Constitutive Equations for Viscoelastic Fluids for Short Deformation Periods and for Rapidly Changing Flows: Significance of the Deborah Number

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The proper forms and asymptotic characteristics of constitutive equations which may be useful for the description of viscoelastic fluids in flow fields of engineering interest are considered. It is seen that the Deborah number emerges as a natural ordering parameter which determines, on the one hand, whether simple approximations explicit in stress may suffice to describe the fluid properties or, on the other hand, whether implicit or integral equations are required. Methods of scale-up are discussed.

While methods for the formulation of constitutive equations for viscoelastic materials undergoing large deformations were introduced by Zaremba (*41*) in 1903, it was not until the publication of the Oldroyd (*19*) and Green and Rivlin (*13*) analyses that a satisfactory understanding of viscoelastic behavior and general constitutive equations relating stress to deformation in an isotropic viscoelastic material were obtained.* Solutions to boundary value problems for large deformations of isotropic viscoelastic materials have been few in number. Rivlin (*25*) has described the solution of the problem of stress relaxation following large complex static deformations of solidlike elastic materials, and Pipkin and Rivlin (*22*) have studied the case of infinitesimal deformations superposed on a finite static strain. Attention has also been paid to steady fluid motions, and Green and Rivlin (*13*) and Coleman and Noll (*9, 10*) have argued that the constitutive equation for this type of deformation is identical to an expansion of acceleration tensors [known for Rivlin and Ericksen (*28*)], which are evaluated at the present instant. Many solutions, both exact (*10, 26*) and approximate (*2, 5, 8, 14, 17, 20, 23, 38, 39*), presently exist in the literature for the Rivlin-Ericksen expansion. However, while the solutions of Rivlin and Pipkin for solid or elastic materials are generally correct, those solutions based on Rivlin-Ericksen expansions may only be useful asymptotically in the case of fluids.

It will be shown in this analysis that for short deformation periods, viscoelastic fluids behave as elastic solids and not as Rivlin-Ericksen materials. Failure to realize this leads to paradoxes (7) and often to mathematical solutions with an uncertain or questionable range of application. It is the purpose of this paper to consider these points and to discuss their implications in the general area of fluid dynamics and design for viscoelastic fluids. Special cases of the results of this note have been realized and discussed by Etter and Schowalter (*11*), White and Tokita (*40*), and Metzner and White (*17*).†

STEADY DEFORMATIONS

The Green-Rivlin theory for viscoelastic materials takes the form of a Frechet expansion of integrals (*11, 40*):

$$\tilde{\sigma} = -p\mathrm{I} + \int_{-\infty}^{t} \Phi(t-s)\ \mathrm{e}\ (s)\ ds$$

* A variety of diverse viewpoints, all with specific merit, of the work in nonlinear viscoelasticity are given by Bogue and Doughty (*4*), Fredrickson (*12*), Truesdell and Noll (*36*), and Walters (*37*).

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† While preparing this manuscript, we discovered that Pipkin has recently come to similar conclusions (*21*).

$$+\int_{-\infty}^{t}\int_{-\infty}^{t} \Psi\,(t-s_1, t-s_2)\ \mathbf{e}\,(s_1)\ \mathbf{e}\,(s_2)\ ds_1\, ds_2$$

$$+\int_{-\infty}^{t}\int_{-\infty}^{t} \sum\,(t-s_1, t-s_2)\ [tr\,\mathbf{e}\,(s_1)]\ \mathbf{e}\,(s_2)\ ds_1 ds_2 + \ldots \tag{1}$$

Here $\mathbf{e}$ is taken to be a Finger strain tensor with the instantaneous state as a reference state (*38*).

By considering the medium to be at rest for all times less than zero and then to be continuously deformed from time zero to the present instant, the strain tensor $\mathbf{e}$ may be written as a Taylor series in time about the present instant. We thus have

$$s < o : \mathbf{e}(s) = \mathbf{E}, \text{ a constant} \tag{2a}$$

$$s \geq o : \mathbf{e}(s) = \sum_n \frac{(-1)^{n+1}(t-s)^n}{2n!}\,\mathbf{B}_n(t) \tag{2b}$$

where (in Cartesian tensor notation)

$$B_{ij}^{(1)} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \tag{3a}$$

$$B_{ij}^{(n+1)} = \frac{D}{Dt}\,B_{ij}^{(n)} - \frac{\partial v_i}{\partial x_m}\,B_{mj}^{(n)} - \frac{\partial v_j}{\partial x_m}\,B_{im}^{(n)} \tag{3b}$$

Substitution of Equation (2) into Equation (1) yields

$$\tilde{\sigma} = -p\mathbf{I} + \left[\int_t^{\infty} \Phi(s)\ ds + \ldots\right]\mathbf{E}$$

$$+\left[\int_t^{\infty}\int_t^{\infty} \Psi\,(s_1, s_2)\ ds_1\, ds_2 + \ldots\right]\mathbf{E}^2$$

$$+\sum_n \frac{(-1)^{n+1}}{2n!}\left[\int_o^t s^n\,\Phi(s)\ ds\right]\mathbf{B}_n$$

$$+\sum_m\sum_n \frac{(-1)^{m+n}}{8m!n!}\left[\int_o^t\int_o^t s_1{}^m\, s_2{}^n\,\Psi\,(s_1, s_2)\ ds_1 ds_2\right]$$

$$[\mathbf{B}_m\mathbf{B}_n + \mathbf{B}_n\mathbf{B}_m] + \ldots \tag{4}$$

If we define new relaxation moduli by

$$\Phi(s) = -2\,\frac{dG(s)}{ds} \tag{5a}$$

$$\Psi(s_1, s_2) = 4\,\frac{\partial^2 K(s_1, s_2)}{\partial s_1\, \partial s_2} \tag{5b}$$

Equation (4) may be integrated by parts to yield

$$\tilde{\sigma} = -p\mathbf{I} + \sum_n \frac{(-1)^{n+1}}{(n-1)!}\left[\int_o^t s^{n-1}\,G(s)\ ds\right]\mathbf{B}_n$$

$$+\sum_m\sum_n \frac{(-1)^{m+n}}{2(m-1)!(n-1)!}$$

$$\left[\int_o^t\int_o^t s_1^{m-1}\,s_2^{n-1}\,K(s_1, s_2) ds_1 ds_2\,[\mathbf{B}_m\mathbf{B}_n + \mathbf{B}_n\mathbf{B}_m] + \ldots \tag{6}$$

Equation (6) is similar in form to the usual Rivlin-Ericksen expansion used for steady flows but there is a significant difference. The coefficients in Equation (6) are not constants but are increasing functions of time. As the moduli $G(s)$ and $K(s_1, s_2), \ldots,$ are approximately exponential, the time dependence of the coefficients is that of an initial rapid increase followed by a gradual approach to an asymptotic value. From a physical viewpoint, Equation (6) differs from the common Rivlin-Ericksen expansion in that it predicts both fluid and solidlike behavior. This may be seen from the following example.

SIMPLE SHEAR

Consider the velocity field

$$\mathbf{v} = \Gamma\, x_2\, \mathbf{e}_1 + 0\, \mathbf{e}_2 + 0\, \mathbf{e}_3 \tag{7}$$

This is the well-known problem of simple shearing flow which was first analyzed for the Rivlin-Ericksen asymptote by Rivlin (*26*) and is described by Coleman and Noll (*10*) and Fredrickson (*12*). Substitution of Equation (7) into Equation (6) yields for the stress components

$$\sigma_{12} = \left[\int_o^t G(s) ds\right]\Gamma + \ldots$$

$$\sigma_{11} = -p + \left[2\int_o^t sG(s) ds + \int_o^t\int_o^t K(s_1, s_2) ds_1 ds_2\right]\Gamma^2 + \ldots$$

$$\sigma_{22} = -p + \left[\int_o^t\int_o^t K(s_1, s_2) ds_1 ds_2\right]\Gamma^2 + \ldots$$

$$\sigma_{33} = -p \tag{8}$$

in which we have only included terms through the second-order approximation. It is easily seen that for long deformation times t such that t is greater than a characteristic relaxation time θ of the material, the stress components in Equation (8) are identical to those of the second-order Rivlin-Ericksen fluid (*8, 9, 14, 38*). For the opposite asymptote of very short deformation times Δt, in which the moduli $G(s)$ and $K(s_1, s_2), \ldots$ may be assumed effectively constant, it follows that

$$\begin{aligned} \sigma_{12} &= GS \\ \sigma_{11} &= -p + [G+K]S^2 \\ \sigma_{22} &= -p + KS^2 \\ \sigma_{33} &= -p \qquad\qquad S = \Gamma\Delta t \end{aligned} \tag{9}$$

which are identical to the results of second-order elasticity theory (*12, 27*) for simple shearing strains. Thus, for short deformation times Equation (6) is seen to predict solidlike behavior. For the intermediate case, it may be seen that the material at first acts as an elastic solid with a decaying modulus and then asymptotically approaches Rivlin-Ericksen fluid behavior.

The characteristic relaxation time θ of the relaxation moduli is thus seen to take on a special significance. When the deformation period is much greater than θ, the usual Rivlin-Ericksen approximations are valid. Conversely, for much shorter deformation periods it is important to employ constitutive relationships which portray stress relaxation and retardation effects correctly. This ordering in the choice of constitutive relationships emphasizes the importance of the characteristic relaxation times of polymeric media; for the case of infinitesimal deformations an extensive literature (*15, 33*) is available on the subject but this has not been extended to processes involving finite deformations save for a single publication (*35*).

CDM PARADOX

After discussion of the form of constitutive equations which describe the motion of viscoelastic fluids during steady deformations of short duration, it is useful to consider boundary value problems. Here, the principal point to be noted is that the usual procedure of simply substituting the Rivlin-Ericksen equations into the equations of motion and then solving, is frequently a questionable one; hence the validity of several such solutions in the literature is in doubt. The best way to illustrate this idea is to call attention to a recent paper by Coleman, Duffin, and Mizel (*7*). In this paper the problem of sudden acceleration of a flat plate parallel to a second plate, with fluid between the plates, is considered. Coleman et al. use the second-order Rivlin-Ericksen fluid as a constitutive equation and find that no solution is possible. The solution to the Coleman-Duffin-Mizel (CDM) paradox lies in the remarks of the previous sections of this paper; that is, in the realization that the Rivlin-Ericksen formulation is an asymptotic approximation valid only for times of deformation which are large as compared to θ, a characteristic relaxation time of the fluid. For the short time periods involved in the sudden acceleration problem Equation (6), which contains within it short time solid-like behavior, represents the proper asymptotic form of the Green-Rivlin theory.

Further, Eulerian sudden accelerations are not the only ones in which the usual Rivlin-Ericksen approximations will not suffice. The same considerations are applicable to all problems which are unsteady from a Lagrangian viewpoint, such as flows around submerged objects; flow in the entry regions of conduits and in conduits in which there is a sudden change in cross section; in oscillatory and turbulent flows; or in processes in which the fluid being handled is suddenly subjected to an intense shearing, as in flow into an atomization nozzle. In all of these instances a fluid element is subjected to sudden, or at least rapidly changing, deformations on a time scale which may be small as compared to the characteristic time of the fluid θ, and Equation (6) or some equivalent relation, rather than the usual Rivlin-Ericksen asymptote, must be used to describe the fluid. Thus, in the case of the developing boundary layers over submerged objects or in the entry region of a conduit, analyses which have employed the Rivlin-Ericksen approximations (*2, 23, 39*) may be valid only asymptotically in that region of the flow field sufficiently far removed from the forward stagnation point or conduit entry in which the residence time of the fluid exceeds the characteristic time θ. The analyses of Tomita (*34*) and of Metzner and White (*17*) have considered this point in somewhat greater detail; it is found that the fluid behaves as an elastic solid near the entrance and as a Rivlin-Ericksen fluid further downstream.

APPLICATION TO SCALE-UP

Scale-up criteria for purely viscous non-Newtonian fluids have been considered by Fredrickson (*12*), Metzner (*16*), and Slattery and Bird (*31*) and the state of the art is rather well defined for these. Discussions for viscoelastic materials, although incomplete, have appeared in the analyses of Astarita (*1*), Bogue and Doughty (*4*), Seyer (*29*), Slattery (*30*), White and Metzner (*17, 38, 39*), and White and Tokita (*40*). The principal point which emerges is that if the flow regime is one in which the Rivlin-Ericksen asymptote is valid then the flow of a viscoelastic material is determined by a Reynolds number, a series of ratios of viscoelastic coefficients, and a series of dimensionless groups containing both kinematic and constitutive parameters:

$$N_{ve} = \frac{\int_0^\infty s^{n+1}\, G(s)\, ds}{\int_0^\infty s^n\, G(s)\, ds} \frac{V}{D} \simeq \theta \frac{V}{D} \tag{10}$$

The first of these ($n = 0$), representing a ratio of elastic to viscous forces, has been termed the Weissenberg number (*17, 38 to 40*).

For deformations in which the residence time t is less than the characteristic relaxation time θ, both the cross ratios (fluid property ratios) and the above parameters become time dependent; for example Equation (10) becomes

$$\frac{\int_0^t s^{n+1}\, G(s)\, ds}{\int_0^t s^n\, G(s)\, ds} \frac{V}{D}$$

The ratio defined by this group differs from that of Equation (10) by an amount which depends upon θ/t, the ratio of the characteristic time of the fluid to the time scale of the process, the latter being determined *not* by the fluid deformation rate as suggested in a recent analysis (*3*), but by the residence time of the fluid in the changing velocity field. When this ratio is small, the fluid has time to accommodate itself to the local stress field or kinematic conditions and the Rivlin-Ericksen approximations in either their full or their abbreviated form (*17*) may be employed. Conversely, for large values of the ratio θ/t the proper asymptotic form of the Rivlin-Ericksen approximation is given by Equation (6) or, alternately, one may use implicit integral equations as discussed by Bogue (*4*) or any of the empirical relationships reviewed recently by Spriggs, Huppler, and Bird (*32*). None of these choices for problems involving large values of the ratio θ/t explicitly gives the stresses in terms of the kinematics of the velocity fields, but involves either convected derivatives or integrals which depend upon the solution of the problem. Thus, analyses of flow fields such as those of the several significant flow problems enumerated in the previous sections, for which the ratio θ/t is large, are likely to involve considerable mathematical difficulties.

The ratio θ/t will be recalled to be related to the Deborah number considered by Reiner* (*24*) and will be so designated.

The preceding sections show that proper scale-up criteria in engineering design for viscoelastic fluids involve, in addition to fluid property and geometric ratios, the Reynolds, Weissenberg, and Deborah numbers. The Reynolds number represents, of course, the ratio of inertial to viscous forces developed in the flow field and the Weissenberg number the corresponding ratio of elastic to viscous forces (*38, 39*). The Deborah number, representing a ratio of time scales involving the fluid properties and the residence time of the fluid, is, at least in steady flows in simple geometries, related to the Weissenberg number through a geometric (L/D) ratio of the processing equipment. As noted in an analysis of turbulent flow fields based on these concepts (*29*), the Weissenberg number

* Actually Reiner considered the reciprocal of this grouping as the Deborah number. The present grouping is perhaps somewhat more natural in that the fluid memory must be considered most carefully for large values of this grouping and this parallel between the complexity of the fluid behavior and the rapidity of the flow is perhaps a natural one. Obviously the choice is largely arbitrary.

describes the innate capacity of the fluid to exhibit both elastic and viscous responses and the magnitude of these, while the Deborah number describes the influence on the flow field of unsteady elastic responses in either a Lagrangian or Eulerian sense. As implied by Slattery (*30*) the difference in the shape of relaxation moduli from material to material may make it difficult if not impossible to apply data on one material to the scaling of another, since the various fluid property ratios may thus be changed. However, if the same fluid is used throughout and if the equipment is geometrically similar then the Reynolds, Weissenberg, and Deborah numbers become the sole dimensionless groups which must be considered.

In special cases, one or more of these three dimensionless ratios may be of negligible importance. Thus, in molten polymers inertial effects are frequently negligible (the Reynolds number is very small and may be neglected) and only the Weissenberg and Deborah numbers are of importance. This observation is of paramount importance as it is impossible to change the scale of equipment, retaining the same material, and obtain constancy of both the Reynolds and Weissenberg numbers. Thus scale-up with a given fluid is not possible unless one of these groups may be shown to be of negligible importance in the problem at hand.

In slowly changing or nearly steady flows, such as encountered in flow through long conduits of constant cross section, or of a cross section which is changing only slowly, only the Reynolds and Weissenberg numbers are of significance in scaling of equipment for a single fluid, as the Deborah number may be too small to be of significance. If under these circumstances the fluid is also only slightly viscoelastic then the Weissenberg number, representing the ratio of elastic to viscous forces, is also too small to be important and only the Reynolds number remains. These considerations are nicely supported by the results recently reported by Christopher and Middleman (*6*) and by Bogue (*4*) for flow through packed beds and in diverging channels, respectively. Under conditions of turbulent flow the analyses of Astarita (*1*), Metzner and Park (*18*), and Seyer (*29*) indicate that all three groups —the Reynolds, Weissenberg, and Deborah numbers— are likely to be significant.

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NOTATION

$\mathbf{B}_n$ = acceleration tensors defined by Equation (3)
$\mathbf{E}$ = strain tensor defined by Equation (*2a*)
$\mathbf{e}_j$ = unit vector
$\mathbf{e}(s)$ = Finger strain tensor (or conjugate metric tensor) (*12, 33*)
$G(s)$ = linear viscoelastic relaxation modulus
$\mathbf{I}$ = unit matrix
$K(s_1, s_2)$ = relaxation modulus
D = characteristic length dimension
p = pressure
S = shear strain
s = dummy time variable
t = deformation time
V = characteristic velocity
$\mathbf{v}$ = velocity vector
$\Phi(s), \Psi(s_1, s_2), \Sigma(s_1, s_2)$ = relaxation moduli
$\underset{\sim}{\sigma}$ = stress tensor
θ = characteristic relaxation time
Γ = shear rate

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