Validity of the First-Order Fluid Model

J. S. VRENTAS, C. M. VRENTAS

Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802

Received 10 April 1998; accepted 9 January 1999

ABSTRACT: The general validity of the first-order fluid model is considered. Conditions are established for which a first-order fluid represents an acceptable approximation to the integral viscoelastic fluid from which it was derived as a Taylor series approximation. The results are applied to two flow problems: generation of flow by the application of a pressure gradient and the growth or dissolution of bubbles in viscoelastic liquids. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 547–552, 1999

Key words: viscoelastic; bubble growth; dissolution

INTRODUCTION

In general, the flow behavior of polymer melts and solutions can best be described by using differential or integral nonlinear viscoelastic constitutive equations.[1] It is sometimes useful, however, to use a simpler rheological model to gain some insight into the importance of elastic effects and of nonlinear viscous effects on the flow behavior of non-Newtonian fluids. An example of a simpler rheological model is the retarded motion expansion, which is thought to be valid for sufficiently small velocity gradients. Bird et al.[1] have noted that in general, retarded motion expansions are valid in the limit of a small Deborah number.

A special constitutive equation based on a special type of retarded motion expansion is the first-order fluid.[2] The first-order fluid represents the first-order term of a Taylor series expansion for linear integral viscoelastic fluids for the special case of unsteady flows of fluids that were at rest for time $t < 0$. The objective of this article is to determine the general validity of this type of unsteady Taylor series expansion. In particular, conditions are established for which the first-order fluid represents an acceptable approximation to the integral viscoelastic fluid from which it was derived as a Taylor series approximation. The theory is developed in the next section, and the results are applied to two flow problems in the third section.

THEORY

As an example of a typical viscoelastic fluid, we consider the constitutive equation for finite linear viscoelasticity, which is the simplest integral constitutive equation that can be derived from simple fluid theory. For an incompressible fluid, the extra stress $\mathbf{S}$ is given by the expression

$$\mathbf{S} = \int_0^\infty \bar{m}(s)[\mathbf{C}_t(t-s) - \mathbf{I}]\, ds \tag{1}$$

where

$$\bar{m}(s) = \frac{dG(s)}{ds} \tag{2}$$

Here t is the present time, s is the backward running time, $\mathbf{I}$ is the identity or unit tensor, $G(t)$

Correspondence to: J. S. Vrentas.

Contract grant sponsor: Dow Chemical Co.

is the shear-stress relaxation modulus of linear viscoelasticity, and $\mathbf{C}_t(t - s)$ is the right Cauchy–Green tensor relative to time t. Also, $\mathbf{C}_t(t - s)$ can be expressed in terms of a Taylor series of the form

$$\mathbf{C}_t(t - s) = \mathbf{I} - s\mathbf{A}_1 + \frac{s^2}{2}\mathbf{A}_2 - \cdots \quad (3)$$

In this expression, $\mathbf{A}_n$ is the nth Rivlin–Ericksen tensor evaluated at time t. Eqs. (1)–(3) can be used to derive a modified form of the constitutive equation for the integral viscoelastic fluid and also to derive the constitutive equation for the first-order fluid.

We now consider unsteady flows for which the fluid is at rest up to zero time. For convenience, we use the following expression for the relaxation modulus:

$$G(s) = a\lambda e^{-s/\lambda} \quad (4)$$

Here a and λ are constants for a given material, and λ is a characteristic relaxation time for the fluid. Integration by parts and introduction of eq. (3) produce the following expression for the integral viscoelastic fluid:

$$\mathbf{S} = \int_0^t G(s)[\mathbf{A}_1 - s\mathbf{A}_2 + \cdots]\, ds \quad (5)$$

The first-order fluid represents the first-order term of the foregoing expansion:

$$\mathbf{S} = \int_0^t G(s)\mathbf{A}_1\, ds \quad (6)$$

These equations can be combined with eq. (4) and put into dimensionless form using the following dimensionless variables:

$$t^* = \frac{t}{\lambda} \quad (7)$$

$$s^* = \frac{s}{\lambda} \quad (8)$$

$$\mathbf{A}_n^* = t_0^n\mathbf{A}_n \quad (9)$$

$$\mathbf{S}^* = \frac{\mathbf{S}t_0}{\eta_0} \quad (10)$$

Here t_0 is the characteristic time for the deformation process for the fluid, and η_0 is the fluid viscosity at zero shear rate. The dimensionless forms of eqs. (5) and (6) are simply

$$\mathbf{S}^* = \int_0^{t^*} e^{-s^*}\Bigg[\mathbf{A}_1^* - s^*N_D\mathbf{A}_2^* + \frac{s^{*2}N_D^2}{2!}\mathbf{A}_3^* - \frac{s^{*3}N_D^3}{3!}\mathbf{A}_4^* + \cdots\Bigg]\, ds^* \quad (11)$$

$$\mathbf{S}^* = \int_0^{t^*} e^{-s^*}\mathbf{A}_1^*\, ds^* \quad (12)$$

where N_D is the Deborah number for the particular deformation process and for the particular fluid of interest:

$$N_D = \frac{\text{characteristic time of fluid}}{\text{characteristic time of process}} = \frac{\lambda}{t_0} \quad (13)$$

It is clear that the dimensionless constitutive equation for the integral viscoelastic fluid [eq. (11)] reduces to the constitutive equation for the first-order fluid [eq. (12)] as $N_D \to 0$. Hence, the first-order fluid is clearly valid for low values of N_D, and this is consistent with the analysis of Bird et al.[1] In addition, however, it is evident from eqs. (11) and (12) that the integral viscoelastic fluid is also approximated well by the first-order fluid when $N_Dt^* \to 0$. Consequently, the first-order fluid not only describes flows at low values of the Deborah number but also at high values of the Deborah number if the deformation field is imposed over a sufficiently small time interval. Consequently, useful Taylor series expansions can be derived from integral constitutive equations when

$$N_D \to 0 \quad t^* > 0 \quad (14)$$

or when

$$N_Dt^* \to 0 \quad (15)$$

The first condition states that the Taylor series expansion is valid for all times if N_D is sufficiently small. The second condition restricts only the product of N_D and t^*, so that rapid deformations involving very elastic fluids can be described by an unsteady Taylor series expansion if the time interval is made sufficiently small.

We now obtain an estimate of the error introduced by using eq. (12) rather than eq. (11) to describe the unsteady flows of fluids that were at rest for $t < 0$. An equation for the variation of this error with Deborah number (N_D) and the time interval of the deformation (t^*) can be derived by using the following equations to provide reasonable approximations for the *dimensionless* Rivlin–Ericksen tensors:

$$\mathbf{A}_1^* \approx \mathbf{A}_2^* \approx \cdots \approx \mathbf{A}_n^* \tag{16}$$

Substitution of this approximation into eq. (11) produces the following simple estimate for the dimensionless extra stress $\mathbf{S}^*$ for the integral viscoelastic fluid:

$$\mathbf{S}^* = \mathbf{A}_1^* \int_0^{t^*} e^{-s^*} \exp[-N_D s^*] \, ds^* \tag{17}$$

Evaluation of the integral in this equation produces the following estimate for $\mathbf{S}^*$ for the integral viscoelastic fluid:

$$\mathbf{S}^* = \frac{\mathbf{A}_1^*}{1 + N_D} \{1 - \exp[-t^*(1 + N_D)]\} \tag{18}$$

The corresponding result for the dimensionless stress for the first-order fluid can be derived from eq. (12):

$$\mathbf{S}^* = \mathbf{A}_1^*[1 - e^{-t^*}] \tag{19}$$

An estimate of the error introduced in using the first-order fluid constitutive equation to analyze a flow field can be calculated by using the ratio R_1 to compare the dimensionless extra stress coefficients in eqs. (18) and (19):

$$R_1 = \frac{\text{extra stress coefficient for integral viscoelastic fluid}}{\text{extra stress coefficient for first-order fluid}} \tag{20}$$

$$R_1 = \frac{1 - \exp[-t^*(1 + N_D)]}{(1 + N_D)(1 - e^{-t^*})} \tag{21}$$

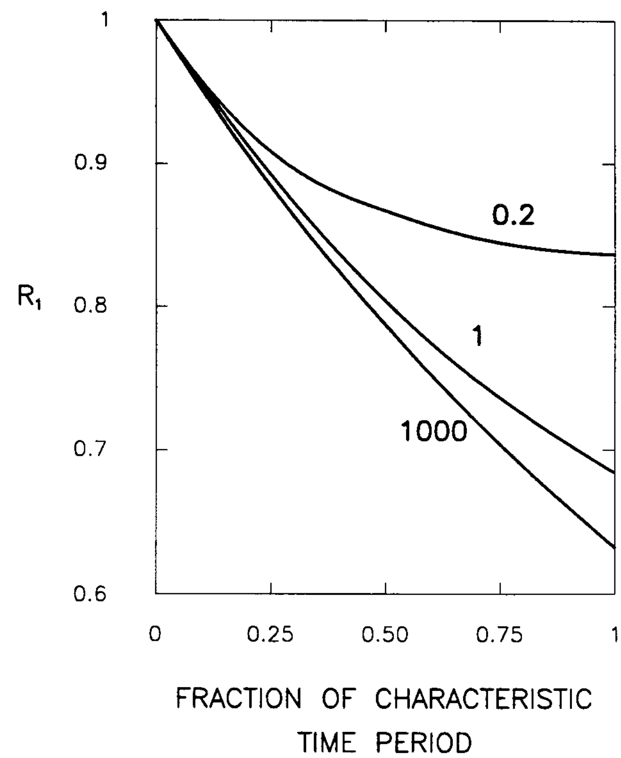

Figure 1 Dependence of R_1 on time and Deborah number. Numbers on the curves refer to values of N_D.

It is evident from eq. (21) that

$$R_1(t^* = \infty) = \frac{1}{1 + N_D}, \tag{22}$$

so that in the long time limit, the first-order fluid provides a good approximation ($R_1 \approx 1$) to the integral viscoelastic fluid only when N_D is sufficiently small. However, in the early part of the deformation process, the first-order fluid can provide reasonable approximations to the stress for large values of N_D if t^* is sufficiently small. For example, a characteristic time t_0 is associated with each unsteady deformation process, and it is reasonable to expect that the more important aspects of the unsteady deformation process occur in the time interval from $t = 0$ to $t = t_0$. Hence it is useful to determine the general validity of the first-order fluid in the characteristic time period ranging from $t^* = 0$ to $t^* = 1/N_D$ (or $t = 0$ to $t = t_0$). A calculation for R_1 based on eq. (21) is illustrated in Figure 1, which presents the dependence of R_1 on N_D and t^*.

It is evident from Figure 1 that for Deborah numbers ranging from 0 to 1,000, the first-order constitutive equation provides excellent predictions over 25% of the characteristic time period (about 10% error), reasonably good predictions for 50% of the characteristic time period (about 20% error), and generally adequate predictions at the end of the characteristic time period (about 35% error). Consequently, it is fair to conclude from Figure 1 and eq. (21) that the first-order fluid yields adequate estimates for the extra stress anywhere in the characteristic time period for all values of the Deborah number.

RESULTS AND DISCUSSION

We now use the results of the foregoing development to examine some characteristics of two important unsteady flow fields. The first flow field involves the generation of flow by the application of a pressure gradient; the second is concerned with the growth or dissolution of bubbles in viscoelastic liquids.

For the first problem, a fluid is at rest between parallel plates separated by a distance L, and a pressure gradient is applied at zero time. For this unsteady flow problem,

$$t_0 = \frac{L^2\rho}{\eta_0} \tag{23}$$

$$N_D = \frac{\lambda\eta_0}{L^2\rho} \tag{24}$$

where ρ is the mass density of the fluid. Solutions for the velocity field for this problem were presented previously[2] for both the integral viscoelastic and first-order fluids. These solutions were obtained for two values of the Deborah number (0.3 and 0.5), and in each case, excellent agreement was obtained between the integral viscoelastic predictions and those of the first-order fluid for 25% of the characteristic time period. In addition, good to adequate predictions were obtained in both cases for the entire characteristic time period. These results clearly show the general validity of the first-order fluid model during the characteristic time period. Furthermore, actual calculations for the integral viscoelastic and first-order fluid models yield error values for early times that are consistent with the estimated error derived using eq. (21).

For the second problem, we study the increase or decrease of the radius of a gas bubble in a viscoelastic fluid as a function of time. This problem is complicated by the presence of a moving boundary and the coupling of rheological and mass transfer effects. Consequently, the utilization of simpler rheological models is particularly important, especially if analytical results are to be developed. For this unsteady flow problem

$$t_0 = \frac{R_0^2}{D|N_a|} \tag{25}$$

$$N_D = \frac{\lambda D|N_a|}{R_0^2} \tag{26}$$

The absolute value sign is needed because the parameter N_a is negative for bubble growth and positive for bubble dissolution. Here R_0 is the initial radius of a gas bubble, and D is the binary mutual diffusion coefficient in the liquid polymer. Also, the dimensionless parameter N_a is defined as

$$N_a = \frac{\rho(\rho_{1E} - \rho_{10})}{\hat{\rho}_0(\rho - \rho_{1E})} \tag{27}$$

where ρ is the total mass density of the liquid phase, ρ_{10} is the initial solute concentration in the liquid phase, $\hat{\rho}_0$ is the initial gas density, and ρ_{1E} is the solute concentration corresponding to the initial pressure. The parameter N_a is 0.03 for the dissolution of oxygen in water and 0.8 for the dissolution of carbon dioxide in water. Typically, $|N_a|$ is on the order of unity or less for bubble–liquid systems.

The results of Figure 1 suggest that the constitutive equation for a first-order fluid should generally provide adequate predictions for the stress when

$$N_D t^* \leqq 1 \tag{28}$$

or, in dimensional form, for bubble growth or dissolution when

$$\frac{Dt|N_a|}{R_0^2} \leqq 1 \tag{29}$$

Calculations carried out using an inviscid liquid phase can be used to give a rough indication of the state of a bubble growth or dissolution process at the end of the characteristic time period. For the range $0 < |N_a| < 1$, the bubble has dissolved for all values of N_a, and for negative values of N_a, the bubble radius has increased by a factor of two to three at the end of the characteristic time period. This suggests that the constitutive equation for a first-order fluid can be used to describe a significant fraction of the bubble dissolution process and a time period for the bubble growth process during which significant bubble growth has occurred. However, the first-order fluid can, of course, be used to describe only a small part of a bubble growth process that involves a 200-fold increase in the bubble radius.[3]

Even though the first-order fluid cannot be used to describe a bubble growth process with a large increase in the bubble radius, the foregoing analysis does suggest another possibility for determining the radius-time behavior at large values of N_D. For the bubble growth or dissolution problem, the mass transfer and rheology are coupled through the extra normal stress terms in the radial component of the equation of motion. If the extra normal stress terms are only a small fraction of the pressure level in the flow field, then they can be neglected, and the fluid can essentially be treated as an inviscid fluid. An estimate of the relative importance of the extra normal stress terms can be obtained by calculating the ratio of the dimensionless extra stress coefficient for the integral viscoelastic fluid to the dimensionless pressure:

$$R_2 = \frac{\text{dimensionless extra stress coefficient}}{\text{dimensionless pressure}} \tag{30}$$

$$R_2 = \frac{N_V |N_a| \{1 - \exp[-t^*(1 + N_D)]\}}{1 + N_D} \tag{31}$$

$$N_V = \frac{\eta_0 D}{p_0 R_0^2} \tag{32}$$

Here p_0 is the initial pressure in the liquid and N_V characterizes the importance of viscous effects in the bubble growth or bubble dissolution process. Clearly,

$$R_2(\text{max}) = \frac{N_V |N_a|}{1 + N_D} \tag{33}$$

and the extra normal stress will be small compared to the pressure level when

$$R_2(\text{max}) \ll 1 \tag{34}$$

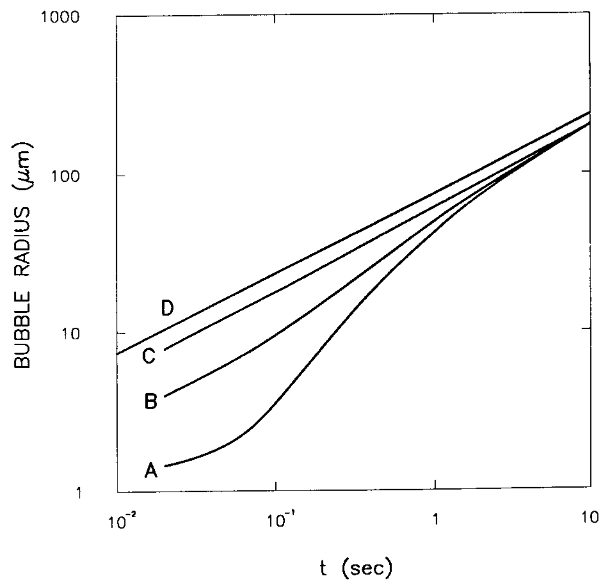

Figure 2 Bubble growth for inviscid and DeWitt fluid models. Curve D is for an inviscid fluid; curves A, B, and C are for the DeWitt model with $N_D = 0, 60.4$, and 3360, respectively.

This will happen when $N_V \to 0$ (low viscosity fluid) and $R_2(\text{max})$ is also very small for $N_D \to \infty$ (very elastic fluid). Consequently, for bubble growth or dissolution in a very elastic fluid, the radius-time behavior can be estimated using an inviscid analysis, and the various solutions that are available at the inviscid limit[4] can be utilized.

The approach of the radius-time curve for an elastic fluid to the radius-time curve for an inviscid fluid as $N_D \to \infty$ is illustrated in Figure 2. From this figure, it is evident that the predictions of the viscoelastic DeWitt model[3] approach the inviscid fluid predictions as the Deborah number N_D is increased. Consequently, simple rheological models can be used to describe bubble growth or dissolution in elastic liquids for two cases. The first-order fluid model [eq. (6)] can be used to provide adequate results when

$$N_D t^* \leqq 1 \tag{35}$$

and the inviscid flow approximation can be used for all time when

$$\frac{N_V |N_a|}{1 + N_D} \ll 1 \tag{36}$$

Although of course there will be conditions for which a more general model must be used, these two simpler approaches will provide very useful results in many cases.

CONCLUSIONS

In this article we have shown that reasonable stress approximations for the simplest integral constitutive equation (finite linear viscoelasticity) can be calculated by using an unsteady Taylor series expansion (the first-order fluid) if either eq. (14) or eq. (28) is satisfied. The first-order fluid should also provide reasonable stress approximations to more general integral constitutive equations for similar restrictions, but the error estimates may be somewhat different. In the present case, the error estimate is based on the utilization of eq. (16). This equation should provide a reasonable approximation for all well-behaved flow fields and hence for most physically realistic problems.

This work was supported by funds provided by the Dow Chemical Company.

REFERENCES

1. Bird, R. B.; Armstrong, R. C.; Hassager, O. Dynamics of Polymeric Liquids, Vol. 1, 2nd ed.; Wiley: New York; 1987.
2. Vrentas, J. S.; Vrentas, C. M. I EC Res 1995, 34, 3203.
3. Han, C. D.; Yoo, H. J. Polym Eng Sci 1981, 21, 518.
4. Vrentas, J. S.; Vrentas, C. M.; Ling, H.-C. Chem Eng Sci 1983, 38, 1927.