation flows, the generalized ZFD model will be inadequate.

3. The field of co-rotational model building has recently been put into proper perspective by the development of a memory-integral expansion by Goddard (1967). The first term in this expansion [the Goddard-Miller (1966) model] is a slight extension of the generalized ZFD model. The Goddard-Miller model can be used to derive many relations among measurable rheological properties. For example, it has been shown that non-Newtonian viscosity data can be used to predict normal stresses using an empiricism based on an analytical relation obtained from the Goddard-Miller model. Similarly, relations among stress relaxation, stress overshoot, steady shear flow

properties, small-amplitude oscillatory functions, and other material functions can be derived from the Goddard-Miller model. For simulation of polymer-process flows, one will probably not want to use a viscoelastic model more complicated than the Goddard-Miller model; when the relaxation modulus in the model is properly chosen, the non-Newtonian viscosity can be reproduced as accurately as needed.

The complete Goddard expansion would, of course, be unwieldy for solving complex hydrodynamics problems. However, it may be very useful for making refined calculations or for analyzing data from diverse rheological experiments. Even then it will probably be advisable to approximate the higher terms in the expansion in some way. For example, by using the first three terms in the series and approximating the kernel functions in a way suggested by molecular theory, one can obtain a somewhat more accurate description of rheological experiments than is provided by the first term alone. The entire Goddard expansion is also very helpful for representing the results of molecular theories of polymer solutions. When the rigid-dumbbell suspension kinetic theory results are written in the form of the co-rotational memory-integral expansion, the results can be extrapolated meaningfully outside the shear-rate range for which the kinetic theory calculations were made. The Goddard (1967) expansion provides a very useful framework for teaching about viscoelastic phenomena, interpreting rheological measurements, and planning the strategy of hydrodynamic calculations; it merits much more attention than it has received in the past seven years.

1. INTRODUCTION

One of the most challenging and rapidly developing areas of transport phenomena is that of non-Newtonian flow, and particularly the non-Newtonian behavior of macromolecular solutions and melts. For many calculations we can assume that these fluids are incompressible so that for isothermal flows the equations of change are

Equation of continuity:

$$(\nabla \bullet \mathbf{v}) = 0 \tag{1.1}$$

Equation of motion:

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p - [\nabla \bullet \boldsymbol{\tau}] + \rho \mathbf{g} \tag{1.2}$$

For structurally simple fluids (gases and liquids of low molecular weight), the momentum-flux tensor $\boldsymbol{\tau}$ is given by the linear relation

$$\boldsymbol{\tau} = -\mu[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\dagger}] \equiv -\mu\dot{\boldsymbol{\gamma}} \tag{1.3}$$

and such fluids are referred to as *Newtonian;* here μ is the Newtonian viscosity, which is independent of the velocity gradient. However, for liquids of very high molecular weight (say, mol.wt. $> 10^4$) striking departures from the simple linear expression above are observed. Other structurally complex materials, such as liquid crystals, soap solutions, and pastes, also deviate markedly from Equation (1.3). All these fluids are then referred to as *non-Newtonian* fluids. In the following discussion we shall be primarily concerned with macromolecular solutions and melts since these fluids have been the subject of most of the research in non-Newtonian fluid dynamics.

The central problem in describing the fluid dynamics of macromolecular fluids is the quest for an analytical expression for the momentum-flux tensor $\boldsymbol{\tau}$. Obtaining an appropriate expression for $\boldsymbol{\tau}$ is an extremely difficult and challenging problem inasmuch as macromolecular fluids are known to differ qualitatively in many ways from Newtonian fluids. Let us summarize a few of the known experimental facts:

1. Shear-rate-dependent viscosity. It has been known for a half-century that macromolecular fluids are shear-thinning, that is, the viscosity drops dramatically as the shear rate increases so that the viscosity may decrease to 10^{-2} to 10^{-4} of the zero-shear-rate viscosity. This property is probably the most important single property for engineers.

2. Normal-stress effects in steady shear flows. Macromolecular fluids exhibit a number of fascinating second-order effects associated with the inequality of normal stresses in steady shear flow (or flows resembling steady shear flows). These include:

(a) the Weissenberg effect, in which a macromolecular fluid climbs up a rotating rod (see for example, Lodge (1964), p. 232; Fredrickson (1964), p. 121);
(b) the reversal of direction of the secondary-flow pattern when a circular disk rotates at the surface of a liquid in a beaker (see Hill, Huppler, and Bird (1966); Hill (1972); Kramer and Johnson (1972);
(c) the slight bulging of the surface of a liquid as it flows down a trough (Wineman and Pipkin (1966), Tanner (1970));
(d) the hole-pressure error inherent in pressure-transducers which are not flush-mounted (Higashitani and Lodge 1974; Baird and Lodge 1974).

3. Transient responses in unsteady shear flows. A wide variety of small-amplitude experiments, such as dynamic testing (that is, oscillatory flows), stress relaxation, creep, and recoil have been used by chemists in order to elucidate molecular structure (Ferry, 1970). In addition, some large-amplitude, time-dependent experiments have also been performed: recoil (see Fredrickson, 1964, p. 120; Lodge, 1964, pp. 236, et seq.), time-dependent pressure gradients in pipe flows with a parametric pumping effect (Barnes, Townsend, and Walters, 1969; Walters and Townsend, 1970; Townsend, 1973); and shear flow with superposed oscillatory motion (Osaki et al., 1965; Booij, 1966; Macdonald and Bird, 1966; Macdonald, 1973).

4. Other phenomena. The above examples involve shearing flows. In nonshearing flows there are additional phenomena, such as swelling of extrudates issuing from a die (see Lodge, 1964, p. 242; Metzner et al., 1961; Graessley et al., 1970); development of a toroidal vortex in the inlet flow of a die (Giesekus, 1968; Metzner et al., 1969); the "Uebler effect", which is the abrupt stopping of large bubbles in the accelerating velocity field where the fluid flows from a reservoir into a tube (Metzner, 1967); the role of stress-overshoot in squeezing flows (Leider and Bird, 1973); the tubeless-siphon effect, in which a siphon continues to operate even though the upstream end has been withdrawn from the fluid (James, 1966); the unsteady state behavior in elongational flow, in which apparently a steady state elongational flow cannot be attained (Meissner, 1971); melt fracture in which very irregular extrudates are produced (Meissner, 1971); the rather weird Kaye phenomenon, wherein a falling stream

of a polymer solution impinging on a puddle of the same fluid seems to bounce from the liquid surface (Kaye, 1963; Lodge, 1964, p. 251); the solid-like behavior of polymeric liquids subjected to high-speed impact tests (Metzner, 1968); the inhibition of vortices by addition of small quantities of polymers to Newtonian fluids (Gordon and Balakrishnan, 1972).

The literature references cited are generally those in which photographs are given or extensive data compilations are presented. The list of phenomena is not complete, but it is sufficient for demonstrating that macromolecular fluids do not obey Newton's law of viscosity and that any expression proposed for $\boldsymbol{\tau}$ will have to be capable of describing a wide variety of observed phenomena. Many of these phenomena have been known for less than one or two decades.

Chemical, mechanical, and plastics engineers have in the past been primarily concerned with describing shear thinning. Consequently, they have used the generalized Newtonian fluid (Reiner, 1960; Bird, 1965):

$$\boldsymbol{\tau} = -\eta(\dot{\gamma})\,\dot{\boldsymbol{\gamma}} \tag{1.4}$$

which is the same as Equation (1.3) except that the viscosity η is now a function of the non-negative scalar $\dot{\gamma}$ which is the magnitude of the tensor $\dot{\boldsymbol{\gamma}}$, defined by $\dot{\gamma} = \sqrt{\tfrac{1}{2}(\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})}$ (see Bird, Stewart, and Lightfoot 1960, pp. 101-106). The most widely used empiricism for $\eta(\dot{\gamma})$ is the power law

$$\eta = m\,\dot{\gamma}^{n-1} \tag{1.5}$$

in which m and n are constants describing the fluid. The power law has been popular since for many macromolecular fluids the viscosity vs. shear-rate curves are linear on a log-log plot (with $0.2 < n < 1$ usually) over a wide range of shear rates. An empiricism which is somewhat preferable to Equation (1.5), since it allows $\eta \to \eta_0$ as $\gamma \to 0$ and $\eta \to \eta_\infty$ as $\gamma \to \infty$, is the following generalization of an equation used earlier by Williams (1966):

$$(\eta - \eta_\infty)/(\eta_0 - \eta_\infty) = [1 + (\lambda\dot{\gamma})^2]^{(n-1)/2} \tag{1.6}$$

in which λ is a time constant and n has the same meaning as in Equation (1.5) for the power-law region. We refer to Equation (1.6) as the *Carreau viscosity equation* (compare Carreau, 1968); it is known to fit experimental data very well as exemplified in Figures 1 and 2. Many other empiricisms have been used (see for example, Bird 1965; Bird, Stewart, and Lightfoot, 1960, Sections 1.2 and 3.6). Keep in mind, however, that the generalized Newtonian fluid models are incapable of describing any of the effects listed in categories 2, 3, and 4 above. As computer-modeling of the polymer-processing operations advances, the need will grow for expressions for $\boldsymbol{\tau}$ which are capable of describing wider ranges of phenomena. Ideally what the polymer engineer needs is an equation for $\boldsymbol{\tau}$ which can describe the most important flow phenomena and whose constants can be determined by a few straightforward and inexpensive laboratory tests.

The quest for useful constitutive equations or rheological equations (of state), as these expressions for $\boldsymbol{\tau}$ are often called, has been going on for some time. To understand the nature of the development, it is convenient to recall some of the older ideas from linear viscoelasticity since, after all, macromolecular fluids are viscoelastic. Over a century ago, Maxwell (who was exploring the idea of elastic effects in gases) observed that for incompressible materials Newton's law of viscosity $\boldsymbol{\tau} = -\mu\dot{\boldsymbol{\gamma}}$ and Hooke's law of elasticity $\boldsymbol{\tau} = -G\boldsymbol{\gamma}$ (here $\boldsymbol{\gamma}$ is the infinitesimal strain tensor) can be combined to give

$$\boldsymbol{\tau} + \lambda_0 \frac{\partial \boldsymbol{\tau}}{\partial t} = -\eta_0\,\dot{\boldsymbol{\gamma}} \tag{1.7}$$

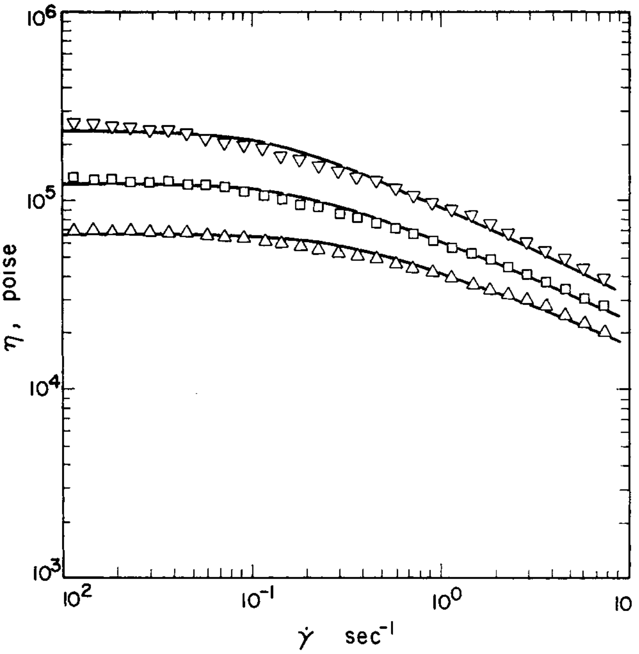

Fig. 1. Non-Newtonian viscosity of low density polyethylene [data of Chen and Bogue (1972)] as fitted by the Carreau viscosity equation, Equation (1.6)

▽ 160°C ($\eta_0 = 2.32 \times 10^5$ poise, $\eta_\infty = 0$, $\lambda = 7.18$ s, $n = 0.520$)
□ 180°C ($\eta_0 = 1.21 \times 10^5$ poise, $\eta_\infty = 0$, $\lambda = 5.23$ s, $n = 0.566$)
△ 200°C ($\eta_0 = 6.43 \times 10^4$ poise, $\eta_\infty = 0$, $\lambda = 2.86$ s, $n = 0.586$)
—— Carreau viscosity equation.

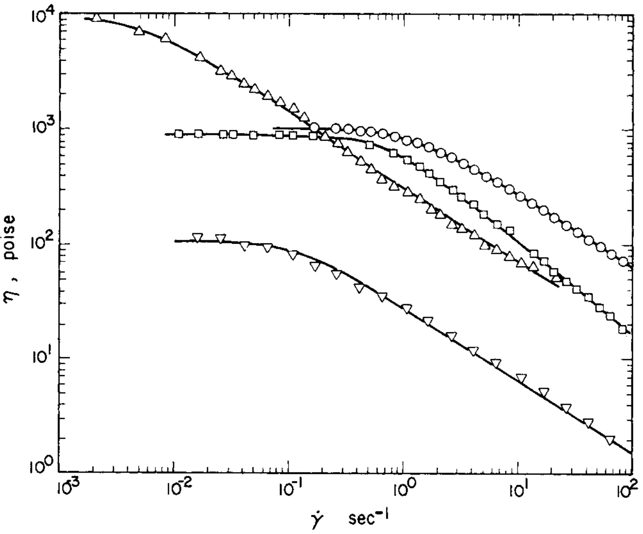

Fig. 2. Non-Newtonian viscosity of three polymer solutions and a soap solution as fitted by the Carreau viscosity equation, Equation (1.6)

△ 2% polyisobutylene, data of Huppler, Ashare, and Holmes, 1967.
($\eta_0 = 9.23 \times 10^3$ poise, $\eta_\infty = 1.50$ poise, $\lambda = 191$ s, $n = 0.358$).

○ 5% polystyrene in Aroclor 1242, data of Ashare (1968) ($\eta_0 = 1.01 \times 10^3$ poise, $\eta_\infty = 0.59$ poise, $\lambda = 0.84$ s, $n = 0.380$).

▽ 0.75% polyacrylamide (SEPARAN-30), data of Marsh, 1967 ($\eta_0 = 1.06 \times 10^2$ poise, $\eta_\infty = 0.10$ poise, $\lambda = 8.04$ s, $n = 0.364$).

□ 7% aluminum soap (Data of Huppler, Ashare, and Holmes 1967).
($\eta_0 = 8.96 \times 10^2$ poise, $\eta_\infty = 0.10$ poise, $\lambda = 1.41$ s, $n = 0.200$).

—— Carreau viscosity equation.

in which $\eta_0 = \mu$, and $\lambda_0 = \mu/G$. For steady state Equation (1.7) reduces to Newton's law and for $\boldsymbol{\tau}$ changing very rapidly with time Equation (1.7), after being integrated with respect to time, reduces to Hooke's law. This is the simplest equation for a linear viscoelastic fluid. We know that macromolecular fluids are mechanically very complex, and thus we would expect to have a whole spectrum of time constants (λ_k) and viscosities (η_k); consequently an improved method for describing linear viscoelastic phenomena is readily obtained by superposing a set of equations of the form Equation (1.7), as shown in Equation (1.8) below. Alternative forms of Equation (1.8) are readily obtained by performing successive differentiations to give Equation (1.9), by integrating to get Equation (1.10), or by integrating the latter by parts to get Equation (1.11)

$$\left\{\begin{aligned} &\boldsymbol{\tau} = \sum_{k=1}^{\infty} \boldsymbol{\tau}_k \\ &\boldsymbol{\tau}_k + \lambda_k \frac{\partial \boldsymbol{\tau}_k}{\partial t} = -\eta_k \dot{\boldsymbol{\gamma}} \end{aligned}\right. \tag{1.8}$$

$$\left[1 + \sum_{n=1}^{\infty} a_n \frac{\partial^n}{\partial t^n}\right] \boldsymbol{\tau} = -\eta_0 \left[1 + \sum_{n=1}^{\infty} b_n \frac{\partial^n}{\partial t^n}\right] \dot{\boldsymbol{\gamma}} \tag{1.9}$$

$$\boldsymbol{\tau} = -\int_{-\infty}^{t} \left\{ \sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_k} \exp\left(-\frac{t-t'}{\lambda_k}\right) \right\} \dot{\boldsymbol{\gamma}}(t')\, dt' \tag{1.10}$$

$$\boldsymbol{\tau} = +\int_{-\infty}^{t} \left\{ \sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_k^2} \exp\left(-\frac{t-t'}{\lambda_k}\right) \right\} \boldsymbol{\gamma}(t')\, dt' \tag{1.11}$$

In Equation (1.11), $\boldsymbol{\gamma}$ is so defined that it is zero at the present time t—that is, the present state is chosen to be the reference state to which the deformations of the fluid at earlier times t' are referred. The quantity in braces in Equation (1.10) is called the *relaxation modulus* and the quantity in braces in Equation (1.11) is termed the *memory function.*

To develop nonlinear viscoelastic constitutive equations, most investigators have chosen to begin with one of the above linear viscoelastic expressions and then to introduce modifications consistent with Oldroyd's rules for constructing rheological equations of state (Oldroyd, 1950, 1958; Fredrickson, 1964; Lodge, 1964, 1974). To indicate the extent of activity in this field we cite in Table 1 some of the rheological models which have been proposed. These models have been compared, to some extent, with each other in order to assess their relative ability to reproduce experimental data (see for example, Spriggs et al., 1966; Lodge, 1974; Yamamoto, 1972, pp. 264-278). However, the recent avalanche of new experimental data and newly discovered phenomena have made these comparisons partially obsolete.

Most of the models listed in Table 1 have been formulated in terms of general tensor calculus, usually using contravariant expressions for the stress tensor; they have been strongly influenced by Oldroyd (1950) in that a convected (co-deforming) coordinate system has been used. Only those marked with an asterisk have taken a co-rotating coordinate system as the basis for the formulation. In the latter approach, orthogonal coordinates can be used and the mathematical description is simpler.

TABLE 1. NONLINEAR RHEOLOGICAL EQUATIONS

Models based on	Rheological equations
Equation (1.8)	Spriggs (1965)
	Giesekus (1966)
Equation (1.9)	Fromm (1947, 1948)*
	Oldroyd (1950, 1958)
	White-Metzner (1963)
	Oldroyd (1964)*
	Roscoe (1964)
	Spriggs-Bird (1965)
	Tanner (1965)
Equation (1.10)	Walters (1960, 1962)
	Fredrickson (1964, p. 123)
	Goddard-Miller (1966)*
	Heindl-Giesekus (1972)
Equation (1.11)	Lodge (1964, p. 103)
	WJFLMB (Spriggs et al., (1966))
	Tanner-Simmons (1967)
	Bird-Carreau (1968)
	Carreau (1972)
	Bogue (1966)
	Chen-Bogue (1972)

* Co-rotational models.

It seems to us that the co-rotational description of rheological phenomena has really not received the attention that it deserves, probably because of the strong influence of the Oldroyd (1950) article and the subsequent textbooks of Fredrickson (1964), Lodge (1964), Middleman (1968) and others, none of which give any particular attention to the co-rotational theories. It is true that Oldroyd in his 1958 paper emphasized the use of the Jaumann derivative and in two later publications (1959, 1964) suggested the use of co-rotational models; however, the rheological data available at that time (particularly the secondary normal-stress data) suggested that co-rotational models were not too promising. It is the purpose of this article to review the past literature on co-rotational theories, summarize some of the key results, add a few hitherto unpublished ideas, and suggest some possible directions for future research. It is our feeling that the co-rotational theories have definite pedagogical advantages and may prove to be quite useful in research and hydrodynamic applications.

2. KINEMATIC CONSIDERATIONS

We consider the flow of an incompressible fluid with velocity field $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$. We define

$$\dot{\boldsymbol{\gamma}} = \nabla \mathbf{v} + (\nabla \mathbf{v})^{\dagger} = \text{rate-of-deformation tensor} \tag{2.1}$$

$$\boldsymbol{\omega} = \nabla \mathbf{v} - (\nabla \mathbf{v})^{\dagger} = \text{vorticity tensor} \tag{2.2}$$

$$\mathbf{w} = \frac{1}{2}[\nabla \times \mathbf{v}] = \text{angular velocity vector} \tag{2.3}$$

Note that $\omega_{jk} = 2\Sigma_i \epsilon_{jki} w_i$ and that $(\nabla \mathbf{v})_{ij} = (\partial/\partial x_i) v_j$ in cartesian coordinates (we use cartesian coordinates throughout this entire review). A flow field is said to be homogeneous if $\mathbf{v} = \boldsymbol{\kappa}(t) \cdot \mathbf{r}$ where the tensor $\boldsymbol{\kappa}$ is position independent. For homogeneous flow $\nabla \mathbf{v} = \boldsymbol{\kappa}^{\dagger}$ and $\mathbf{w} = \frac{1}{2}[\boldsymbol{\varepsilon} : \boldsymbol{\kappa}]$.

We now introduce the notion of two reference frames moving with a fluid particle P in a flow field (see Figure 3). One frame, described by a triad of mutually orthogonal unit vectors $\boldsymbol{\delta}_1$, $\boldsymbol{\delta}_2$, $\boldsymbol{\delta}_3$, moves along with the particle in fixed orientation. A second frame, described by a second triad of mutually orthogonal unit vectors $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$ moves along with the particle but rotates with an angular velocity $\mathbf{W}$; later on we will let $\mathbf{W}$ be the local fluid angular velocity $\mathbf{w} = (\frac{1}{2})[\nabla \times \mathbf{v}]$. The rotating frame coincides with

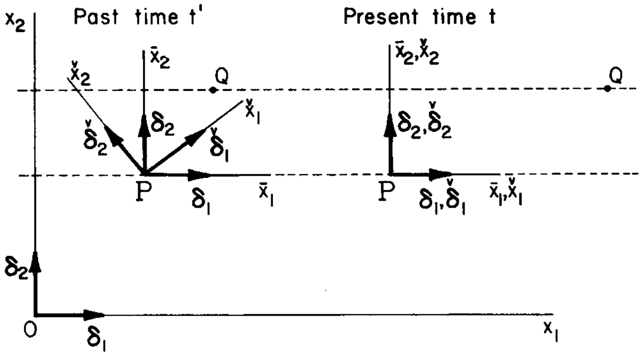

Fig. 3. Motion of particles *P* and *Q* moving with the fluid in steady shearing flow $v_1 = \gamma x_2$. The velocity v and the local fluid angular velocity w as seen by observers in the three coordinate frames are

Fixed: $\mathbf{v} = \boldsymbol{\delta}_1 \dot{\gamma} x_2$ $\qquad \mathbf{w} = \boldsymbol{\delta}_3(-\dot{\gamma}/2)$

Co-translating: $\bar{\mathbf{v}} = \boldsymbol{\delta}_1 \dot{\gamma} \bar{x}_2$ $\qquad \bar{\mathbf{w}} = \boldsymbol{\delta}_3(-\dot{\gamma}/2)$

Co-Rotating: $\check{\mathbf{v}} = \check{\boldsymbol{\delta}}_1(\dot{\gamma}/2)[\check{x}_1 \sin \dot{\gamma}(t-t') + \check{x}_2 \cos \dot{\gamma}(t-t')]$ $\qquad \check{\mathbf{w}} = \mathbf{0}$

$+ \check{\boldsymbol{\delta}}_2(\dot{\gamma}/2)[\check{x}_1 \cos \dot{\gamma}(t-t') + \check{x}_2 \sin \dot{\gamma}(t-t')]$

the nonrotating frame at the present time t.

Let us now consider the steady state shear flow $v_1 = \dot{\gamma} x_2$, with the rotating frame having a constant angular velocity $\mathbf{W} = \boldsymbol{\delta}_3 W$. Then an observer in the rotating frame would see velocity components, in terms of his own coordinates $\check{x}_1, \check{x}_2, \check{x}_3$, which would look like this at time t':

$$\check{v}_1 = \dot{\gamma}\,[-\check{x}_1 \sin W(t-t') + \check{x}_2 \cos W(t-t')] \cos W(t-t') + W \check{x}_2 \tag{2.4}$$

$$\check{v}_2 = \dot{\gamma}\,[-\check{x}_1 \sin W(t-t') + \check{x}_2 \cos W(t-t')] \sin W(t-t') - W \check{x}_1 \tag{2.5}$$

In each of these expressions the first term is what the observer would see if his frame were translating but rotated through a fixed angle $-W(t-t')$ with respect to the $\boldsymbol{\delta}_1 \boldsymbol{\delta}_2 \boldsymbol{\delta}_3$-frame; the second term is the additional contribution associated with rotation. From Equations (2.4) and (2.5) we can get the components of the velocity gradient tensor as seen by the rotating observer

$$\left[\frac{\partial}{\partial \check{x}_i} \check{v}_j\right] = \begin{bmatrix} -\tfrac{1}{2}\sin 2W(t-t') & -\sin^2 W(t-t') & 0 \\ \cos^2 W(t-t') & \tfrac{1}{2}\sin 2W(t-t') & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \qquad \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} W \tag{2.6}$$

from which $\check{\dot{\gamma}}_{ij}$, $\check{\omega}_{ij}$, and $\check{w}_i$ can be obtained. The only nonvanishing component of the angular velocity vector as seen by the rotating observer is the 3-component

$$\check{w}_3 = \frac{1}{2}\left(\frac{\partial}{\partial \check{x}_1}\check{v}_2 - \frac{\partial}{\partial \check{x}_2}\check{v}_1\right) = \frac{1}{2}(-\dot{\gamma} - 2W) \tag{2.7}$$

If now we specialize to the case where the $\check{\boldsymbol{\delta}}_1 \check{\boldsymbol{\delta}}_2 \check{\boldsymbol{\delta}}_3$-frame is rotating with the local fluid angular velocity $w_3 = -(\dot{\gamma}/2)$, then we shall speak of a co-rotating frame; all the principal results for the co-rotating frame are shown in the caption to Figure 3.

Next we turn our attention to a general flow history $\mathbf{v}(\mathbf{r}, t')$, where $-\infty < t' \leqq t$, in which t is the present time. Once again we consider two sets of unit vectors going along with the fluid particle, the set $\check{\boldsymbol{\delta}}_i$ rotating in some arbitrary fashion; the $\check{\boldsymbol{\delta}}_i$ and $\boldsymbol{\delta}_i$ are related by

$$\begin{cases} \check{\boldsymbol{\delta}}_i(t') = \sum\limits_j Q_{ij}(t, t')\, \boldsymbol{\delta}_j & (2.8) \\ \check{\boldsymbol{\delta}}_i(t) = \boldsymbol{\delta}_i \quad \text{or} \quad Q_{ij}(t, t) = \delta_{ij} & (2.9) \end{cases}$$

That is, the two triads of unit vectors coincide at the present time t. The Q_{ij} are the elements of an orthogonal matrix so that $\Sigma_m Q_{im} Q_{jm} = \Sigma_m Q_{mi} Q_{mj} = \delta_{ij}$. For the moment we do not specify $Q_{ij}(t, t')$ further.

An observer in the $\bar{x}_1 \bar{x}_2 \bar{x}_3$-frame will specify the position of a particle Q (relative to particle P) and the velocity of particle Q as follows:

$$\begin{cases} \mathbf{x} = \sum\limits_i \boldsymbol{\delta}_i \bar{x}_i & (2.10) \\ \bar{v}_i = \dfrac{D}{Dt'} \bar{x}_i = \sum\limits_j (\overline{\nabla \mathbf{v}})_{ji}\, \bar{x}_j + \ldots & (2.11) \end{cases}$$

Here and in the following equations D/Dt' is a time derivative following the particle (the material (or substantial) derivative) and vector and tensor components are evaluated at time t' (where $-\infty < t' \leqq t$). If the flow is homogeneous the higher terms indicated by "+ . . ." are zero.

The observer in the $\check{x}_1 \check{x}_2 \check{x}_3$-frame will give the location and velocity of Q in terms of different components

$$\begin{cases} \mathbf{x} = \sum\limits_i \check{\boldsymbol{\delta}}_i \check{x}_i & (2.12) \\ \check{v}_i = \dfrac{D}{Dt'} \check{x}_i = \sum\limits_j (\check{\nabla} \check{\mathbf{v}})_{ji}\, \check{x}_j + \ldots & (2.13) \end{cases}$$

From Equations (2.10) and (2.12) we find that $\check{x}_i = \Sigma_j Q_{ij} \bar{x}_j$ so that

$$\check{v}_i = \frac{D}{Dt'}\left(\sum_j Q_{ij} \bar{x}_j\right) = \sum_j Q_{ij} \bar{v}_j + \sum_j \left(\frac{D}{Dt'} Q_{ij}\right) \bar{x}_j \tag{2.14}$$

This result should be compared with Equations (2.4) and (2.5) for steady shear flow; here again we see that $\check{v}_i$ has one term $(\Sigma_j Q_{ij} \bar{v}_j)$ associated with the instantaneous tilt of the $\check{x}_1 \check{x}_2 \check{x}_3$-frame and a second term arising from the rotary movement of the frame. Now by inserting $\bar{v}_i$ from Equation (2.11) into Equation (2.14) and then equating to the right side of Equation (2.13), we obtain (using the fact that the Q_{ij} are orthogonal):

$$(\check{\nabla} \check{\mathbf{v}})_{ij} = \sum_m \sum_n Q_{im} (\bar{\nabla} \bar{v})_{mn} Q_{jn} + \sum_n Q_{in}\left(\frac{D}{Dt'} Q_{jn}\right) \tag{2.15}$$

It can be seen that this has the same two contributions encountered in Equation (2.6)—one associated with the instantaneous tilt of the $x_1 x_2 x_3$ frame and another associated to the rotary movement of the $x_1 x_2 x_3$ axes. Hence the rotating observer sees the following components of the rate-of-deformation and vorticity tensors

$$\left\{\begin{array}{ll} \check{\dot{\gamma}}_{ij} = \sum\limits_m \sum\limits_n Q_{im}\,\bar{\dot{\gamma}}_{mn}\,Q_{jn} & (2.16) \\ \check{\omega}_{ij} = \sum\limits_m Q_{im}\left(\sum\limits_n \bar{\omega}_{mn}\,Q_{jn} + 2\left(\frac{D}{Dt'} Q_{jm}\right)\right) & (2.17) \end{array}\right.$$

We see that the transformation rule for $\dot{\boldsymbol{\gamma}}$ is quite simple since it deals with internal deformations only.

We now specialize by choosing the matrix $Q_{ij}(t, t')$ so that $\check{\omega}_{ij} = 0$; that is, we require

$$\left\{\begin{array}{ll} \left(\frac{D}{Dt'} Q_{ij}\right) = +\frac{1}{2} \sum\limits_m Q_{im}\,\bar{\omega}_{mj}\,(t') & (2.18) \\ Q_{ij}\,(t, t') = \delta_{ij} \quad \text{when} \quad t' = t & (2.19) \end{array}\right.$$

Hence for this choice of Q_{ij} the rotating observer will observe that the entire flow history in his immediate neighborhood has been irrotational for $-\infty < t' \leqq t$; if the flow is homogeneous he will have seen an irrotational flow throughout the entire flow field because the "+ . . ." terms in Equation (2.13) will be zero.

Combination of Equation (2.18) with Equation (2.8) shows that the above choice of Q_{ij} is such that the $\check{\boldsymbol{\delta}}_i$ change with time in the following way:

$$\frac{D}{Dt'} \check{\boldsymbol{\delta}}_i(t)') = [\mathbf{w}(t') \times \check{\boldsymbol{\delta}}_i(t')]$$

$$= -\frac{1}{2}\,[\boldsymbol{\omega}(t') \bullet \check{\boldsymbol{\delta}}_i(t')] \qquad (2.20)$$

Thus we see that the Q_{ij} have been so chosen that the $\check{\boldsymbol{\delta}}_i$ vectors rotate with the angular velocity equal to ½[$\nabla \times \mathbf{v}$].

The total stress tensor $\boldsymbol{\pi}$ is defined in terms of the force per unit area f transmitted across a surface of unit normal **n** from the negative to the positive side thus:

$$\mathbf{f} = [\mathbf{n} \bullet \boldsymbol{\pi}] = [\mathbf{n} \bullet (p\boldsymbol{\delta} + \boldsymbol{\tau})] \qquad (2.21)$$

in which $\boldsymbol{\delta}$ is the unit tensor, p is an isotropic pressure, and $\boldsymbol{\tau}$ is the extra stress tensor which must be determined from the rheological equation of state. After decomposing the vectors **f** and **n** as was done for **x** in Equations (2.10) and (2.12) we find

$$\check{\tau}_{ij} = \sum_m \sum_n Q_{im}\,\bar{\tau}_{mn}\,Q_{jn} \qquad (2.22)$$

for the relation between the components of $\boldsymbol{\tau}$ in the $\bar{x}_1\,\bar{x}_2\,\bar{x}_3$ and $\check{x}_1\,\check{x}_2\,\check{x}_3$ systems. From Equations (2.22) and (2.18) we can obtain the relation for the time rate of change of the stress components $\check{\tau}_{ij}$ following a fluid particle at $t' = t$:

$$\frac{D}{Dt'} \check{\tau}_{ij} = \frac{D}{Dt'} \bar{\tau}_{ij} + \frac{1}{2} \sum_m (\bar{\omega}_{im}\,\bar{\tau}_{mj} - \bar{\tau}_{im}\,\bar{\omega}_{mj}); \quad (t' = t) \qquad (2.23)$$

It is now convenient to have an abbreviation for the collection of terms on the right side—that is, the substantial derivative plus the extra terms involving the instantaneous local rotation. We now drop the overlines since components of $\boldsymbol{\omega}$ and $\boldsymbol{\gamma}$ in the $\bar{x}_1\,\bar{x}_2\,\bar{x}_3$ system are the same as those in the $x_1\,x_2\,x_3$ system and define the co-rotational (or Jaumann, 1905, 1911) derivative

$$\frac{\mathcal{D}}{\mathcal{D}t'} \tau_{ij} \equiv \frac{D}{Dt'} \tau_{ij} + \frac{1}{2} \sum_m (\omega_{im}\,\tau_{mj} - \tau_{im}\,\omega_{mj}); \quad (t' = t) \qquad (2.24)$$

(see also Prager, 1961). A relation of the form of Equation (2.23) also holds for the substantial derivatives of the components of the rate-of-deformation tensor $\dot{\boldsymbol{\gamma}}$ in the two frames. We see that, although $\check{\tau}_{ij} = \tau_{ij}$ at $t' = t$, the two substantial derivatives are unequal. The inverse of this Jaumann differentiation is called *Jaumann integration;* this latter terminology was first used by Goddard and Miller (1966).

Let us now return to the question of determining the Q_{ij} from Equation (2.18). For any flow field Goddard and Miller (1966) showed that a perturbation solution can be found

$$\begin{aligned} Q_{ij} = \delta_{ij} &+ \left(-\frac{1}{2}\right) \int_{t'}^{t} \omega_{ij}(t'')\,dt'' \\ &+ \left(-\frac{1}{2}\right)^2 \int_{t'}^{t} \int_{t''}^{t} \sum_m \omega_{im}(t''')\,\omega_{mj}(t'')\,dt'''\,dt'' \\ &+ \ldots \end{aligned} \qquad (2.25)$$

This solution is easily verified by substitution into Equation (2.18). For flows in which $\boldsymbol{\omega}$ is independent of time as we follow a fluid particle Equation (2.25) simplifies to

$$\begin{aligned} Q_{ij} &= \delta_{ij} - \frac{1}{2}\,\omega_{ij}(t - t') + \frac{1}{8} \sum_m \omega_{im}\,\omega_{mj}(t - t')^2 - \ldots \\ &\equiv e^{-\frac{1}{2}\,\omega_{ij}(t-t')} \end{aligned} \qquad (2.26)$$

where the exponential notation has to be interpreted as a matrix shorthand notation. For unsteady state shearing flows $v_1 = \dot{\gamma}(t')x_2$, $v_2 = 0$, $v_3 = 0$, we have

$$[Q_{ij}] = \begin{bmatrix} \cos \frac{1}{2} \int_{t'}^{t} \dot{\gamma}(t'')dt'' & \sin \frac{1}{2} \int_{t'}^{t} \dot{\gamma}(t'')dt'' & 0 \\ -\sin \frac{1}{2} \int_{t'}^{t} \dot{\gamma}(t'')dt'' & \cos \frac{1}{2} \int_{t'}^{t} \dot{\gamma}(t'')dt'' & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad (2.27)$$

For complex flows the determination of Q_{ij} will be a difficult problem.

3. CO-ROTATIONAL MODELS

In this section we discuss the evolution of co-rotational rheological equations. We take more or less a historical approach, beginning with the elementary two-constant model of Zaremba (1903), Fromm (1947, 1948), and DeWitt (1955) and ending with the co-rotational memory-integral expansion of Goddard (1967). By so doing we go from simple equations with rather transparent physical meaning all the way to the results of a formal development.

In Section 1 it was pointed out that the simplest rheological equation containing the notions of viscosity and elasticity is the Maxwell model [Equation (1.7)]. Zaremba (1903) seems to have been the first to suggest that the Maxwell model should be formulated in such a way that there is no unwanted dependence on the instantaneous local rotation of a fluid element. This means that the Maxwell model should be written in a co-rotating coordinate system following a fluid element. The same idea surfaced again a half-century later when Fromm (1947, 1948) and DeWitt (1955) published more readable accounts with specific applications. We therefore refer to the co-rotating Maxwell equation as the ZFD model and write accordingly,

$$\begin{cases} \check{\tau}_{ij} + \lambda_0 \dfrac{D}{Dt} \check{\tau}_{ij} = - \eta_0 \check{\dot{\gamma}}_{ij} & (3.1) \\[2ex] \check{\tau}_{ij} = - \displaystyle\int_{-\infty}^{t} \left\{ \frac{\eta_0}{\lambda_0} e^{-\left(\frac{t-t'}{\lambda_0}\right)} \right\} \check{\dot{\gamma}}_{ij}(t')\, dt' & (3.2) \end{cases}$$

the second form being obtained from the first by integration in the co-rotating frame following the fluid particle from $t' = -\infty$ (when the fluid is presumed to be at rest) to the present time $t' = t$. When Equations (3 1) and (3.2) are translated into fixed coordinates at time t (when $\check{\tau}_{ij} = \tau_{ij}$, *and* $D\, \check{\tau}_{ij}/Dt = \mathcal{D}\, \tau_{ij}/\mathcal{D}t$) we get

$$\begin{cases} \boldsymbol{\tau} + \lambda_0 \dfrac{\mathcal{D}}{\mathcal{D}t} \boldsymbol{\tau} = - \eta_0 \dot{\boldsymbol{\gamma}} & (3.3) \\[2ex] \boldsymbol{\tau} = - \displaystyle\int_{-\infty}^{t} \left\{ \frac{\eta_0}{\lambda_0} e^{-\left(\frac{t-t'}{\lambda_0}\right)} \right\} \dot{\boldsymbol{\Gamma}}'\, dt' & (3.4) \end{cases}$$

in which we have introduced

$$\dot{\Gamma}_{ij}' = \dot{\Gamma}_{ij}(t, t') = \sum_m \sum_n Q_{im}(t, t')\, Q_{jn}(t, t')\, \dot{\gamma}_{mn}(t') \tag{3.5}$$

Equations (3.3) and (3.4) are alternative forms of the ZFD model. The model contains two constants: a zero-shear-rate viscosity η_0 and a time constant λ_0. This ZFD equation occupies somewhat the same position in rheology as the two-constant van der Waals equation enjoys in thermodynamics. It contains the main ideas: viscosity, elasticity, and freedom from unwanted dependence on spatial rotation.

We shall not tabulate the main results for this elementary model since they can all be obtained as special cases of the results given in the next section. However, we will summarize qualitatively the main good and bad points about the ZFD model thus:

1. It gives a viscosity $\eta = \eta_0/(1 + \lambda_0^2 \dot{\gamma}^2)$ which decreases as $\dot{\gamma}^{-2}$ for large $\dot{\gamma}$ which is unrealistic since it is implied that τ_{yx} goes through a maximum as $\dot{\gamma}$ goes from 0 to ∞.

2. It gives shear-rate-dependent normal stresses and also gives $(\tau_{22} - \tau_{33}) = - \frac{1}{2} (\tau_{11} - \tau_{22})$ for $v_1 = v_1(x_2)$; the best recent experimental data seem to give a proportionality coefficient of $- 1/10$ to $- 2/5$ rather than $- 1/2$ (see Ginn and Metzner, 1969; Pritchard, 1971; Higashitani and Pritchard, 1972; Tanner, 1973; Harris, 1973, Christiansen and Leppard, 1974). It should be pointed out that the proportionality coefficient $- 1/2$ would correspond to a uniform pressure distribution in the cone-and-plate viscometer, whereas it is known that the pressure decreases linearly with log r [see, for example, Lodge (1964), p. 209 (Equation 9.64) and p. 235 (Figure 10.5).]

3. For sudden startup of steady shear flow it can describe stress overshoot, with the normal-stress maximum appearing later than the shear-stress maximum, as it should (Meissner, 1972; Hansen, 1974). The model shows that the stresses undergo damped oscillations after the overshoot, but this seems to be in disagreement with most data except those of Laufer (1974).

4. Stress relaxation after cessation of steady shear flow is described, but not properly; shear stresses are known to relax more rapidly than normal stresses, and both are known to relax faster as the steady-shear-flow shear rate is increased—but the model is incapable of describing either (Lodge, 1964; Carreau et al., 1968; Harris, 1970).

5. The model gives a constant elongational viscosity in agreement with some data (Radushkevich et al., 1968; Stevenson, 1972) but in disagreement with others (Meissner, 1971).

6. In elongational stress growth approaching steady elongational flow, the model shows no stress overshoot in agreement with experiment (Stevenson, 1972).

It is therefore evident that this simple two-constant model has many attractive features, as well as several drawbacks (the same might be said of the van der Waals equation).

Suppose next that we begin to generalize in the same fashion that we did for linear viscoelasticity in Section 1. For example if we write Equation (1.9) in co-rotational form (with $a_1 = \lambda_1$, $b_1 = \lambda_2$, and all other a's and b's equal to zero) and then transform to fixed coordinates, we obtain the co-rotational Jeffreys model [see Equation (10) of Oldroyd (1959) and Equations (53) and (59) of Goddard and Miller (1966)]

$$\begin{cases} \boldsymbol{\tau} + \lambda_1 \dfrac{\mathcal{D}}{\mathcal{D}t} \boldsymbol{\tau} = - \eta_0 \left(\dot{\boldsymbol{\gamma}} + \lambda_2 \dfrac{\mathcal{D}}{\mathcal{D}t} \dot{\boldsymbol{\gamma}} \right) & (3.6) \\[2ex] \boldsymbol{\tau} = - \displaystyle\int_{-\infty}^{t} \left\{ \frac{\eta_0}{\lambda_1} \left[2\lambda_2 \delta(t - t') + \left(1 - \frac{\lambda_2}{\lambda_1} \right) e^{-\left(\frac{t-t'}{\lambda_1}\right)} \right] \right\} \dot{\boldsymbol{\Gamma}}'\, dt' & (3.7) \end{cases}$$

in which $\delta(t - t')$ is the Dirac delta function.[*] [In this model we must specify that $\lambda_1 > \lambda_2$, as can be seen from Equation (4.2).] This three-parameter model represents a considerable improvement over the ZFD model, but, aside from its mention by Goddard and Miller (1966) and Oldroyd (1959), does not seem to have been used in rheology. Oldroyd (1964) suggested using the analog of Equation (1.9), with many derivatives on both sides, but further efforts in this direction were not made, possibly because of criticism leveled by de Vries (1965) and perhaps others who felt that this kind of rheological equation led to unrealistic results. We must remember, however, that up until about 1965 it was generally agreed that $(\tau_{22} - \tau_{33})/(\tau_{11} - \tau_{22})$ was positive, and experimental data on transient phenomena (aside from small-amplitude oscillatory flow) and elongational flow were very scanty. [It is interesting to note that Equation (3.7) has exactly the same form as the first term in the Goddard expansion for rigid-dumbbell kinetic theory, see Equation (8.2). Hence the co-rotational Jeffreys model is amenable to a molecular interpretation.]

Rather than patterning our thinking after Equation (1.9), which led to the co-rotational Jeffreys model and the Oldroyd (1964) model, we could consider the co-rotational analogs of Equations (1.8) or (1.10). Such an

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[*] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Oxford University Press (1947), Third Edit., pp. 58-61. Here we use the statement of M. J. Lighthill, *Fourier Analysis and Generalised Functions*, Cambridge University Press (1964), p. 17, that

$$\delta(x) = \lim_{n \to \infty} \sqrt{\frac{n}{\pi}}\, e^{-nx^2} \tag{3.7a}$$

From this it follows that

$$\int_{-a}^{a} f(x)\delta(x)dx = 2 \int_{0}^{a} f(x)\delta(x)dx = f(0) \tag{3.7b}$$

$$\int_{-a}^{a} f(x)\delta'(x)dx = - f'(0) \tag{3.7c}$$

in which $a > 0$ and the prime denotes differentiation with respect to x. Note particularly the occurrence of the factor of 2 in Equation (3.7c) when the integral is over the region from 0 to a. This explains the occurrence of the factors of 2 in the δ-function terms in Equation (3.7).

obvious extension, which does not seem to have been suggested, leads to a generalized ZFD model

$$\left\{\begin{aligned} &\boldsymbol{\tau} = \sum_{k=1}^{\infty} \boldsymbol{\tau}_k; \quad \boldsymbol{\tau}_k + \lambda_k \frac{\mathcal{D}}{\mathcal{D}t} \boldsymbol{\tau}_k = -\eta_k \dot{\boldsymbol{\gamma}} && (3.8) \\ &\boldsymbol{\tau} = -\int_{-\infty}^{t} \left\{ \sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_k} e^{-\left(\frac{t-t'}{\lambda_k}\right)} \right\} \dot{\boldsymbol{\Gamma}}'\, dt' && (3.9) \end{aligned}\right.$$

This contains too many constants to be of much practical use, and so one would have to seek some kind of empiricism for reducing the number of constants. Methods for doing this are suggested in Section 5. Goddard and Miller (1966) went one step beyond Equation (3.9) and replaced the quantity in braces by an arbitrary function of $t - t'$; this Goddard-Miller equation is discussed in Section 6 and some of its properties are explored.

Finally, as the last development in the sequence, we come to the memory-integral expansion of Goddard (1967) which includes all of the previous models of this section as special cases. Goddard showed that a formal expansion can be made for any incompressible, isotropic viscoelastic fluid for which the stress at a particular particle depends on the deformation history of that particle only and not on that of adjacent particles; the resulting series is

$$\begin{aligned} \boldsymbol{\tau} = &-\int_{-\infty}^{t} G_I\,(t-t')\ \dot{\boldsymbol{\Gamma}}'\, dt' \\ &-\frac{1}{2}\int_{-\infty}^{t}\int_{-\infty}^{t} G_{II}\,(t-t', t-t'') \\ &\qquad [\dot{\boldsymbol{\Gamma}}' \cdot \dot{\boldsymbol{\Gamma}}'' + \dot{\boldsymbol{\Gamma}}'' \cdot \dot{\boldsymbol{\Gamma}}']\, dt''\, dt' \\ &-\frac{1}{2}\int_{-\infty}^{t}\int_{-\infty}^{t}\int_{-\infty}^{t} \{2\, G_{III}\,(t-t',\ t-t'',\ t-t''') \\ &\qquad \dot{\boldsymbol{\Gamma}}'\, \dot{\boldsymbol{\Gamma}}'' : \dot{\boldsymbol{\Gamma}}''' + G_{IV}\,(t-t',\ t-t'',\ t-t''') \\ &\qquad [\dot{\boldsymbol{\Gamma}}' \cdot \dot{\boldsymbol{\Gamma}}'' \cdot \dot{\boldsymbol{\Gamma}}''' + \dot{\boldsymbol{\Gamma}}''' \cdot \dot{\boldsymbol{\Gamma}}'' \cdot \dot{\boldsymbol{\Gamma}}']\}\, dt'''\, dt''\, dt' \\ &- \ldots \end{aligned} \qquad (3.10)^{*}$$

The first term of this expansion is the Goddard-Miller (1966) model. Equation (3.10) contains an infinite number of kernel functions G_I, G_{II}, etc. In Section 10 we explore one method of simplifying the series by approximating the G's in a way suggested by the molecular theory in Section 9.

Goddard (1967, p. 396) has emphasized that this expansion converges—at least for steady shearing flow—much more rapidly than similar expansions developed earlier by Green, Rivlin, and Spencer (1957, 1959, 1960), Coleman and Noll (1961), and Pipkin (1964). We strongly concur in this and summarize in Section 8 supporting kinetic theory evidence provided by Abdel-Khalik et al. (1974). Unfortunately the Goddard paper seems to have been overlooked, and several recent reviews of continuum mechanics (Rivlin and Sawyers, 1971; Truesdell, 1974) make no mention of it.

4. THE CO-ROTATIONAL JEFFREYS MODEL

In this section we examine the behavior of the three-parameter co-rotational Jeffreys model given in Equation (3.6) or Equation (3.7). This model may be useful for exploring polymer behavior in complex flow problems where a simple, but fairly realistic, model is needed. It will be seen that the model gives qualitatively the correct behavior in many situations. By setting λ_2 equal to zero and replacing λ_1 by λ_0, one can obtain the results for the older ZFD model.

Steady Shearing Flow

Equation (2.27) can be specialized for the steady shearing flow $v_x = \dot{\gamma}\, y$, and then $\dot{\Gamma}'_{ij}$ can be obtained from Equation (3.5)

$$[\dot{\Gamma}'_{ij}] = \begin{bmatrix} \dot{\gamma} \sin \dot{\gamma}\,(t-t') & \dot{\gamma} \cos \dot{\gamma}\,(t-t') & 0 \\ \dot{\gamma} \cos \dot{\gamma}\,(t-t') & -\dot{\gamma} \sin \dot{\gamma}\,(t-t') & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad (4.1)$$

Substitution of this into Equation (3.7) and performing the integration gives

$$\tau_{xy} = -\eta\, \dot{\gamma} = -\eta_0\, \dot{\gamma}\, \frac{1 + \lambda_1 \lambda_2\, \dot{\gamma}^2}{1 + (\lambda_1\, \dot{\gamma}\,)^2} \qquad (4.2)$$

$$\tau_{xx} - \tau_{yy} = -\theta\, \dot{\gamma}^2 = -2\eta_0\, \dot{\gamma}^2\, \frac{\lambda_1 - \lambda_2}{1 + (\lambda_1\, \dot{\gamma}\,)^2} \qquad (4.3)$$

$$\tau_{yy} - \tau_{zz} = -\beta\, \dot{\gamma}^2 = +\eta_0\, \dot{\gamma}^2\, \frac{\lambda_1 - \lambda_2}{1 + (\lambda_1\, \dot{\gamma}\,)^2} \qquad (4.4)$$

Since $\lambda_2 < \lambda_1$, the non-Newtonian viscosity decreases from η_0 to $\eta_\infty = \eta_0(\lambda_2/\lambda_1)$ as $\dot{\gamma}$ goes from 0 to ∞. The primary normal stress function θ, which indicates that there is an extra tension in the x-direction, also decreases with increasing $\dot{\gamma}$. The fact that β is negative means that there is an extra tension in the z-direction, in agreement with the tilted trough experiment (Tanner, 1970) and numerous other experiments, which seem to indicate that $-\beta/\theta$ is about 0.1 to 0.4. For many hydrodynamic problems an exact portrayal of β is probably not necessary; the only problems we know of where β plays a key role are high-speed wire-coating (Tadmor and Bird, 1974) and the orbits of elongated particles suspended in a sheared viscoelastic continuum (Leal, 1974).

Small-Amplitude Oscillatory Motions

Next we examine the small-amplitude oscillatory flow given by $\dot{\gamma}(t') = \dot{\gamma}^0 \cos \omega t'$, where ω is the frequency and $\dot{\gamma}^0$ is a real positive quantity denoting the amplitude of the velocity gradient. Use of Equations (2.27) and (3.5) then gives

$$\dot{\boldsymbol{\Gamma}}' = \begin{bmatrix} \sin\left[\frac{\dot{\gamma}^0}{\omega}(\sin \omega t - \sin \omega t')\right] & \cos\left[\frac{\dot{\gamma}^0}{\omega}(\sin \omega t - \sin \omega t')\right] & 0 \\ \cos\left[\frac{\dot{\gamma}^0}{\omega}(\sin \omega t - \sin \omega t')\right] & -\sin\left[\frac{\dot{\gamma}^0}{\omega}(\sin \omega t - \sin \omega t')\right] & 0 \\ 0 & 0 \end{bmatrix} \dot{\gamma}^0 \cos \omega t'$$

(Continued on next page)

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[*] Our G_I, G_{II}, G_{III}, G_{IV} correspond to Goddard's $\psi_1^{(1)}$, $\frac{1}{2}\,\psi_2^{(2)}$, $\frac{1}{4}\,\psi_1^{(3)}$, $\frac{1}{4}\,\psi_3^{(3)}$ respectively, where $\psi_1^{(3)} = \psi_{1,1,1}^{(3)} + \psi_{1,1,3}^{(3)} + \psi_{1,3,3}^{(3)}$, and $\psi_2^{(2)} \equiv \psi_{2,2}^{(2)}$, and $\psi_3^{(3)} \equiv \psi_{3,3,3}^{(3)}$.

$$\approx \begin{bmatrix} \frac{\dot\gamma^0}{\omega}(\sin \omega t - \sin \omega t') & 1 & 0 \\ 1 & -\frac{\dot\gamma^0}{\omega}(\sin \omega t - \sin \omega t') & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot\gamma^0 \cos \omega t' \qquad (4.5)$$

The second, approximate, form retains only those terms which contribute to first and second order in γ^0. Substituting this last expression into Equation (3.7), one obtains the following result for the shear stress:

$$\begin{aligned}\tau_{yx} &= -\eta' \dot\gamma^0 \cos \omega t - \eta'' \dot\gamma^0 \sin \omega t \\ &= -\eta_0 \frac{1 + \lambda_1\lambda_2 \omega^2}{1 + (\lambda_1 \omega)^2} \dot\gamma^0 \cos \omega t \\ &\quad - \eta_0 \frac{(\lambda_1 - \lambda_2)\omega}{1 + (\lambda_1 \omega)^2} \dot\gamma^0 \sin \omega t \qquad (4.6)\end{aligned}$$

This gives the expressions for $\eta'(\omega)$ and $\eta''(\omega)$, the in-phase and out-of-phase components of the complex viscosity $\eta^* = \eta' - i\eta''$. The shapes of η' and η'' given by the model are qualitatively correct. Note that $\eta(\gamma)$ and $\eta'(\omega)$ are identical functions as predicted by this model; also the model says that η'' and $\theta \dot\gamma/2$ should be identical. These two sets of functions are not found experimentally to be identical, but they are rather similar in shape and usually begin to depart from their zero-shear rate values at about the same value of the argument (within a factor of two). In Equation (4.6) we have shown how the shear stress oscillates with time; a similar calculation can be made for the normal stresses [compare Equations (7.7) to (7.12)].

Stress Growth at Inception of Steady State Shear Flow

Next we study the consequences of suddenly starting a steady state shear flow $v_x = \gamma y$ when the fluid has been at rest for $t < 0$. For this case $\dot\Gamma'_{ij}$ is given by Equation (4.1) for $t' \geqq 0$ and $\Gamma'_{ij} = 0$ for $t' < 0$. Substitution of this into Equation (3.7) then gives for the growth of the shear and normal stresses

$$\begin{aligned}\tau_{yx} &= -\eta^+ \dot\gamma = -\eta_0 \dot\gamma \frac{1 + \lambda_1\lambda_2 \dot\gamma^2}{1 + (\lambda_1 \dot\gamma)^2} \\ &\quad - \eta_0 \dot\gamma \frac{1 - (\lambda_2/\lambda_1)}{1 + (\lambda_1 \dot\gamma)^2} (\lambda_1 \dot\gamma \sin \dot\gamma t - \cos \dot\gamma t)\, e^{-t/\lambda_1}\end{aligned} \qquad (4.7)$$

$$\begin{aligned}\tau_{xx} - \tau_{yy} &= -\theta^+ \dot\gamma^2 = -2\eta_0 \dot\gamma^2 \frac{\lambda_1 - \lambda_2}{1 + (\lambda_1 \dot\gamma)^2} \\ &\quad + 2\eta_0 \lambda_1 \dot\gamma^2 \frac{1 - (\lambda_2/\lambda_1)}{1 + (\lambda_1 \gamma)^2} \left(\frac{1}{\lambda_1 \dot\gamma} \sin \dot\gamma t + \cos \dot\gamma t \right) e^{-t/\lambda_1}\end{aligned} \qquad (4.8)$$

According to Equation (4.7), τ_{yx} always rises to a maximum at a value of the strain $\dot\gamma t = \pi/2$ and then undergoes damped oscillations about the steady state value. Similarly, Equation (4.8) shows that $\tau_{xx} - \tau_{yy}$ rises to a maximum at $\dot\gamma t = \pi$ and then undergoes damped oscillations. Experimentally it has been found that the maximum in $\tau_{xx} - \tau_{yy}$ occurs at a larger value of the strain than that in τ_{xy} (Meissner, 1972; Hansen, 1974). However, the experimental curves do not oscillate except for the recent data taken by Laufer (1974). Also it is found experimentally that τ_{yx} rises monotonically to its steady state value for small values of γ (Huppler et al., 1967).

Stress Relaxation after Cessation of Steady Shear Flow

We next explore the relaxation of the stresses for $t > 0$ after a steady shearing flow $v_x = \dot\gamma y$ has suddenly been stopped at $t = 0$. Then the $\dot\Gamma'_{ij}$ are zero for all $t' > 0$, but for $t' < 0$ are given by Equation (4.1) with t set equal to zero. Then for this case Equation (3.7) gives

$$\tau_{yx} = -\eta^- \dot\gamma = -\eta_0 \dot\gamma \frac{1 - (\lambda_2/\lambda_1)}{1 + (\lambda_1 \dot\gamma)^2} e^{-t/\lambda_1} \qquad (4.9)$$

$$\begin{aligned}\tau_{xx} - \tau_{yy} &= -\theta^- \dot\gamma^2 \\ &= -2\eta_0 \lambda_1 \dot\gamma^2 \frac{1 - (\lambda_2/\lambda_1)}{1 + (\lambda_1 \dot\gamma)^2} e^{-t/\lambda_1}\end{aligned} \qquad (4.10)$$

By comparison with Equations (4.2) and (4.3) we find that $\tau_{yx}(t > 0)/\tau_{yx}(t < 0)$ has a discontinuity at $t = 0$ whereas the ratio $(\tau_{xx} - \tau_{yy})(t > 0)/(\tau_{xx} - \tau_{yy})(t < 0)$ does not. Thus the shear-stress relaxation curves lie below the corresponding normal-stress relaxation curves. Experimentally it is found (for example, Huppler et al., 1967) that the normal stresses relax slower than the shear stresses so that there is a point of agreement here. It is also known experimentally that the $\tau_{yx}(t > 0)/\tau_{yx}(t < 0)$ and the corresponding normal-stress-difference ratio both relax faster with increasing $\dot\gamma$. Equation (4.9) correctly predicts this for the shear stresses, but Equation (4.10) does not agree with experiment in this regard.

Steady Elongational Flow

For this irrotational flow $v_z = \dot\epsilon z$, $v_x = -\frac{1}{2} \dot\epsilon x$, $v_y = -\frac{1}{2} \dot\epsilon y$ where $\dot\epsilon$ is constant so that

$$\dot{\mathbf{\Gamma}}' = \begin{bmatrix} -\dot\epsilon & 0 & 0 \\ 0 & -\dot\epsilon & 0 \\ 0 & 0 & +2\dot\epsilon \end{bmatrix} \qquad (4.11)$$

Then from Equation (3.7) we find that

$$\tau_{xx} - \tau_{zz} = \bar\eta \dot\epsilon = 3\eta_0 \dot\epsilon \qquad (4.12)$$

That is, the elongational viscosity $\bar\eta$ (compare Lodge, 1964, p. 98) is just three times the zero-shear-rate viscosity. This kind of behavior—$\bar\eta$ independent of $\dot\epsilon$ and η decreasing with increasing $\dot\gamma$—has been observed by Stevenson (1972) and by Vinogradov et al. (1970) for several undiluted polymers. It is not difficult to show that when a sample at rest and unstressed prior to $t = 0$ is suddenly made to undergo steady state elongational flow after $t = 0$, Equation (3.7) predicts that the buildup to the steady state value in Equation (4.12) will take place as follows:

$$\tau_{xx} - \tau_{zz} = 3\eta_0 \dot\epsilon \left[1 - \left(1 - \frac{\lambda_2}{\lambda_1} \right) e^{-t/\lambda_1} \right] \qquad (4.13)$$

That is, the model predicts that the stresses develop in a monotone-increasing fashion (that is, with no overshoot), and this is qualitatively in accord with the experimental data on those fluids which can attain a steady state flow (Stevenson, 1972).

It is thus seen that the co-rotational Jeffreys model describes qualitatively most of the observed rheological phenomena. It may be useful as a simple 3-parameter model for doing exploratory hydrodynamic calculations in order to search for new phenomena or to estimate the order of magnitude of elastic effects.

5. THE GENERALIZED ZFD MODEL

Next we turn to the superposition of ZFD models given in Equations (3.8) and (3.9), which contains a set of time constants λ_k and a set of viscosity constants η_k, with $k = 1, 2, \ldots \infty$. Much is known about how these constants vary with k, both from molecular theories and from previous empirical studies on nonlinear viscoelastic models (see, for example, Spriggs and Bird, 1965; Spriggs, 1965; Bird and Carreau, 1968). We illustrate the technique of reducing the number of constants in Equation (3.9) by the following empiricism:

$$\eta_k = \eta_0 \frac{\lambda_k}{\Sigma\, \lambda_k}; \quad \lambda_k = \frac{\lambda}{k^\alpha} \tag{5.1}$$

This then gives a constitutive equation with three material constants

η_0 = zero-shear-rate viscosity
λ = characteristic time [not same as λ in Equation (1.6)]
α = dimensionless index

These constants have simple physical meanings and are easy to determine from $\eta(\dot{\gamma})$.

Let us now examine the steady state shearing flow material functions $\eta(\dot{\gamma})$ and $\theta(\gamma)$ [keep in mind that $\beta(\gamma) = -(1/2)\theta(\dot{\gamma})$]. These functions are obtained directly from Equations (4.2) and (4.3) by setting $\lambda_2 = 0$, replacing η_0 and λ_1 by η_k and λ_k, and then summing on k; this gives

$$\eta = \sum_{k=1}^{\infty} \frac{\eta_k}{1 + (\lambda_k \gamma)^2} = \frac{\eta_0}{\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{k^\alpha}{k^{2\alpha} + (\lambda \dot{\gamma})^2} \tag{5.2}$$

$$\theta = \sum_{k=1}^{\infty} \frac{2\eta_k \lambda_k}{1 + (\lambda_k \gamma)^2} = \frac{2\eta_0 \lambda}{\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{1}{k^{2\alpha} + (\lambda \dot{\gamma})^2} \tag{5.3}$$

in which $\zeta(\alpha)$ is the Riemann zeta function $\zeta(\alpha) = \sum_{1}^{\infty} k^{-\alpha}$, for which tables are available. These functions are identical to those given by Spriggs [1965, Equations (41) and (42)]. For large $\dot{\gamma}$ these summations can be performed by using the Euler-Maclaurin expansion to give

$$\frac{\eta}{\eta_0} = \frac{1}{\zeta(\alpha)} \left[\frac{\pi(\lambda \dot{\gamma})^{(1/\alpha)-1}}{2\alpha \sin\left(\frac{(\alpha+1)\pi}{2\alpha}\right)} \right] \quad [\text{large } \dot{\gamma}] \tag{5.4}$$

$$\frac{\theta \dot{\gamma}}{2\eta_0} = \frac{1}{\zeta(\alpha)} \left[\frac{\pi(\lambda \dot{\gamma})^{(1/\alpha)-1}}{2\alpha \sin\left(\frac{\pi}{2\alpha}\right)} - \frac{(\lambda \dot{\gamma})^{-1}}{2} \right] \quad [\text{large } \dot{\gamma}] \tag{5.5}$$

Equations (5.4) and (5.5) describe the power-law regions of the curves. From the above results we see that $\eta \rightarrow \eta_0$ for $\dot{\gamma} \rightarrow 0$ and that $(1/\alpha)$ corresponds to the power-law index in Equations (1.5) and (1.6). The time constant λ can be determined from the value of $\dot{\gamma}$ at which the power-law asymptote intersects the line $\eta = \eta_0$. Equations (5.2) and (5.3) describe the $\eta(\dot{\gamma})$ and $\theta(\dot{\gamma})$ curves fairly well. Some improvement might be obtained by replacing Equations (5.1) by more complicated expressions. The above procedure yields a constitutive equation which describes $\eta(\dot{\gamma})$ adequately for hydrodynamic calculations and will do a moderately good job of describing other material functions.

A somewhat different approach has been taken by Heindl and Giesekus (1972) who have used a continuous spectrum of relaxation times in lieu of our discrete spectrum in Equation (5.1). They chose their continuous spectrum so that η is described by a power-law [Equation (1.5)] for all $\dot{\gamma}$—that is, there is no η_0 in their constitutive equation, which then exhibits some strange behavior in the linear viscoelastic region.

6. THE GODDARD-MILLER MODEL

In this section we explore some of the consequences of using the first term of Equation (3.10), which we refer to as the Goddard-Miller model (1966). We make no assumptions as to the relaxation modulus $G_I(t - t')$. First we give the results for several shear-flow material functions in terms of G_I, and then we show how relations among these material functions can be obtained by eliminating G_I. In later sections we examine the higher terms in the Goddard expansion in Equation (3.10), but here we want to see to what extent rheological phenomena can be explained by the first term alone.

Steady Shear Flow, Oscillatory Shearing Motion, and Their Superposition

From Equations (4.1) and (4.5) and the definitions of the material functions above, it is not difficult to show that

$$\eta^* \equiv \eta' - i\eta'' = \int_0^\infty G_I(s)\, e^{-i\omega s}\, ds \tag{6.1}$$

$$\eta^\# \equiv \eta - i\frac{\theta \dot{\gamma}}{2} = \int_0^\infty G_I(s)\, e^{-i\dot{\gamma} s}\, ds \tag{6.2}$$

Here $\eta^*(\omega)$ is the complex viscosity, and for $\eta^\#(\dot{\gamma})$ we propose the name *complex viscometric function.* From Equations (6.1) and (6.2) we see that $\eta^*(\omega) = \eta^\#(\dot{\gamma})|_{\dot{\gamma} = \omega}$.

Next we want to study the rheological response when steady shear flow and oscillatory shearing motion are superposed so that the velocity gradient is given by

$$\dot{\gamma}(t) = \dot{\gamma}_m + Re\,\{\dot{\gamma}^0\, e^{i\omega t}\} \tag{6.3}$$

Here $\dot{\gamma}_m$ is the mean velocity gradient about which oscillations are performed; $\dot{\gamma}^0$ is a complex quantity which contains information about the amplitude and phase of the oscillatory motion. The matrix elements Q_{ij} are then given by Equation (2.27) with

$$\frac{1}{2}\int_{t'}^{t} \dot{\gamma}(t'')\, dt'' = \frac{1}{2}\gamma_m\,(t - t') + \frac{1}{2} Re \left\{ \frac{\dot{\gamma}^0}{i\omega} (e^{i\omega t} - e^{-i\omega t'}) \right\} \tag{6.4}$$

and

$$\dot{\mathbf{\Gamma}} = \begin{bmatrix} 2Q_{11}Q_{12} & Q_{11}Q_{22} + Q_{12}Q_{21} & 0 \\ Q_{11}Q_{22} + Q_{12}Q_{21} & 2Q_{22}Q_{21} & 0 \\ 0 & 0 & 0 \end{bmatrix} (\dot{\gamma}_m + Re\,\{\dot{\gamma}^0\, e^{i\omega t'}\}) \tag{6.5}$$

When this is substituted into the Goddard-Miller model and terms in the zeroth and first order of $\dot{\gamma}^0$ are retained, we find for the shear stress:

$$\tau_{yx} = -\int_0^\infty G_I(s) \Big[\dot{\gamma}_m \cos \dot{\gamma}_m s + (\cos \dot{\gamma}_m s)\, Re\,\{\dot{\gamma}^0\, e^{i\omega(t-s)}\} - \dot{\gamma}_m (\sin \dot{\gamma}_m s)\, Re \left\{ \frac{\dot{\gamma}^0}{i\omega} (e^{i\omega t} - e^{i\omega(t-s)}) \right\} \Big] ds \tag{6.6}$$

which is of the form $\tau_m + Re\,\{\tau^0\, e^{i\omega t}\}$ where τ_m is real and τ^0 is complex. Hence

$$\tau_m = -\,\dot{\gamma}_m \int_0^\infty G_I(s)\,\cos \dot{\gamma}_m\, s\, ds = -\,\eta(\,\dot{\gamma}_m)\,\dot{\gamma}_m \quad (6.7)$$

as expected; the effect of the superposed oscillations is contained in τ^0 which becomes

$$\begin{aligned}\tau^0 = -\,\dot{\gamma}^{\,0} \int_0^\infty G_I(s)\,[\,(\cos \gamma_m\, s)\; e^{-i\omega s} \\ -\,(\,\dot{\gamma}_m/i\omega)\,(\sin \dot{\gamma}_m\, s)\,(1 - e^{-i\omega s})\,]\; ds \\ \equiv -\,\eta^*\,(\omega;\,\dot{\gamma}_m)\;\dot{\gamma}^{\,0} \quad (6.8)\end{aligned}$$

Here a new complex material function $\eta^*(\omega;\,\dot{\gamma}_m)$ has been defined, analogously to η^* [see text after Equation (4.6); note that $\eta^*(\omega;\,0)$ is identical to $\eta^*(\omega)$]. The in-phase and out-of-phase components of $\eta^*(\omega;\,\dot{\gamma}_m)$ are then

$$\begin{aligned}\eta'(\omega;\,\dot{\gamma}_m) = \int_0^\infty G_I(s)\;[\cos \dot{\gamma}_m\, s\; \cos \omega s \\ -\,(\,\dot{\gamma}_m/\omega)\;\sin \dot{\gamma}_m\, s\; \sin \omega s]\; ds \quad (6.9)\end{aligned}$$

$$\begin{aligned}\eta''(\omega;\,\dot{\gamma}_m) = \int_0^\infty G_I(s)\;[\cos \dot{\gamma}_m\, s\; \sin \omega s \\ -\,(\,\dot{\gamma}_m/\omega)\;\sin \dot{\gamma}_m\, s\,(1 - \cos \omega s)]\; ds \quad (6.10)\end{aligned}$$

These functions have been studied experimentally by Osaki et al. (1965), Booij (1966), and Macdonald (1973); that $\eta''(\omega;\,\dot{\gamma}_m)$ should be negative for small ω and high $\dot{\gamma}_m$ was first predicted by Macdonald and Bird (1966), and experiments by Booij (1966) and Macdonald (1973) confirmed this prediction. Such negative values can also be described by Equation (6.10).

Stress-Growth and Stress-Relaxation in Shearing Flow

The growth and relaxation functions defined in Equations (4.7) to (4.10) are, for the Goddard-Miller model,

$$\left\{\begin{aligned} \eta^+\,(\,\dot{\gamma}, t) &= \int_0^t G_I(s)\;\cos \dot{\gamma} s\; ds \quad (6.11) \\ \frac{1}{2}\,\dot{\gamma}\,\theta^+(\,\dot{\gamma}, t) &= \int_0^t G_I(s)\;\sin \dot{\gamma} s\; ds \quad (6.12)\end{aligned}\right.$$

$$\left\{\begin{aligned} \eta^-(\,\dot{\gamma}, t) &= \int_t^\infty G_I(s)\;\cos \dot{\gamma}(s - t)\; ds \quad (6.13) \\ \frac{1}{2}\,\dot{\gamma}\,\theta^-(\,\dot{\gamma}, t) &= \int_t^\infty G_I(s)\;\sin \dot{\gamma}(s - t)\; ds \quad (6.14)\end{aligned}\right.$$

Equation (6.11) gives the first maximum of η^+ at a strain of $\dot{\gamma}\, t = \pi/2$ and the maximum of θ^+ at $\dot{\gamma} t = \pi$.

In connection with the stress growth experiment it is interesting to examine the behavior of the van Es and Christensen function (1973):

$$E(\,\dot{\gamma}, t) = \theta^+(\,\dot{\gamma}, t) - t\,\eta^+(\,\dot{\gamma}, t) + \int_0^\infty \eta^+(\,\dot{\gamma}, t')\; dt' \quad (6.15)$$

If the right side of Equation (6.15) is calculated for rheological models of the Bird-Carreau (1968) type, the result is (1) independent of $\dot{\gamma}$, and (2) a monotone increasing function of t. Result (1) is in disagreement with the experiments according to van Es and Christensen (1973) and Hansen (1974), and result (2) disagrees with the experimental data of van Es and Christensen, but not with those of Hansen. Hence the Bird-Carreau type of model is believed to be unsuitable for describing stress-growth experiments. This had already been expected from the calculations of Carreau, Macdonald, and Bird (1968). For the Goddard-Miller model we find

$$E(\,\dot{\gamma}, t) = \int_0^t G_I(s)\left[\frac{2}{\dot{\gamma}}\,\sin \dot{\gamma} s - \cos \dot{\gamma} s\right] ds \quad (6.16)$$

This function is (i) dependent on $\dot{\gamma}$, and (ii) not a monotone increasing function of t. Hence the Goddard-Miller model does not suffer from the same deficiency as the Bird-Carreau model. However, the η^+ and θ^+ functions obtained from the Goddard-Miller model exhibit oscillations with respect to time [see, for example, the graphs presented by Heindl and Giesekus (1972)], and such oscillatory behavior has not been observed except by Laufer (1974).

Relaxation between η and θ

Up to this point we have given several material functions in terms of G_I. Next we turn to the question of whether or not relations between two material functions can be obtained by eliminating G_I. The first one we examine is the relation between η and θ.

First we note that Equations (6.1) and (6.2) can be inverted by Fourier transformation to give $G_I(s)$ in terms of the material functions; for example,

$$G_I(s) = \frac{2}{\pi}\int_0^\infty \eta(\,\dot{\gamma}\,)\;\cos \dot{\gamma} s\; d\dot{\gamma} \qquad (s \geqq 0) \quad (6.17)$$

$$G_I(s) = \frac{1}{\pi}\int_0^\infty \dot{\gamma}\,\theta(\,\dot{\gamma}\,)\;\sin \dot{\gamma} s\; d\dot{\gamma} \quad (s > 0) \quad (6.18)$$

and similar expressions could be written for $\eta'(\omega)$ and $\eta''(\omega)$. If the Goddard-Miller equation gave a perfect representation of the rheological behavior of the fluid, then G_I could in principle be determined equally well from data on any one of the properties η, θ, η', or η''; however, data must be available over an enormously wide range of γ or ω. But the Goddard-Miller equation (only the first term of the Goddard expansion) cannot describe simultaneously both steady shear flow and oscillatory properties arbitrarily well. Hence in determining G_I, one has to decide which property one wishes most to describe accurately. If G_I is determined from Equation (6.17), then the viscosity can be described with arbitrarily good precision.

If Equations (6.17) and (6.18) are substituted into the expressions for η and θ given by Equation (6.2), then the following reciprocal relations are obtained:

$$\theta(\,\dot{\gamma}\,) = \frac{4}{\pi}\int_0^\infty \frac{\eta(\,\dot{\gamma}\,) - \eta(\,\dot{\gamma}')}{\dot{\gamma}'^2 - \dot{\gamma}^{\,2}}\; d\dot{\gamma}' \qquad (\dot{\gamma} > 0) \quad (6.19)$$

$$\eta(\,\dot{\gamma}\,) - \eta_\infty = \frac{1}{\pi}\int_0^\infty \frac{\dot{\gamma}'^2\,\theta(\,\dot{\gamma}')}{\dot{\gamma}'^2 - \dot{\gamma}^{\,2}}\; d\dot{\gamma}' \quad (\dot{\gamma} \geqq 0) \quad (6.20)$$

in which η_∞ stands for the limit of $\eta(\,\dot{\gamma}\,)$ as $\dot{\gamma}$ goes to ∞. (To get these relations one needs to know the integral $\int_0^\infty \sin xs \cos ys\, ds = x/(x^2 + y^2)$.) The relations for $\eta'(\omega)$ and $\eta''(\omega)$ (or for associated linear viscoelastic functions) analogous to Equations (6.19) and (6.20) are slight generalizations of the Kramers-Kronig relations (compare Ferry, 1970, p. 74) in that we do not assume that η goes to 0 as $\dot{\gamma}$ goes to ∞; relations of this type were used by Kramers (1927) and Kronig (1926) in connection with the atomic theory of dispersion of light.

Equation (6.19) is interesting since it suggests that normal stresses can be predicted from viscosity measurements. Recently Abdel-Khalik, Hassager, and Bird (1974) have compared this equation with experimental data on the fluids given in Table 2. It was found that for six polymer

Table 2. Relation Between η and θ

$$\theta(\gamma) = K \cdot \frac{4}{\pi} \int_0^\infty \frac{\eta(\dot\gamma) - \eta(\gamma')}{\dot\gamma'^2 - \dot\gamma^2}\, d\dot\gamma$$

Fluid	Authors	Constant K needed in above equation to get best agreement with data
I. Polymer melts		
1. LDPE 160°C	Chen and Bogue (1972)	3
2. LDPE 180°C	Chen and Bogue (1972)	3
3. LDPE 200°C	Chen and Bogue (1972)	3
4. HDPE 160°C	Ballenger et al. (1971)	3
5. Polystyrene 180°C	Ballenger et al. (1971)	3
6. Phenoxy-A 212°C	Marsh (1967)	2
II. Polymer solutions		
1. 5% Polystyrene in Aroclor 1242	Ashare (1968)	2
2. 2% PIB in Primol 355	Huppler, Ashare, and Holmes (1967)	2
3. 0.75% Polyacrylamide in 95-5 water-glycerine	Marsh (1967)	2
III. 7% Aluminum soap in decalin and *m*-cresol	Huppler, Ashare, and Holmes (1967)	2

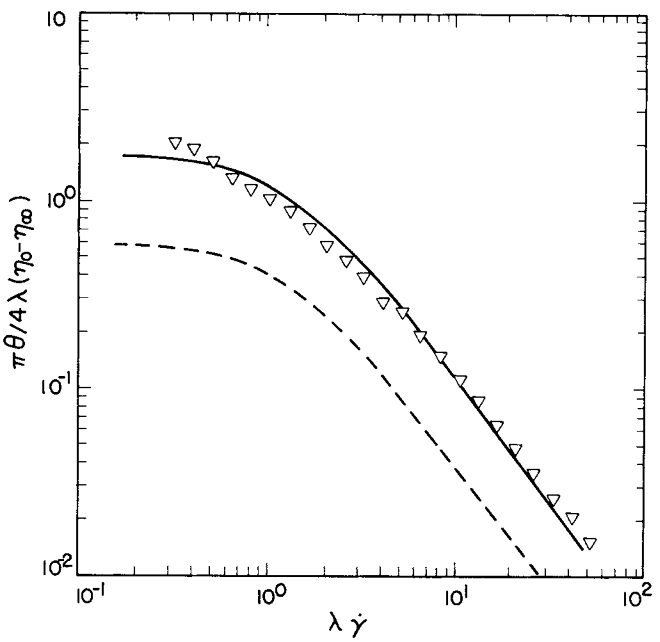

Fig. 4. Primary normal stress function for low density polyethylene at 160°C (η_0, η_∞, and λ are parameters in the Carreau viscosity equation, Equation (1.6), given in the caption of Figure 1)

▽ Experimental data (Chen and Bogue, 1972).

--- The Goddard-Miller Model, Equation (6.19); viscosity data given in Figure 1.

—— Equation (6.19) multiplied by the empirical constant $K = 3$

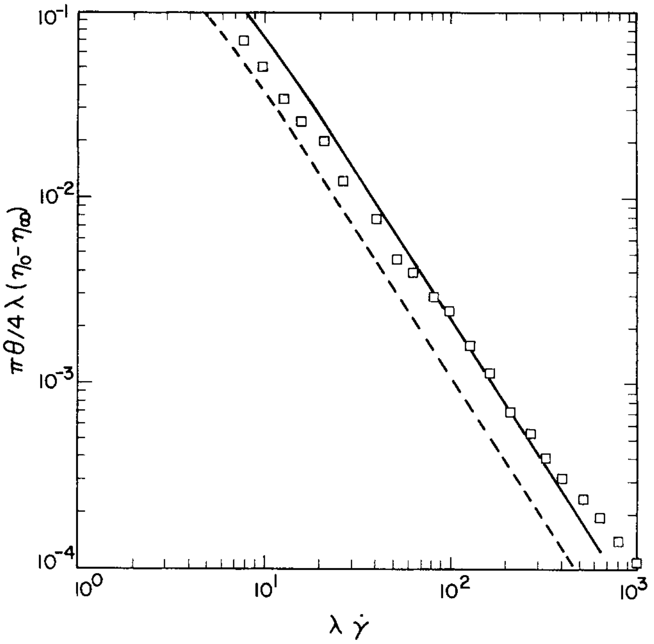

Fig. 5. Primary normal stress function for 2% polyisobutylene in Primol 355 (η_0, η_∞, and λ are given in the caption of Figure 2).

□ Experimental data (Huppler, Ashare, and Holmes, 1967).

--- The Goddard-Miller Model, Equation (6.19); viscosity data given in Figure 2).

—— Equation (6.19) multiplied by the empirical constant $K = 2$.

melts, three polymer solutions, and one soap solution, with a wide range of physical and chemical properties, Equation (6.19) consistently predicted θ-values lower than the experimental values by a factor of about 2 or 3. Some sample comparisons are shown in Figures 4 to 6. It seems that Equation (6.19) with $4/\pi$ replaced by $8/\pi$ for solutions and $12/\pi$ for melts can be a useful relation for estimating $\theta(\dot\gamma)$ when $\eta(\dot\gamma)$ is known. The fact that fluids of such diverse properties have $\theta(\dot\gamma)$ related in such a simple way to $\eta(\dot\gamma)$ gives additional support to the method proposed earlier by Bird (1965), in which a time constant determined from $\eta(\dot\gamma)$ is used for the correlation of elastic effects. Additionally, the study of Equation (6.19) has established the fact that melts and solutions behave in a similar way, thereby supporting the idea that information known about the solution phenomena can be taken over for melts.

Relations Between Other Shear-Flow Functions

Many other relations can be derived which connect the various material functions. According to the Goddard-Miller equation, η^- and θ^- are related by

$$\frac{\partial}{\partial t}\theta^- = -2\eta^- \qquad (6.21)$$

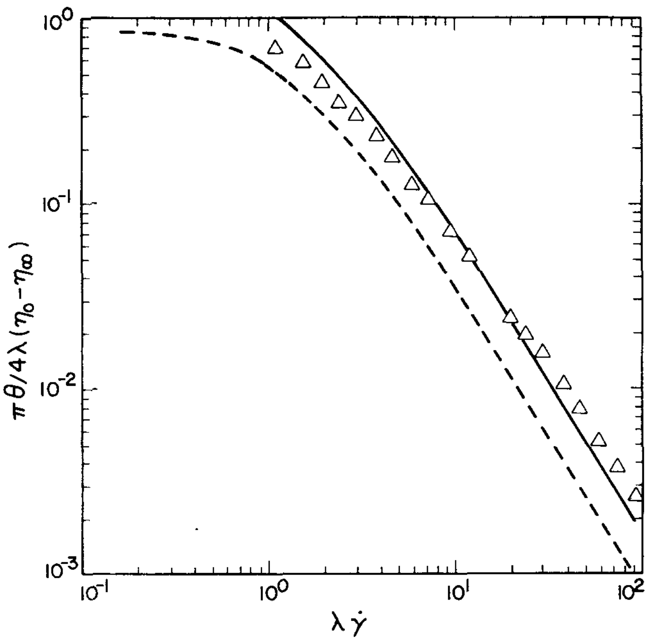

Fig. 6. Primary normal stress function for 7% aluminum soap in decalin and *m*-cresol (η_0, η_∞, and λ are given in the caption of Figure 2).

△ Experimental data (Huppler, Ashare, and Holmes, 1967).

--- The Goddard-Miller Model, Equation (6.19); viscosity data given in Figure 3).

—— Equation (6.19) multiplied by the empirical constant $K = 2$.

When this is integrated from $t = 0$ to $t = \infty$ and when it is assumed that the stresses are continuous at $t = 0$, we get

$$\theta(\dot{\gamma}) = 2\int_0^\infty \eta^-(\dot{\gamma}, t)\, dt \qquad (6.22)$$

This same relation can be derived by comparing Equations (6.13) and (6.2). Equation (6.22) has also been derived by Hassager and Bird (1972) from kinetic theory arguments for a dilute solution of flexible macromolecules with nonlinear stretchability and hydrodynamic interaction. Experiments by Harris (1970) and by Stratton and Butcher (1971) indicate, however, that the time-integral of η^- in Equation (6.22) exceeds the steady state normal stress function $\theta(\dot{\gamma})$ by 20 to 100%.

Several other relations which have to our knowledge not been tested are

$$\left\{\begin{aligned} \eta^+(\dot{\gamma}, t) &= \frac{1}{\pi}\int_0^\infty \eta(\dot{\gamma}')\left[\frac{\sin(\dot{\gamma}'+\dot{\gamma})t}{\dot{\gamma}'+\dot{\gamma}} + \frac{\sin(\dot{\gamma}'-\dot{\gamma})t}{\dot{\gamma}'-\dot{\gamma}}\right] d\dot{\gamma}' \qquad (6.23) \\ \frac{1}{2}\dot{\gamma}\,\theta^+(\dot{\gamma}, t) &= \frac{1}{\pi}\int_0^\infty \eta(\dot{\gamma}')\left[\frac{1-\cos(\dot{\gamma}'+\dot{\gamma})t}{\dot{\gamma}'+\dot{\gamma}} - \frac{1-\cos(\dot{\gamma}'-\dot{\gamma})t}{\dot{\gamma}'-\dot{\gamma}}\right] d\dot{\gamma}' \qquad (6.24) \end{aligned}\right.$$

which relate the stress-growth functions to the steady-flow material functions, and

$$\left\{\begin{aligned} (\eta - \eta^+) &= \eta^- \cos\dot{\gamma}t - \frac{1}{2}\dot{\gamma}\,\theta^- \sin\dot{\gamma}t \qquad (6.25) \\ \frac{1}{2}\dot{\gamma}(\theta - \theta^+) &= \eta^- \sin\dot{\gamma}t + \frac{1}{2}\dot{\gamma}\,\theta^- \cos\dot{\gamma}t \qquad (6.26) \end{aligned}\right.$$

which interrelate the stress-growth and stress-relaxation functions.

Equations (6.19) through (6.26) do not contain $G_1(t - t')$. Although they are not found to be exactly followed experimentally, empirical modifications of them may have predictive value. Also systematic studies of deviations from these relations may be useful in learning how to approximate higher terms in the Goddard expansion. This will be discussed further in Section 10.

In this section we have discussed only shearing flows. It is expected that similar interrelations can be obtained within other classes of flows. The Goddard-Miller model predicts a constant elongational viscosity given by

$$\bar{\eta} = 3\int_0^\infty G_1(s)\, ds = 3\eta_0 \qquad (6.27)$$

Hence the Goddard-Miller model is consistent with the data of Stevenson (1972) and others which show η decreasing with $\dot{\gamma}$ but $\bar{\eta}$ independent of the elongation rate (see Figure 7).

Our conclusion is that the Goddard-Miller (1966) model [that is, the first term of Equation (3.10)] with $G_1(t - t')$ so chosen that the non-Newtonian viscosity $\eta(\dot{\gamma})$ is well described, is a very useful constitutive equation for hydrodynamic calculations, particularly for those flows in which an accurate portrayal of $\eta(\dot{\gamma})$ is essential and in which viscoelastic phenomena play a secondary role. The function $G_1(t - t')$ can be realistically approximated by a superposition of exponentials (the generalized ZFD model) or roughly approximated by a single exponential added to a delta function (the co-rotational Jeffreys model). What is really needed to test the utility of the Goddard-Miller model is a series of well-chosen nonviscometric flow experiments coupled with the necessary computer solutions.

7. THE GODDARD MEMORY-INTEGRAL EXPANSION

As the final step in the generalization process we arrive at the Goddard memory-integral expansion in Equation (3.10). $G_1(t - t')$ is then identical to the relaxation modulus of linear viscoelasticity (compare Ferry, 1970, p. 8); that is, $G_1(t - t')$ is determined from η^*-data by inversion of Equation (6.1) or from the appropriate analysis of other linear viscoelastic data. The higher G's describe the nonlinear viscoelastic effects. However, as was seen in the foregoing section even the first term alone gives a very good qualitative description of many rheological phenom-

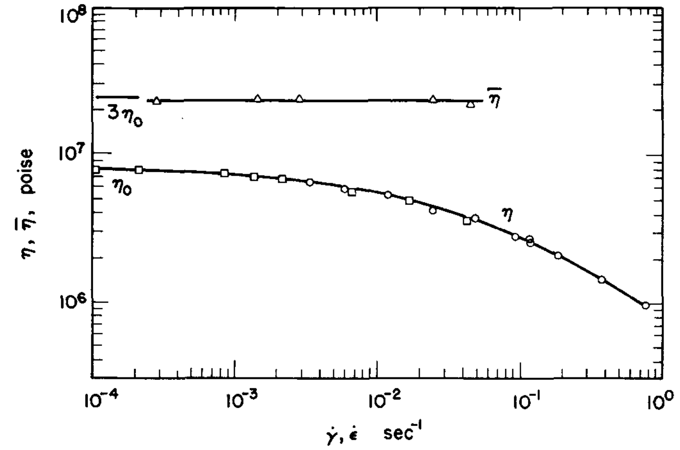

Fig. 7. Stevenson's (1972) data on Butyl 035 at 100°C (Enjay Chemical Company's 97% isobutylene and 3% isoprene), showing $\bar{\eta}$ to be constant and η undergoing shear thinning.

ena. Consequently, we feel that the complete Goddard expansion will prove useful for the following purposes:

1. It is possible that for some categories of flows the expansion can be collapsed; in fact, Goddard (1967) has already shown that for steady-shearing flows his series gives, after a lengthy derivation, the Criminale-Ericksen-Filbey (1958) or "CEF" equation [see also Ericksen (1960)]:

$$\boldsymbol{\tau} = - \eta\dot{\boldsymbol{\gamma}} - \frac{1}{2}(\theta + 2\beta)\dot{\boldsymbol{\gamma}}^2 + \frac{1}{2}\theta\frac{\mathcal{D}}{\mathcal{D}t}\dot{\boldsymbol{\gamma}} \quad (7.1)$$

in which the viscometric material functions $\eta(\dot{\gamma})$, $\theta(\dot{\gamma})$, and $\beta(\dot{\gamma})$ are consistent with the definitions given in Equations (4.2), (4.3), (4.4); the scalar $\dot{\gamma}$ is defined as the magnitude of the tensor $\dot{\boldsymbol{\gamma}}$ $\left(\text{that is } \dot{\gamma} = \sqrt{\frac{1}{2}(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}})}\right)$

2. It has already been pointed out by Rivlin and Sawyers (1971) that if one assumes that various strain events in the past do not interact with one another then the Green-Rivlin and Coleman-Noll expansions can be collapsed into the K-BKZ fluid (Kaye, 1962, 1965); Bernstein, Kearsley, and Zapas, 1964); in doing this use is made of theorems provided by Chacon and Friedman (1965) and by Martin and Mizel (1964). A similar collapsing of the Goddard series yields

$$\boldsymbol{\tau} = - \int_{-\infty}^{t} [\alpha_1 (II_{\dot{\gamma}}, III_{\dot{\gamma}})\ \dot{\boldsymbol{\Gamma}}(t')$$
$$+ \alpha_2(II_{\dot{\gamma}}, III_{\dot{\gamma}})\ \dot{\boldsymbol{\Gamma}}(t') \bullet \dot{\boldsymbol{\Gamma}}(t')]:dt' \quad (7.2)$$

in which α_1 and α_2 are functions of the second and third invariants of the $\dot{\boldsymbol{\gamma}}$-tensor. Equation (7.2), which was suggested recently by LeRoy and Pierrard (1973) may prove helpful as a basis for useful empiricisms.

3. Because the first term in the Goddard expansion gives a major contribution to many rheological properties, it seems reasonable to expect that molecular theories should be expressed in terms of this expansion rather than in terms of other expansions which are available. This point is discussed at length in the next two sections.

4. It may be possible to approximate G_{II}, G_{III}, G_{IV}, . . . by using the results of molecular theories as a guide. If so, such a method would enable one systematically to interrelate higher-order effects, thereby winning a certain amount of predictive power. An example of what we mean by this is given in Section 10.

The earlier memory-integral expansions of Green and Rivlin (1957) and Coleman and Noll (1961) appear to be less useful than the Goddard expansion inasmuch as in those earlier expansions the first term does not have shear-rate-dependent material functions in steady shear flow, nor can the first term describe stress overshoot and other phenomena. Goddard has made several comments about the previously proposed expansions which are worth quoting: ". . . above some critical shear rate, the 'higher order' fluid models previously proposed could never accurately represent the behavior of certain fluids, *no matter how many higher-order terms were retained*" (Goddard, 1967, p. 396); "The difference between the present *n*th order fluid model and that of previous workers is now more evident. For steady viscometric flows the present model gives higher-order terms for the material functions, each of which is composed of a power of $\dot{\gamma}$ multiplied by a *Fourier* integral of a hereditary function. On the other hand, the expansions of Coleman and Noll, or of Green and Rivlin, consist simply of a series in powers of $\dot{\gamma}$" (Goddard, 1967, p. 395).

Let us now give for later use a sampling of results for the Goddard series. For steady state shearing flow:

$$\eta = \int_0^\infty G_I(s) \cos \dot{\gamma}s\, ds$$
$$+ \dot{\gamma}^2 \int_0^\infty \int_0^\infty \int_0^\infty [2G_{III}(s, s', s'') \cos \gamma s \cos \gamma(s' - s'')$$
$$+ G_{IV}(s, s', s'') \cos \dot{\gamma}(s'' - s' + s)]\, ds''\, ds'\, ds + \ldots \quad (7.3)$$

$$\frac{1}{2}\dot{\gamma}\,\theta = \int_0^\infty G_I(s) \sin \gamma s\, ds$$
$$+ \dot{\gamma}^2 \int_0^\infty \int_0^\infty \int_0^\infty [2G_{III}(s, s', s'') \sin \dot{\gamma}s \cos \dot{\gamma}(s' - s'')$$
$$+ G_{IV}(s, s', s'') \sin \dot{\gamma}(s'' - s' + s)]\, ds''\, ds'\, ds + \ldots \quad (7.4)$$

$$\dot{\gamma}\,\beta = - \int_0^\infty G_I(s) \sin \gamma s\, ds$$
$$+ \dot{\gamma} \int_0^\infty \int_0^\infty G_{II}(s, s') \cos \dot{\gamma}(s - s')\, ds'\, ds + \ldots \quad (7.5)$$

[compare Goddard (1967), Equations (3.25), (3.26), (3.29) to (3.32)]. These expressions illustrate the second of Goddard's quotations above.

For small-amplitude oscillatory motion, the η' and η'' defined in Equation (4.6) are given by Equation (6.1). The corresponding second-order quantities (θ', θ'', θ^d) describing the oscillatory normal stresses are defined by

$$\tau_{xx} - \tau_{yy} = - \theta' \dot{\gamma}^{02} \cos 2\omega t - \theta'' \dot{\gamma}^{02} \sin 2\omega t - \theta^d \dot{\gamma}^{02} \quad (7.6)$$

with a similar expression for $\tau_{yy} - \tau_{zz}$ and the quantities β', β'', β^d. The Goddard expansion gives

$$\left\{\begin{aligned} \theta' &= \frac{1}{\omega}\int_0^\infty G_I(s)\ (\sin 2\omega s - \sin \omega s)\, ds && (7.7)\\ \theta'' &= \frac{1}{\omega}\int_0^\infty G_I(s)\ (\cos \omega s - \cos 2\omega s)\, ds && (7.8)\\ \theta^d &= \frac{1}{\omega}\int_0^\infty G_I(s) \sin \omega s\, ds && (7.9) \end{aligned}\right.$$

$$\left\{\begin{aligned} \beta' &= -\frac{1}{2}\theta' + \frac{1}{2}\int_0^\infty \int_0^\infty G_{II}(s, s') \\ &\qquad \cos \omega(s + s')\, ds'\, ds && (7.10)\\ \beta'' &= -\frac{1}{2}\theta'' + \frac{1}{2}\int_0^\infty \int_0^\infty G_{II}(s, s') \\ &\qquad \sin \omega(s + s')\, ds'\, ds && (7.11)\\ \beta^d &= -\frac{1}{2}\theta^d + \frac{1}{2}\int_0^\infty \int_0^\infty G_{II}(s, s') \\ &\qquad \cos \omega(s - s')\, ds'\, ds && (7.12) \end{aligned}\right.$$

From the first set of relations we find

$$\omega\, \theta^d = \eta'' \quad (7.13)$$

$$i\omega\theta^* = \eta^*(\omega) - \eta^*(2\omega) \quad (7.14)$$

in which $\theta^* = \theta' - i\theta''$. Equation (7.13) was obtained by Lodge (1961, 1964) for his rubberlike liquid model and by Williams and Bird (1964) for an Oldroyd model; Spriggs (1966) obtained Equation (7.14) from the Coleman-Noll (1961) theory of second-order viscoelasticity. Both of these relations have been experimentally confirmed by Christiansen and Leppard (1974), who also made the first experimental measurements of β', β'', β^d. Earlier experiments by Akers and Williams (1969) verified Equation (7.13) and, in the very low frequency region, Equation (7.14). Additional confirming data have been reported by Kajiura, Endō, and Nagasawa (1973).

For steady elongational flow the Goddard expansion gives

$$\bar{\eta} = 3 \int_0^\infty G_I(s)\, ds + 3\dot{\epsilon} \int_0^\infty \int_0^\infty G_{II}(s, s')\, ds'\, ds + 9\dot{\epsilon}^2 \int_0^\infty \int_0^\infty \int_0^\infty (2G_{III}(s, s', s'') + G_{IV}(s, s', s''))\, ds''\, ds'\, ds + \ldots \tag{7.15}$$

Hence the Trouton relation $\bar{\eta}/\eta_0 = 3$ is given at the first approximation, with higher contributions given as a power series in the elongation rate $\dot{\epsilon}$. Stevenson (1972) has summarized the $\bar{\eta}$ data on undiluted polymers taken up through 1971 and found that the experimental $\bar{\eta}(0)/\eta_0$ values varied from 2.6 to 3.2; a few fluids studied showed an increase in $\bar{\eta}$ with $\dot{\epsilon}$.

It will clearly be very difficult to deduce the form of G_{II}, G_{III}, G_{IV}, . . . from rheological data using expressions such as Equations (7.3) through (7.15). The possibility of guessing reasonable forms for the G's is discussed in Section 10.

Finally we must not lose sight of the fact that the stress-tensor expression must be inserted into the equation of motion in order to solve fluid dynamical problems. An expression as complicated as the Goddard expansion in Equation (3.10) presents formidable obstacles. For the present we visualize the principal value of the Goddard series as providing a useful framework for interpreting and interrelating rheological data. But we feel that the first term, that is, the Goddard-Miller model, merits consideration as a helpful empiricism for use in computer solution of flow problems.

8. COMPARISON WITH RIGID-DUMBBELL KINETIC THEORY

In this and the next section we obtain some additional information about the Goddard expansion [Equation (3.10)] by using kinetic-theory results for dilute solutions of macromolecules. By writing the kinetic-theory expression for the stress tensor in the form of the Goddard series, we can obtain expressions for the G's in terms of the structural parameters describing the macromolecular solutions. We can also get some insight as to the convergence of the Goddard expansion in various flow situations. In this section we summarize the comparison with the kinetic-theory results for rigid-dumbbell solutions made by Abdel-Khalik, Hassager, and Bird (1974), and in the next section with those for elastic-dumbbell solutions, these models being sufficiently simple that extensive kinetic-theory results are available.

A macromolecule is here idealized as a rod of length L with a bead at each end. Each bead of this dumbbell has a friction coefficient ζ, and there are n_0 macromolecules per unit volume, and the solution is so dilute that macromolecule-macromolecule interactions may be neglected. The solvent is Newtonian with a viscosity η_s. The structural parameters ζ and L always appear in the grouping $\lambda = \zeta L^2/12kT$, which is a time constant for the macromolecular solution.

For this simple dilute solution model Armstrong and Bird (1973) obtained a perturbation solution for arbitrary time-dependent, irrotational flows [see Equation (22) of their paper]. That result may now be reinterpreted, in light of Section 2 of this paper, as being the tensor components as seen by an observer in a co-rotating frame. The Armstrong-Bird expression may then be made applicable to any flows by replacing $\dot{\gamma}_{ij}(t')$ everywhere by $\dot{\Gamma}_{ij}(t')$. When this is done, one obtains directly

$$\boldsymbol{\tau} = \boldsymbol{\tau}_s - n_0\, kT\, \lambda \Big[\frac{2}{5} \dot{\mathbf{\Gamma}} + \frac{3}{5\lambda} \int_{-\infty}^{t} \exp\left(-\frac{t - t'}{\lambda}\right) \dot{\mathbf{\Gamma}}'\, dt' + \frac{6}{35} \int_{-\infty}^{t} \exp\left(-\frac{t - t'}{\lambda}\right) (\dot{\mathbf{\Gamma}} \bullet \dot{\mathbf{\Gamma}}' + \dot{\mathbf{\Gamma}}' \bullet \dot{\mathbf{\Gamma}})\, dt' + \frac{9}{70\lambda} \int_{-\infty}^{t} \int_{-\infty}^{t'} \exp\left(-\frac{t - t''}{\lambda}\right) (\dot{\mathbf{\Gamma}}' \bullet \dot{\mathbf{\Gamma}}'' + \dot{\mathbf{\Gamma}}'' \bullet \dot{\mathbf{\Gamma}}')\, dt''\, dt' + \ldots \Big] \tag{8.1}$$

in which $\dot{\Gamma}_{ij} \equiv \dot{\Gamma}_{ij}(t, t) = \dot{\gamma}_{ij}(t)$, and $\boldsymbol{\tau}_s = -\eta_s \dot{\boldsymbol{\gamma}}$ is the solvent contribution to the stress tensor. The complete third-order term may be written out as well by analogy with Equation (22) of Armstrong and Bird (1973).

When the result in Equation (8.1) is compared with the Goddard expansion, one finds after some minor rearrangements that (compare Abdel-Khalik, Hassager, and Bird, 1974):

$$G_I(t - t') = 2\eta_s\, \delta(t - t') + \frac{n_0\, kT\, \lambda}{5} \left[4\delta(t - t') + \frac{3}{\lambda} \exp\left(-\frac{t - t'}{\lambda}\right) \right] \tag{8.2}$$

$$G_{II}(t - t', t - t'') = \frac{n_0\, kT\, \lambda}{70} \left[24\delta(t - t') + \frac{9}{\lambda} g(t', t'') \right] \exp\left(-\frac{t - t''}{\lambda}\right) \tag{8.3}$$

$$\vdots$$

in which $g(t', t'')$ is 1 if $-\infty < t'' \leqq t'$ and is zero otherwise. The first two terms of the Goddard series with G_I and G_{II} given by Equations (8.2) and (8.3) thus reproduce all the first- and second-order viscoelastic results known for rigid-dumbbell solutions (compare Bird, Warner, and Evans, 1971). Note that $G_I(t - t')$ for the rigid-dumbbell expansion has the same form as the relaxation modulus for the co-rotational Jeffreys model in Equation (3.7).

All that has been done so far is to recast the kinetic theory results into the form provided by the Goddard series. There are, as we have indicated earlier, other memory-integral expansions available, and one might well inquire as to whether the Goddard expansion offers any special advantage in the representation of kinetic theory results. In the Armstrong-Bird (1973) paper, the kinetic theory results were recast in the form provided by a memory integral expansion of the form developed by Green and Rivlin (1957, 1960), Green, Rivlin, and Spencer (1959), Coleman and Noll (1961), and Pipkin (1964). This GRSCNP expansion, given as Equation (3) in the publication of Armstrong and Bird (1973), has the same general form as the Goddard expansion except that the kinematic tensor used is $\boldsymbol{\gamma}^{[1]}$ instead of $\dot{\mathbf{\Gamma}}$; here $\boldsymbol{\gamma}^{[1]}$ is the time derivative of the Cauchy strain tensor [defined by Equation (A8)].

In Figures 8 to 11 we show the exact kinetic theory results for η, θ, β, and $\bar{\eta}$, along with the results obtained using one, two, or three terms in the Goddard and GRSCNP expansions. For shear flow the Goddard series has been given explicitly in Equations (7.3), (7.4), and

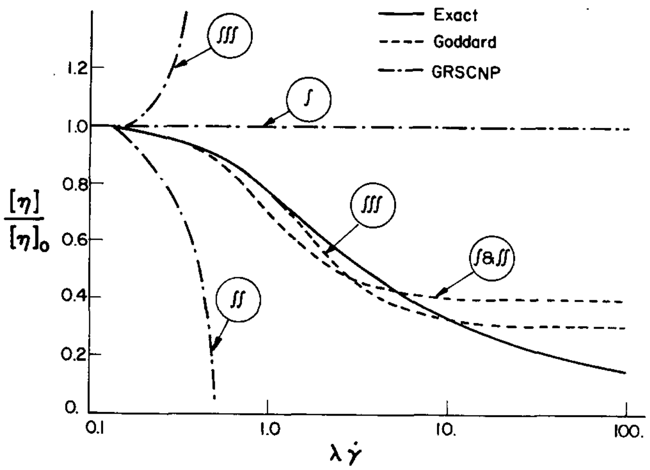

Fig. 8. Comparison of the exact intrinsic viscosity [as computed by Stewart and Sørensen (1972)] for solutions of rigid dumbbells with the results obtained using a finite number of terms of the Goddard and the GRSCNP expansions. The number of integrals indicates the number of terms used in the expansions.

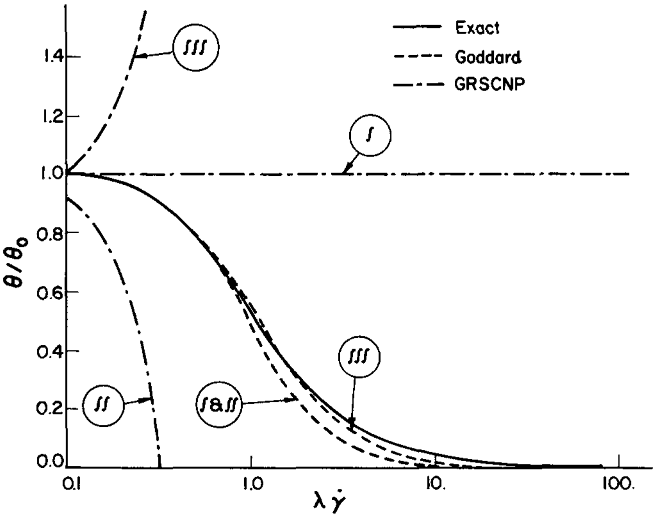

Fig. 9. Comparison similar to Figure 8, for primary normal stress function $\theta(\dot{\gamma})$.

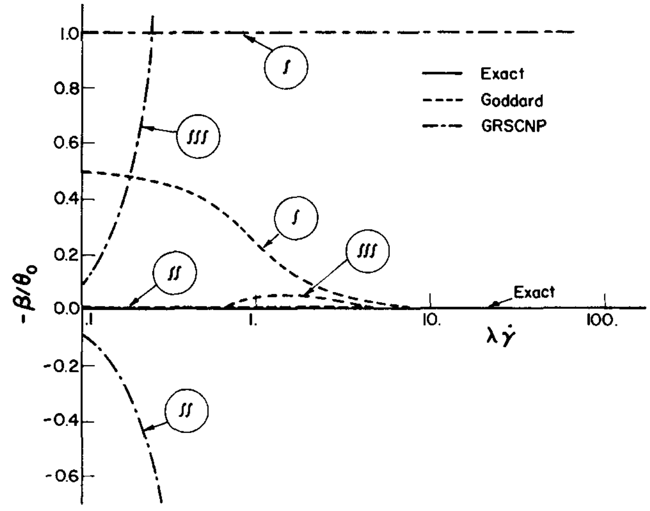

Fig. 10. Comparison similar to Figure 8, for secondary normal stress function $\beta(\dot{\gamma})$.

(7.5). It is evident that each successive term in the Goddard series gives an improved representation of the η, θ, and β curves and that the series provides a useful extrapolation beyond the range for which the original kinetic theory calculations are valid (the Armstrong-Bird third-order kinetic-theory expressions are probably valid only up to at most $\lambda\dot{\gamma} = 0.4$). For elongational flow the Goddard expansion, as may be seen in Equation (7.15), becomes a power series and thus has a radius of convergence of $\lambda\dot{\epsilon} = 1$. Nonetheless, this expansion does seem to be better than the GRSCNP-expansion in the range $\lambda\dot{\epsilon} < 1$.

From the above development we can conclude that (1) the Goddard series is useful for presenting macromolecular kinetic theory results; (2) comparison of kinetic theory with the Goddard expansion enables us to get some information about the form of the G's, which might later provide useful empirical expressions for the G's; (3) the choice of the kinematic tensor used in a memory-integral expansion is quite important as far as the convergence of the series is concerned; and (4) although a memory-integral expansion may have excellent convergence properties for one flow it may not necessarily have such excellent properties for all other flows.

9. COMPARISON WITH ELASTIC DUMBBELL KINETIC THEORY

In this section we wish to show how a classical constitutive equation, the equation for a dilute suspension of elastic dumbbells (or alternatively the Lodge (1964) rubberlike liquid with a single exponential memory function) may be put in the form of a Goddard expansion. As in the previous section, a macromolecule is idealized as a dumbbell suffering Brownian motion. The two beads, however, are connected by a Hookean spring of zero natural length and force constant H. This model has a zero shear rate viscosity $\eta_0 = \eta_s + \eta_0 kT \lambda_H$ with the time constant $\lambda_H = \zeta/4H$. The model exhibits shear-rate-independent viscosity and primary normal stress coefficient and may therefore be expected not to fit very naturally into the co-rotational formalism. In particular, we are here thinking of the fact that the Goddard-Miller equation (the first term of the Goddard expansion) will always predict that a fluid with a shear rate independent viscosity exhibits no normal stress effects [Equation (6.19)], contrary to the behavior of the elastic dumbbell suspension. When more terms in the Goddard expansion are included, however, the approximation is systematically improved as we shall see.

It is well known (for example, Lodge and Wu, 1971) that the rheological equation of state for an elastic dumbbell suspension is

$$\boldsymbol{\tau} = \boldsymbol{\tau}_s - \frac{\eta_0}{\lambda_H}\int_{-\infty}^{t} \exp\left(-\frac{t-t'}{\lambda_H}\right)\boldsymbol{\gamma}'_{[1]}\,dt' \quad (9.1)$$

where $\dot{\boldsymbol{\gamma}}'_{[1]} = \boldsymbol{\gamma}_{[1]}(t, t')$ is the negative of the derivative of the Finger strain tensor with respect to t' (defined by Equation (A8) of Appendix A). By use of Equation (A11) we may immediately rewrite Equation (9.1) formally as

$$\boldsymbol{\tau} = \boldsymbol{\tau}_s - \frac{\eta_0}{\lambda_H}\int_{-\infty}^{t} \exp\left(-\frac{t-t'}{\lambda_H}\right)\mathbf{R}'\cdot\dot{\boldsymbol{\Gamma}}'\cdot\mathbf{R}'^{\dagger}\,dt' \quad (9.2)$$

in which $\mathbf{R}' = \mathbf{R}(t, t')$ is given by Equations (A13) to (A15):

$$\mathbf{R}' = \sum_{n=0}^{\infty} \mathbf{R}'_n \quad (9.3)$$

where

$$\mathbf{R}'_0 = \boldsymbol{\delta}\,, \quad (9.4)$$

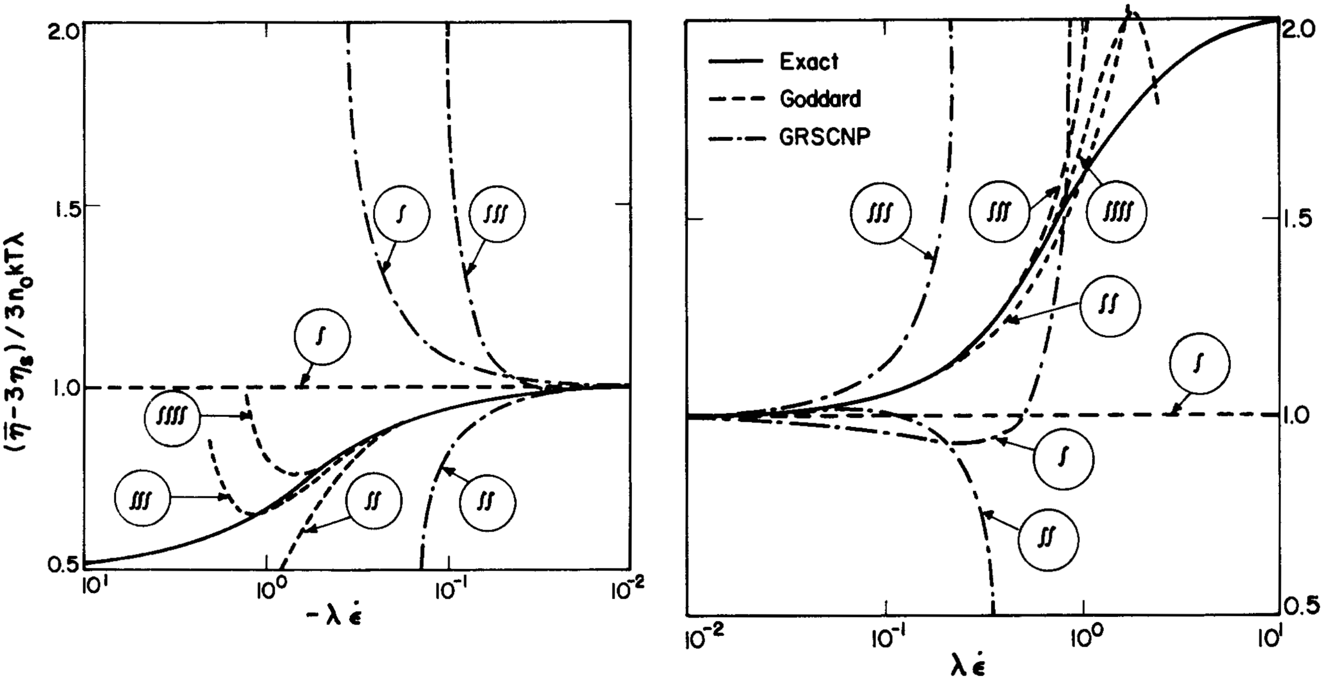

Fig. 11. Comparison of the exact elongational viscosity [as computed from the results of Bird, Johnson, and Stevenson (1970)] for solutions of rigid dumbbells with the results obtained using a finite number of terms of the Goddard and the GRSCNP expansions.

$$\mathbf{R}_n' = \left(\frac{1}{2}\right)^n \int_{t'}^{t}\int_{t'}^{t_1}\cdots\int_{t'}^{t_{n-1}} \dot{\boldsymbol{\Gamma}}_1 \bullet \dot{\boldsymbol{\Gamma}}_2 \bullet \cdots \dot{\boldsymbol{\Gamma}}_n \, dt_n \cdots dt_2 dt_1 ; \quad n \geqq 1 \tag{9.5}$$

and $\dot{\boldsymbol{\Gamma}}_i = \dot{\boldsymbol{\Gamma}}(t, t_i)$. Equations (9.2) to (9.5) represent the constitutive equation for the Hookean dumbbell suspension written in terms of the co-rotational rate of strain tensor. In order to obtain explicitly the kernel functions of the Goddard expansion, a slight rewriting of the integrals is necessary. For the Rouse model with N beads and $N-1$ freely-jointed Hookean springs (a generalization of the Hookean dumbbell model), one obtains

$$G_I(t-t') = n_0 kT \sum_{i=1}^{N-1} \exp\left(-\frac{t-t'}{\lambda_i}\right) \tag{9.6}$$

$$G_{II}(t-t',\, t-t'') = n_0 kT\, g(t', t'') \sum_{i=1}^{N-1} \exp\left(-\frac{t-t''}{\lambda_i}\right) \tag{9.7}$$

$$G_{III}(t-t',\, t-t'',\, t-t''') = 0 \tag{9.8}$$

$$G_{IV}(t-t', t-t'', t-t''') = \frac{1}{2} n_0 kT \sum_{i=1}^{N-1} \left[g(t''', t', t'') \exp\left(-\frac{t-t''}{\lambda_i}\right) + g(t', t'', t''') \exp\left(-\frac{t-t'''}{\lambda_i}\right)\right] \tag{9.9}$$

where $g(t', t'')$ is 1 if $-\infty < t'' \leqq t'$ and is zero otherwise, and $g(t', t'', t''')$ is 1 if $-\infty < t''' \leqq t'' \leqq t'$ and is 0 otherwise. For computational purposes the form given by Equations (9.2) to (9.5) is easier to use than the Goddard expansion with the above determined kernel functions. In the following we will investigate the convergence properties when only a finite number of terms is included for two specific flows: steady elongational flow and steady shear flow.

Steady Elongational Flow

For the steady elongational flow defined in Section 4 the $\dot{\boldsymbol{\Gamma}}$ tensor is given by Equation (4.11). In order to evaluate the tensor $\mathbf{R}_n'$ of Equation (9.5), we note first of all that

$$\dot{\boldsymbol{\Gamma}}_1 \bullet \dot{\boldsymbol{\Gamma}}_2 \cdots \dot{\boldsymbol{\Gamma}}_n = \begin{bmatrix} (-1)^n & 0 & 0 \\ 0 & (-1)^n & 0 \\ 0 & 0 & 2^n \end{bmatrix} \dot{\epsilon}^n \tag{9.10}$$

Consequently from Equations (9.5) and (9.10)

$$\mathbf{R}_n' = \left(\frac{\dot{\epsilon}}{2}\right)^n \begin{bmatrix} (-1)^n & 0 & 0 \\ 0 & (-1)^n & 0 \\ 0 & 0 & 2^n \end{bmatrix} \int_{t'}^{t}\int_{t'}^{t_1}\cdots\int_{t'}^{t_{n-1}} dt_n \ldots dt_2 dt_1$$

$$= \left(\frac{\dot{\epsilon}}{2}\right)^n \frac{(t-t')^n}{n!} \begin{bmatrix} (-1)^n & 0 & 0 \\ 0 & (-1)^n & 0 \\ 0 & 0 & 2^n \end{bmatrix} \tag{9.11}$$

In evaluating the integrals above, the change of variables $s_0 = t_n - t', \ldots s_{n-1} = t_1 - t'$ is useful. It then follows from Equations (4.11) and (9.11) that

$$\mathbf{R}_n' \bullet \dot{\boldsymbol{\Gamma}}' \bullet \mathbf{R}_m' = \dot{\epsilon}\left(\frac{\dot{\epsilon}}{2}\right)^{n+m} \frac{(t-t')^{n+m}}{n!\, m!} \begin{bmatrix} (-1)^{n+m+1} & 0 & 0 \\ 0 & (-1)^{n+m+1} & 0 \\ 0 & 0 & 2^{n+m+1} \end{bmatrix} \tag{9.12}$$

The complete expression for the stress tensor then follows from Equations (9.2), (9.3), and (9.12) after a single integration:

$$\boldsymbol{\tau} = \boldsymbol{\tau}_s - \eta_0 \dot{\epsilon} \lim_{N\to\infty} \sum_{\substack{n=0 \\ (n+m<N)}} \sum_{m=0} \left(\frac{\lambda_H \dot{\epsilon}}{2}\right)^{n+m} \frac{(n+m)!}{n!\, m!} \begin{bmatrix} (-1)^{n+m+1} & 0 & 0 \\ 0 & (-1)^{n+m+1} & 0 \\ 0 & 0 & 2^{n+m+1} \end{bmatrix} \tag{9.13}$$

Table 3. The Elongational Viscosity of Hookean Dumbbell Suspensions as Approximated by the Goddard Expansion up to and Including the N Fold Integrals, $\bar{\eta}^{(N)}$. Here $x = \lambda_H \dot{\epsilon}$

N	$\bar{\eta}^{(N)} - 3\eta_s$
1	$3\eta_0$
2	$3\eta_0(1 + x)$
3	$3\eta_0(1 + x + 3x^2)$
4	$3\eta_0(1 + x + 3x^2 + 5x^3)$
5	$3\eta_0(1 + x + 3x^2 + 5x^3 + 11x^4)$
N	$\eta_0 \sum_{n=0} \sum_{m=0} \left(\frac{x}{2}\right)^{n+m} \frac{(n+m)!}{n!\,m!} [2^{n+m+1} + (-1)^{n+m}]$, $n+m<N$
∞	$3\eta_0(1 - 2x)^{-1}(1 + x)^{-1}$

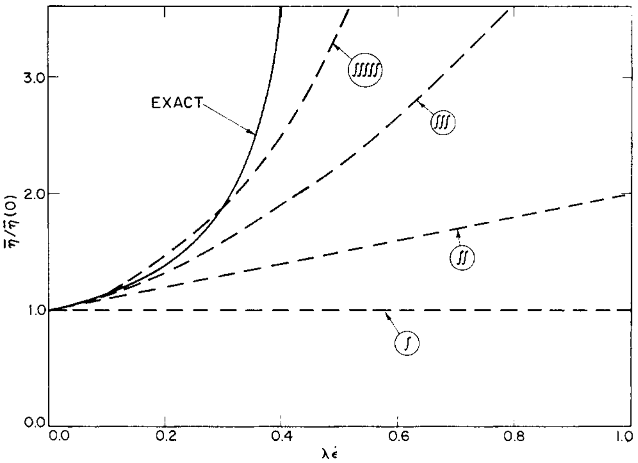

Fig. 12. Comparison of the exact elongational viscosity for solutions of elastic dumbbells with the results obtained using a finite number of terms in the Goddard expansion (compare Table 3).

In order to explore the consequences of including only a finite number of terms in the Goddard expansion, the exact result has been written as a limit with respect to N. The quantity N corresponds to the number of terms included in the Goddard expansion. Table 3 and Figure 12 show the elongational viscosity as given to the Nth approximation compared with the exact result. With just one term in the Goddard expansion the approximation is rather poor; when more terms are included, however, the approximation is improved. In case $N \to \infty$ the summation converges in the range $-1 < \lambda\dot{\epsilon} < \frac{1}{2}$ to the correct elongational viscosity for Hookean dumbbell suspensions:

$$\bar{\eta} = 3[\eta_s + \eta_0 (1 - 2\lambda_H \dot{\epsilon})^{-1} (1 + \lambda_H \dot{\epsilon})^{-1}] \tag{9.14}$$

(compare Bird, Warner, Evans, 1971, p. 74).

Steady Shearing Flow

For a steady shearing flow $v_x = \dot{\gamma} y$, a suspension of elastic dumbbells is known to have the following viscometric functions, η, θ, and β:

$$\eta = \eta_s + \eta_0 \tag{9.15}$$

$$\theta = 2\lambda_H \eta_0 \tag{9.16}$$

$$\beta = 0 \tag{9.17}$$

The Goddard approximations to the material functions will be given here through the three-fold integrals. For this flow $\mathbf{\Gamma}'$ is given by Equation (4.1); we find then for the tensors $\mathbf{R}_1'$ and $\mathbf{R}_2'$ of Equation (9.5):

$$\mathbf{R}_1(t, t') = \frac{1}{2} \begin{bmatrix} 1 - \cos \dot{\gamma}s & \sin \dot{\gamma}s & 0 \\ -\sin \dot{\gamma}s & -(1 - \cos \dot{\gamma}s) & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.18}$$

$$\mathbf{R}_2(t, t') = \frac{1}{4} \begin{bmatrix} 1 - \cos \dot{\gamma}s & \sin \dot{\gamma}s - \dot{\gamma}s & 0 \\ \dot{\gamma}s - \sin \dot{\gamma}s & 1 - \cos \dot{\gamma}s & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.19}$$

where $s = t - t'$. The approximations to the stress tensor now follow from Equations (9.2), (9.3), (9.4), (9.18), and (9.19). The approximations to the viscometric functions $\eta^{(N)}$, $\theta^{(N)}$, and $\beta^{(N)}$ resulting from including terms in the Goddard expansion through the N fold integrals have been arranged in Table 4. Notice that $2\lambda_H \eta^{(N)} = \theta^{(N)}$ for all values of N. The functions are also shown in Figure 13. Again with just one term in the Goddard expansion we see that the correct viscometric functions are approximated rather poorly; when more terms are included, however, the approximation is improved.

10. A TRUNCATED GODDARD EXPANSION

As was shown in Section 6, the first term of the Goddard expansion is probably adequate for making engineering hydrodynamic calculations for flows in which non-Newtonian viscosity must be described accurately but the elastic properties need be described only approximately. If one needs a more refined rheological description of the fluid, then one could consider including a few more terms in the expansion, but perhaps making some crude estimates of the form of G_{II}, G_{III}, G_{IV}, ... In this section we

Table 4. The Viscometric Functions of Hookean Dumbbell Suspensions as Approximated by the Goddard Expansion up to and Including the N Fold Integrals, $\eta^{(N)}$, $\theta^{(N)}$, $\beta^{(N)}$. Here $x = \lambda_H \dot{\gamma}$

N	$(\eta^{(N)} - \eta_s)\eta_0^{-1}$	$\theta^{(N)}(2\lambda_H \eta_0)^{-1}$	$\beta^{(N)}(\lambda_H \eta_0)^{-1}$
1	$\frac{1}{1 + x^2}$	$\frac{1}{1 + x^2}$	$\frac{-1}{1 + x^2}$
2	$\frac{1}{1 + x^2}$	$\frac{1}{1 + x^2}$	0
3	$\frac{1 + \frac{x^2}{1 + x^2}}{1 + x^2}$	$\frac{1 + \frac{x^2}{1 + x^2}}{1 + x^2}$	$\frac{-x^2}{(1 + x^2)^2}$

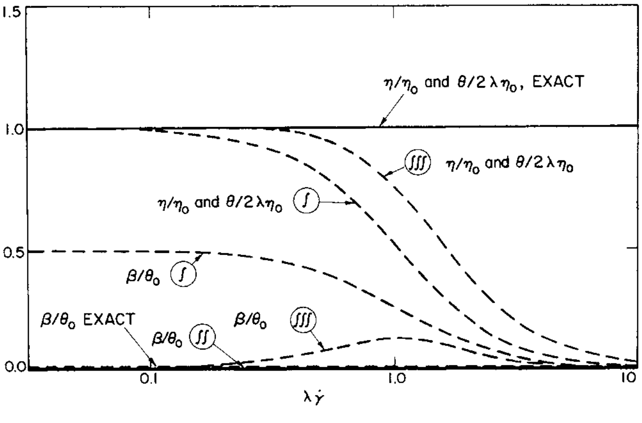

Fig. 13. Comparison of the exact steady state material functions for solutions of elastic dumbbells with the results obtained using a finite number of terms in the Goddard expansion (compare Table 4).

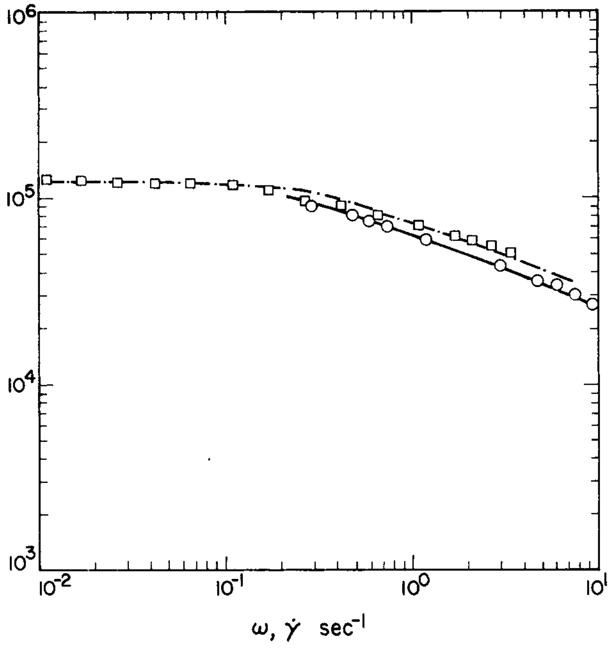

Fig. 14. Comparison between experimental data of viscosity η for Phenoxy-A melt and the predicted values from Equation (10.9)

○ η' Experimental, data of Marsh, 1967.

□ η Experimental, data of Marsh, 1967.

—— Fitted Carreau viscosity equation for η' data [Equation (1 6)] with η, λ, n, and $\dot{\gamma}$ replaced by η', λ', n', and ω, respectively, and $\eta_\infty = 0$) ($\eta_0 = 1.24 \times 10^5$ poise, $\lambda' = 5.75$ s, $n' = 0.616$).

– · – Predicted values of η using Equation (10.9)

give one illustration of what we mean by this, recognizing that our example does not represent a completely successful attempt.

We try here including terms in the Goddard expansion up through the triple-integral terms. We simplify these terms by setting

$$G_{II}(t-t', t-t'') = b\, g(t' t'') \quad G_I(t-t'') \qquad (10.1)$$

$$G_{III}(t-t', t-t'', t-t''') = 0 \qquad (10.2)$$

$$G_{IV}(t-t', t-t'', t-t''') = \frac{1}{2} c\,[g(t''', t', t'') \, G_I(t-t'') + g(t', t'', t''')\, G_I(t-t''')] \qquad (10.3)$$

in which b and c are constants characteristic of the fluid. Here $g(t', t'', t''') = 1$ for $-\infty < t''' \leqq t'' \leqq t'$ and zero otherwise. This choice is based on the results in Section 9, where it was shown that for the Rouse model G_{II}, G_{III}, G_{IV} are given by Equations (10.1), (10.2), (10.3) with $b = c = 1$. Then the truncated Goddard expansion becomes

$$\boldsymbol{\tau} = -\int_{-\infty}^{t} G_I(t-t')\, \dot{\mathbf{\Gamma}}'\, dt' - \frac{1}{2} b \int_{-\infty}^{t} G_I(t-t') \left[\int_{-\infty}^{t} (\dot{\mathbf{\Gamma}}' \bullet \dot{\mathbf{\Gamma}}'' + \dot{\mathbf{\Gamma}}'' \bullet \dot{\mathbf{\Gamma}}')\, dt''\right] dt'$$
$$- \frac{1}{4} c \int_{-\infty}^{t} G_I(t-t') \left[\int_{t'}^{t}\int_{t'}^{t} \dot{\mathbf{\Gamma}}'' \bullet \dot{\mathbf{\Gamma}}' \bullet \dot{\mathbf{\Gamma}}'''\, dt'''\, dt'' + \int_{t'}^{t}\int_{t'}^{t''} \dot{\mathbf{\Gamma}}'' \bullet \dot{\mathbf{\Gamma}}''' \bullet \dot{\mathbf{\Gamma}}'\, dt'''\, dt'' + \int_{t'}^{t}\int_{t'}^{t'''} \dot{\mathbf{\Gamma}}' \bullet \dot{\mathbf{\Gamma}}''' \bullet \dot{\mathbf{\Gamma}}''\, dt'''\, dt''\right] dt' \qquad (10.4)$$

It is understood that $G_I(s)$ is so chosen as to describe the linear viscoelastic properties of the fluid.

If the flow field is known, the evaluation of the quantities inside the brackets is straightforward. We now consider several flow fields briefly:

1. For small-amplitude oscillations we need only the first term to get η' and η'' as given in Equation (6.2).
2. For steady state shear flow Equation (10.4) gives

$$\eta = \int_0^\infty G_I(s) \left[\cos \dot{\gamma}s + \frac{1}{2} c\, \dot{\gamma}s \sin \dot{\gamma}s\right] ds \qquad (10.5)$$

$$\frac{\theta \dot{\gamma}}{2} = \int_0^\infty G_I(s) \left[\sin \dot{\gamma}s + \frac{1}{2} c\, (\sin \dot{\gamma}s - \dot{\gamma}s \cos \dot{\gamma}s)\right] ds \qquad (10.6)$$

$$-\beta \dot{\gamma} = \int_0^\infty G_I(s) \left[\sin \dot{\gamma}s - b \sin \dot{\gamma}s + \frac{1}{2} c\, (\sin \dot{\gamma}s - \dot{\gamma}s \cos \dot{\gamma}s)\right] ds \qquad (10.7)$$

From this we see that, approximately,

$$\beta \approx -\frac{\theta}{2}(1-b) \qquad (10.8)$$

Hence by suitable choice of the constant b for various fluids, one can describe the fact that the ratio $-\beta/\theta$ varies from 0.1 to 0.4 from fluid to fluid.

Also by combining the above steady-shear flow results with the oscillatory results, it is easy to show that

$$\eta = \left\{\eta' \left[1 - \frac{c}{2} \frac{d \ln \eta'}{d \ln \omega}\right]\right\}_{\omega = \dot{\gamma}} \qquad (10.9)$$

$$\frac{\theta \dot{\gamma}}{2} = \left\{\eta'' \left[\left(1 + \frac{c}{2}\right) - \frac{c}{2} \frac{d \ln \eta''}{d \ln \omega}\right]\right\}_{\omega = \dot{\gamma}} \qquad (10.10)$$

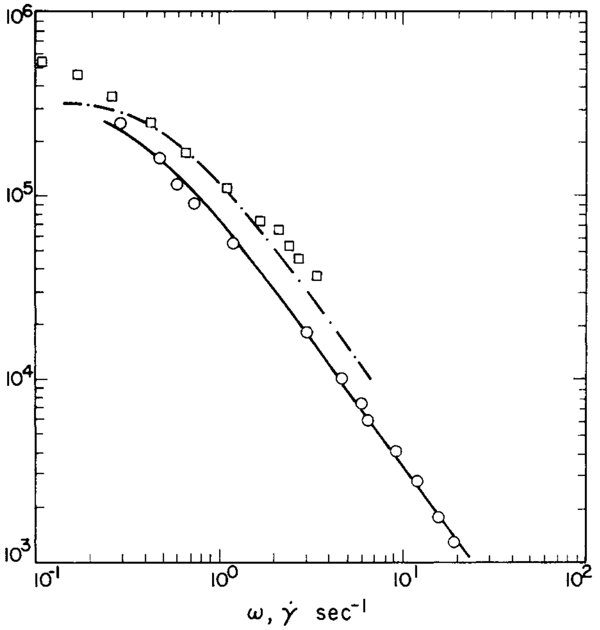

Fig. 15. Comparison between experimental data of primary normal stress function, θ, for Phenoxy-A melt and the predicted values from Equation (10.10).

○ $2\eta''/\omega$ Experimental, data of Marsh (1967).

□ θ Experimental, data of Marsh (1967).

—— Fitted Carreau viscosity equation for $2\eta''/\omega$ data [Equation (1.6)] with η, η_0, λ, n, and $\dot{\gamma}$ replaced by $2\eta''/\omega$, A, λ'', n'', and ω, respectively, and $\eta_\infty = 0$) ($A = 3.18 \times 10^5$ g/cm, $\lambda'' = 2.79$ s, $n'' = -0.372$).

– · – Predicted values of θ using Equation (10.10).

which says that for $c > 0$ the $\eta(\dot\gamma)$ curve should lie above the $\eta'(\omega)$ curve and that the $\frac{1}{2}\,\theta\,\dot\gamma$ curve should lie above the $\eta''(\omega)$ curve, as is observed experimentally. We have to rule out c values greater than 1 since such choices produce spurious maxima in η and θ. In Figures 14 to 19 are shown some plots illustrating the use of Equations (10.9) and (10.10) for $c = 1$. It can be seen that these equations give a correction in the right direction, but that the experimentally-observed differences in slopes of the $\eta(\gamma)$ and $\eta'(\omega)$ curves (and the other pair) are not reproduced.

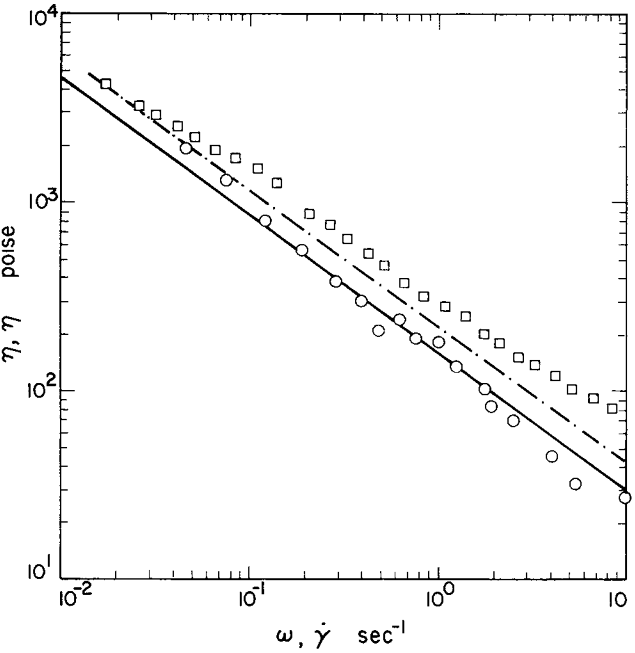

Fig. 16. Comparison similar to Figure 14 for 2% polyisobutylene in Primol 355, data of Huppler, Ashare, and Holmes, 1967. ($\eta_0 = 9.23 \times 10^3$ poise, $\lambda' = 265.0$ s, $n' = 0.272$).

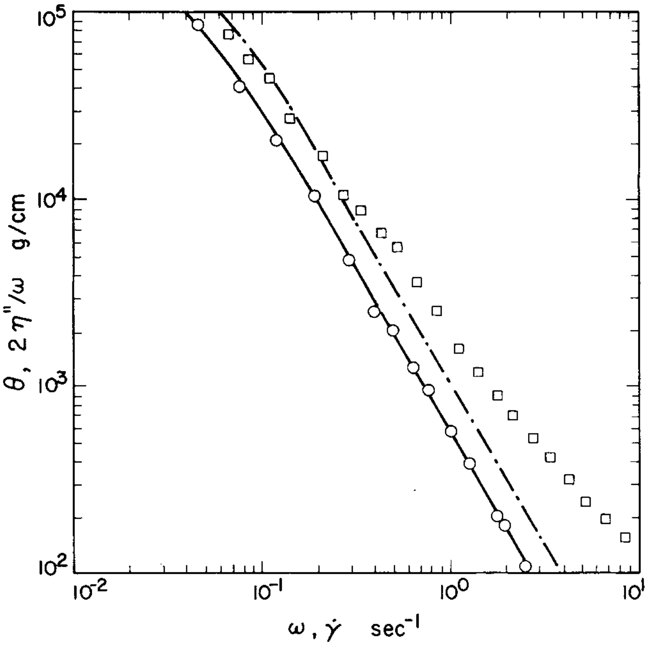

Fig. 17. Comparison similar to Figure 15 for 2% polyisobutylene in Primol 355, data of Huppler, Ashare, and Holmes (1967). ($A = 1.94 \times 10^5$ g/cm, $\lambda'' = 280.3$ s, $n'' = -0.760$).

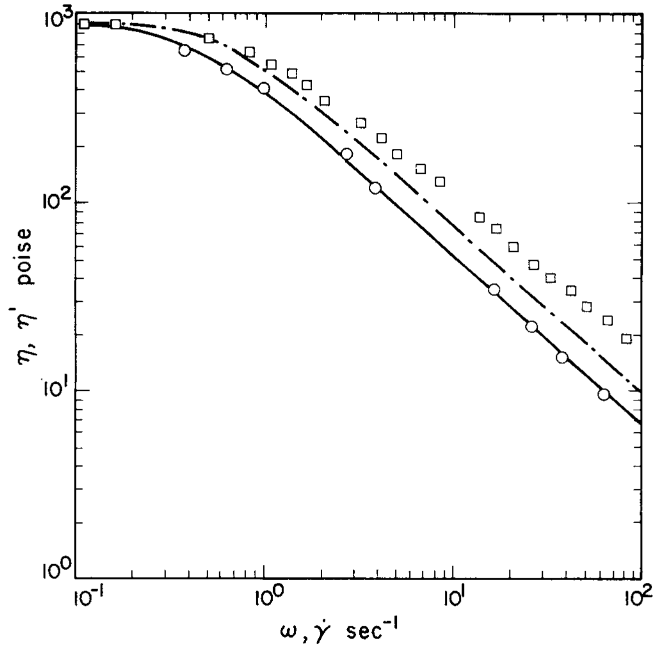

Fig. 18. Comparison similar to Figure 14 for 7% aluminum soap, data of Huppler, Ashare, and Holmes (1967). ($\eta_0 = 8.96 \times 10^2$ poise, $\lambda' = 2.41$ s, $n' = 0.106$).

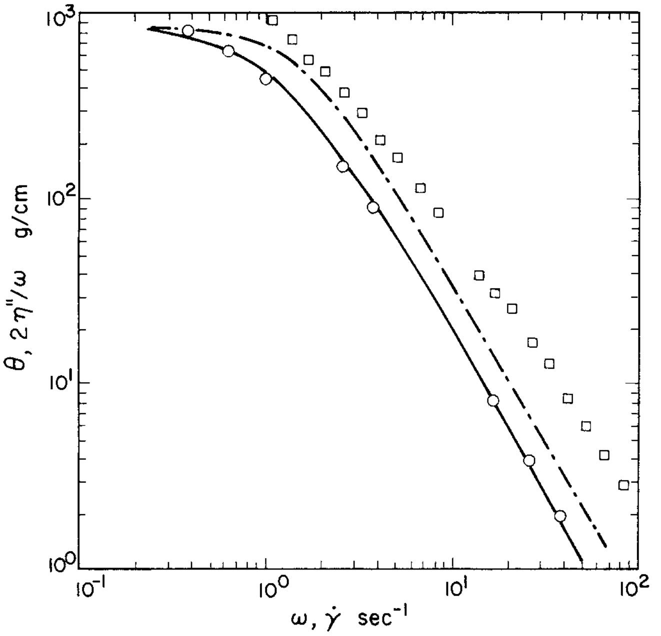

Fig. 19. Comparison similar to Figure 15 for 7% aluminum soap, data of Huppler, Ashare, and Holmes (1967). ($A = 8.10 \times 10^2$ g/cm, $\lambda'' = 0.896$ s, $n'' = -0.728$).

3. For stress relaxation after cessation of steady shear flow we find

$$\eta^- = \int_t^\infty G_I(s)\left[\cos \dot\gamma\,(t-s) + \frac{1}{2}\,c\,\dot\gamma(t-s)\,\sin\dot\gamma(t-s)\right] ds \qquad (10.11)$$

which leads once again to Equation (6.22).

4. For elongational stress growth the fluid is at rest for time $t < 0$ and undergoes a constant rate of elongation $\dot\epsilon = dv_z/dz$ for $t > 0$. Then

$$\tau_{xx} - \tau_{zz} = \bar\eta^{+}(\dot\epsilon, t)\,\dot\epsilon \qquad (10.12)$$

defines the material function $\bar{\eta}^+$. For this function Equation (10.4) gives

$$\bar{\eta}^+ = 3\int_0^t G_I(s)\,ds + 3\,b\,\dot{\epsilon}\int_0^t sG_I(s)\,ds + \frac{9}{2}c\,\dot{\epsilon}^2\int_0^t s^2\,G_I(s)\,ds \qquad (10.13)$$

This expression for $\bar{\eta}^+(\dot{\epsilon}, t)$ is compared with the experimental values of Meissner (1971) in Figure 20. In this comparison we have let $b = 0.5$, $c = 1.0$ and $G_I(s)$ has been expressed by

$$G_I(s) = \sum_{i=1}^{5} a_i\lambda_i\, e^{-s/\lambda_i} \qquad (10.14)$$

i	1	2	3	4	5	
λ_i	100	10	1	0.1	0.01	(s)
a_i	19.03	2306	62410	3.299×10^6	3.72×10^7	dyn cm^{-2} s^{-1}

(10.15)

This is the same relaxation modulus as was used by Chang and Lodge (1972) in their comparison of the data of Meissner with the predictions of the rubberlike liquid (Lodge, 1964). This spectrum was chosen to fit the linear viscoelastic behavior ($\bar{\eta}^+(0, t)$) of the L.D.P.E. melt (see Chang and Lodge, 1972). From Figure 20 we can see that the truncated Goddard expansion seems to fit the data quantitatively. Note however that the upward-sweeping curves cannot be described at all by the single-integral Goddard-Miller model. Hence in this key experiment we find that higher-order terms in the Goddard expansion are imperative.

5. For stress growth at inception of steady shear flow we find

$$\eta^+ = \int_0^t G_I(s)\left[\cos\dot{\gamma}s + \frac{1}{2}c\,\dot{\gamma}s\sin\dot{\gamma}s\right]ds \qquad (10.16)$$

The effect of positive values of c is to shift the maxima towards larger values of time and to increase the oscillations after the first maximum. Equation (10.16) is compared with the experimental values of Meissner (1972) in Figure 21. The fluid tested is the L.D.P.E. melt used in the elongational test described above, and we have therefore used the same values of b and c, and the same relaxation spectrum as used in 4. As the imposed shear rate is increased the response of the truncated Goddard expansion becomes increasingly more oscillatory. For an imposed shear rate of 10 s^{-1} the transient viscosity function $\eta^+(\dot{\gamma}, t)$ oscillates extremely wildly, and even attains negative values, a prediction that is certainly unrealistic.

From the results in Equations (10.9), (10.10), (10.11), and (10.13) we conclude that further studies on truncating the memory integral expansion should prove fruitful.

The question which one faces when confronting a macromolecular hydrodynamic problem is: "What expression

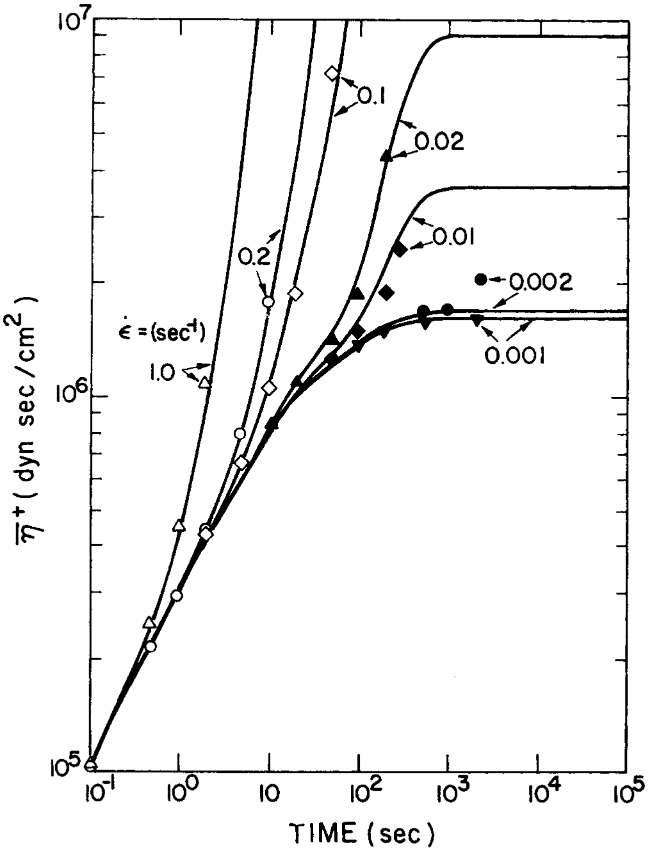

Fig. 20. Comparison between experimental data of the elongational stress growth function $\bar{\eta}^+(\dot{\epsilon},t)$ for L.D.P.E. and the predicted values from the truncated Goddard expansion, Equation (10.13).

△○◇▲○◆▼ Experimental, data of Meissner (1971).

—— Truncated Goddard expansion, Equation (10.13) with $b = 0.5$, $c = 1.0$, and $G(s)$ given by Equations (10.14) and (10.15).

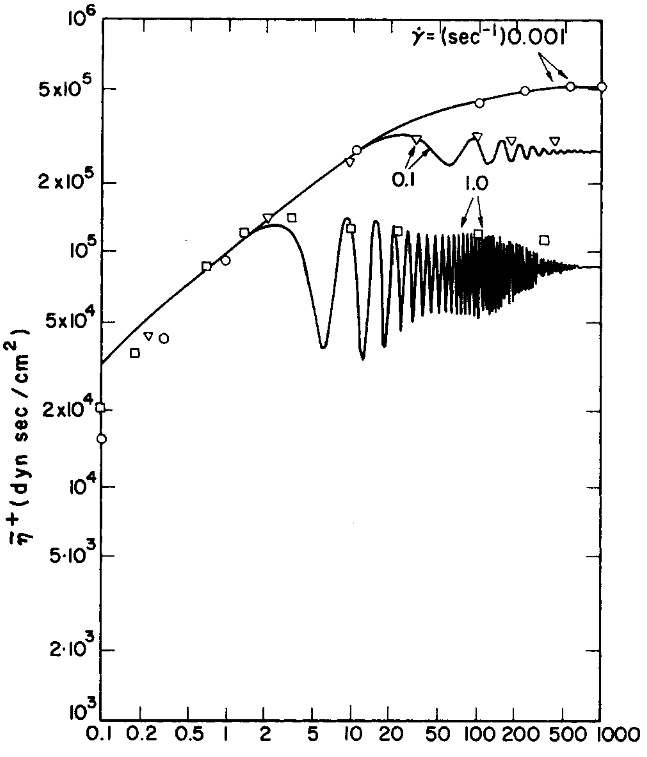

Fig. 21. Comparison between experimental data of the shear stress growth function $\eta^+(\dot{\gamma},t)$ for L.D.P.E. melt and the predicted values from the truncated Goddard expansion, Equation (10.16).

○▽□ Experimental, data of Meissner (1972).

—— Truncated Goddard expansion, Equation (10.16), with $c = 1.0$, and $G(s)$ given by Equations (10.14) and (10.15).

shall we use for the stress tensor?" The answer to this question will depend on several factors:

1. Importance of non-Newtonian Viscosity: If this property is the most important property for describing the flow, then the power law [Equation (1.5)] or the Carreau viscosity function [Equation (1.6)] used in the generalized Newtonian model [Equation (1.4)] should be adequate. If some elastic effects appear to be important, then the Goddard-Miller model may be needed.
2. Need for Simplicity: Sometimes one wishes only to make a probing calculation, to explore for new effects, or to chart regions in which elastic terms will be important. For such calculations the co-rotational Jeffreys model may serve well.
3. Need for Accuracy: In basic rheological studies one may wish for refined relationships among rheological properties, or one may require a precise hydrodynamic study. Then the Goddard series, or some simplification of it, may be needed. This approach has been illustrated in Section 10.
4. Type of Flow: For steady state shear flow the CEF equation [Equation (7.1)] is the most general equation available. For first and second-order viscoelasticity the first and second terms of the Goddard series are needed. As pointed out in connection with Equation (10.13), for some flows the use of higher-order terms in the Goddard series is required.
5. Time and Money: It must be kept in mind that the stress tensor has to be inserted into the equations of motion. The solution of these nonlinear equations is a formidable task. The time requirements and monetary needs must be kept in mind before embarking on extensive calculations.

Finally we point out that to date the co-rotational models have, as far as we know, not been used for any hydrodynamic calculations. We feel, however, that these models merit much more attention than they have received in the past.

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NOTATION

a_n = parameters in Equation (1.9)
b = parameter in Equation (10.1)
$\mathbf{B}$, $\dot{\mathbf{B}}$ = finger strain tensor, and its time derivative, Equations (A7) and (A9)
b_n = parameters in Equation (1.9)
c = parameter in Equation (10.3)
$\mathbf{C}$, $\dot{\mathbf{C}}$ = Cauchy strain tensor, and its time derivative, Equations (A6) and (A8)
$E(\dot{\gamma}, t)$ = Van Es and Christensen function, Equation (6.15)
$\mathbf{E}$ = kinematic tensor ($= \mathbf{F}^{-1}$)
$\mathbf{F}$ = kinematic tensor defined by Equation (A1)
$\mathbf{f}$ = traction vector, force per unit area
$\mathbf{g}$ = gravitational acceleration
$g(t', t'')$ = function introduced in Equation (8.3); = 1 for $-\infty < t'' \leqq t'$ and = 0 for $t' < t'' \leqq t$
$g(t', t'', t''')$ = function introduced in Equation (10.3); = 1 for $-\infty < t''' \leqq t'' \leqq t'$ and = 0 for $t'' < t''' \leqq t$ or $t' < t'' \leqq t$
G = elastic modulus, just before Equation (1.7)
G_I, G_{II}, G_{III}, G_{IV} . . = kernel functions in the Goddard expansion Equation (3.10)
K = empirical constant, Table 2
m, n = power law parameters, Equation (1.5)
$\mathbf{n}$ = unit normal
n_0 = number density of macromolecules in solution
p = pressure
Q_{ij} = elements of the rotation matrix
$\mathbf{R}$, $\mathbf{R}_n$ = tensors defined by Equations (A13) to (A15)
$\mathbf{r}$ = position vector
s, s', s'' = dummy variables
$\mathbf{S}$, $\mathbf{S}_n$ = tensors defined by Equations (A16) to (A18)
t, t', t'' = time
v = velocity
$\mathbf{w}$ = angular velocity vector
$\mathbf{W}$ = angular velocity vector
x_i = position coordinate in a fixed reference frame
$\bar{x}_i$ = position coordinate in a co-translating reference frame
$\check{x}_i$ = position coordinate in a co-rotating reference frame
X_i = material coordinate

Greek Letters

α = dimensionless index in Equation (5.1)
α_1, α_2 = functions in Equation (7.2)
β = secondary normal stress function $= -(\tau_{22} - \tau_{33})/\dot{\gamma}^2$
β', β'' β^d = oscillatory secondary normal stress functions, Equations (7.10) to (7.12)
$\boldsymbol{\gamma}$ = infinitesimal strain tensor
$\dot{\boldsymbol{\gamma}}$ = rate of deformation tensor
$\dot{\gamma}$ = shear rate
$\dot{\gamma}^0$ = amplitude of shear rate in oscillatory shear flow, Equation (4.5)
$\dot{\gamma}_m$ = mean shear rate, Equation (6.3)
$\bar{\dot{\gamma}}_{ij}$ = components of the rate of deformation tensor in the co-translating frame
$\check{\dot{\gamma}}_{ij}$ = components of the rate of deformation tensor in the co-rotating frame
$\dot{\boldsymbol{\Gamma}}$ = co-rotating rate of deformation tensor
δ_{ij} = Kronecker delta function
$\boldsymbol{\delta}_i$ = space-fixed unit vectors
$\check{\boldsymbol{\delta}}_i$ = co-rotating unit vectors
$\boldsymbol{\varepsilon}$ = alternating unit tensor
$\dot{\epsilon}$ = elongation rate
$\zeta(\ )$ = Riemann zeta function
η = non-Newtonian viscosity
η', η'' = real and imaginary parts of complex viscosity η^*
$\bar{\eta}$ = elongational viscosity
$\bar{\eta}^+$ = transient elongational viscosity function, Equation (10.12)
η^- = transient viscosity function, Equation (4.9)
η^+ = transient viscosity function, Equation (4.7)
$\eta^\#$ = complex viscometric function, Equation (6.2)
$\eta'(\omega; \dot{\gamma}_m)$, $\eta''(\omega; \dot{\gamma}_m)$ = real and imaginary parts of the complex material function $\eta^*(\omega; \gamma_m)$
η_0 = zero-shear-rate viscosity
η_∞ = infinite-shear-rate viscosity
η_k = viscosity constants, Equation (1.10)
η_s = (Newtonian) solvent viscosity
θ = primary normal stress function $= -(\tau_{11} - \tau_{22})/\dot{\gamma}^2$

θ', θ'', θ^d = oscillatory primary normal stress functions, Equations (7.7) to (7.9)

θ^+ = transient primary normal stress function, Equation (4.8)

θ^- = transient primary normal stress function, Equation (4.10)

$\boldsymbol{\varkappa}$ = second-order tensor

λ, λ_H, λ_k, λ_0, λ_1, λ_2 = time constants

μ = Newtonian viscosity

$\boldsymbol{\pi}$ = total stress tensor

ρ = density

$\boldsymbol{\tau}$ = extra stress tensor

$\bar{\tau}_{ij}$ = components of the extra stress tensor in the co-translating frame

$\check{\tau}_{ij}$ = components of the extra stress tensor in the co-rotating frame

τ_m = mean shear stress, Equation (6.7)

$\tau_{11} - \tau_{22}$ = primary normal stress difference

$\tau_{22} - \tau_{33}$ = secondary normal stress difference

τ^0 = amplitude of oscillatory part of shear stress, Equation (6.8)

$\boldsymbol{\omega}$ = vorticity tensor

ω = frequency

$\bar{\omega}_{ij}$ = components of the vorticity tensor in the co-translating frame

$\check{\omega}_{ij}$ = components of the vorticity tensor in the co-rotating frame

$II_{\dot{\gamma}}$, $III_{\dot{\gamma}}$ = second and third invariants of the rate of deformation tensor $\dot{\boldsymbol{\gamma}}$

Superscripts

$\dagger$ = transpose

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APPENDIX A

When formulating rheological equations of state for viscoelastic materials undergoing large deformations, it is imperative that the rheological predictions for a material element be independent of its motion as a whole in space. For the corotational models this aim is achieved by having the equations formulated by an observer rotating with the local angular velocity of the fluid element. This observer will not detect a superposed rigid rotation, and the necessary invariance properties are consequently assured. This idea, however, is by no means the only way of achieving the correct invariance properties, and two other methods have traditionally been employed. Oldroyd (1950) and Lodge (1974) formulate constitutive equations in a convected coordinate system in which the coordinate surfaces are chosen as surfaces drawn in the material and deforming continuously with it. On the other hand, Rivlin and Ericksen (1955), Green and Rivlin (1957), and Coleman and Noll (1961) introduce the idea of a change of observer or reference frame and derive the restrictions imposed on the constitutive relations by requiring that they be independent of such a change. In any of these treatments the so-called "Cauchy strain tensor," the "Finger strain tensor," and their time derivatives appear naturally. These tensors are defined and related to the $\dot{\boldsymbol{\Gamma}}$ tensor below. An example of the application of the relations was given in Section 9.

We introduce a set of cartesian space coordinates $\{x_i\} = x$, and a set of material (or convected) coordinates $\{X_i\} = X$ with the property that a material particle with convected coordinates X_i at any one time has the same convected coordinates at any other time. The X_i are specified by requiring that $X = x$ at the present time t. The motion of the fluid is then given by the functions $x_i = x_i(X, t')$ with $-\infty < t' \leq t$. We introduce a tensor $\mathbf{F} = \mathbf{F}(X, t, t')$ as the transpose of the deformation gradient tensor:

$$F_{ij} = \frac{\partial x_i(X, t')}{\partial X_j} \tag{A1}$$

It may be shown that $\mathbf{F}$ is the solution of the initial value problem:

$$\frac{D}{Dt'}\mathbf{F} = (\nabla\mathbf{v})^\dagger \bullet \mathbf{F} \tag{A2}$$

$$\mathbf{F} = \boldsymbol{\delta} \quad \text{for} \quad t' = t \tag{A3}$$

where $\boldsymbol{\delta}$ is the unit tensor, $\nabla\mathbf{v} = \nabla\mathbf{v}(X, t')$, and D/Dt' denotes differentiation with respect to t' keeping the material coordinates constant, that is, following a particle. Let us introduce also the orthogonal tensor $\mathbf{Q} = \mathbf{Q}(X, t, t')$ as the solution of

$$\frac{D}{Dt'}\mathbf{Q} = \frac{1}{2}\mathbf{Q} \bullet \boldsymbol{\omega} \tag{A4}$$

$$\mathbf{Q} = \boldsymbol{\delta} \quad \text{for} \quad t' = t \tag{A5}$$

where $\boldsymbol{\omega} = \boldsymbol{\omega}(X, t')$. In Equation (A3) $\mathbf{Q} = \sum_i \sum_j Q_{ij}\boldsymbol{\delta}_i\boldsymbol{\delta}_j$ where the Q_{ij} are the matrix elements defined by Equations (2.18) and (2.19).

The Cauchy strain tensor $\mathbf{C} = \mathbf{C}(X, t, t')$, Finger strain tensor $\mathbf{B} = \mathbf{B}(X, t, t') = \mathbf{C}^{-1}$, and their time derivatives $\dot{\mathbf{C}} = \frac{D}{Dt'}\mathbf{C}$, and $\dot{\mathbf{B}} = \frac{D}{Dt'}\mathbf{B}$ are defined by

$$\mathbf{C} - \boldsymbol{\delta} = \mathbf{F}^\dagger \bullet \mathbf{F} - \boldsymbol{\delta} = \boldsymbol{\gamma}^{[0]} \tag{A6}$$

$$\mathbf{B} - \boldsymbol{\delta} = \mathbf{E} \bullet \mathbf{E}^\dagger - \boldsymbol{\delta} = -\boldsymbol{\gamma}_{[0]} \tag{A7}$$

$$\dot{\mathbf{C}} = \mathbf{F}^\dagger \bullet \dot{\boldsymbol{\gamma}} \bullet \mathbf{F} = \boldsymbol{\gamma}^{[1]} \tag{A8}$$

$$\dot{\mathbf{B}} = -\mathbf{E} \bullet \dot{\boldsymbol{\gamma}} \bullet \mathbf{E}^\dagger = -\boldsymbol{\gamma}_{[1]} \tag{A9}$$

in which $\dot{\boldsymbol{\gamma}} = \dot{\boldsymbol{\gamma}}(X, t')$ and $\mathbf{E} = \mathbf{E}(X, t, t') = \mathbf{F}^{-1}$. The tensors $\boldsymbol{\gamma}_{[0]} = \boldsymbol{\gamma}_{[0]}(X, t, t')$, $\boldsymbol{\gamma}^{[0]} = \boldsymbol{\gamma}^{[0]}(X, t, t')$, $\boldsymbol{\gamma}_{[1]} = \boldsymbol{\gamma}_{[1]}(X, t, t')$ and $\boldsymbol{\gamma}^{[1]} = \boldsymbol{\gamma}^{[1]}(X, t, t')$ are those used by Armstrong and Bird (1973). The $\dot{\boldsymbol{\Gamma}}$ tensor is defined in terms of the $\mathbf{Q}$ tensor:

$$\dot{\boldsymbol{\Gamma}} = \mathbf{Q} \bullet \dot{\boldsymbol{\gamma}} \bullet \mathbf{Q}^\dagger \tag{A10}$$

where again $\dot{\boldsymbol{\gamma}}$ is evaluated at time t' and at the same particle as $\mathbf{Q}$ and $\dot{\boldsymbol{\Gamma}}$. We see that $\dot{\boldsymbol{\Gamma}}$ is a very different rate of strain measure than the more conventional $\dot{\mathbf{B}}$ and $\dot{\mathbf{C}}$ tensors; in particular, $\dot{\boldsymbol{\Gamma}}$ may not be expressed as a linear combination of $\dot{\mathbf{B}}$ and $\dot{\mathbf{C}}$.

The $\boldsymbol{\gamma}_{[1]}$ and $\boldsymbol{\gamma}^{[1]}$ tensors may be expressed in terms of the $\dot{\boldsymbol{\Gamma}}$ tensor by

$$\boldsymbol{\gamma}_{[1]} = \mathbf{R} \bullet \dot{\boldsymbol{\Gamma}} \bullet \mathbf{R}^\dagger \tag{A11}$$

$$\boldsymbol{\gamma}^{[1]} = \mathbf{S}^\dagger \bullet \dot{\boldsymbol{\Gamma}} \bullet \mathbf{S} \tag{A12}$$

in which the tensors $\mathbf{R} = \mathbf{R}(X, t, t')$, and $\mathbf{S} = \mathbf{S}(X, t, t') = \mathbf{R}^{-1}$ may be expressed by

$$\mathbf{R} = \sum_{n=0}^{\infty} \mathbf{R}_n \tag{A13}$$

$$\mathbf{R}_0 = \boldsymbol{\delta} \tag{A14}$$

$$\mathbf{R}_n = \left(\frac{1}{2}\right)^n \int_{t'}^{t} \int_{t'}^{t_1} \dots \int_{t'}^{t_{n-1}} \dot{\mathbf{\Gamma}}_1 \bullet \dot{\mathbf{\Gamma}}_2 \bullet \dots \dot{\mathbf{\Gamma}}_n \, dt_n \dots dt_2 \, dt_1; \quad n \geqq 1 \tag{A15}$$

and

$$\mathbf{S} = \sum_{n=0}^{\infty} \mathbf{S}_n \tag{A16}$$

$$\mathbf{S}_0 = \boldsymbol{\delta} \tag{A17}$$

$$\mathbf{S}_n = \left(\frac{1}{2}\right)^n \int_{t}^{t'} \int_{t}^{t_1} \dots \int_{t}^{t_{n-1}} \dot{\mathbf{\Gamma}}_1 \bullet \dot{\mathbf{\Gamma}}_2 \bullet \dots \dot{\mathbf{\Gamma}}_n \, dt_n \dots dt_2 \, dt_1; \quad n \geqq 1 \tag{A18}$$

where $\dot{\mathbf{\Gamma}}_i = \dot{\mathbf{\Gamma}}(X, t, t_i)$. Equations (A11) to (A18) may be proven, for example, by considering first an observer moving with a fluid particle and rotating with the vorticity of the fluid, and then rewriting the equations for a space fixed observer. An illustration of the use of Equations (A11) and (A13) to (A15) is given in Section 9.

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JOURNAL REVIEW

A Semimicro Thermomechanical Technique for Characterizing Polymeric Materials: Torsional Braid Analysis

An overview of a nondestructive semimicro mechanical technique—pioneered, developed, and exploited by the author—which is used for characterizing phase transitions and transformations in polymeric materials is presented. Particular attention is given to literature published since January, 1972, which pertains to advances in automation, data acquisition and processing, and application to polymeric systems. The instrument has been consolidated as a powerful and convenient mechanical spectrometer in this short period.

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SCOPE

An understanding of the relationships between bulk properties and molecular architecture is a major goal of polymer science. Dynamic mechanical methods, particularly those involving low-deformation oscillatory experiments which are used to generate mechanical spectra, have been important in this endeavor. The mechanical spectra consist of two parameters, one related to the storage and the other to the loss of energy on mechanical deformation, which are presented as functions of temperature or time. Attempts are being made to relate (for example) the loss peaks to the onset of particular localized intra- and intermolecular motions on the one hand and to changes in macroscopic bulk properties on the other hand.

The torsional pendulum is commonly used for characterizing the thermomechanical behavior of polymeric materials. However, it would be used even more extensively were it not for problems with data reduction, difficulties with specimen fabrication, and the inherently low thermal conductivity of organic materials which limits the rate of heating and cooling during measurements. The tedium of the experiment has resulted in its scattered use by experimenters who have constructed their own apparatus. Although the torsional pendulum technique is old, in the field of plastics it only became a full standard (ASTM D-2236) of the American Society for Testing Materials in 1969.