

# SMALL SHEARING OSCILLATIONS SUPERPOSED ON LARGE STEADY SHEAR OF THE BKZ FLUID

BARRY BERNSTEIN

Illinois Institute of Technology, Chicago

**Abstract**—This is a theoretical discussion of methods which could be used to determine, according to the BKZ elastic fluid theory, the shearing stress and normal stress responses of a non-Newtonian fluid to simple shearing histories for which the rate of shear varies arbitrarily with time. In order to do this for any given fluid, certain information is needed about the fluid. It is shown how this information could be obtained if one knew merely the shearing stress responses to simple shearing motions of any one of the following types; stress relaxation, suddenly imposed steady shear, or small oscillations superposed on steady shearing flow. For each such type of flow some rheological relations are derived. These are relations between directly measurable quantities and do not involve material properties, but hold only for given classes of motions. It is also shown how, according to the BKZ perfect elastic fluid theory, a change in temperature affects the results. Thence it is argued how a variation in temperature could be used to supplement data obtained when the range of mechanical parameters is limited.

## NOTATION

$x_i$	Cartesian coordinates of position
$X_i$	particle labels
$t$	present time
$\gamma$	amount of shear
$\dot{\gamma}$	rate of shear
$\sigma_{ij}$	true stress tensor
$\sigma$	shearing stress
$K[\gamma, t]$	stress relaxation function
$K_*[\gamma, t]$	partial derivative of $K$ with respect to $t$
$K'[\gamma, t]$	partial derivative of $K$ with respect to $\gamma$
$K', K''$ etc	second partial derivatives of $K$ , etc.
$v$	normal stress difference
$\kappa$	constant rate of shear
$G(t)$	shear relaxation modulus from linear visco-elasticity
$A$	amplitude of oscillation
$\omega$	frequency of oscillation
$\Gamma[\kappa, \omega]$	complex shear-dependent dynamic shear modulus
$\Gamma_1, \Gamma_2$	real and imaginary parts of $\Gamma$ respectively
$\sigma_0(\kappa)$	stress for steady shear of rate $\kappa$
$\sigma_{\text{complex}}$	complex form of oscillating shear stress
$v_{\text{complex}}$	complex form of oscillating normal stress
$v_0(\kappa)$	normal stress for steady shear of rate $\kappa$
$N[\kappa, \omega]$	complex shear-dependent dynamic normal stress modulus
$N_1, N_2$	real and imaginary parts of $N$ respectively
$G'(\omega), G''(\omega)$	real and imaginary parts of dynamic shear modulus in linear viscoelasticity
$T$	absolute temperature
$T_0$	reference temperature
$a_T$	time-temperature superposition coefficient
$b_T$	$1/a_T$
$\rho$	mass density
$\rho_0$	mass density at temperature $T_0$
$\Gamma[\kappa, \omega; T]$	shear and temperature dependent dynamic shear modulus.

$\sigma_0[\kappa, T]$	shear stress at constant rate of shear $\kappa$ and temperature $T$
$G'_\kappa(\omega), G''_\kappa(\omega)$	$\Gamma_1[\kappa, \omega], \Gamma_2[\kappa, \omega]$ respectively as used by other authors
$p_{11} - p_{22}$	$v$ as used by other authors

## 1. INTRODUCTION

WE are concerned here with the development of methods to determine the behavior of a *non-Newtonian* viscoelastic fluid when subjected to a simple shearing motion with arbitrary shear history.<sup>†</sup> In particular we shall discuss the BKZ<sup>‡</sup> fluid theory [1, 2] in order to see how, in terms of this theory, data obtained in certain particular simple shearing motions could be used to predict the shear and normal stress responses in any other simple shearing motion. It should be understood at the outset that although we have chosen to phrase our results in terms of analysis of data in order to indicate the useful value of our work, this is a strictly theoretical discussion of the BKZ fluid and actual analysis of data will be left for later efforts. On the other hand it should also be understood that the BKZ fluid theory is one which has shown itself to agree very well with experimental data on both polymers and polymer solutions [3, 4], and therefore is deserving of our interest in it as a tool for describing non-Newtonian behavior of such substances.

Three methods will be discussed. The first involves stress relaxation. This method has already been used successfully for simple extension of bulk polymers [3], but would not be expected to be of much use for rapidly relaxing polymer solutions. The second method involves the sudden imposition of a steady shearing motion on a fluid previously at rest. Such a motion involves a discontinuity in rate of shear, a discontinuity which is less severe than one imposed in the shear strain itself. Nevertheless it could be desirable to have a method which deals with smooth motions. This brings us, then, to the third method, the one to be discussed at some length here, namely that of small shearing oscillations superposed on steady shearing flows with rates of shear of arbitrary magnitude, including large rates of shear.

Indeed there is current interest in such motions. Recent work, including experimental results, has been published by Booij [5] and by Osaki, Tamura, Kurata and Kotaka [6]. What we wish to show here is that in terms of the BKZ theory, the information obtained from measurements of this type give in principle all information that can be obtained in simple shear.

In order not to complicate our discussion initially, we shall deal at first with the incompressible isothermal form of the BKZ theory. Later we shall bring in results from the thermodynamic BKZ theory, the Perfect Elastic Fluid [1], in order to discuss the dependence of our results on temperature and to point out how one may use a temperature variation to increase the information obtained from a use of a limited range of mechanical parameters.

In the course of our discussion, we shall derive some new rheological relations. Section 5 is devoted to some such relations which are appropriate to small oscillations on large steady shear. These relations are significant for non-Newtonian behavior and are derived in terms of the BKZ theory.

## 2. SIMPLE SHEAR OF THE BKZ FLUID

In order to be precise about the class of motions which we shall consider under the

<sup>†</sup> This work was supported by the National Science Foundation under grant number GP 7141.

<sup>‡</sup> The abbreviation BKZ will be used here for the Bernstein, Kearsley, and Zapas theory, Ref. [1].

heading of simple shear, let us begin by defining these motions. To this end, let us have in mind a fixed Cartesian coordinate system  $x_i$ ,  $i = 1, 2, 3$ . Let us label the particles or material points of the fluid by the positions  $X_i$ ,  $i = 1, 2, 3$  which they take at some particular time during the motion. We may then conveniently describe a simple shearing motion in terms of a single function of time  $t$ , say  $\gamma(t)$ , as follows: The particle  $X_i$  has the position  $x_i$  at time  $t$  given by

$$x_1 = X_1 + \gamma(t)X_2, \quad x_2 = X_2, \quad x_3 = X_3 \quad (2.1)$$

The quantity  $\gamma(t)$  is called the *amount of shear* and its derivative, which we denote by  $\dot{\gamma}(t)$ , is called the *rate of shear*.

Let the components of the *true stress tensor* be denoted by  $\sigma_{ij}$ . In the coordinate system in which the motion is described by (2.1), the component  $\sigma_{12}$  is usually called the *shearing stress*. Since we shall be dealing extensively with the component of stress, we shall find it convenient to denote it simply by  $\sigma$ , i.e.  $\sigma = \sigma_{12}$ . In the incompressible isothermal form of the BKZ Theory [2] the value of  $\sigma$  at time  $t$  is related to history of  $\gamma(\tau)$ ,  $\tau \leq t$ , through a relation of the form

$$\sigma = - \int_{-\infty}^t K_*[\gamma(t) - \gamma(\tau), \quad t - \tau] d\tau \quad (2.2)$$

where  $K_*[\gamma, \xi]$  is a function of the real variable  $\gamma$  and the non-negative real variable  $\xi$  such that

$$K_*[0, \xi] = 0 \quad (2.3)$$

In (2.2) as henceforth, we adopt the convention that  $t$  is the present time and that when we do not specify a time at which a given quantity is to be evaluated, we shall understand it to be evaluated at the present time  $t$ . Thus in (2.2)  $\sigma$  means  $\sigma(t)$ . The function  $K_*$  is not specified by the theory. To each material described by the theory there corresponds exactly one such function. If it could be measured by, say, performing a specific set of simple shearing motions experimentally, then the values of  $\sigma$  for all other simple shearing flows can be calculated from (2.2). Indeed, we can now clarify our statements in Section 1 to the effect that we shall be discussing methods to determine the behavior of non-Newtonian visco-elastic fluids in simple shear. As far as the behavior of  $\sigma$  is concerned, our task is seen to be then, to discuss methods of determining  $K_*$  for a given fluid. Similar considerations would apply to the other stress components. Indeed, it has been shown [2] that  $\sigma_{13} = \sigma_{23} = 0$  and that the values  $\sigma_{11} - \sigma_{33}$  as well as  $\sigma_{22} - \sigma_{33}$  at time  $t$  are related to the history of  $\gamma(\tau)$ ,  $\tau \leq t$ , through relations entirely similar in form to (2.2) but involving, in general, a different function than the  $K_*$  which figures in the equation (2.2). (Since in the incompressible theory stress is determined only to within a hydrostatic pressure by the history of  $\gamma(\tau)$ , the stress components and differences mentioned above constitute a complete set of those which can be related to  $\gamma(\tau)$ ,  $\tau \leq t$  with this theory.) In general, we could apply the considerations pertaining to  $\sigma$  to the normal stress differences as well. However, there is one normal stress difference which will deserve a more thorough discussion, as will be seen below. This is the quantity  $\sigma_{11} - \sigma_{22}$ , to which we shall assign the symbol  $v$  here, i.e.  $v = \sigma_{11} - \sigma_{22}$ . Now,  $v$  is a normal stress difference which could be measured, for example, by the Padden-De Witt [7] apparatus.† But in terms of the BKZ

† For a more thorough discussion of normal stresses and their measurement see Markovitz [8].

theory, the quantity  $v$  has a special interest in that it is determined by  $K_*$  alone. Indeed, it could readily be shown that in terms of the BKZ theory,<sup>†</sup>

$$v = - \int_{-\infty}^t [\gamma(t) - \gamma(\tau)] K_* [\gamma(t) - \gamma(\tau), t - \tau] d\tau \quad (2.4)$$

With these preliminaries over, we proceed now to the discussion of particular forms of the function  $\gamma(\tau)$ , i.e. to particular shear histories.

### 3. SINGLE-STEP STRESS RELAXATION AND SUDDENLY APPLIED STEADY SHEAR

The inclusion of a short discussion on *single step stress relaxation* here is done for the sake of completeness and so that we may state an operational interpretation of the function  $K_*$ . Indeed, effective use has already been made of this type of history for the case of simple extension of bulk polymers [3], in which case the predictions of the theory were verified by experiment.

A single step stress relaxation in simple shear may be specified by

$$\left. \begin{aligned} \gamma(\tau) &= 0, & \tau < 0 \\ \gamma(\tau) &= \gamma = \text{const}, & \tau > 0 \end{aligned} \right\} \quad (3.1)$$

for which (2.2) gives, for  $t > 0$ ,

$$\sigma = - \int_{-\infty}^0 K_* [\gamma, t - \tau] d\tau \quad (3.2)$$

when we make use of (2.3) and the fact that  $\gamma(t) - \gamma(\tau) = 0$  when  $t, \tau > 0$ . Under a change in variable of integration to  $\xi = t - \tau$ , (3.2) becomes

$$\sigma = - \int_t^{\infty} K_* [\gamma, \xi] d\xi = K[\gamma, t], \quad (3.3)$$

where the second equality in (3.3) constitutes the definition of the function  $K$ . Indeed, we see that  $K[\gamma, t]$  is the shear stress in single step stress relaxation with step  $\gamma$  at time  $t$  after the step. Furthermore, differentiation of the second equality in (3.3) with respect to  $t$  yields

$$K_* [\gamma, t] = \partial K[\gamma, t] / \partial t \quad (3.4)$$

Thus in addition to telling us how to determine  $K_*$  from  $K$ , (3.4) gives an operational interpretation of  $K_* [\gamma, t]$  namely the time rate of change of the shear stress during a stress relaxation of stress  $\gamma$  at time  $t$  after the step.

Now we also remark that (2.3) and (3.3) give

$$K[0, t] = 0 \quad (3.4 \text{ bis.})$$

We may also note in passing that similar considerations apply to the normal stress difference  $v$ . Furthermore, if we evaluate (2.4) for the motion (3.1), we get

$$v = K[\gamma, t] \gamma \quad (3.5)$$

<sup>†</sup> Our equation (2.4) follows immediately from equations (5.9) and (5.10) of Bernstein [2].

as the value of  $v$  at time  $t$  after the step. Indeed, (3.3) and (3.5) give us a relation of the type which we shall call a *rheological relation*, namely that

$$v = \sigma\gamma \quad (3.6)$$

in stress relaxation. By a *rheological relation* we shall mean here one between rheological quantities which has the following properties: It does not require a knowledge of specific material properties (e.g. a knowledge of  $K[\gamma, t]$ ), but in general is valid only for particular motions, (i.e. for particular classes of the function  $\gamma(\tau)$  in our context). Risking redundancy, we emphasize here that the rheological relation (3.6) has been shown to be valid only for single step relaxation and should not be expected thereby to hold for other histories  $\gamma(\tau)$ .

We now turn to consideration of *suddenly applied steady shear*. Such a motion may be described by, say,

$$\left. \begin{aligned} \gamma(\tau) &= 0, \quad \tau \leq 0 \\ \gamma(\tau) &= \kappa\tau, \quad \kappa = \text{const.}, \quad \tau \geq 0 \end{aligned} \right\} \quad (3.7)$$

or, alternatively

$$\left. \begin{aligned} \dot{\gamma}(\tau) &= 0, \quad \tau < 0 \\ \dot{\gamma}(\tau) &= \kappa = \text{const.}, \quad \tau > 0 \end{aligned} \right\}$$

and the condition that  $\gamma(\tau)$  is continuous at  $\tau = 0$ . Thus  $\kappa$  is the rate of shear which is suddenly applied.

Insertion of (3.7) into (2.2) yields

$$\sigma = - \int_{-\infty}^0 K_*[\kappa t, t - \tau] d\tau - \int_0^t K_*[(t - \tau)\kappa, t - \tau] d\tau \quad (3.8)$$

We make the change of variable of integration to  $\xi = t - \tau$  in both of the integrals in (3.8) and find, after comparison with (3.3),

$$\sigma = K[\kappa t, t] - \int_0^t K_*[\kappa\xi, \xi] d\xi \quad (3.9)$$

In (3.4) we have already a special notation for the partial derivative of  $K[\gamma, \xi]$  with respect to  $\xi$  holding  $\gamma$  constant, namely  $K_*$ . We shall now introduce a notation for the partial derivative of  $K$  with respect to  $\gamma$  holding  $\xi$  constant, viz.

$$K'[\gamma, \xi] \equiv \partial K[\gamma, \xi] / \partial \gamma$$

We shall compound this notation. Thus

$$\left. \begin{aligned} K'_*[\gamma, \xi] &= \partial^2 K[\gamma, \xi] / \partial \gamma \partial \xi \\ K''[\gamma, \xi] &= \partial^2 K[\gamma, \xi] / \partial \xi^2 \end{aligned} \right\} \quad (3.10)$$

etc. Now with this notation we may write

$$K_*[\kappa\xi, \xi] = \frac{d}{d\xi} K[\kappa\xi, \xi] - \kappa K'[\kappa\xi, \xi]$$

whence (3.9) yields

$$\sigma = K[\kappa t, t] - \int_0^t \frac{d}{d\xi} K[\kappa\xi, \xi] d\xi + \kappa \int_0^t K'[\kappa\xi, \xi] d\xi \quad (3.11)$$

The first integration in (3.11) is readily carried out, the result of which gives for the second term in (3.11)  $-K[\kappa t, t] + K[0, 0] = -K[\kappa t, t]$  where the last equality follows from (3.4 bis). Thus (3.11) becomes simply

$$\sigma = \kappa \int_0^t K'[\kappa\xi, \xi] d\xi \quad (3.12)$$

(We may remark parenthetically here that as  $t \rightarrow \infty$  the stress  $\sigma$  approaches that in steady shearing flow, whence the non-Newtonian viscosity is given by

$$\int_0^\infty K'[\kappa\xi, \xi] d\xi$$

as can be seen from (3.12).)

Similarly  $v$  may be determined by the same process with  $\gamma K[\gamma, \xi]$  substituted for  $K[\gamma, \xi]$ . Then  $K[\gamma, \xi] + \gamma K'[\gamma, \xi]$  will take the place of  $K'[\gamma, \xi]$  so that in a manner similar to that by which we derived (3.12) we get

$$v = \kappa \int_0^t \{ \kappa\xi K'[\kappa\xi, \xi] + K[\kappa\xi, \xi] \} d\xi \quad (3.13)$$

Now differentiation of (3.12) with respect to  $t$  yields

$$\dot{\sigma}/\dot{\gamma} = \dot{\sigma}/\kappa = K'[\kappa t, t] \quad (3.14)$$

Thus  $K'$  and thence, with the extra condition (3.4 bis),  $K$  may be determined from measurements of  $\sigma$  in motions of the form (3.7) for various values of  $\kappa$  and  $t$ . In a similar manner, one could use (3.13) to determine  $\gamma K[\gamma, t]$ , and thence  $K$ , by using measurements of  $v$ . Once we know the function  $K$ , we can then determine  $\sigma$  and  $v$  for any simple shearing motion through the use of (3.4), (2.2) and (2.4).

Actually for the motions (3.7) we can find a rheological relation from which  $v$  can be determined from  $\sigma$  or vice versa. Now as long as we restrict ourselves to these motions, there is one value of  $\sigma$  and of  $v$  for each  $\kappa$  and each  $t$  and therefore, within the framework of the motions (3.7) we regard  $\sigma$  and  $v$  as functions of  $\kappa$  and  $t$ , say

$$\left. \begin{aligned} \sigma &= \sigma(\kappa, t), & v &= v(\kappa, t) \\ \dot{\sigma} &= \partial\sigma(\kappa, t)/\partial t, & \dot{v} &= \partial v(\kappa, t)/\partial t \end{aligned} \right\} \quad (3.15)$$

Now (3.13) yields upon differentiation with respect to  $t$

$$\dot{v}/\kappa = \kappa t K'[\kappa t, t] + K[\kappa t, t] \quad (3.16)$$

whence follows, with the use of (3.14) and (3.15)

$$\frac{\partial}{\partial t} \frac{v}{\kappa} - t \frac{\partial \sigma}{\partial t} = \frac{\dot{v}}{\kappa} - t \dot{\sigma} = K[\kappa t, t] \quad (3.17)$$

Differentiation of (3.17) with respect to  $\kappa$  and use of (3.2) yields

$$\frac{\partial^2}{\partial \kappa \partial t} \left( \frac{\nu}{\kappa} \right) - t \frac{\partial^2 \sigma}{\partial \kappa \partial t} = \frac{t}{\kappa} \frac{\partial \sigma}{\partial t} \quad (3.18)$$

which is a rheological relation.

If we are to be able to use the rheological relation (3.18) to determine  $\nu(\kappa, t)$  from a knowledge of  $\sigma(\kappa, t)$ , or vice versa, we would need, in addition to the differential equation (3.18), sufficient conditions to determine a solution. One of these is readily obtained from (3.13) namely  $\nu(\kappa, 0)/\kappa = 0$ . The other is obtained by observing that (3.13) and (3.4 bis) imply that  $\nu/\kappa$  must have the value zero for  $\kappa = 0$ . These, then, supply sufficient conditions to uniquely determine  $\sigma(\kappa, t)$  from a knowledge of  $\nu(\kappa, t)$ . We first observe that (3.18) may also be written

$$\frac{\partial}{\partial \kappa} \kappa t \frac{\partial \sigma}{\partial t} = \kappa \frac{\partial^2}{\partial \kappa \partial t} \left( \frac{\nu}{\kappa} \right) \quad (3.19)$$

Now  $\kappa t \cdot \partial \sigma / \partial t = 0$  at  $\kappa = 0$ . Also  $\sigma = 0$  at  $t = 0$ , as seen from (3.12). These conditions suffice, together with (3.19), to allow us to determine  $\sigma(\kappa, t)$  from a knowledge of  $\nu(\kappa, t)$ .

We have seen how the motions discussed in this section can be used to determine  $\sigma$  and  $\nu$  for an arbitrary simple shearing motion. But before we leave these flows, let us relate our results to the classical result of the linear theory of viscoelasticity. Now in the linear theory [9] the stress  $K[\gamma, t]$  in stress relaxation is proportional to the shear  $\gamma$ , namely

$$K[\gamma, t] = G(t) \gamma \quad (3.20)$$

where  $G(t)$ , which is a function of  $t$  alone, is called the shear relaxation modulus. Indeed, if we use (3.20) in those of our above formulas which involve  $\sigma$ , we shall obtain the results of linear viscoelasticity. In particular (2.2) then becomes

$$\sigma = G(0) \gamma(t) + \int_0^\infty \dot{G}(t - \tau) \gamma(\tau) d\tau$$

(where we have made use of the fluid-type assumption that  $G(\infty) = 0$ ). The formula (3.14) becomes

$$\dot{\sigma} / \dot{\gamma} = \dot{\sigma} / \kappa = G(t)$$

which is a well-known result.

The linear theory of viscoelasticity is intended for small enough values of  $\gamma$  that  $\gamma^2$  may be neglected relative to  $\gamma$ . Comparison of (2.2) with (2.4) illustrates, then, why normal stresses do not figure in the linear theory.

#### 4. SMALL OSCILLATIONS ON LARGE STEADY SHEAR

We now discuss a smooth steady state type of motion, namely

$$\gamma(\tau) = \gamma \tau + A \cos \omega \tau, \quad -\infty < \tau \quad (4.1)$$

where  $\kappa$ ,  $A$  and  $\omega$  are constants. The basic rate of shear  $\kappa$ , may be of any magnitude, but the amplitude of oscillation,  $A$ , will be assumed to be as small as we need for our discussion below. If we insert (4.1) into (2.2), we obtain

$$\sigma = - \int_{-\infty}^t K_*[(t - \tau)\kappa + A(\cos \omega t - \cos \omega \tau), t - \tau] d\tau \quad (4.2)$$

We now consider the integrand of (4.2), which we expand in  $A(\cos \omega t - \cos \omega \tau)$  and neglect terms of order greater than unity in this quantity. The result is

$$\left. \begin{aligned} & K_*[(t - \tau)\kappa + A(\cos \omega t - \cos \omega \tau), t - \tau] \\ & = K_*[(t - \tau)\kappa, t - \tau] + K'_*[(t - \tau)\kappa, t - \tau] A(\cos \omega t - \cos \omega \tau) \end{aligned} \right\} \quad (4.3)$$

We shall not belabor the question here of when it is legitimate to substitute (4.3) for the integrand of (4.2) within acceptable approximation. This is not to be construed to imply that we do not consider this question to be important. Rather, we mean that we wish to devote ourselves to this discussion only to the case where this approximation is valid and to obtain the consequences of its validity. Similar considerations will apply to our manipulations below.

Before substituting (4.3) into (4.2) let us note that one may verify from standard trigonometric relationships that

$$\cos \omega t - \cos \omega \tau = (1 - \cos \omega(t - \tau)) \cos \omega t - \sin \omega(t - \tau) \sin \omega t$$

whence we obtain

$$\sigma = - \int_{-\infty}^t K_*[(t - \tau)\kappa, t - \tau] d\tau + A\Gamma_1[\kappa, \omega] \cos \omega t - A\Gamma_2[\kappa, \omega] \sin \omega t \quad (4.4)$$

where

$$\begin{aligned} \Gamma_1[\kappa, \omega] &= - \int_{-\infty}^t K'_*[(t - \tau)\kappa, t - \tau] (1 - \cos \omega(t - \tau)) d\tau \\ &= - \int_0^\infty K'_*[\kappa\xi, \xi] (1 - \cos \omega\xi) d\xi \\ \Gamma_2[\kappa, \omega] &= - \int_0^\infty K'_*[\kappa\xi, \xi] \sin \omega\xi d\xi \end{aligned} \quad (4.5)$$

where appropriate changes of the variable of integration to  $\xi = t - \tau$  have been made.

In (4.4) we recognize that the first integral term on the right gives the stress when  $A = 0$ , namely the steady shearing stress corresponding to constant rate of shear  $\kappa$ . We denote this stress here by  $\sigma_0(\kappa)$  and obtain, after change of variable of integration to  $\xi = t - \tau$ ,

$$\sigma_0(\kappa) = - \int_0^\infty K_*[\kappa\xi, \xi] d\xi \quad (4.6)$$

Let us note then, that (4.4) may be written

$$\sigma - \sigma_0(\kappa) = A\Gamma_1[\kappa, \omega] \cos \omega t - A\Gamma_2[\kappa, \omega] \sin \omega t \quad (4.7)$$

In complex notation, we may write  $\Gamma[\kappa, \omega] = \Gamma_1[\kappa, \omega] + i\Gamma_2[\kappa, \omega]$  and obtain from (4.7)

$$\sigma - \sigma_0(\kappa) = \Re(A\Gamma e^{i\omega t})$$

If we then define  $\sigma_{\text{complex}}$  by

$$\sigma_{\text{complex}} - \sigma_0(\kappa) = A\Gamma e^{i\omega t} \quad (4.8)$$



we see that  $\sigma$  is then given by the real part of  $\sigma_{\text{complex}}$ . (Note that  $\sigma_0(\kappa)$  is real.) We can then avail ourselves of complex notation. In particular (4.5) becomes

$$\Gamma[\kappa, \omega] = - \int_0^{\infty} K'_*[\kappa\xi, \xi] (1 - e^{-i\omega\xi}) d\xi. \quad (4.9)$$

As can be seen from (4.7) or (4.8), one criterion of whether our linearization approximations are valid for a given experimental situation is, in fact, whether or not the measured stress response is actually sinusoidal. If it is, then  $\Gamma_1[\kappa, \omega]$  and  $\Gamma_2[\kappa, \omega]$  can be determined from a knowledge of the amplitude of  $\sigma_{\text{complex}} - \sigma_0(\kappa)$  and the phase angle between it and the real part of  $\gamma(t)$ , viz.  $A \cos \omega t$ . This type of analysis is quite standard.

The point that is to be made here is that *from a knowledge of  $\Gamma_1[\kappa, \omega]$  or  $\Gamma_2[\kappa, \omega]$  the function  $K'_*[\kappa\xi, \xi]$  may be determined with the use of fourier analysis*. Indeed, we may first apply the Riemann–Lebesgue theorem† to (4.5) to obtain

$$\Gamma[\kappa, \infty] = \Gamma_1[\kappa, \infty] = \lim_{\omega \rightarrow \infty} \Gamma_1[\kappa, \omega] = - \int_0^{\infty} K'_*[\kappa\xi, \xi] d\xi \quad (4.10)$$

whence

$$\left. \begin{aligned} \Gamma_1[\kappa, \omega] - \Gamma_1[\kappa, \infty] &= \int_0^{\infty} K'_*[\kappa\xi, \xi] \cos \omega\xi d\xi \\ \Gamma_2[\kappa, \omega] &= - \int_0^{\infty} K'_*[\kappa\xi, \xi] \sin \omega\xi d\xi \end{aligned} \right\} \quad (4.11)$$

Then, according to the theory of Fourier integrals,

$$\begin{aligned} K'_*[\kappa\xi, \xi] &= \frac{1}{2\pi} \int_0^{\infty} \{\Gamma_1[\kappa, \omega] - \Gamma_1[\kappa, \infty]\} \cos \omega\xi d\omega \\ K'_*[\kappa\xi, \xi] &= - \frac{1}{2\pi} \int_0^{\infty} \Gamma_2[\kappa, \omega] \sin \omega\xi d\omega \end{aligned} \quad (4.12)$$

Writing  $\gamma$  for  $\kappa\xi$  in (4.12), we may then in principle obtain  $K'_*[\gamma, \xi]$  for all values of  $\gamma$  and  $\xi$  from a knowledge of either of the functions  $\Gamma_1$  or  $\Gamma_2$ . From (3.10) and (3.4) follows

$$K'_*[\gamma, \xi] = \partial K_*[\gamma, \xi] / \partial \gamma$$

from which we may obtain  $K_*$  from  $K'_*$  with the use of the additional condition (2.3). According to (2.2) and (2.4), this will now suffice to allow us to determine the shearing stress response  $\sigma$  or the normal stress response  $\nu$  to *any* simple shearing flow history (2.1). As we have set out to do, we have now shown how data taken from small oscillations superposed on arbitrary steady shearing flow will allow us to calculate the shearing or normal stress response to any simple shearing history.

Quite similar considerations may be carried through for the oscillatory part of the normal stress  $\nu$ . We shall leave the details to the reader, but we may state that in a manner

† The Riemann–Lebesgue theorem may be applied under the condition of absolute convergence of the right-hand side of (4.10).

quite similar to that used to deal with the shear stresses we may arrive at an expression similar to (4.8) namely

$$\frac{v_{\text{complex}} - v_0(\kappa)}{A e^{i\omega t}} = N[\kappa, \omega] = N_1[\kappa, \omega] + iN_2[\kappa, \omega] \quad (4.13)$$

where  $v_0(\kappa)$  is the normal stress corresponding to the steady shearing flow with rate of shear  $\gamma$  and where the complex function  $N[\gamma, \omega]$  as well as its real and imaginary parts  $N_1$  and  $N_2$  are defined by (4.13). For  $N$  we also arrive at an expression similar to (4.9) in which  $K_*[\gamma, \xi]$  is replaced by  $\gamma K_*[\gamma, \xi]$ . Indeed, the said expression may be written

$$N = - \int_0^\infty \{ \kappa \xi K'_*[\kappa \xi, \xi] + K_*[\kappa \xi, \xi] \} (1 - e^{-i\omega \xi}) d\xi \quad (4.14)$$

or

$$\left. \begin{aligned} N_1[\kappa, \omega] &= - \int_0^\infty \{ \kappa \xi K'_*[\kappa \xi, \xi] + K_*[\kappa \xi, \xi] \} (1 - \cos \omega \xi) d\xi \\ N_2[\kappa, \omega] &= - \int_0^\infty \{ \kappa \xi K'_*[\kappa \xi, \xi] + K_*[\kappa \xi, \xi] \} \sin \omega \xi d\xi \end{aligned} \right\} \quad (4.15)$$

We also record here

$$v_0(\kappa) = - \int_0^\infty \kappa \xi K_*[\kappa \xi, \xi] d\xi \quad (4.16)$$

Let us now return to a discussion of the function  $\Gamma[\kappa, \omega]$  for the purpose of discussing alternate ways in which a knowledge of it may be used to obtain  $K_*$ . Also let us see how our results relate to those in linear viscoelasticity. To this end we note that we may write

$$K'_*[\kappa \xi, \xi] = \frac{d}{d\xi} K'[\kappa \xi, \xi] - \kappa K''[\kappa \xi, \xi]$$

whence (4.9) yields

$$\Gamma[\kappa, \omega] = - \int_0^\infty (1 - e^{-i\omega \xi}) \frac{d}{d\xi} K[\kappa \xi, \xi] d\xi + \kappa \int_0^\infty K''[\kappa \xi, \xi] (1 - e^{-i\omega \xi}) d\xi \quad (4.17)$$

An integration by parts in the first integral of (4.17), yields

$$\Gamma[\kappa, \omega] = i\omega \int_0^\infty K'[\kappa \xi, \xi] e^{-i\omega \xi} d\xi + \kappa \int_0^\infty K''[\kappa \xi, \xi] (1 - e^{-i\omega \xi}) d\xi \quad (4.18)$$

where we have used the conditions  $K[0, 0] = 0$  and  $K[\infty, \infty] = 0$ . The former of these conditions follows from (3.4 bis). Although we shall regard the latter condition here as an assumption, a word is necessary about conditions under which it could be derived from the foregoing relations. To this end, we remark that it would follow from (3.3) under the assumption that  $K_*[\gamma, t]$  is bounded for large enough  $\gamma$  and  $t$  by an expression of the form  $P(\gamma) e^{-\alpha t}$  where  $P(\gamma)$  is a polynomial in  $\gamma$  and  $\alpha$  is a positive number.

Now let us note that for  $\kappa = 0$  the function  $\gamma(\tau)$  in (4.1), under the assumption of small enough  $A$ , satisfies the same conditions that are usually assumed for the validity of the

linear theory. Indeed to apply the linear theory one may either use (3.20) or one may write instead

$$K[\gamma, t] = G(t)\gamma + \text{terms of higher order in } \gamma$$

whence to first order in  $\gamma$

$$\left. \begin{aligned} K[0, t] &= 0 \\ K'[0, t] &= G(t) \\ K_*[0, t] &= \dot{G}(t)\gamma \\ K_*'[0, t] &= \dot{G}(t) \end{aligned} \right\} \quad (4.19)$$

Substitution of the formulas (4.19) into equations in this section should then give standard results from the linear theory. We note in particular that for  $\kappa = 0$  (4.18) becomes

$$\Gamma[0, \omega] = i\omega \int_0^\infty G(\xi) e^{-i\omega\xi} d\xi \equiv G'(\omega) + iG''(\omega) \quad (4.20)$$

where  $G'(\omega)$  and  $G''(\omega)$  are standard notations for the real and imaginary part of the complex dynamic shear modulus. (The primes do not denote differentiation here). We note that (4.20) has the desirable property that the method of Fourier transforms applies directly if one wishes to solve for  $G(\omega)$  in terms of the dynamic moduli  $G'$  or  $G''$ , i.e.  $\Gamma_1[0, \omega]$  or  $\Gamma_2[0, \omega]$ . This property does not carry over to the case  $\kappa \neq 0$  because of the second integral term which appears in (4.18).

It could, however, be useful to have, in addition to (4.12)<sub>2</sub>, another way of obtaining  $K_*[\gamma, \xi]$  by a method which does not involve  $\Gamma[\kappa, \infty]$  explicitly, as does (4.12)<sub>1</sub>. To this end note that differentiation of (4.9) yields

$$\frac{\partial \Gamma[\kappa, \omega]}{\partial \omega} = -i \int_0^\infty K_*'[\kappa\xi, \xi] \xi e^{-i\omega\xi} d\xi$$

whence we may obtain

$$K_*'[\kappa\xi, \xi] = -\frac{1}{2\pi\xi} \int_0^\infty \frac{\partial \Gamma_1[\kappa, \omega]}{\partial \omega} \sin \omega\xi d\omega$$

and

$$K_*'[\kappa\xi, \xi] = -\frac{1}{2\pi\xi} \int_0^\infty \frac{\partial \Gamma_2[\kappa, \omega]}{\partial \omega} \cos \omega\xi d\omega$$

This provides us with an additional way of doing the calculations necessary to determine  $\sigma$  and  $\nu$  in any simple shearing history.

## 5. SOME RHEOLOGICAL RELATIONS

From the equations in the previous section there arise immediately a number of rheological relations, namely

$$\lim_{\omega \rightarrow 0} \frac{\Gamma_2[\kappa, \omega]}{\omega} = \frac{d\sigma_0(\kappa)}{d\kappa} \quad (5.1)$$

$$\lim_{\omega \rightarrow 0} \frac{2\Gamma_1[\kappa, \omega]}{\omega^2} = \frac{d}{d\kappa} \frac{\nu_0(\kappa)}{\kappa} \quad (5.2)$$

$$\lim_{\omega \rightarrow 0} \frac{N_2[\kappa, \omega]}{\omega} = \frac{d}{d\kappa} \nu_0(\kappa) \quad (5.3)$$

$$N_1[\kappa, \infty] = \lim_{\omega \rightarrow \infty} N_1[\kappa, \omega] = \frac{d}{d\kappa} \kappa \sigma_0(\kappa) \quad (5.4)$$

Before discussing how these relations are obtained, let us see what well known relations they generalize.

For  $\kappa = 0$ , (5.1) becomes

$$\lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega} = \text{zero shear viscosity,}$$

which is a classical statement in linear visco-elasticity. At  $\kappa = 0$ , (5.2) reduces to

$$\lim_{\omega \rightarrow 0} \frac{2G'(\omega)}{\omega^2} = \lim_{\kappa \rightarrow 0} \frac{\nu_0(\kappa)}{\kappa^2}$$

which has been proven by Coleman and Markovitz [10] for simple fluids. As far as we know, (5.3) and (5.4) do not relate to any known relations, but of course, (5.3) is formally similar to (5.1).

We shall now obtain the above rheological relations. To arrive at (5.1) note that differentiation of (4.6) yields

$$\frac{d\sigma_0(\kappa)}{d\kappa} = - \int_0^\infty K'_*[\kappa\xi, \xi] d\xi \quad (5.5)$$

On the other hand, (4.5)<sub>2</sub> yields

$$\frac{\Gamma_2[\kappa, \omega]}{\omega} = - \int_0^\infty K'_*[\kappa\xi, \xi] \xi \frac{\sin \omega\xi}{\omega\xi} d\xi \quad (5.6)$$

We may take the limits of both sides of (5.6) as  $\omega$  goes to zero and interchange the processes of integration and taking the limit on the right-hand side of (5.6) to obtain<sup>†</sup>

$$\lim_{\omega \rightarrow 0} \frac{\Gamma_2[\kappa, \omega]}{\omega} = - \int_0^\infty K'_*[\kappa\xi, \xi] \xi \lim_{\omega \rightarrow 0} \frac{\sin \omega\xi}{\omega\xi} d\xi = - \int_0^\infty K'_*[\kappa\xi, \xi] \xi d\xi \quad (5.7)$$

Comparison of (5.5) and (5.7) now establishes the relation (5.1).

<sup>†</sup> It is a simple exercise to show that absolute convergence of the improper integral in (5.5) suffices to allow our procedures.

We now proceed to relation (5.2). To this end we start with (4.16) and obtain

$$\frac{d}{d\kappa} \left( \frac{v_0}{\kappa} \right) = - \int_0^{\infty} K_*'[\kappa\xi, \xi] \xi^2 d\xi \quad (5.8)$$

Also from (4.5) we get

$$\frac{2\Gamma_1[\kappa, \omega]}{\omega^2} = - \int_0^{\infty} K_*'[\kappa\xi, \xi] \xi^2 \frac{2(1 - \cos \omega\xi)}{\omega^2 \xi^2} d\xi \quad (5.9)$$

Again, taking the limits as  $\omega \rightarrow 0$  and interchanging the process of integration with that of taking the limit as above, we obtain from (5.9).

$$\lim_{\omega \rightarrow 0} \frac{2\Gamma_1[\kappa, \omega]}{\omega^2} = - \int_0^{\infty} K_*'[\kappa\xi, \xi] \xi^2 \lim_{\omega \rightarrow 0} \frac{2(1 - \cos \omega\xi)}{\omega^2 \xi^2} d\xi = - \int_0^{\infty} K_*'[\kappa\xi, \xi] \xi^2 d\xi \quad (5.10)$$

Comparison of (5.8) with (5.10) then establishes (5.2) as we set out to do.

Next we consider the relation (5.3). The derivation of this is formally identical to that of (5.1) and we shall leave the details to the reader.

Finally we consider relation (5.4). In a manner quite analogous to the way (4.10) was obtained, we get from (4.15)<sub>1</sub>.

$$N_1[\kappa, \infty] = - \int_0^{\infty} \{ \kappa\xi K_*'[\kappa\xi, \xi] + K_*[\kappa\xi, \xi] \} d\xi \quad (5.11)$$

On the other hand, (4.6) yields

$$\frac{d}{d\kappa} \kappa \sigma_0(\kappa) = - \int_0^{\infty} \frac{d}{d\kappa} \kappa K_*[\kappa\xi, \xi] d\xi \quad (5.12)$$

A formal application of the rules of differentiation shows that the right hand sides of (5.11) and (5.12) are identical. This establishes (5.4) and thus all of the above rheological relations have been obtained.

In addition to (5.1–4) we may obtain the following relations between  $N[\kappa, \omega]$  and  $\Gamma[\kappa, \omega]$ , namely

$$\frac{\partial}{\partial \kappa} \{ N_1[\kappa, \omega] - N_1[\kappa, \infty] \} = - \frac{\partial}{\partial \kappa} \kappa \frac{\partial \Gamma_2}{\partial \omega} - \frac{\partial \Gamma_2}{\partial \omega} \quad (5.13)$$

$$\frac{\partial}{\partial \kappa} N_2[\kappa, \omega] = \frac{\partial}{\partial \kappa} \kappa \frac{\partial \Gamma_1}{\partial \omega} + \frac{\partial \Gamma_1}{\partial \omega} \quad (5.14)$$

From these relations together with (5.4) one could compute  $N_1[\kappa, \omega]$  and  $N_2[\kappa, \omega]$  from a knowledge of  $\Gamma_1[\kappa, \omega]$ ,  $\Gamma_2[\kappa, \omega]$ , the function  $\sigma_0(\kappa)$  and the condition that  $N$  vanishes when  $\kappa = 0$ . Alternatively, one might compute  $\Gamma_1$  and  $\Gamma_2$  from a knowledge of the dynamic modulus  $G'(\omega) + iG''(\omega) = \Gamma(0, \omega)$  and conditions that  $\Gamma[\kappa, 0] = 0$ , as could be seen, for example, from (5.1) and (5.2). A word about such a computation is necessary here. Given the left hand side of say, (5.13), one could then start by regarding

(5.13) for each fixed  $\omega$  as an ordinary differential equation for  $\partial\Gamma_2/\partial\omega$  as a function of  $\kappa$ . Initial conditions are provided by  $\partial\Gamma_2[0, \omega]/\partial\omega = dG''(\omega)/d\omega$ . Standard methods then allow one to integrate this equation for each  $\omega$ , thus yielding a determination of  $\partial\Gamma_2/\partial\omega$  as a function of  $\kappa$  and  $\omega$ . Thence one may readily determine  $\Gamma_2[\kappa, \omega]$  given that  $\Gamma_2[\kappa, 0] = 0$ . Similar considerations apply to (5.14).

The derivation of (5.13) and (5.14) follow in a straightforward manner by evaluating both sides of these equations in terms of (4.5) and (4.15) with the right-hand side of (5.11) substituted for  $N[\kappa, \infty]$ . It can thus be shown that the right- and left-hand sides of (5.13) and (5.14) become identically equal. We leave this simple task to the reader.

## 6. THE EFFECT OF TEMPERATURE: TIME-TEMPERATURE SUPERPOSITION

In the situation in which the classical linear theory of viscoelasticity applies (e.g. the case  $\kappa = 0$  in (4.1)), it has long been realized that the temperature provides a parameter which may be utilized to extend the effective range of a laboratory instrument which has been designed for a limited range of mechanical parameters (e.g. a limited range of shear rates  $\kappa$  and frequencies  $\omega$  in (4.1)). We shall show here how in the non-linear case one could make similar use of the temperature dependence incorporated into the BKZ perfect elastic fluid theory [1] for general rates of shear  $\kappa$ .

For a fuller discussion of temperature dependence, we refer the reader to previous work [1]. Here we shall only deal with isothermal simple shearing flows for which the temperature may be different for different flows. We shall need a reference temperature, say absolute temperature  $T_0$ . (*A priori* it does not matter which temperature is taken for reference.) We shall take  $K[\gamma, t]$  to be the relaxation function (3.3) at temperature  $T_0$ .

The principle of time-temperature superposition [9] enters our theory. According to this principle, there is a function of the absolute temperature  $T$ , often denoted by  $a_T > 0$ , which figures in formulating the effect of temperature in the stress-shear history relations and which may, without loss of generality, be taken to have the value unity at the reference temperature  $T_0$ . We shall then assume  $a_T = 1$  at  $T = T_0$ . The specific manner in which  $a_T$  depends on  $T$  for a given material is itself a property of the material. The WLF equation [11] often used as an empirical fit for  $a_T$  over an appropriate range of temperatures. In order to simplify the typesetting, we shall adopt the notation  $b_T = 1/a_T$ .

We may now formulate the manner in which the shearing stress depends on temperature in simple shear according to the BKZ theory, as can be readily derived by introducing the temperature dependence of the perfect elastic fluid theory [1] into our above results. For an isothermal motion (2.1), the relation (2.2) becomes

$$\sigma = -\frac{\rho T}{\rho_0 T_0} \int_t^\infty K_*[\gamma(t) - \gamma(\tau), (t - \tau)b_T] b_T d\tau \quad (6.1)$$

where  $\rho$  is the mass density at temperature  $T$  and  $\rho_0$  is the density at  $T_0$ .

For stress relaxation at temperature  $T$ , we use (6.1) in place of (2.2) and obtain instead of (3.3)

$$\sigma = -\frac{\rho T}{\rho_0 T_0} \int_t^\infty K_*[\gamma, b_T \xi] b_T d\xi = -\frac{\rho T}{\rho_0 T_0} \int_{b_T t}^\infty K_*[\gamma, \zeta] d\zeta = \frac{\rho T}{\rho_0 T_0} K[\gamma, b_T t] \quad (6.2)$$

where the second equality in (5.2) results from the change of variable  $\tau = b_T \xi$  and where the third equality results from (3.3). Thus (6.2) gives the stress relaxation response for different temperatures in terms of the BKZ theory.

For suddenly imposed constant rate of strain (3.7) we get in place of (3.9)

$$\sigma = \frac{\rho T}{\rho_0 T_0} K[\kappa t, b_T t] - \frac{\rho T}{\rho_0 T_0} \int_0^t K[\kappa \xi, b_T \xi] b_T d\xi$$

whence instead of (3.12) there follows

$$\sigma = \frac{\kappa \rho T}{\rho_0 T_0} \int_0^t K'[\kappa \xi, b_T \xi] d\xi$$

and in place of (3.14) we get

$$\frac{\dot{\sigma}}{\dot{\gamma}} = \frac{\dot{\sigma}}{\kappa} = \frac{\rho T}{\rho_0 T_0} K'[\kappa \xi, b_T \xi] \quad (6.3)$$

We note that (6.2) and (6.3) gives a way of varying the second argument in  $K$  or  $K'$  respectively beyond that permissible for experiments conducted over limited durations of time; i.e. by changing the temperature of the experiment, and thus adjusting  $b_T$ , we may obtain information for larger or smaller values of  $t$  than actually occur during the time interval in which data are taken in a given set of experiments. Let us now see how varying the temperature parameter affects the information obtained from small oscillations superposed on steady shearing flow.

When (4.1) is inserted into (6.1) instead of (2.2) the steps by which we arrive at (4.9) lead instead to

$$\Gamma[\kappa, \omega; T] = -\frac{\rho T}{\rho_0 T_0} \int_0^\infty K'_*[\kappa \xi, b_T \xi] (1 - e^{-i\omega \xi}) b_T d\xi \quad (6.4)$$

where  $\Gamma[\kappa, \omega; T]$  is the value of  $\Gamma[\kappa, \omega]$  at temperature  $T$ . If in (6.4) we make the change of variable to  $\zeta = b_T \xi$ , i.e.  $\xi = a_T \zeta$  we obtain

$$\Gamma[\kappa, \omega, T] = -\frac{\rho T}{\rho_0 T_0} \int_0^\infty K'_*[\kappa a_T \zeta, \zeta] (1 - e^{-i\omega a_T \zeta}) d\zeta \quad (6.5)$$

whence

$$\Gamma[a_T \kappa, a_T \omega; T_0] = \frac{\rho_0 T_0}{\rho T} \Gamma[\kappa, \omega; T] \quad (6.6)$$

This, then, is the result which gives the temperature dependence of  $\Gamma$ .

Finally let us mention that if one defined  $\sigma_0[\kappa; T]$  to be the steady shearing stress at rate of shear  $\kappa$ , and temperature  $T$  one could derive by methods similar to those just described

$$\sigma_0[\kappa; T] = \frac{\rho T}{\rho_0 T_0} \sigma_0[a_T \kappa; T_0] \quad (6.7)$$

This result has already been derived elsewhere and compared favorably with data [1].

Results formally identical to (6.6) and (6.7) can be obtained for  $N$  and  $v_0$  respectively. These results (6.6) and (6.7), as well as their counterparts of  $N$  and  $v_0$ , can be used to supplement the effective ranges of the variables  $\kappa$  and  $\omega$  for small oscillations on steady shearing flow (or simply steady flow in the case of  $\sigma_0$  and  $v_0$ ) by comparison of data at different temperatures.

## 7. CONCLUDING REMARKS

In terms of the BKZ theory we have shown methods of obtaining the information necessary to predict the response of a non-Newtonian fluid to an arbitrary simple shearing history. We have concentrated on the shearing stress  $\sigma$  and the normal stress difference  $v$  as defined above. The particular normal stress difference chosen is that measured in such standard instruments as the Padden-De Witt apparatus [7] or the Weissenberg Rheogenerator. However, considerations similar to those discussed for, say,  $\sigma$  alone would also apply to other normal stress differences as well. Indeed normal stress differences other than  $v$  could not be predicted from measurements on  $\sigma$  or  $v$  for a given fluid if one knew that it is a fluid of the general BKZ type. The reader may verify the statement from the equations for simple shear displayed in Ref. [2].

A more serious drawback is that, unlike the case of the linear viscous fluid, the behavior of the general BKZ fluid in arbitrary flow cannot be determined merely from simple shearing measurements. Zapas [4] has dealt with this difficulty by proposing a more specific form of the BKZ fluid equations. His specification of the form was obtained empirically and its success depends on how good his empirical fit turns out to be. As far as he has been able to check it against data, he has found the fit to be excellent. However, it would be well to have direct methods of determining the response to flows other than simple shearing one, not only to help check or improve the empirical fit but, even more, to be able to operate without relying on an empirical fit, as we can in simple shear. (General biaxial stress relaxation would give all information required, but such motions are hardly appropriate to polymer solutions).

Finally let us recall for a moment the rheological relations (5.1-4). It would seem that they should be among the most directly experimentally verifiable results of our foregoing work. A preliminary check of the data of Booij [5] seems to indicate that (5.1) agrees with it. Booij does not give sufficient data conclusively to check or disprove (5.2). However we may make the following observation, namely that (5.2) may also be written

$$\lim_{\omega \rightarrow 0} \frac{2\Gamma_1[\kappa, \omega]}{\omega^2} = \frac{v_0(\kappa)}{\kappa^2} \left[ \frac{d \ln v_0}{d \ln \kappa} - 1 \right] \quad (7.1)$$

It would seem, then, that as  $\omega$  goes to zero,  $\Gamma_1[\kappa, \omega]/\omega^2$  should approach a positive or negative value depending on whether the slope of the curve of  $\ln v_0$  vs.  $\ln \kappa$  is greater than or less than unity respectively. The data of Booij suggests consistency with this result. (We mention, for those readers who wish to check this result, that Booij uses the notation  $G'_\kappa(\omega)$ ,  $G''_\kappa(\omega)$  and  $p_{11} - p_{22}$  where we use the notation  $\Gamma_1[\kappa, \omega]$ ,  $\Gamma_2[\kappa, \omega]$  and  $v_0$  respectively.)

We have found no data on  $N[\kappa, \omega]$  and so have at present no experimental check for (5.3) or (5.4).



Finally we remark that we believe that (5.1) should hold for any Coleman–Noll Simple Fluid [12], but that (5.2) should not. If this be true, then verification of (5.2) would be evidence in favor of the BKZ theory. We must leave to future work these questions as well as questions of the extent of generality of the rheological relations.

#### REFERENCES

- [1] B. BERNSTEIN, E. A. KEARSLEY and L. J. ZAPAS, Thermodynamics of perfect elastic fluids. *J. Res. natn. Bur. Stand.* **68B**, 103 (1964).
- [2] B. BERNSTEIN, Time dependent behavior of an incompressible elastic fluid. *Acta Mechanica* **II**/4, p. 329 (1966).
- [3] L. J. ZAPAS and T. CRAFT, Correlation of large longitudinal deformations with different strain histories. *J. Res. natn. Bur. Stand.* **69A**, 541 (1965).
- [4] L. J. ZAPAS, Viscoelastic behavior under large deformations. *J. Res. natn. Bur. Stand.* **70A**, 525 (1966).
- [5] H. C. BOOIJ, Influence of superimposed steady shear flow on the dynamic properties of non-Newtonian fluids. *Rheol. Acta* **5**, 216 (1966).
- [6] K. OSAKI, M. TAMURA, M. KURATA and T. KOTAKA, Complex modulus of concentrated polymer solutions in steady shear. *J. phys. Chem.* **69**, 4183 (1965).
- [7] F. J. PADDEN and T. W. DEWITT, Some rheological properties of concentrated polyisobutylene solutions. *J. appl. Phys.* **25**, 1086 (1954).
- [8] H. MARKOVITZ, Normal stress measurements on polymer solutions. *Proc. 4th Int. Congr. on Rheology*, Part I, p. 189 (1963).
- [9] J. D. FERRY, *Viscoelastic Properties of Polymers*. Wiley (1961).
- [10] B. D. COLEMAN and H. MARKOVITZ, Normal stress effects in second order fluids. *J. appl. Phys.* **35**, 1 (1964).
- [11] M. L. WILLIAMS, R. F. LANDEL and J. P. FERRY, The temperature dependence of relaxation mechanisms in amorphous polymer and other glass-forming liquids, *J. Am. chem. Soc.* **77**, 3701 (1955).
- [12] W. NOLL, A mathematical theory of the behavior of continuous media. *Archs ration. Mech. Analysis* **2**, 197 (1958).

(Received 7 May 1968)

**Résumé**—On discute théoriquement des méthodes qui pourraient être utilisées pour déterminer, d'après la théorie BKZ des fluides élastiques, la contrainte de cisaillement et la contrainte normale réponses d'un fluide non Newtonien à une série de cisaillements simples pour laquelle la vitesse de cisaillement varie arbitrairement avec le temps. Pour faire ceci avec n'importe quel fluide on a besoin de certaines informations sur le fluide. On montre que ces informations pourraient être obtenues si on connaissait seulement la contrainte de cisaillement réponse à un cisaillement simple de n'importe lequel des types suivants: relaxation de contrainte, cisaillement constant imposé brusquement ou petites oscillations superposées à un flux de cisaillement constant. On démontre quelques relations rhéologiques pour chacun de ces types de flux. Ces relations sont des relations entre des quantités directement mesurables et ne font pas intervenir les propriétés des matériaux, mais elles ne sont valables que pour certaines catégories de mouvements. On montre aussi comment, d'après la théorie BKZ des fluides parfaitement élastiques, un changement de température affecte les résultats. A partir de là on discute comment un changement de température pourrait être utilisé pour compléter les données obtenues lorsque l'étendue des paramètres mécaniques est limitée.

**Zusammenfassung**—Es werden solche Methoden theoretisch behandelt, mit denen gemäss der BKZ-Theorie elastischer Flüssigkeiten die Scher- und Normalspannungen bestimmt werden können, die in einer nicht-Newton'schen Flüssigkeit unter einfacher Scherung auftreten, wobei die Schergeschwindigkeit sich willkürlich mit der Zeit ändert. Für jede gegebene Flüssigkeit müssen dazu bestimmte Informationen über die Flüssigkeit zur Verfügung stehen. Es wird gezeigt, wie man diese Informationen erhalten kann, wenn nur die Scherspannungen bekannt sind, die von einer der nachfolgenden Scherbewegungen hervorgerufen werden: Spannungsrelaxation, plötzlich aufgebrachte stetige Scherung, oder stetige Scherströmung mit überlagerten kleinen Schwankungen. Für jeden dieser Strömungstypen werden einige rheologische Beziehungen abgeleitet. Es sind dies Beziehungen zwischen direkt messbaren Grössen, d.h. sie enthalten keine Materialeigenschaften, gelten jedoch nur für gegebene Bewegungsarten. Ebenfalls wird gezeigt, wie gemäss der BKZ-Theorie vollkommen elastischer Flüssigkeiten eine Temperaturänderung die Ergebnisse beeinflusst. Damit kann die Möglichkeit diskutiert werden, durch Temperaturänderung die Messergebnisse zu erweitern, die im Falle einer begrenzten Anzahl von mechanischen Parametern zur Verfügung stehen.

**Абстракт**—Это теоретическое обсуждение методов, которые могли бы применяться для определения — согласно теории ВКЗ упругой жидкости — касательные и нормальные давления напряжения вызванные в жидкости неудовлетворяющей теории Ньютона простыми измерениями касательных напряжений по времени, для которых скорость изменения касательных напряжений произвольным образом со временем. Для того, чтобы это сделать для произвольной (данной) жидкости, необходима некоторая информация относительно этой жидкости. Показывается как эта информация может быть получена если известны только касательные напряжения вызванные простыми сдвигами каждого из следующих видов: релаксация напряжений, мгновенно приложенное установившееся касательное напряжение, или же малые колебания наложенные на установившийся поток жидкости, со сдвигом. Для каждого из этих типов течения выводятся некоторые реологические соотношения. Это соотношение между непосредственно измеряемыми величинами и не зависят от свойств материала, но справедливы для данных классов движений. Показывается, тоже каким образом изменение температуры, согласно теории идеально упругой жидкости ВКЗ влияет на результаты. В связи с этим обсуждается вопрос, как можно использовать температурные изменения для получения добавочных данных в случае, когда предел механических параметров ограничен.