On the Limit of Linear Viscoelastic Response in the Flow Between Eccentric Rotating Disks

R. J. J. JONGSCHAAP, K. H. KNAPPER, *and* J. S. LOPULISSA

Department of Applied Physics
Twente University of Technology
Enschede, The Netherlands

The dependence on frequency of the limiting value of strain, ψ_L, for which linear viscoelastic response occurs in eccentric rotating disks (ERD) flow is studied theoretically and experimentally. The theoretical investigations are based upon the general simple-fluid theory of Coleman and Noll. It is shown that according to this theory ψ_L becomes independent of angular velocity, ω, at relatively high frequencies, whereas ψ_L becomes inversely proportional to ω at sufficiently low frequencies. The results of previous investigations, based upon some special rheological models, are discussed. The behavior predicted by the simple-fluid theory is confirmed by experiments on polyisobutylene solutions.

INTRODUCTION

If a polymeric liquid is subjected to finite deformations, the relation between the stress response and the history of deformations is in general non-linear and complicated. At sufficiently small deformations, however, the response of the material becomes linear and is described by the classical theory of linear viscoelasticity. Although this discipline is already very well established theoretically and experimentally, there still exists some confusion about the limiting value of strain up to which it is applicable. In the instance of an oscillatory shear flow, the problem can be stated as follows: does the limiting value of strain amplitude, ψ_L, upon to which linear viscoelastic response occurs, depend on frequency or not? Systematic experimental evidence about this problem was reported first by Philippoff (1), who performed large-amplitude oscillatory shear experiments on a variety of polymeric liquids and observed that ψ_L was independent of frequency. A different way of investigating the problem experimentally is offered by the so-called "eccentric rotating disks flow" (ERD), in which the deformation of a fluid element is effectively one of oscillatory shear. This type of flow will be described in the following section. It has been used for the determination of $\psi_L(\omega)$ by Gross and Maxwell (2) for a series of polymer melts. Again no frequency dependence of the strain limit was found. These results were used by Gross and Maxwell for checking the validity of some non-linear constitutive equations. This is a way of checking indeed, for Gordon and Schowalter (3) have proved that different classes of constitutive equations lead to different predictions about the behavior of $\psi_L(\omega)$. Some of these predictions will be reviewed in the section on Special Models.

In the present investigations, rather than using some special rheological models, we took as a basis the more general theory of simple fluids with fading memory of Coleman and Noll (4). In the section on Simple-Fluid Theory, it will be shown that according to this theory, a shape of the $\psi_L(\omega)$ curve is obtained which is qualitatively different from the ones obtained for the special models. In order to check our theoretical results, experiments similar to those of Gordon and Schowalter have been performed. At present only some preliminary results are available. These results, which support the predictions of the simple-fluid theory, will be presented in the Experimental Section.

ECCENTRIC ROTATING DISKS FLOW

A schematic diagram of the eccentric rotating disks (or Maxwell orthogonal flow) is given in *Fig. 1*. The fluid is contained between two parallel plates on a distance h from each other, rotating with an angular velocity ω

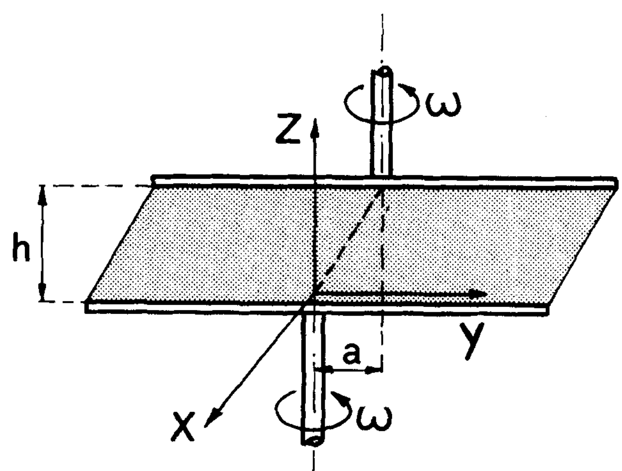

Fig. 1. Schematic diagrams of the ERD flow.

about axes which are shifted an amount a with respect to each other. It can be shown (5, 6) that although the motion is stationary the material elements are performing a sinusoidal deformation with a strain amplitude equal to

$$\psi = \frac{a}{h} \tag{1}$$

In the region of linear response the horizontal forces F_y and F_x on the plates are given by the expressions (7-10):

$$\begin{aligned} F_y &= \pi R^2 T_{yz} = \pi R^2 \psi G' \\ F_x &= \pi R^2 T_{xz} = \pi R^2 \psi G'' \end{aligned} \tag{2}$$

R is the radius of the plates and G' and G'' are the real and imaginary part of the complex dynamic shear modulus $G^*(\omega)$. For our purpose only some kinematic properties of the flow are needed. It will be assumed that the effect of the free edges (11), of inertia (12) and of a possible velocity lag (13) between the plates upon the flow profile are negligible, as has been shown to be allowed under the usual experimental conditions. In that case, the fluid particles make a circular motion around centers that are located on a straight line between the centers of the two disks. The relative deformation function which relates the coordinates $x(t-s)$, $y(t-s)$, $z(t-s)$ of a particle at a (past) time $t-s$ $(s > 0)$ with the coordinates at the (present) time t is given then (8) by the equations:

$$\begin{aligned} x(t-s) &= x(t)\cos\omega s + [y(t) - \psi z(t)]\sin\omega s \\ y(t-s) &= -x(t)\sin\omega s + [y(t) - \psi z(t)]\cos\omega s + \psi z(t) \\ z(t-s) &= z(t) \end{aligned} \tag{3}$$

For the relative deformation gradient

$$\underline{F}_t(t-s) = \frac{\partial \underline{x}(t-s)}{\partial \underline{x}(t)} \tag{4}$$

we obtain from these:

$$[\underline{F}_t(t-s)] = \begin{bmatrix} c & s & -\psi s \\ -s & c & \psi(1-c) \\ 0 & 0 & 1 \end{bmatrix}$$

where

$$c \equiv \cos\omega s \quad \text{and} \quad s \equiv \sin\omega s. \tag{5}$$

For the strain tensors $\underline{\Gamma}$ and $\underline{\bar{\Gamma}}$, defined as

$$\begin{aligned} \underline{\Gamma}(t-s) &= \underline{1} - \underline{C}_t(t-s) \\ \underline{\bar{\Gamma}}(t-s) &= \underline{C}_t^{-1}(t-s) - \underline{1} \end{aligned} \tag{6}$$

where

$$\underline{C}_t(t-s) = \underline{F}_t^T(t-s)\cdot\underline{F}_t(t-s) \tag{7}$$

the relative Cauchy strain tensor, we obtain:

$$[\underline{\Gamma}] = \begin{bmatrix} 0 & 0 & \psi s \\ 0 & 0 & \psi(1-c) \\ \psi s & \psi(1-c) & 2\psi^2(c-1) \end{bmatrix} \tag{8}$$

$$[\underline{\bar{\Gamma}}] = \begin{bmatrix} \psi^2 s^2 & \psi^2 s(1-c) & \psi s \\ \psi^2 s(1-c) & \psi^2(1-c)^2 & \psi(1-c) \\ \psi s & \psi(1-c) & 0 \end{bmatrix} \tag{9}$$

where again the abbreviations of *Eq 5* have been used.

From *Eq 3* the Cartesian components of the velocity field are calculated to be:

$$\underline{v} = (-\omega y + \omega\psi z,\ \omega x,\ 0) \tag{10}$$

The rate-of-strain tensor

$$\underline{D} = \frac{1}{2}[grad\ \underline{v} + (grad\ \underline{v})^T] \tag{11}$$

therefore becomes:

$$[\underline{D}] = \begin{bmatrix} 0 & 0 & \frac{1}{2}\omega\psi \\ 0 & 0 & 0 \\ \frac{1}{2}\omega\psi & 0 & 0 \end{bmatrix} \tag{12}$$

For later reference we finally note that

$$\overline{II}_{\underline{D}} \equiv tr\ \underline{D}^2 = \frac{1}{2}\omega^2\psi^2 \tag{13}$$

SPECIAL MODELS

In this section we briefly review some results (2) about the frequency dependence of the strain limit of linear viscoelastic response ψ_L for some special rheological models. As an example of a model of the integral type with a strain dependent memory function we consider Tanner's network rupture model (14, 15)*. The constitutive equation is of the form

$$\underline{T} = -p\,\underline{1} + \int_0^\infty K[\underline{\Gamma}(t-s)]\,\mu(s)\Big[\Big(1+\frac{\epsilon}{2}\Big)\,\underline{\bar{\Gamma}}(t-s) - \frac{\epsilon}{2}\,\underline{\Gamma}(t-s)\Big]\,ds \tag{14}$$

where ϵ is a constant and the function $K(\underline{\Gamma})$ has the following properties:

$$K(\underline{\Gamma}) = \begin{Bmatrix} 0 \\ 1 \end{Bmatrix} \text{ if } tr\Big[\Big(1+\frac{\epsilon}{2}\Big)\,\underline{\Gamma} - \frac{\epsilon}{2}\,\underline{\Gamma}\Big] \begin{Bmatrix} > \\ < \end{Bmatrix} (1+\epsilon)\,B^2 \tag{15}$$

Physically this means that network rupture occurs when the magnitude of strain exceeds some critical value, determined by the constant B.

In ERD flow using *Eqs 8* and *9* we obtain from *Eq 15*:

$$K(\underline{\Gamma}) = \begin{Bmatrix} 0 \\ 1 \end{Bmatrix} \text{ if } 2\psi^2(1-\cos\omega s) \begin{Bmatrix} > \\ < \end{Bmatrix} B^2 \tag{16}$$

In the case that the $<$ sign applies for all values of s, i.e., if

$$\psi < \frac{B}{2} \tag{17}$$

we obtain from *Eqs 2, 14* and *16* the following expressions for the forces on the plates:

* Since Tanner's model is a special case of a simple fluid the fact that the result, *Eq 19*, is inconsistent with *Eq 40* seems at first sight a paradox. This point has been discussed recently in a paper by Astarita and Jongschaap (18). It turns out that in the case of Tanner's model *Eq 19* applies only at relatively high frequencies and that at low frequencies the behavior is similar to one predicted by *Eq 40*.

$$F_y = \pi R^2 \psi \int_0^\infty \mu(s)\,(1 - \cos \omega s)\, ds$$
$$F_x = \pi R^2 \psi \int_0^\infty \mu(s) \sin \omega s\, ds \tag{18}$$

So these values of ψ are in the range of linear viscoelastic response.

In the case that the > sign in *Eq 16* applies the function $K(\underline{\Gamma})$ becomes zero for some values of s and therefore non-linear terms will appear in the expressions corresponding to *Eq 18*. Thus we arrive at the conclusion that, in this model, the strain limit of linear viscoelastic response is given by

$$\psi_L = \frac{B}{2} \tag{19}$$

independently of ω (cf., *Fig. 2a*).

As an example of a model of the integral type with a rate-of-strain dependent memory function we now consider the Bird-Carreau model (16). The constitutive equation of this model is of the form

$$\underline{T} = -p\,\underline{1} + \int_0^\infty \mu[s, \overline{II}_{\underline{D}}(t-s)] \left[\left(1 + \frac{\epsilon}{2}\right) \overline{\underline{\Gamma}}(t-s) - \frac{\epsilon}{2}\, \underline{\Gamma}(t-s)\right] ds \tag{20}$$

with a memory function given by the expression

$$\mu[s, \overline{II}_{\underline{D}}(t-s)] = \sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_{2k}^2}\, \frac{e^{-\frac{s}{\lambda_{2k}}}}{1 + 2\lambda_{1k}^2\, \overline{II}_{\underline{D}}(t-s)} \tag{21}$$

where $\overline{II}_{\underline{D}}$ is defined as in *Eq 13*, and

$$\eta_k = \eta_o \frac{\lambda_{1k}}{\sum_{m=1}^{\infty} \lambda_{1m}};\quad \lambda_{1k} = \lambda_1 \left(\frac{1 + n_1}{k + n_1}\right)^{\alpha_1}$$
$$\lambda_{2k} = \lambda_2 \left(\frac{1 + n_2}{k + n_2}\right)^{\alpha_2} \tag{22}$$

The model contains 8 material parameters: the time constants λ_1 and λ_2, 2 dimensionless integers: n_1 and n_2, 3 dimensionless scalars: α_1, α_2 and ϵ, and the zero-shear-rate viscosity, η_0. Using *Eqs 8, 9, 13, 20,* and *21*,

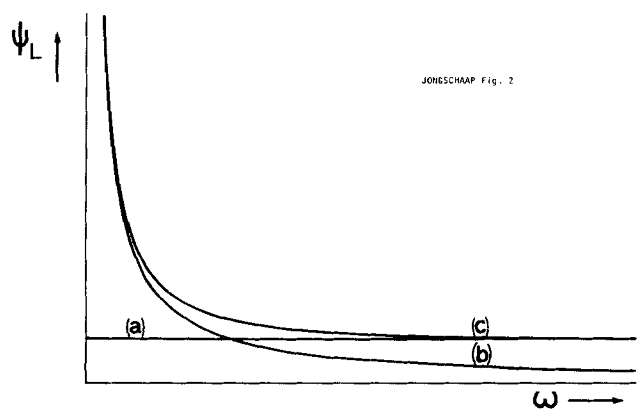

Fig. 2. Strain limit of linear viscoelastic response as a function of frequency according to (a) Tanner's network rupture model, (b) the Bird-Carreau model and (c) the simple-fluid theory.

the following expressions for the forces on the plates are obtained:

$$F_y = \pi R^2 \psi \sum_{k=1}^{\infty} \frac{\omega^2 \lambda_{2k} \eta_k}{(1 + \omega^2 \psi^2 \lambda_{1k}^2)(1 + \omega^2 \lambda_{2k}^2)} \tag{23}$$

$$F_z = \pi R^2 \psi \sum_{k=1}^{\infty} \frac{\omega \eta_k}{(1 + \omega^2 \psi^2 \lambda_{1k}^2)(1 + \omega^2 \lambda_{2k}^2)} \tag{24}$$

These expressions become linear in ψ if

$$\omega^2 \psi^2 \lambda_{1k}^2 << 1 \tag{25}$$

So in this case the extent of the linear region depends on the value of $\omega\psi$ instead of ψ alone, as it was the case in Tanner's model. This implies that the strain limit of linear viscoelastic response ψ_L becomes inversely proportional to ω:

$$\psi_L = \frac{A}{\omega} \tag{26}$$

where A is a constant (cf., *Fig. 2b*).

SIMPLE-FLUID THEORY

In the theory of simple fluids having fading memory (4) the stress response at (the present) time t is assumed to be a functional of the history of strain up to time t. As a measure of strain the strain tensor $\underline{\Gamma}$ (*Eq 6*) may be used. Thus we have:

$$\underline{T} = -p\,\underline{1} + \underset{s=0}{\overset{\infty}{\underline{F}}} [\underline{\Gamma}(t-s)] \tag{27}$$

The stress response is assumed to be smaller and smaller if the history of strain is taken more and more close to the rest history. In other words: the functional $\underline{F}$ in *Eq 27* is assumed to be continuous at the rest history. However, in order to make such a statement meaningful one has to define under which conditions the distance between two deformation histories becomes diminishingly small. That is to say, a topology in the space of deformation histories should be defined. In the theory of Coleman and Noll, this is achieved by introduction of a norm in this space. The norm is defined as

$$\| \underline{\Gamma} \| = \sqrt{\int_0^\infty h^2(s)\, tr\, \underline{\Gamma}^2(t-s)\, ds} \tag{28}$$

where $h(s)$ is the so-called influence function (or obliviator). This function by definition has the following properties:

$$h(0) = 1$$
$$h(s) \geq 0 \qquad (0 \leq s < \infty) \tag{29}$$
$$\lim_{s \to \infty} s^r h(s) = 0 \text{ for some } r > 0$$

The right-hand side of *Eq 28* represents a weight average of the magnitude of the strain history over the entire past, where in view of *Eq 29* much less weight is assigned to the distant than to the recent past. By the assumed continuity of the response functional $\underline{F}$ this means that two deformation histories showing significant differences only in the distant past will give about the same stress response. This is in accordance with the so-called principle of "fading memory", which states that the influence of deformations in the past on the present stress becomes weaker as they took place in a more distant past. The choice of the influence function $h(s)$ is not unique. Different influence functions may correspond to the same topology in the space of deformation histories. In the present paper in order to obtain explicit results we make a special choice for $h(s)$:

$$h(s) = e^{-\alpha s},\ (\alpha > 0) \tag{30}$$

This function clearly obeys the requirements (*Eq 29*); physically the constant α^{-1} may be viewed as a characteristic time for the memory of the material.

In addition to the continuity mentioned above, the response functional $\underline{F}$ is also assumed to be Frechet differentiable at the rest history. From this assumption it follows (4) that *Eq 27* may be expanded in the form

$$\underline{T} = -p\,\underline{1} + \int_0^\infty \mu(s)\,\underline{\Gamma}(t-s)\,ds + \underline{R}(\underline{\Gamma}) \tag{31}$$

where the "remainder" $\underline{R}$ is a functional of the history of deformation, which approaches zero faster than the norm of $\underline{\Gamma}$ in the sense that

$$\lim_{\|\underline{\Gamma}\|\to 0} \frac{\underline{R}(\underline{\Gamma})}{\|\underline{\Gamma}\|} = 0 \tag{32}$$

This may also be stated as

$$\underline{R}(\underline{\Gamma}) = o(\|\underline{\Gamma}\|) \tag{33}$$

We now return to the problem of the limit of linear viscoelastic response in ERD flow. If in *Eq 30* the term $\underline{R}(\underline{\Gamma})$ is neglected, by using *Eqs 8* and *2* we obtain the result, *Eq 18* for the forces on the plates. So in this case the response is linear. Non-linear response will occur if the relative magnitude of the remainder $\underline{R}$ exceeds some preassigned small value. Since by *Eq 32* for each ϵ being such that

$$\frac{\underline{R}(\underline{\Gamma})}{\|\underline{\Gamma}\|} < \epsilon \tag{34}$$

there exists a δ being such that

$$\|\underline{\Gamma}\| < \delta \tag{35}$$

and by *Eq 31* the left-hand side of *Eq 34* is a measure of the relative magnitude of $\underline{R}$, non-linear response will occur if the norm of the deformation history no longer obeys the inequality of *Eq 35*. This norm can be calculated explicitly in the present case as a function of ψ and ω. For the limit of linear viscoelastic response we then obtain an equation of the form

$$\|\underline{\Gamma}\|(\omega, \psi_L) = \delta \tag{36}$$

From *Eqs 8* and *28* the norm of the deformation history is calculated to be:

$$\|\underline{\Gamma}\| = \sqrt{\int_0^\infty e^{-2\alpha s}\, 4\psi^2\{1 + \psi^2 - (1 + 2\psi^2)\cos \omega s + \psi^2 \cos^2 \omega s\}\, ds}$$

$$= 2\psi\sqrt{\frac{1+\psi^2}{2\alpha} - \frac{2\alpha(1+2\psi^2)}{4\alpha^2+\omega^2} + \frac{2\alpha^2+\omega^2}{4\alpha(\alpha^2+\omega^2)}\psi^2} \tag{37}$$

From *Eqs 36* and *37* we obtain the following equation for ψ_L:

$$\psi_L^4 + \frac{2}{3}\left(\frac{\alpha^2}{\omega^2} + 1\right)\psi_L^2 - \frac{1}{3}\alpha\left(4\frac{\alpha^2}{\omega^2} + 1\right)\left(\frac{\alpha^2}{\omega^2} + 1\right)\delta^2 = 0 \tag{38}$$

with the solution

$$\psi_L^2 = \frac{1}{3}\left(\frac{\alpha^2}{\omega^2} + 1\right)\left(\sqrt{1 + 3\alpha\,\frac{4\frac{\alpha^2}{\omega^2} + 1}{\frac{\alpha^2}{\omega^2} + 1}\,\delta^2} - 1\right) \tag{39}$$

We thus see that according to the simple-fluid theory the shape of the $\psi_L(\omega)$ curve is as indicated in *Fig. 2c*.

Two limiting cases are of interest:

$$\omega \ll \alpha \rightarrow \psi_L^2 = \frac{1}{3}\frac{\alpha^2}{\omega^2}(\sqrt{1 + 12\alpha\delta^2} - 1) \tag{40}$$

in this region of frequencies ψ_L is inversely proportional to ω. On the other hand:

$$\omega \gg \alpha \rightarrow \psi_L^2 = \frac{1}{3}(\sqrt{1 + 3\alpha\delta^2} - 1) \tag{41}$$

In this region ψ_L is independent of ω.

It is interesting to note that the predictions of the Bird-Carreau model are in accordance with the predictions of the simple-fluid theory in the low-frequency region only and those of Tanner's theory in the high frequency region.

EXPERIMENTAL

As stated in the Introduction, all experimental evidence available in literature seems to indicate that ψ_L is independent of ω. Gross and Maxwell (2), who used their experiments as a test of constitutive equations, concluded from their results that in this test the Bird-Carreau model is incorrect, whereas Tanner's theory tends to be substantiated. In view of the theoretical results obtained in the preceding section a different interpretation of their results is possible now. We have seen there that according to the simple-fluid theory the shape of the $\psi_L(\omega)$ plot strongly depends on the frequency region which is considered.

The experiments of Gross and Maxwell show the behavior expected for high frequencies. According to our point of view this result supports the general simple-fluid theory. That ψ_L was found to be independent of ω indicates that the inverse of the characteristic times of the material lies in a region below the range of frequencies used in the experiments. In our experiments we attempted to enter into the region where the frequency dependence of $\psi_L(\omega)$ becomes significant. Since about the same frequency range as in the experiments of Gross and Maxwell on polymer melts was available, materials with relatively short characteristic times were needed.

If the characteristic time needed here is assumed to be of the order of magnitude of the longest relaxation time of the material, this time, according to the modified Rouse theory (17), will be proportional to the viscosity of the fluid. Therefore, in order to obtain systems with relatively short characteristic times, polymer solutions were used (a 3 and a 7 percent solution of poly(isobutylene) PIB (BASF Opanol 200) in paraffin oil (Baker)) instead of polymer melts. The measurements were performed with a Rheometrics mechanical spectrometer in a frequency range between 10^{-1} and 10 rad/s. For the determination of ψ_L from the plots of $F_y(\psi)$ the method described in reference (2) was used.

At present only some preliminary results are available, which however at least qualitatively confirm the predictions of the simple-fluid theory. The results are shown in *Figs. 3* and *4*. In further investigations on this subject we will try to improve the accuracy of determination of ψ_L and to perform experiments on other polymeric systems.

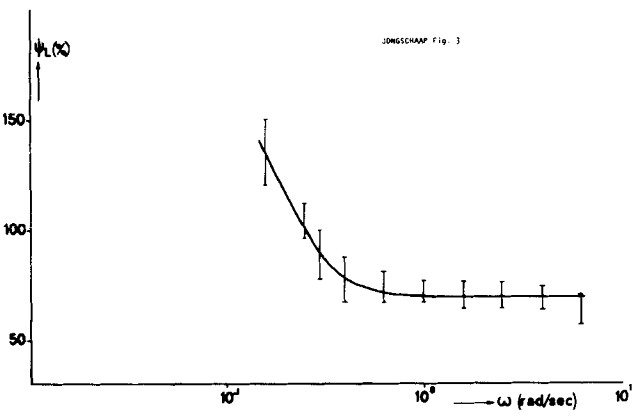

Fig. 3. Strain limit of linear viscoelastic response determined from the elastic response $F_y(\psi)$ curve for a solution of 3 percent PIB in paraffin oil; temperature: 30°C.

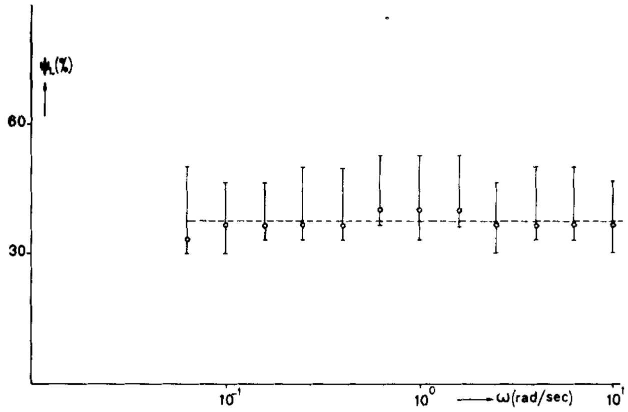

Fig. 4. As Fig. 3, for a 7 percent solution of PIB in paraffin oil; temperature: 30°C.

ACKNOWLEDGMENT

The authors are indebted to Professor P. F. Mijnlieff for many helpful discussions.

REFERENCES

1. W. Philippoff, *Trans. Soc. Rheol.*, **10**, 317 (1966).
2. L. H. Gross and B. Maxwell, *Trans. Soc. Rheol.*, **16**, 577 (1972).
3. R. J. Gordon and W. R. Schowalter, *A.I.Ch.E. J.*, **16**, 318 (1970).
4. B. D. Coleman and W. Noll, *Rev. Mod. Phys.*, **33**, 239 (1961).
5. B. Maxwell and R. P. Chartoff, *Trans. Soc. Rheol.*, **9**, 41 (1965).
6. C. W. Macosko and W. M. Davies, *Rheol. Acta*, **13**, 814 (1974).
7. L. L. Blyler, Jr. and S. J. Kurtz, *J. Appl. Phys.*, **11**, 127 (1967).
8. R. B. Bird and E. K. Harris, Jr., *A.I.Ch.E. J.*, **14**, 758 (1968).
9. T. N. G. Abbott and K. Walters, *J. Fluid Mech.*, **40**, 205 (1970).
10. R. R. Huilgol, *Trans. Soc. Rheol.*, **13**, 513 (1969).
11. R. J. J. Jongschaap and P. F. Mijnlieff, *Rheol. Acta*, **15**, 623 (1976).
12. T. N. G. Abbott and K. Walters, *J. Fluid Mech.*, **40**, 205 (1970).
13. P. Payvar and R. I. Tanner, *Trans. Soc. Rheol.*, **17**, 449 (1973).
14. R. I. Tanner and J. M. Simmons, *Chem. Eng. Sci.*, **22**, 1803 (1967).
15. R. I. Tanner, *A.I.Ch.E. J.*, **15**, 177 (1969).
16. R. B. Bird and P. J. Carreau, *Chem. Eng. Sci.*, **23**, 427 (1968).
17. J. D. Ferry, R. F. Landel and M. L. Williams, *J. Appl. Phys.*, **26**, 359 (1955).
18. G. Astarita and R. J. J. Jongschaap, *J. Non-Newtonian Fluid Mech.*, accepted for publication (1977).