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NON-NEWTONIAN FLOW IN INCOMPRESSIBLE FLUIDS

Part III. Some problems in transient flow

by

A. Kaye

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A. Kaye, M.A.

SUMMARY

Some transient flows are investigated, using a rheological equation of state for an incompressible fluid of the form:

$$p_{ij} - p\delta_{ij} = 2\int_{-\infty}^{t} \left(\frac{\partial\Omega}{\partial J_1} S_{ij} - \frac{\partial\Omega}{\partial J_2} S_{ij}^{-1}\right) dt'$$

where Ω is a function of J_1 and J_2, the invariants of the Cauchy-Green deformation tensor S_{ij}, which relates the deformation at the present time t with that at some past time t'. Ω is also a function of t and t'. It is found that a material obeying the above equation of state will show elastic and stress relaxation effects and may be of some use in investigating these properties in concentrated polymer solutions and melts.

Contents

List of Symbols

This list defines the additional symbols used in this Note, and should be taken in conjunction with the list in College of Aeronautics Note No. 134.

f_i	the acceleration of a particle at x_i
F_i	the body force per unit volume on the body at x_i
v_i	the velocity of a particle at x_i
$A_{ij}(t)$ or $\underline{\underline{A}}(t)$ or $\underline{\underline{A}}$ $A_{ij}(t')$ or $\underline{\underline{A}}(t')$ or $\underline{\underline{A}}'$	the matrices defining a given homogeneous deformation.
$\underline{\underline{I}}$	the unit matrix.
$\underline{\underline{P}}$	the matrix of the stress tensor.
$J_1^* \; J_2^* \; J_3^*$	the invariants of the tensor S_{ij}^{-1}
diag (a,b,c)	a matrix whose only non-zero terms are the leading diagonal terms a, b, c.
$\lambda_1, \lambda_2, \lambda_3$	the extension ratios on deformation of the sides of a parallelopiped whose sides are parallel to the principal directions.
$(p_{ij})_T$	the transient stress.
$(Z^*)_T$	the transient normal force.
M, N, m, n	constants in the definition of a particular form of Ω.
$\underline{\underline{A}}_o$	$\underset{t \to o_+}{\mathrm{Lt}} \; \underline{\underline{A}}$
p, q, r, s a, b, c, d	constants used for particular forms of $\underline{\underline{A}}_o$
τ	$t-t'$
a_i or $\underline{a}$ (a_i' or $\underline{a}'$)	the position of a particle just before (or just after) a change in stress.
σ	the shear stress in constrained flow.
F(t)	a function defining the amount of shear in constrained flow.
γ_1, γ_1^*	the recovery in constrained flow.

a) Introduction

In Part I of this series (CoA Note 134) a rheological equation of state for an incompressible fluid was obtained by a formal generalisation of the rheological equation of state for an incompressible elastic solid capable of sustaining large strains. The complete physical significance of this generalisation is not understood but, since the elastic equation of state has been used to describe the elastic behaviour of rubber-like polymers at large strains, it seems possible that this equation of state for an incompressible fluid may be used to describe the properties of materials such as polymer melts, concentrated polymer solutions and even 'solid' rubber-like polymers which show time-dependent properties.

In Part II (CoA Note 134) the equation of state was used to obtain solutions to some problems in steady flow in which the velocity and stress at any point in the fluid were independent of time.

In this Note (Part III) we investigate some problems in which the stress and velocity are not independent of time. In particular we investigate problems in which there is an instantaneous change in the deformation, the rate of deformation, or the applied stress. Such transient flow phenomena are of interest because they provide further insight into the behaviour of the class of fluids which may be characterized by the general equation of state, and also because many experiments involve flow of this type; for example, creep under constant load, stress relaxation under constant deformation, and elastic recovery.

Many polymeric substances show marked elastic recovery in the sense that the sudden removal of an applied stress, even after the steady flow under this stress has been achieved, results in further deformation, even when the inertia forces may be neglected. It is important to develop a general formalism for the description and inter-relation of all these phenomena.

The mathematical problem can be represented as that of finding a solution to the equation of motion

$$\frac{\partial p_{ij}}{\partial x_j} = \rho f_i - F_i \tag{3.1}$$

subject to the equation of continuity

$$\frac{\partial v_i}{\partial x_i} = 0 \tag{3.2}$$

for the rheological equation of state

$$p_{ij} - p\delta_{ij} = 2\int_{-\infty}^{t} \left\{ \frac{\partial \Omega}{\partial J_1} s_{ij} - \frac{\partial \Omega}{\partial J_2} s_{ij}^{-1} \right\} dt' \tag{3.3}$$

when the boundary conditions are specified and may be discontinuous with respect to time t.

In these equations, p_{ij} is the stress tensor at the point x_i referred to the rectangular cartesian co-ordinate system OX_i. F_i is the body force per unit volume at x_i and f_i is given by

$$f_i = v_m \frac{\partial v_m}{\partial x_i} + \frac{\partial v_i}{\partial t} \qquad (3.4)$$

where v_i is the velocity of the particle at x_i. The equation of state (3.3) is discussed in detail in Part I, where a definition of Ω, J_1, J_2, S_{ij}^{-1} and S_{ij} will be found. The equation of continuity is the mathematical expression of the assumption that the material is incompressible. The general problem is, of course, too difficult and it will be simplified by making the following assumptions; (1) body forces do not exist ($F_i = 0$) and (2) inertial forces are negligible ($f_i = 0$). In addition, we shall consider only homogeneous deformations (see Appendix I). For slow moving viscous liquids it is reasonable to ignore inertial forces and most physical experiments are designed to produce a deformation as nearly homogeneous as possible.

The effect of equating F_i and f_i to zero in the equation of motion is to reduce it to the form

$$\frac{\partial p_{ij}}{\partial x_j} = 0 \qquad (3.5)$$

and it is shown in section (b) that, for homogeneous deformation, the stress, p_{ij}, is not a function of position, but only of time; therefore, the equation of motion of the form (3.5) must be satisfied. Hence any homogeneous deformation, for which the equation of continuity is satisfied, is a possible deformation, and the stress may be calculated directly from the equation of state. Similarly, any stress which is not a function of position gives rise to a homogeneous deformation which may be calculated directly from the equation of state, using as a subsidiary condition the fact that the material is incompressible.

b) A special form of the equation of state when the deformations are homogeneous.

We now consider only those deformations, (homogeneous deformations) which convert any set of parallel planes into another set of parallel planes, and in which the origin of co-ordinates remains fixed. It can be shown, (Appendix I), that the most general deformation of this type can be expressed by,

$$A_{ij}\ x_j = A'_{ij}\ x'_j \tag{3.6}$$

where x_i and x'_i are, as in Part I, the rectangular cartesian coordinates of a particle at times t and t′ respectively and

$$A_{ij} = A_{ij}(t) \tag{3.7}$$

$$A'_{ij} = A_{ij}(t') \tag{3.8}$$

We denote the matrix whose element in the i^{th} row and j^{th} column is A_{ij} by $\underline{\underline{A}}$, and define $\underline{\underline{A}}'$ in a similar manner. If $\underline{x}$ is the column matrix of x_i and $\underline{x}'$ the column matrix of x'_i, then

$$\underline{\underline{A}}\ \underline{x} = \underline{\underline{A}}'\ \underline{x}' \tag{3.9}$$

or

$$\underline{x} = \underline{\underline{A}}^{-1}\ \underline{\underline{A}}'\ \underline{x}' \tag{3.10}$$

The matrix of

$$\frac{\partial x_i}{\partial x'_j} \quad \text{is} \quad \underline{\underline{A}}^{-1}\ \underline{\underline{A}}' \tag{3.11}$$

and therefore the matrix of

$$S_{ij} = \frac{\partial x_i}{\partial x'_\alpha}\ \frac{\partial x_j}{\partial x'_\alpha} \quad \text{is} \quad \underline{\underline{A}}^{-1}\ \underline{\underline{A}}'\,(\widetilde{\underline{\underline{A}}^{-1}\ \underline{\underline{A}}'}) = \underline{\underline{A}}^{-1}\ \underline{\underline{A}}'\ \tilde{\underline{\underline{A}}}'\ \tilde{\underline{\underline{A}}}^{-1} \tag{3.12}$$

Similarly, the matrix of

$$S^{-1}_{ij} \quad \text{is} \quad \tilde{\underline{\underline{A}}}\ \tilde{\underline{\underline{A}}}'^{-1}\ \underline{\underline{A}}'^{-1}\ \underline{\underline{A}} \tag{3.13}$$

For homogeneous deformations the equation of state (3.3) can be expressed in matrix form where $\underline{\underline{P}}$ is the matrix of p_{ij}, $\underline{\underline{I}}$ is the matrix of δ_{ij} by

$$\underline{\underline{P}} - p\underline{\underline{I}} = \int_{-\infty}^{t} 2\{\frac{\partial\Omega}{\partial J_1}\ \underline{\underline{A}}^{-1}\ \underline{\underline{A}}'\ \tilde{\underline{\underline{A}}}'\ \tilde{\underline{\underline{A}}}^{-1} - \frac{\partial\Omega}{\partial J_2}\ \underline{\underline{A}}\ \tilde{\underline{\underline{A}}}'^{-1}\ \tilde{\underline{\underline{A}}}'^{-1}\ \underline{\underline{A}}\}dt' \tag{3.14}$$

Noting that $\underline{\underline{A}}$ is a function of t only, this has the alternative form,

$$\underline{\underline{P}} - p\underline{\underline{I}} = \underline{\underline{A}}^{-1}\left\{\int_{-\infty}^{t} 2\ \frac{\partial\Omega}{\partial J_1}\ \underline{\underline{A}}'\ \tilde{\underline{\underline{A}}}'\ dt'\right\}\tilde{\underline{\underline{A}}}^{-1} - \tilde{\underline{\underline{A}}}\left\{\int_{-\infty}^{t} 2\ \frac{\partial\Omega}{\partial J_2}\ \tilde{\underline{\underline{A}}}'^{-1}\ \underline{\underline{A}}'^{-1}\ dt'\right\}\underline{\underline{A}} \tag{3.15}$$

It must be remembered that, in general, Ω is a function of t and J_1, J_2 are functions of t; therefore the integrands are not simply functions of t′ unless $\frac{\partial\Omega}{\partial J_1}, \frac{\partial\Omega}{\partial J_2}$ are constants. We also note that the condition $J_3 = 1$ implies, for all t,

$$\det \underline{\underline{A}} = \text{constant} \tag{3.16}$$

and this constant may be taken to be one.
Moreover, since $\underline{\underline{A}}$, J_1 and J_2 are not functions of position, $\underline{\underline{P}}$ is not a function of position. In fact J_1, J_2 and J_3 are defined by

$$\begin{aligned} J_1 &= S_{\alpha\alpha} = \text{trace } S_{ij} \\ J_2 &= \tfrac{1}{2}(S^2_{\alpha\alpha} - S_{\alpha\beta}\, S_{\beta\alpha}) \\ J_3 &= \det S_{ij} \end{aligned} \tag{3.17}$$

and, if J_1^* J_2^* and J_3^* are similarly defined invariants of S_{ij}^{-1}, it can be shown that

$$J_1^* = \frac{J_2}{J_3} \tag{3.18}$$

$$J_2^* = \frac{J_1}{J_3} \tag{3.19}$$

$$J_3^* = \frac{1}{J_3} \tag{3.20}$$

The incompressibility condition gives

$$J_3^* = J_3 = 1 \tag{3.21}$$

and therefore

$$J_1^* = J_2 \tag{3.22}$$

$$J_2^* = J_1 \tag{3.23}$$

and hence, using (3.12) and (3.13), for a homogeneous deformation we have

$$J_1 = \text{trace } S_{ij} = \text{trace } \underline{\underline{A}}^{-1}\, \underline{\underline{A}}'\, \tilde{\underline{\underline{A}}}'\, \tilde{\underline{\underline{A}}}^{-1} \tag{3.24}$$

$$J_2 = J_1^* = \text{trace } S_{ij}^{-1} = \text{trace } \tilde{\underline{\underline{A}}}\, \tilde{\underline{\underline{A}}}'^{-1}\, \underline{\underline{A}}'^{-1}\, \underline{\underline{A}} \tag{3.25}$$

c) Stress relaxation

i) Consider a deformation defined by $\underline{\underline{A}}$ where

$$\left.\begin{aligned} \underline{\underline{A}} &= \underline{\underline{I}} \quad t < o \\ \underline{\underline{A}} &= \text{diag}\,\{\lambda_1^{-1}, \lambda_2^{-1}, \lambda_3^{-1}\} \quad t > o \\ \lambda_1\lambda_2\lambda_3 &= 1 \end{aligned}\right\} \tag{3.26}$$

where λ_1, λ_2, λ_3 are constants independent of time. It can be seen, by examining the equation (A9) in this special case, that the physical meaning of this deformation is that the body is at rest until $t = 0$, when it is given an instantaneous extension of amount λ_i along the x_i direction. If the stress is now measured as a function of time, this represents a stress relaxation experiment.

Therefore,

$$\left.\begin{aligned} \underline{\underline{A}}\,\tilde{\underline{\underline{A}}} &= \underline{\underline{I}} \quad t < o \\ \underline{\underline{A}}\,\tilde{\underline{\underline{A}}} &= \text{diag}\{\lambda_1^{-2}, \lambda_2^{-2}, \lambda_3^{-2}\} \quad t > o \end{aligned}\right\} \tag{3.27}$$

$$\begin{matrix} t > o \\ t' < o \end{matrix}\left\{\begin{aligned} J_1 &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\ J_2 &= \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} \end{aligned}\right. \qquad \begin{matrix} t > o \\ t' > o \end{matrix}\left\{\begin{aligned} J_1 &= 3 \\ J_2 &= 3 \end{aligned}\right. \tag{3.28}$$

Inserting these results in the equation of state (3.15) we obtain, for t less than zero,

$$\underline{\underline{P}} = p'\underline{\underline{I}} \tag{3.29}$$

and for t greater than zero,

$$\begin{aligned} \underline{\underline{P}} - p\,\underline{\underline{I}} = {} & \text{diag}\{\lambda_1^2, \lambda_2^2, \lambda_3^2\}\int_{-\infty}^{o} 2\,\frac{\partial\Omega}{\partial J_1}dt' - \text{diag}\{\lambda_1^{-2}, \lambda_2^{-2}, \lambda_3^{-2}\}\int_{-\infty}^{o} 2\,\frac{\partial\Omega}{\partial J_2}dt' \\ & + \text{diag}\{\lambda_1^2, \lambda_2^2, \lambda_3^2\}\int_{o}^{t} 2\,\frac{\partial\Omega}{\partial J_1}\text{diag}\{\lambda_1^{-2}, \lambda_2^{-2}, \lambda_3^{-2}\}dt' \\ & - \text{diag}\{\lambda_1^{-2}, \lambda_2^{-2}, \lambda_3^{-2}\}\int_{o}^{t} 2\,\frac{\partial\Omega}{\partial J_2}\text{diag}\{\lambda_1^2, \lambda_2^2, \lambda_3^2\}dt' \end{aligned} \tag{3.30}$$

where we have used the fact that diagonal matrices commute; hence we obtain, for $t > o$,

$$\underline{\underline{P}} - p''\underline{\underline{I}} = \mathrm{diag}\{\lambda_1^2, \lambda_2^2, \lambda_3^2\}\int_{-\infty}^{0} 2\frac{\partial\Omega}{\partial J_1}dt' - \mathrm{diag}\{\lambda_1^{-2}, \lambda_2^{-2}, \lambda_3^{-2}\}\int_{-\infty}^{0} 2\frac{\partial\Omega}{\partial J_2}dt' \tag{3.31}$$

and,

$$p'' = p + \int_0^t 2\frac{\partial\Omega}{\partial J_1}dt' - \int_0^t 2\frac{\partial\Omega}{\partial J_2}dt' \tag{3.32}$$

If such a stress relaxation experiment is carried out, the quantities which can be measured practically are $p_{11} - p_{22}$, $p_{22} - p_{33}$, and $p_{11} - p_{33}$. These depend on $\int_{-\infty}^{0} \frac{\partial\Omega}{\partial J_1}dt'$ and $\int_{-\infty}^{0} \frac{\partial\Omega}{\partial J_2}dt'$ which, of course, depend on t. Since, in this stress relaxation experiment, J_1 and J_2 can be varied independently by changing λ_1, λ_2, λ_3, a measurement of $\int_{-\infty}^{0} \frac{\partial\Omega}{\partial J_1}dt'$ and $\int_{-\infty}^{0} \frac{\partial\Omega}{\partial J_2}dt'$ for various J_1 and J_2 will be sufficient to determine Ω completely as a function of J_1, J_2 and $\tau = (t-t')$. Thus, if we consider the case where Ω is given by (2.20) (Part II) and the initial deformation is a simple elongation, that is,

$$\lambda_1 = \lambda \qquad \lambda_2 = \lambda_3 = \lambda^{-\frac{1}{2}} \tag{3.33}$$

we find,

$$\left.\begin{aligned} P_{22} - P_{33} &= P_{21} = P_{13} = P_{32} = 0 \\ P_{11} - P_{22} &= 2(\lambda^2 - \frac{1}{\lambda})\left\{\frac{C_1}{K_1} e^{-K_1 t} + \frac{1}{\lambda}\ \frac{C_2}{K_2} e^{-K_2 t}\right\} \end{aligned}\right\} \tag{3.34}$$

and we note that $p_{11} - p_{22}$ falls to zero as t tends to infinity, as we would expect for a liquid. A measurement of $p_{11} - p_{22}$ as a function of t for various values of λ will enable C_1, C_2, K_1 and K_2 to be found.

The equation of state (3.3) may be useful in investigating the properties of 'solid' substances. By a solid we mean that, in the stress relaxation experiment outlined above, the stress does not become isotropic as t tends to infinity, as it must if it is of the form given by (1.10) and (2.22). The equation of state could be altered by suitably changing the form of Ω in equation 2.22, as a function of t-t', in such a manner that the stress does not tend to zero as t tends to infinity. In this case, an experiment on homogeneous stress relaxation may throw some light on the remarks by Cifferi and Flory (1961) on the connection between the C_2 term (see equation (2.20)) and hysteresis.

ii) <u>Stress relaxation in simple shear</u>

Consider the deformation defined by

$$\left.\begin{aligned} \underline{\underline{A}} &= \underline{\underline{I}} \quad t < o \\ \underline{\underline{A}} &= \begin{pmatrix} 1 & -\alpha & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad t > o \end{aligned}\right\} \qquad (3.35)$$

therefore,

$$x_i = x_i' \quad \begin{array}{l} \text{if} \quad t < o \;\; t' < o \\ \text{or} \quad t > o \;\; t' > o \end{array} \qquad (3.36)$$

$$\begin{aligned} x_1' &= x_1 - \alpha x_2 \\ x_2' &= x_2 \qquad\qquad \text{if } t' < o \quad t > o \\ x_3' &= x_3 \end{aligned} \qquad (3.37)$$

By examining the physical meaning of equations (3.36) and (3.37) we see that the deformation is such that the body is at rest until t = 0, when it is given an instantaneous simple shear of amount α.

We find, for $t > o$, that

$$\left.\begin{aligned} \underline{\underline{S}} &= \begin{pmatrix} 1+\alpha^2 & \alpha & 0 \\ \alpha & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad t' < o \\ \underline{\underline{S}} &= \underline{\underline{I}} \qquad\qquad\qquad t' > o \end{aligned}\right\} \qquad (3.38)$$

$$\left.\begin{aligned} \underline{\underline{S}}^{-1} &= \begin{pmatrix} 1 & -\alpha & 0 \\ -\alpha & 1+\alpha^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad t' < o \\ \underline{\underline{S}}^{-1} &= \underline{\underline{I}} \qquad\qquad\qquad t' > o \end{aligned}\right\} \qquad (3.39)$$

$$\left.\begin{aligned} J_1 &= J_2 = 3 + \alpha^2 \quad t' < o \quad t > o \\ J_1 &= J_2 = 3 \qquad\quad t' > o \quad t > o \end{aligned}\right\} \qquad (3.40)$$

and the equation of state becomes, for $t > o$,

$$\underline{\underline{P}} - p''\underline{\underline{I}} = \int_{-\infty}^{o} 2\frac{\partial\Omega}{\partial J_1}\begin{pmatrix} \alpha^2+1 & \alpha & 0 \\ \alpha & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}dt' - \int_{-\infty}^{o} 2\frac{\partial\Omega}{\partial J_2}\begin{pmatrix} 1 & -\alpha & 0 \\ -\alpha & 1+\alpha^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}dt' \qquad (3.41)$$

where $\frac{\partial\Omega}{\partial J_1}$ and $\frac{\partial\Omega}{\partial J_2}$ are evaluated with $J_1 = J_2 = 3 + \alpha^2$

Hence,

$$p_{11} - p_{33} = \alpha^2 \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_1} \, dt' \tag{3.42}$$

$$p_{22} - p_{33} = -\alpha^2 \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_2} \, dt' \tag{3.43}$$

$$p_{12} = \alpha \left\{ \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_1} \, dt' + \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_2} \, dt' \right\} \tag{3.44}$$

Thus a simple shear stress relaxation experiment is sufficient to find Ω when $J_1 = J_2$. It is probably more convenient to carry out the experiment either by the torsion of a cylinder of the fluid between parallel plates or the torsion of the fluid between a cone and plate. Although these deformations are not homogeneous, they give essentially the same information as a simple shear experiment and it will be convenient to quote the results here.

In the parallel plate experiment, the normal force Z^* per unit area on the plate is given by

$$Z^* = \frac{\omega_o^2 r^2}{L^2} \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_2} \, dt' + \frac{\omega_o^2}{L^2} \int_{r}^{a} r \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_1} \, dt' . \, dr \tag{3.45}$$

and the tangential force, T, per unit area on the plate is given by

$$T = \frac{r\omega_o}{L} \left\{ \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_1} \, dt' + \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_2} \, dt' \right\} \tag{3.46}$$

where $J_1 = J_2 = 3 + \frac{r^2\omega_o^2}{L^2}$ and ω_o is the angle the cylinder is twisted about its axis; L is the distance between the ends of the cylinder, which are held at a fixed distance apart, and r is the distance between a point on the end plate and the axis of rotation.

In the cone and plate experiment, the normal force Z^* per unit area on the plate is given by

$$Z^* = \frac{\omega_o^2}{\beta^2} \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_2} \, dt' + \frac{\omega_o^2}{\beta^2} \{\log \frac{a}{r}\} \left\{ \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_1} \, dt' - \int_{-\infty}^{0} 2 \frac{\partial\Omega}{\partial J_2} \, dt' \right\} \tag{3.47}$$

and the tangential force, T, per unit area is given by

$$T = \frac{\omega_o}{\beta}\left\{\int_{-\infty}^{o} 2\,\frac{\partial\Omega}{\partial J_2}\,dt' + \int_{-\infty}^{o} 2\,\frac{\partial\Omega}{\partial J_1}\,dt'\right\} \tag{3.48}$$

where $J_1 = J_2 = 3 + \frac{\omega_o^2}{\beta^2}$, ω_o is the angle the cone turns through about its axis and β is the complement of the semivertical angle of the cone. Hence, in both these experiments, measurements of Z^* and T as functions of radius will enable Ω to be found as a function of J_1, J_2 and $t-t'$, when $J_1 = J_2$.

d) Simple shear flow

i) Instantaneous application of simple shear flow

Let us envisage a situation in which the fluid has been at rest until $t = o$, when a deformation corresponding to a simple shear flow is suddenly applied. We proceed to investigate how the stress varies with time.

It is easy to see that in this case we have,

$$\left.\begin{array}{l} \underline{\underline{A}} = \underline{\underline{I}} \quad t < o \\ A = \begin{pmatrix} 1 & -tG & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} t > o \end{array}\right\} \tag{3.49}$$

where G is the shear rate. Obviously, for $t < o$, p_{ij} is just an isotropic pressure. For $t > o$ we find

$$\left.\begin{array}{ll} t' < o & J_1 = J_2 = 3 + t^2G^2 \\ t' > o & J_1 = J_2 = 3 + (t-t')^2G^2 \end{array}\right\} \tag{3.50}$$

Inserting the value of $\underline{\underline{A}}$ into (3.15) we find,

$$\underline{\underline{P}} - p\,\underline{\underline{I}} = \begin{pmatrix} 1+t^2G^2 & tG & 0 \\ tG & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \int_{-\infty}^{o} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'<o} dt' - \int_{-\infty}^{o} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o} \begin{pmatrix} 1+(t-t')^2G^2 & (t-t')G & 0 \\ (t-t')G & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt'$$

$$- \begin{pmatrix} 1 & -tG & 0 \\ -tG & 1+t^2G^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \int_{-\infty}^{o} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o} dt' + \int_{-\infty}^{o} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o} \begin{pmatrix} 1 & -(t-t')G & 0 \\ -(t-t')G & 1+(t-t')^2G^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt'$$

$$+ \int_{-\infty}^{t} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o} \begin{pmatrix} 1+(t-t')^2G^2 & (t-t')G & 0 \\ (t-t')G & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt' - \int_{-\infty}^{t} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o} \begin{pmatrix} 1 & -(t-t')G & 0 \\ -(t-t')G & 1+(t-t')^2G^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt' \tag{3.51}$$

where $\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'<o}$ is the value of $\frac{\partial\Omega}{\partial J_1}$ when $J_1 = J_2 = 3 + t^2G^2$

and $\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o}$ is the value of $\frac{\partial\Omega}{\partial J_1}$ when $J_1 = J_2 = 3 + (t-t'^2)G^2$

and $\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'<o}$, $\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o}$ have similar meanings.

We recognise the last pair of integrals as the stress that is obtained when a simple shear flow has been maintained for an infinite time. The other integrals therefore represent the transient stress, due to starting the flow at t=o, which decays to zero as t tends to infinity.

This transient stress $(P_{ij})_T$ cannot be evaluated until the form of Ω is known. Using the form (2.20) (Part II) we find,

$$(p_{12})_T = -G\left\{\frac{2C_1}{K_1^2}e^{-K_1t} + \frac{2C_2}{K_2^2}e^{-K_2t}\right\}$$

$$(p_{11}-p)_T = -4C_1\left\{\frac{e^{-K_1t}}{K_1^3} + \frac{t}{K_1^2}e^{-K_1t}\right\}G^2 \qquad (3.52)$$

$$(p_{22}-p)_T = 4C_2\left\{\frac{e^{-K_2t}}{K_2^3} + \frac{t}{K_2^2}e^{-K_2t}\right\}G^2$$

$$(p_{33}-p)_T = 0$$

Once again, the most convenient way to examine these simple shear transients is to carry out experiments in a cone and plate or parallel plate viscometer. It can be shown that the transient force on the plate of a cone and plate viscometer is given by,

$$(Z^*)_T = 4C_2\frac{\omega^2}{\beta^2}e^{-K_2t}\left\{\frac{1}{K_2^3} + \frac{t}{K_2^2}\right\}$$
$$+ \frac{\omega^2}{\beta^2}\left\{\log\frac{a}{r}\right\}\left\{4C_2\,e^{-K_2t}\left(\frac{1}{K_2^3}+\frac{t}{K_2^2}\right) - 4C_1\,e^{-K_1t}\left(\frac{1}{K_1^3}+\frac{t}{K_1^2}\right)\right\}$$
$$(3.53)$$

where ω is the angular velocity of the cone. Now the sign of $(Z^*)_T$ is determined, for sufficiently small r, by

$$e^{-K_2 t} C_2 \left\{ \frac{1}{K_2^3} + \frac{t}{K_2^2} \right\} - e^{-K_1 t} C_1 \left\{ \frac{1}{K_1^3} + \frac{t}{K_1^2} \right\} \qquad (3.54)$$

It can be shown that this function of t can change sign as t goes from 0 to ∞. We observe that $(Z^*)_T$ becomes zero as t tends to infinity; we would expect this, since the steady state force distribution is produced at large times. The fact that $(Z^*)_T$ may change sign as t increases means that the force on the plate may go through a maximum, which is higher than the steady state value of the force when the transient has died away. This effect has been observed by Lodge and Adams during experiments on polymethylmethacrylate dissolved in dimethyl phthalate.

Considering now the shear stress in the case of simple shear, using the form of Ω given by (2.20) (Part II), the shear stress is given by,

$$p_{12} = \frac{2C_1}{K_1} G \left\{ 1 - e^{-K_1 t} \right\} + \frac{2C_2}{K_2} G \left\{ 1 - e^{-K_2 t} \right\} \qquad (3.55)$$

This shows that the shear stress grows monotonically from 0 at t=o to the steady state value of

$$\left(\frac{2C_1}{K_1} + \frac{2C_2}{K_2} \right) G \qquad (3.56)$$

at large times.

If we define the viscosity $\eta(t) = \frac{p_{12}}{G}$, we see that the viscosity increases monotonically with time, becoming constant after a very long time. The variation of viscosity with time is usually called thixotropy; an increase of viscosity with time we call negative thixotropy, and a fall of viscosity with time we call positive thixotropy. It is more usual to observe positive thixotropy. We can express the time behaviour of p_{12} in equation (3.54) by saying that if Ω takes the form given by (2.20) (Part II), then the fluid shows negative thixotropy. Of course, whether the variation of p_{12} with time could be observed experimentally would depend on the relative values of C_1, C_2, K_1 and K_2.

It can be shown (see Appendix II) that if Ω takes the form given by (2.6) (Part II) then it is not possible for the liquid to show positive thixotropy if S'_{10} and S'_{01} are non-negative for all τ.

However, this is not true for all forms of Ω, as we can see by an example.

Let

$$\Omega = M\, e^{-m(t-t')}\{J_1 - 3\} - \frac{N}{2}\, e^{-n(t-t')}\{J_1 - 3\}^2 \qquad (3.57)$$

$$M, N, m, n > o$$

Evaluating the shear stress, using equation (3.51), we find

$$p_{12} = \frac{MG}{m^2}\{1 - e^{-mt}\} - \frac{6NG^3}{n^4}\{1 - e^{-nt}\} + \frac{3NG^3}{n^4}\{2tn\, e^{-nt} + t^2n^2e^{-nt}\} \qquad (3.58)$$

The steady state viscosity is given by,

$$\underset{t\to\infty}{\mathrm{Lt}} \left\{ \frac{p_{12}}{G} \right\} = \frac{M}{m^2} - \frac{6NG^2}{n^4} \qquad (3.59)$$

We note that the steady state viscosity falls with G, as is usually found in practice. Obviously we must have

$$\frac{M}{m^2} - \frac{6NG^2}{n^4} > o \qquad (3.60)$$

or the form (3.57) can only be valid for sufficiently small G. Now it can be shown that, if $m > n$ and condition (3.60) is obeyed, then p_{12}, given by (3.57), does not tend monotonically to the steady state value (3.59) but first passes it and then slowly falls to the value given by (3.59). Moreover, if $m \gg n$ the initial rise may only take a very short time and experimentally we would only observe the positive thixotropy. Figs. 1 and 2 demonstrate this effect.

ii) Instantaneous stopping of simple shear flow

In this case, $\underline{\underline{A}}$ is defined by,

$$\left.\begin{array}{ll} \underline{\underline{A}} = \begin{pmatrix} 1 & -tG & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & -\infty < t < o \\ \underline{\underline{A}} = \underline{\underline{I}} & t > o \end{array}\right\} \qquad (3.61)$$

Obviously for $t < o$ we get the stress for steady flow. For $t > o$ we get,

$$\underline{\underline{P}} - p'\underline{\underline{I}} = \int_{-\infty}^{o} 2\frac{\partial\Omega}{\partial J_1}\begin{pmatrix} 1+t'^2G^2 & -t'G & 0 \\ -t'G & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}dt' - \int_{-\infty}^{o} 2\frac{\partial\Omega}{\partial J_2}\begin{pmatrix} 1 & t'G & 0 \\ t'G & 1+G^2t'^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}dt' \qquad (3.62)$$

where $\frac{\partial\Omega}{\partial J_1}$ and $\frac{\partial\Omega}{\partial J_2}$ are evaluated with

$$J_1 = J_2 = 3 + G^2t'^2 \qquad (3.63)$$

This is obviously a transient which starts at t=o as the steady state stress, and decays to an isotropic stress as t tends to infinity. Evaluating this for the simple form of Ω in equation (2.20) (Part II) we find,

$$\begin{aligned}
p_{11}-p' &= 2C_1\left\{\frac{1}{K_1}+\frac{2G^2}{K_1^3}\right\}e^{-K_1t} - 2C_2\left\{\frac{1}{K_2}\right\}e^{-K_2t}\\
p_{22}-p' &= 2C_1\left\{\frac{1}{K_1}\right\}e^{-K_1t} - 2C_2\left\{\frac{1}{K_2}+\frac{2G^2}{K_2^3}\right\}e^{-K_2t}\\
p_{33}-p' &= 2C_1\left\{\frac{1}{K_1}\right\}e^{-K_1t} - 2C_2\left\{\frac{1}{K_2}\right\}e^{-K_2t}\\
p_{21} &= G\left\{\frac{2C_1}{K_1^2}e^{-K_1t} + \frac{2C_2}{K_2^2}e^{-K_2t}\right\}\\
p_{31} &= p_{32} = 0
\end{aligned} \qquad (3.64)$$

We first note that the transient obtained when the simple shear is removed is different from that obtained when it is applied. Lodge (1956) has shown that in the case of the removal of simple shear flow, the stress decays in such a manner that the normal stress, $p_{11}-p_{22}$, falls to zero less rapidly than does the shear stress, p_{12}, when $\Omega = S_{1o}'(t-t')$.

This result is not true for all forms of Ω in the general equation of state.

e) Elongational flow

In Part II we have examined elongational flow (Trouton flow) in the steady state and we now consider the transients associated with starting and stopping this type of flow.

i) Instantaneous application of elongational flow

In this case we have

$$\left.\begin{aligned}
\underline{\underline{A}} &= \underline{\underline{I}} \quad t < o\\
\underline{\underline{A}} &= \mathrm{diag}\,\{e^{-at}, e^{\frac{a}{2}t}, e^{\frac{at}{2}}\} \quad t > o
\end{aligned}\right\} \qquad (3.65)$$

For $t > o$ we have

$$t' < o \quad J_1 = e^{2at} + 2e^{-at} \quad J_2 = e^{-2at} + 2e^{at} \qquad (3.66)$$

$$t' > o \quad J_1 = e^{2a(t-t')} + 2e^{-a(t-t')} \quad J_2 = e^{-2a(t-t')} + 2e^{a(t-t')}$$

$$(3.67)$$

Inserting this value of $\underline{\underline{A}}$ into (3.15) we find,

$$\underline{\underline{P}} - p\underline{\underline{I}} = \mathrm{diag}\{e^{2at}, e^{-at}, e^{-at}\}\Big\{\int_{-\infty}^{0} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'<o} dt'$$

$$- \int_{-\infty}^{0} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o} \mathrm{diag}(e^{-2at'}, e^{at'}, e^{at'})dt'\Big\}$$

$$- \mathrm{diag}\{e^{-2at}, e^{at}, e^{at}\}\Big\{\int_{-\infty}^{0} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'<o} dt'$$

$$- \int_{-\infty}^{0} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o} \mathrm{diag}(e^{2at'}, e^{-at'}, e^{-at'})dt'\Big\}$$

$$+ \Big\{\mathrm{diag}\{e^{2at}, e^{-at}, e^{-at}\}\int_{-\infty}^{t} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o} \mathrm{diag}(e^{-2at'}, e^{at'}, e^{at'})dt'$$

$$- \mathrm{diag}\{e^{-2at}, e^{at}, e^{at}\}\int_{-\infty}^{t} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o} \mathrm{diag}(e^{2at'}, e^{-at'}, e^{-at'})dt'\Big\} \tag{3.68}$$

where $\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'<o}$ is the value of $\frac{\partial\Omega}{\partial J_1}$ when J_1 and J_2 are given by (3.66)

$\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o}$ is the value of $\frac{\partial\Omega}{\partial J_1}$ when J_1 and J_2 are given by (3.67)

and $\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'<o}$ and $\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o}$ are similarly defined.

The last two integrals in (3.68) give the stress due to the steady state flow already obtained in equation (2.19) (Part II). For the transient flow, assuming the form of Ω in equation (2.20) (Part II), we obtain $p_{22} = p_{33}$ $p_{12} = p_{23} = p_{31} = 0$

$$(p_{11} - p_{22})_T = 2C_1\, e^{-K_1 t}\left\{e^{2at}\left(\frac{1}{K_1} - \frac{1}{K_1 - 2a}\right) - e^{-at}\left(\frac{1}{K_1} - \frac{1}{K_1+a}\right)\right\}$$

$$- 2C_2\, e^{-K_2 t}\left\{\underline{e}^{-2at}\left(\frac{1}{K_2} - \frac{1}{K_2+2a}\right) - e^{at}\left(\frac{1}{K_2} - \frac{1}{K_2 - a}\right)\right\} \tag{3.69}$$

and we note that at $t = o$, this reduces to minus the stress for steady Trouton flow, as it should.

ii) Instantaneous stopping of elongational flow

We now consider the situation when a steady elongational flow is suddenly stopped. In this case we have

$$\left.\begin{array}{ll} -\infty < t < o & \underline{\underline{A}} = \mathrm{diag}(e^{-at}, e^{a/2\,t}, e^{a/2\,t}) \\ t > o & \underline{\underline{A}} = \underline{\underline{I}} \end{array}\right\} \qquad (3.70)$$

Obviously for $t < o$ we have the steady state stress; and for $t > o$ we have

$$t' < o \quad J_1 = e^{-2at'} + 2e^{at'} \quad J_2 = e^{2at'} + 2e^{-at'} \qquad (3.71)$$

$$t' > o \quad J_1 = J_2 = 3 \qquad (3.72)$$

By inserting the value of $\underline{\underline{A}}$ in equation (3.15), we find, for $t > o$,

$$\underline{\underline{P}} - p\underline{\underline{I}} = \int_{-\infty}^{o} 2\frac{\partial\Omega}{\partial J_1}\,\mathrm{diag}\,(e^{-2at'}, e^{at'}, e^{at'})dt'$$

$$- \int_{-\infty}^{o} 2\frac{\partial\Omega}{\partial J_2}\,\mathrm{diag}(e^{2at'}, e^{-at'}, e^{-at'})dt' \qquad (3.73)$$

This gives, in the simple case when Ω is of the form (2.20) (Part II)

$$p_{11} - p_{22} = 2C_1\, e^{-K_1 t}\left\{\frac{1}{K_1-2a} - \frac{1}{K_1+a}\right\} - 2C_2\, e^{-K_2 t}\left\{\frac{1}{K_2+2a} - \frac{1}{K_2-a}\right\}$$

$$p_{22} - p_{33} = p_{23} = p_{31} = p_{12} = 0 \qquad (3.74)$$

Again we note the difference between the transients in the 'switch on' and 'switch off' cases.

(f) Shear stress

We have so far considered the application of transient deformations. We now consider the application of impulsive stresses and investigate the deformations that arise from them.

i) Instantaneous application of a shear stress

We have seen that the stress in the case of uniform steady simple shear is given by equation (2.3) (Part II). We investigate the deformation when the stress $\underline{\underline{P}}$ is isotropic for all $t < o$, and equal to the simple steady state shear stress for all $t > o$. That is,

$$\underline{\underline{P}} = p\underline{\underline{I}} \text{ when } t < o \qquad (3.75)$$

and $\underline{\underline{P}}$ is given by equation (2.3) (Part II) when $t > o$. Since for an isotropic stress there is no deformation, for $t < o$ we get

$$\underline{\underline{A}} = \underline{\underline{I}}$$

For $t > o$, $\underline{\underline{A}}(t)$ is to be determined, and it must satisfy the equation

$$\underline{\underline{P}} - p\underline{\underline{I}} = \underline{\underline{A}}^{-1} \left\{ \int_{-\infty}^{o} 2 \frac{\partial\Omega}{\partial J_1} \underline{\underline{I}} \, dt' + \int_{o}^{t} 2 \frac{\partial\Omega}{\partial J_1} \underline{\underline{A}}' \, \underline{\underline{\tilde{A}}}' dt' \right\} \underline{\underline{\tilde{A}}}^{-1}$$

$$- \underline{\underline{\tilde{A}}} \left\{ \int_{-\infty}^{o} 2 \frac{\partial\Omega}{\partial J_2} \underline{\underline{I}} \, dt' + \int_{o}^{t} 2 \frac{\partial\Omega}{\partial J_2} \underline{\underline{\tilde{A}}}'^{-1} \, \underline{\underline{A}}'^{-1} \, dt' \right\} \underline{\underline{A}} \qquad (3.76)$$

This equation for $\underline{\underline{A}}$ is subject to the condition

$$\det\underline{\underline{A}} = 1 \qquad (3.77)$$

$\underline{\underline{A}}$ need not change continuously with t. In fact, $\underset{t\to o-}{Lt} \underline{\underline{A}} = \underline{\underline{I}}$ need not be equal to $\underset{t\to o+}{Lt} \underline{\underline{A}}$. We investigate the instantaneous change in $\underline{\underline{A}}$ when the stress is applied. Mathematically, we look for a solution of (3.60) for $\underline{\underline{A}}$ (t) when $t \to o_+$

$$\text{Let } \underline{\underline{A}}_o = \underset{t\to o_+}{Lt} \underline{\underline{A}}(t) \qquad (3.78)$$

and therefore

$$\underline{\underline{P}} - p\underline{\underline{I}} = \underline{\underline{A}}_o^{-1} \, \underline{\underline{\tilde{A}}}_o^{-1} \int_{-\infty}^{o} 2 \frac{\partial\Omega}{\partial J_1} dt' - \underline{\underline{\tilde{A}}}_o \, \underline{\underline{A}}_o \int_{-\infty}^{o} 2 \frac{\partial\Omega}{\partial J_2} dt' \qquad (3.79)$$

subject to $\det\underline{\underline{A}}_o = 1$

$$\text{and } \underline{\underline{P}} = \begin{pmatrix} G^2N_2+N_o-M_o & G(N_1+M_1) & 0 \\ G(N_1+M_1) & N_o-G^2M_2-M_o & 0 \\ 0 & 0 & N_o-M_o \end{pmatrix} \qquad (3.80)$$

We now consider the special case when Ω is given by (2.6), in this case

$$\left. \begin{aligned} \underset{t\to o_+}{Lt} \int_{-\infty}^{o} 2 \frac{\partial\Omega}{\partial J_1} dt' &= N_o' \\ \underset{t\to o_+}{Lt} \int_{-\infty}^{o} 2 \frac{\partial\Omega}{\partial J_2} dt' &= M_o' \end{aligned} \right\} \qquad (3.81)$$

(see equations (2.4) and (2.5)).

Hence we required to find a solution of

$$\underline{\underline{P}}' - p\underline{\underline{I}} = \underline{\underline{A}}_o^{-1}\,\tilde{\underline{\underline{A}}}_o^{-1}\,N_o' - \tilde{\underline{\underline{A}}}_o\,\underline{\underline{A}}_o\,M_o' \qquad (3.82)$$

subject to condition (3.77)

$$\text{where } \underline{\underline{P}}' = \begin{pmatrix} G^2N_2'+N_0'-M_0' & G(N_1'+M_1') & 0 \\ G(N_1'+M_1') & N_0-G^2M_2'-M_0' & 0 \\ 0 & 0 & N_0'-M_0' \end{pmatrix} \qquad (3.83)$$

We consider two special cases; when $\Omega = S_{10}'(J_1-3)$(Case I), and when $\Omega = S_{01}'(J_2-3)$(Case II). The more general case is discussed in Appendix III.

Case I

$\underline{\underline{A}}_o$ is not uniquely determined by equation (3.82). It is instructive to find a solution in the form

$$\underline{\underline{A}}_o^{-1} = \begin{pmatrix} p & q & 0 \\ 0 & r & 0 \\ 0 & 0 & s \end{pmatrix} \qquad (3.84)$$

It will be found that it is possible to satisfy (3.82) when $\Omega = S_{10}'(J_1-3)$ with this form of $\underline{\underline{A}}_o$. This solution can be interpreted physically by examining the meaning of $\underline{\underline{A}}_o^{-1}$. A particle which was at a position $\underline{a}'$ just before time zero moves to $\underline{a}$ just after time zero where

$$\underline{\underline{A}}_o\,\underline{a} = \underline{a}' \qquad (3.85)$$

or

$$\left.\begin{aligned} a_1 &= pa_1' + qa_2' \\ a_2 &= ra_2' \\ a_3 &= sa_3' \end{aligned}\right\} \qquad (3.86)$$

or

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} 1 & {}^q/r & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} p & 0 & 0 \\ 0 & r & 0 \\ 0 & 0 & s \end{pmatrix}\begin{pmatrix} a_1' \\ a_2' \\ a_3' \end{pmatrix} \qquad (3.87)$$

This deformation has the physical meaning that a unit cube of material, whose edges are parallel to the axes, is given two successive deformations at t=o; firstly, an instantaneous deformation so that it becomes a rectangular parallelopiped with edges of length p, r, s, parallel to the co-ordinate axes, and secondly, a simple shear whose angle is

$\tan^{-1}\frac{q}{r}$ (See Fig. III).

We find, using (3.84), (3.83) and (3.82) with $\Omega = S'_{1o}(J_1-3)$ and condition (3.77) that

$$s = r \tag{3.89}$$
$$p = {}^1/r^2 \tag{3.90}$$
$$q = \frac{N'_1 G r}{N'_o} \tag{3.91}$$

where r is a root of

$$r^6 + r^4\left\{\frac{N'_2 G^2}{N'_o}\right\} - r^2\left\{\frac{N'^2_1 G^2}{N'^2_o}\right\} - 1 = 0 \tag{3.92}$$

It is shown in Appendix IV that this cubic in r^2 has only one positive root and that this positive root is greater or less than one according to whether $N'_2N'_o - N'^2_1$ is negative or positive. Lodge (1958) has shown that when Ω takes the form

$$\Omega = S'_{1o}(J_1-3) \quad S'_{1o}(t-t') > o \text{ all } t-t' > o \tag{3.93}$$

then

$$N'_2N'_o - N'^2_1 > o \tag{3.94}$$

In this case, $r < 1$ and therefore $p > 1$; thus the instant the stress is applied there is an elongation in the x_1 direction with equal instantaneous contractions in the x_2 and x_3 directions, followed by an instantaneous simple shear.

Case 2

When Ω takes the form $S'_{o1}(J_2-3)$, let us suppose

$$\underline{\underline{A}}_o = \begin{pmatrix} a & d & o \\ o & b & o \\ o & o & c \end{pmatrix} \tag{3.95}$$

where a, b, c, and d are to be determined. We find from (3.82) and (3.77) that

$$a = c \quad b = 1/a^2 \quad ad = -\frac{M'_1 G}{M'_o} \tag{3.96}$$

where a is a root of

$$a^6 + \frac{M'_2 G^2}{M'_o}a^4 - \frac{M'^2_1 G^2}{M'^2_o}a^2 - 1 = 0 \tag{3.97}$$

Again we see that this has only one positive root. Whether this root is greater or less than one is determined by the sign of $M_2' M_0' - M_1'^2$. If we suppose this is positive, then $a < 1$. It may be shown, in the same manner as Lodge (1958), that $M_2' M_0' - M_1'^2 > 0$ when Ω takes the form,

$$\Omega = S_{01}'(J_2 - 3) \qquad S_{01}'(t-t') > 0 \quad \text{all } (t-t') > 0 \tag{3.98}$$

In this particular case we have,

$$0 < a < 1 \qquad 0 < c < 1 \qquad b > 1 \tag{3.99}$$

By considering the meaning of $\underline{\underline{A}}_0$, we see that the instant stress is applied there is an elongation in the x_1 direction, an elongation in the x_3 direction, a contraction in the x_2 direction, and an instantaneous simple shear.

It seems plausible, therefore, that when Ω is given by (2.6), in addition to the simple shear there will be an elongation in the x_1 direction and a contraction in the x_2 direction, with the behaviour in the x_3 direction being dependent on the relative magnitudes of the M_i' and N_i'.

ii) Instantaneous removal of shear stress

Let us suppose that the stress (2.3) needed to maintain a simple shear flow has been applied for all time in the past and is suddenly removed at time zero.

In this case,

$$\underline{\underline{A}} = \begin{pmatrix} 1 & -Gt & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \; t < o \tag{3.100}$$

since the shear stress has been applied for an infinite time and therefore the steady state deformation must have been established.

On removal of the steady state shear stress we must be left with an isotropic pressure.

$$\underline{\underline{p}} = p' \, \underline{\underline{I}} \qquad t > o \tag{3.101}$$

$\underline{\underline{A}}(t)$ for $t > o$ is unknown and to be determined. For $t > o$, $\underline{\underline{A}}$ is determined by,

$$\underline{\underline{I}}(p'-p) = \underline{\underline{A}}^{-1}\left\{\int_{-\infty}^{t} 2\frac{\partial\Omega}{\partial J_1}\underline{\underline{A}}'\,\underline{\underline{\tilde{A}}}'\,dt'\right\}\underline{\underline{\tilde{A}}}^{-1} - \underline{\underline{\tilde{A}}}\left\{\int_{-\infty}^{t} 2\frac{\partial\Omega}{\partial J_2}\underline{\underline{\tilde{A}}}'^{-1}\,\underline{\underline{A}}'^{-1}\,dt'\right\}\underline{\underline{A}} \tag{3.102}$$

and

$$\det \underline{\underline{A}} = 1 \tag{3.103}$$

Again we only consider the behaviour at the instant the stress is removed for the special case when $\Omega = S'_{10}(J_1-3) + S'_{01}(J_2-3)$

Let, $\underline{\underline{A}}_o = \underset{t\to o_+}{Lt} \underline{\underline{A}}$

If $t\to o_+$ in equation (3.102) we get,

$$(p'_o - p_o)\underline{\underline{I}} = \underline{\underline{A}}_o^{-1} \begin{pmatrix} N'_o+N'_2G^2 & N'_1G & 0 \\ N'_1G & N'_o & 0 \\ 0 & 0 & N'_o \end{pmatrix} \underline{\underline{\tilde{A}}}_o^{-1}$$

$$- \underline{\underline{\tilde{A}}}_o \begin{pmatrix} M'_o & -M'_1G & 0 \\ -M'_1G & M'_o+M'_2G^2 & 0 \\ 0 & 0 & M'_o \end{pmatrix} \underline{\underline{A}}_o \tag{3.104}$$

with $\det \underline{\underline{A}}_o = 1$.

Let us consider the special cases when $\Omega = S'_{10}(J_1-3)$ (case 1) and $\Omega = S'_{01}(J_2-3)$ (case 2).

Case 1

Lodge (1958) has investigated the particular case when,

$$\Omega = S'_{10}(J_1 - 3)$$

Let us suppose that,

$$\underline{\underline{A}}_o = \begin{pmatrix} a & d & o \\ o & b & o \\ o & o & c \end{pmatrix} \tag{3.105}$$

where a, b, c and d are to be determined. We find from equations (3.104) and (3.105) that

$$a = \left\{1 + (N'_2N'_o - N'^2_1)\frac{G^2}{N'^2_o}\right\}^{1/3}$$

$$b = c = \left\{1 + (N'_2N'_o - N'^2_1)\frac{G^2}{N'^2_o}\right\}^{-1/6} \tag{3.106}$$

$$d = \frac{GN'_1}{N'_o}\left\{1 + (N'_2N'_o - N'^2_1)\frac{G^2}{N'^2_o}\right\}^{-1/6}$$

If we examine the meaning of $\underline{\underline{A}}_o$, we find that when the shearing forces are removed, the liquid suffers an instantaneous deformation which may be considered to be composed of two successive deformations such that a unit cube of material whose edges are parallel to the co-ordinate axes first changes to a rectangular parallelopiped whose edges are parallel to the co-ordinate axes and whose lengths are $\frac{1}{a}, \frac{1}{b}, \frac{1}{c}$, this parallelopiped being then sheared by an angle $-\tan^{-1}\frac{d}{a}$. Since $N_2'N_0' - N_1'^2 > o$, we have

$$a > 1 \quad b = c < 1 \tag{3.107}$$

and we find that there is an instantaneous contraction in the direction of flow and instantaneous expansions in the two perpendicular directions followed by an instantaneous simple shear recovery of angle $\tan^{-1}\frac{d}{a}$.

Case 2

When Ω is of the form $S\delta_1(J_2 - 3)$, let,

$$\underline{\underline{A}}_o^{-1} = \begin{pmatrix} p & q & o \\ o & r & o \\ o & o & s \end{pmatrix} \tag{3.108}$$

We then find,

$$r = \left\{1 + \frac{G^2}{M_o'^2}\left(M_2'M_o' - M_1'^2\right)\right\}^{1/3}$$

$$p = s = \left\{1 + \frac{G^2}{M_o'^2}\left(M_2'M_o' - M_1'^2\right)\right\}^{-1/6} \tag{3.109}$$

$$q = -\frac{M_1'G}{M_o'}\left\{1 + \frac{G^2}{M_o'^2}\left(M_2'M_o' - M_1'^2\right)\right\}^{-1/6}$$

when,

$$M_2'M_o' - M_1'^2 > o$$

$$r > 1 \quad o < p = s < 1 \tag{3.110}$$

The meaning of $\underline{\underline{A}}_o$ shows that, as well as an instantaneous simple shear, there are equal contractions in the x_1 and x_3 directions, and an expansion in the x_2 direction immediately the stress is removed.

It has been pointed out by Lodge (1960) that when

$$\Omega = C_1 e^{-K_1 t}(J_1 - 3) \tag{3.111}$$

the instantaneous solution is true for all time. That is, when the stress is removed, there is an instantaneous deformation, after which the fluid does not move. It can be shown that a similar state of affairs exists for a more general equation of state defined by

$$\Omega = C_1 e^{-K_1 t}(J_1 - 3) + C_2 e^{-K_2 t}(J_2 - 3) \tag{3.112}$$

if $K_1 = K_2$.

The above analysis has a certain practical significance. Consider a liquid which has been pumped through a long pipe and which suddenly emerges from the end of the pipe. While it was in the pipe it was being sheared, the walls exerting shearing force on the liquid. When the liquid emerges from the end of the pipe the shearing force is suddenly removed, and the situation considered by the above analysis is realized. Of course the comparison is only descriptive, since the geometries are different and the deformation of the liquid flowing through the tube is certainly inhomogeneous. However, it is found in practice that an expansion usually takes place as the liquid emerges from the pipe. This expansion is to be expected, in a qualitative manner, if the liquid was governed by an equation of state for which $\Omega = S_{10}(J_1 - 3)$.

g) Stress whose principal directions remain constant in time

We choose the co-ordinate axes to be along the principal directions; the stress $\underline{\underline{P}}$ is given by diag. $(P_1(t), P_2(t), P_3(t))$.

i) Suddenly applied stress

We consider what happens when such a stress is suddenly applied to the fluid; that is, we have,

$$\begin{aligned} \underline{\underline{P}} &= p\underline{\underline{I}} \quad t < o \quad \text{and hence } \underline{\underline{A}} = \underline{\underline{I}} \text{ all } t < o \\ \underline{\underline{P}} &= \text{diag}\,(P_1, P_2, P_3) \quad t > o \end{aligned} \tag{3.113}$$

and $\underline{\underline{A}}(t)$ is to be determined for $t > o$. For $t > o$, the equation which determined $\underline{\underline{A}}$ is

$$\begin{aligned} \text{diag}\Big(P_1(t), P_2(t), P_3(t)\Big) - p\underline{\underline{I}} &= \underline{\underline{A}}^{-1}\Big\{\int_{-\infty}^{o} 2\,\frac{\partial\Omega}{\partial J_1}\,\underline{\underline{I}}\;dt' \\ &+ \int_{o}^{t} 2\,\frac{\partial\Omega}{\partial J_1}\,\underline{\underline{A}}'\,\underline{\underline{\tilde{A}}}'\;dt'\Big\}\,\underline{\underline{\tilde{A}}}^{-1} - \underline{\underline{\tilde{A}}}\Big\{\int_{-\infty}^{o} 2\,\frac{\partial\Omega}{\partial J_2}\,\underline{\underline{I}}\;dt' + \int_{o}^{t} 2\,\frac{\partial\Omega}{\partial J_2}\,\underline{\underline{\tilde{A}}}'^{-1}\,\underline{\underline{A}}'^{-1}\;dt'\Big\}\,\underline{\underline{A}} \end{aligned} \tag{3.114}$$

Consider first the instantaneous deformation. If $t \to o_+$, $\underline{\underline{A}} \to \underline{\underline{A}}_o$, $P_i(t) \to P_i(0)$ and Ω is of the form (2.6), we obtain

$$\text{diag}\left\{P_1(0),\ P_2(0),\ P_3(0)\right\} - p\underline{\underline{I}} = \underline{\underline{A}}_o^{-1}\ \tilde{\underline{\underline{A}}}_o^{-1}\ N'_o - \tilde{\underline{\underline{A}}}_o\ \underline{\underline{A}}_o\ M'_o \qquad (3.115)$$

where $\det \underline{\underline{A}}_o = 1$ (3.116)

and N'_o, M'_o are given by equations (2.7) and (2.8). Obviously $\underline{\underline{A}}_o$ is diagonal, say

$$A_o \quad = \quad \text{diag.}\left(\frac{1}{\lambda_1^o}, \frac{1}{\lambda_2^o}, \frac{1}{\lambda_3^o}\right) \qquad (3.117)$$

and we obtain

$$P_i(o) \quad = \quad \lambda_i^{o2}\ N'_o - M'_o\ \lambda_i^{o-2} \qquad i = 1, 2, 3 \qquad (3.118)$$

with $\quad \overset{o}{\lambda_1}\ \overset{o}{\lambda_2}\ \overset{o}{\lambda_3} \quad = \quad 1$ (3.119)

λ_i^o is the instantaneous extension on applying the stress; if we consider the particular case of simple elongation, that is, $\underline{\underline{P}}(0) =$ diag(P, 0, 0), we find that

$$\lambda_1^o = \lambda_o \qquad \lambda_2^o = \frac{1}{\sqrt{\lambda_o}} \qquad \lambda_3^o = \frac{1}{\sqrt{\lambda_o}} \qquad (3.120)$$

where λ_o is the positive root of

$$P \quad = \quad \left(\lambda_o^2 - \frac{1}{\lambda_o}\right)\left(N'_o + \frac{1}{\lambda_o} M'_o\right) \qquad (3.121)$$

For $t > o$ we consider a special case.

$$\left.\begin{aligned} P \quad &= \quad \text{diag }(P,\ 0,\ 0)\ P \text{ is constant for all } t \\ P \quad &= \quad p'\underline{\underline{I}} \qquad t < o \end{aligned}\right\} \qquad (3.122)$$

and Ω is given by the special form (2.20).

Inserting these values in equation (3.114) and noting that

$$\underline{\underline{A}} = \text{diag}\left(\lambda^{-1}(t),\ \lambda^{\frac{1}{2}}(t),\ \lambda^{\frac{1}{2}}(t)\right) \qquad (3.123)$$

we find, with some manipulation,

$$P = (\lambda^2 - \frac{1}{\lambda}) \frac{2C_1}{K_1} e^{-K_1 t} - (\frac{1}{\lambda^2} - \lambda) \frac{2C_2}{K_2} e^{-K_2 t}$$

$$+ \int_0^t 2C_1 \, e^{-K_1(t-t')} \left(\frac{\lambda^2}{\lambda'^2} - \frac{\lambda'}{\lambda}\right) dt' - \int_0^t 2C_2 \, e^{-K_2(t-t')} \left(\frac{\lambda'^2}{\lambda^2} - \frac{\lambda}{\lambda'}\right) dt' \quad (3.124)$$

where

$$\lambda = \lambda(t) \quad \lambda' = \lambda(t') \quad (3.125)$$

This equation is to be solved for $\lambda(t)$. We note that as $t \to o_+$, (3.124) tends to the equation (3.121) where N'_o and M'_o are evaluated using (2.20) and $\lambda \to \lambda_o$. Now equation (3.124) has an approximate solution for large values of t. We have already solved the problem of steady state elongation flow, Part II, and obviously the solution of (3.124) must tend to this solution, for after a long time, the fluid will have 'forgotten' the effect of starting the flow at time zero. Mathematically we expect that there will be an asymptotic solution to equation (3.124) of the form,

$$\lambda = Be^{at} \quad (3.126)$$

where a is given by

$$P = \frac{6aC_1}{(K_1+a)(K_2-2a)} + \frac{6aC_2}{(K_2+2a)(K_2-a)} \quad (3.127)$$

and B is a constant.

That this is an asymptotic solution can be verified analytically. Inserting (3.126) in equation (3.124) we find,

$$2C_1 \left(\frac{e^{-(K_1-2a)t}}{K_1-2a} - \frac{e^{-(K_1+a)t}}{K_1+a}\right) - 2C_2 \left(\frac{e^{-(K_2+2a)t}}{K_2+2a} - \frac{e^{-(K_2-a)t}}{K_2-a}\right)$$

$$= \left(B^2 e^{2at} - \frac{1}{B} e^{-at}\right) \frac{2C_1}{K_1} e^{-K_1 t} - \left(\frac{1}{B^2} e^{-2at} - B e^{at}\right) \frac{2C_2}{K_2} e^{-K_2 t} \quad (3.128)$$

This cannot be satisfied by any constant value of B, so $\lambda = Be^{at}$ is not an exact solution. However, we can choose B so that (3.126) is a good fit for large values of t. For large values of t,

$$e^{-(K_2-a)t} > e^{-(2a+K_2)t} \text{ and } e^{-(K_1-2a)t} > e^{-(a+K_1)t} \quad (3.129)$$

and if (K_2-a) is greater than (K_1-2a) say,

$$e^{-(K_2-a)t} < e^{-(K_1-2a)t} \tag{3.130}$$

and hence we get the best fit for large t by taking,

$$B = \sqrt{\frac{K_1}{K_1-2a}} \tag{3.131}$$

i.e., equation (3.124) has an asymptotic solution of the form

$$\lambda(t) \sim \sqrt{\frac{K_1}{K_1-2a}}\, e^{at} \tag{3.132}$$

ii) Instantaneous removal of stress

We have considered the case of the sudden application of stress whose principal directions remain constant in time. We now consider what happens when such a stress is suddenly removed. We have

$$\left.\begin{array}{ll} \underline{\underline{P}} = \mathrm{diag}(P_1(t),\ P_2(t),\ P_3(t)) & t < o \\ \underline{\underline{P}} = p'\underline{\underline{I}} & t > o \end{array}\right\} \tag{3.133}$$

The value of $\underline{\underline{A}}$ for $t < o$ must be found by solving

$$\mathrm{diag}(P_1,\ P_2,\ P_3) - p\underline{\underline{I}} = \underline{\underline{A}}^{-1}\left(\int_{-\infty}^{t} 2\,\frac{\partial\Omega}{\partial J_1}\,\underline{\underline{A}}'\ \underline{\underline{\tilde{A}}}'\,dt'\right)\underline{\underline{\tilde{A}}}^{-1} - \underline{\underline{\tilde{A}}}\left(\int_{-\infty}^{t} 2\,\frac{\partial\Omega}{\partial J_2}\,\underline{\underline{\tilde{A}}}'^{-1}\ \underline{\underline{A}}'^{-1}dt'\right)\underline{\underline{A}} \tag{3.134}$$

For $t > o$, we have

$$(p-p')\underline{\underline{I}} = \underline{\underline{A}}^{-1}\left(\int_{-\infty}^{t} 2\,\frac{\partial\Omega}{\partial J_1}\,\underline{\underline{A}}'\ \underline{\underline{\tilde{A}}}'\ dt'\right)\underline{\underline{\tilde{A}}}^{-1} - \underline{\underline{\tilde{A}}}\left(\int_{-\infty}^{t} 2\,\frac{\partial\Omega}{\partial J_2}\,\underline{\underline{\tilde{A}}}'^{-1}\ \underline{\underline{A}}'^{-1}\ dt'\right)\underline{\underline{A}} \tag{3.135}$$

Now $\underline{\underline{A}}$ must be diagonal, say

$$\underline{\underline{A}} = \mathrm{diag}\ (A_1(t),\ A_2(t),\ A_3(t))$$

and for the instantaneous deformation we have, letting $t \to o_+$,

$$\underset{t\to o_+}{\mathrm{Lt}}\ \underline{\underline{A}} = \mathrm{diag}(A_1^o,\ A_2^o,\ A_3^o) \tag{3.136}$$

and

$$\underline{\underline{I}}(p-p') = \mathrm{diag}\left(\frac{1}{A_1^{o2}}, \frac{1}{A_2^{o2}}, \frac{1}{A_3^{o2}}\right)\mathrm{diag}(n_1, n_2, n_3) - \mathrm{diag}\left(A_1^{o2}, A_2^{o2}, A_3^{o2}\right)\mathrm{diag}(m_1, m_2, m_3) \tag{3.137}$$

subject to

$$\det \underline{\underline{A}} = 1$$

where

$$\mathrm{diag}(n_1, n_2, n_3) = \underset{t\to 0}{\mathrm{Lt}} \int_{-\infty}^{0} \mathrm{diag}(A_1'^2, A_2'^2, A_3'^2)\, 2\, \frac{\partial\Omega}{\partial J_1}\, dt' \tag{3.138}$$

and

$$\mathrm{diag}(m_1, m_2, m_3) = \underset{t\to 0}{\mathrm{Lt}} \int_{-\infty}^{0} \mathrm{diag}(A_1'^{-2}, A_2'^{-2}, A_3'^{-2})\, 2\, \frac{\partial\Omega}{\partial J_2}\, dt' \tag{3.139}$$

It must not be forgotten that n_i and m_i are not only functions of the flow history up to time zero, but also functions of A_1^o, A_2^o, A_3^o.

If the instantaneous change is elongation λ_i^o along the x_i axis, then

$$A_i^o = \frac{1}{\lambda_i^o} \tag{3.140}$$

To find λ_i^o we must solve

$$p-p' = \lambda_i^{o2}\, n_i - \lambda_i^{o-2}\, m_i \quad i = 1, 2, 3 \text{ (not summed)} \tag{3.141}$$

subject to

$$\lambda_1^o\, \lambda_2^o\, \lambda_3^o = 1 \tag{3.142}$$

If we consider the particular case when $\underline{\underline{P}} = \mathrm{diag}(P, 0, 0)$, where P is constant for all time, we have simple elongational flow with the stress suddenly removed. Using the form of Ω given by equation (2.20) we obtain

$$(p-p')\underline{\underline{I}} = \mathrm{diag}(\lambda_1^{o2}\, \lambda_2^{o2}\, \lambda_3^{o2})\, \mathrm{diag}\left(\frac{2C_1}{K_1-2a}, \frac{2C_1}{K_1+a}, \frac{2C_1}{K_1+a}\right)$$

$$- \mathrm{diag}(\lambda_1^{o-2}\, \lambda_2^{o-2}\, \lambda_3^{o-2})\mathrm{diag}\left(\frac{2C_2}{K_2+2a}, \frac{2C_2}{K_2-a}, \frac{2C_2}{K_2-a}\right) \tag{3.143}$$

Obviously, using $\det \underline{\underline{A}} = 1$, we may take

$$\mathrm{diag}(\lambda_1^o, \lambda_2^o, \lambda_3^o) = \mathrm{diag}\left(\lambda_o, \frac{1}{\sqrt{\lambda_o}} \frac{1}{\sqrt{\lambda_o}}\right) \quad (3.144)$$

and we find an equation for λ_o,

$$\lambda_o^2\left(\frac{C_1}{K_1-2a}\right) - \frac{1}{\lambda_o}\left(\frac{C_1}{K_1+a}\right) - \frac{1}{\lambda_o^2}\left(\frac{C_2}{K_2+2a}\right) + \lambda_o\left(\frac{C_2}{K_2-a}\right) = 0 \quad (3.145)$$

The solution of this quartic gives λ_o, the instantaneous extension along the axis x_1.

Again it can be shown that, if $K_1 = K_2$ in the particular form of Ω in equation (2.20), then $\underline{\underline{A}}$ is a solution for all time.

h) Constrained flow

We have considered so far those problems in which either the deformation is given for all time and the stress is to be determined, or those in which the stress is defined and the deformation is to be determined. However, it is possible that a situation might arise in which only some of the components of the stress tensor are defined, and the deformation is restricted by constraints. Such a situation is commonly investigated in some recovery experiments. For example, if a liquid is sheared in a concentric cylinder viscometer by rotating the inner cylinder, and the torque is suddenly removed from the inner cylinder, we are effectively defining the shear stress for all time. Since the distance between the cylinders is fixed, the liquid is constrained in such a manner that only a simple shear recovery is possible. Of course, the problem is not restricted to recovery; the transients associated with the sudden application of a constant shear stress can be similarly investigated.

We now investigate this situation mathematically.

1) Application of a shear stress to a constrained system

Let us suppose we apply a shear stress p_{12}, which is given by,

$$\begin{aligned} p_{12} &= 0 \quad t < o \\ p_{12} &= \sigma \quad t > o \end{aligned} \quad (3.146)$$

to a system which is constrained in such a manner that only a simple shear deformation is possible. Physically we may think of the liquid as being constrained between two infinite parallel plates whose distance apart is fixed. We must have

$$\underline{\underline{A}} = \underline{\underline{I}} \quad t < o \quad (3.147)$$

since there is no force on the liquid for all $t < o$.

and

$$\underline{\underline{A}} = \begin{pmatrix} 1 & -F(t) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad t > o \tag{3.148}$$

where F(t) is to be determined, since the only allowed deformation is a simple shear. Moreover, we wish to find p_{11}, p_{22}, p_{33} as functions of t. This problem has been considered by Lodge (1958 B) for the case where $\Omega = S_{10}'(J_1-3)$. We shall follow his method. Evaluating S_{ij} and S_{ij}^{-1} from (3.12) and (3.13) and using (3.14), we find for $t > o$.

$$\begin{aligned}\underline{\underline{P}}-p\underline{\underline{I}} = &\int_{-\infty}^{o} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'<o} \begin{pmatrix} 1+F^2 & F & 0 \\ F & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt' + \int_{o}^{t} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o} \begin{pmatrix} 1+(F-F')^2 & F-F' & 0 \\ F-F' & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt' \\ &- \int_{-\infty}^{o} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'<o} \begin{pmatrix} 1 & -F & 0 \\ -F & 1+F^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt' - \int_{o}^{t} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o} \begin{pmatrix} 1 & -(F-F') & 0 \\ -(F-F') & 1+(F-F')^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt'\end{aligned} \tag{3.149}$$

where

$$F = F(t), \quad F' = F(t') \tag{3.150}$$

$$t > o \quad t' < o \qquad J_1 = J_2 = 3 + F^2 \tag{3.151}$$

$$t > o \quad t' > o \qquad J_1 = J_2 = 3 + (F-F')^2 \tag{3.152}$$

$\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'<o}$ is evaluated using equation (3.151)

$\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o}$ is evaluated using equation (3.152)

$\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'<o}$ and $\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o}$ are evaluated in a similar manner.

$$\underline{\underline{P}} = \begin{pmatrix} p_{11} & p_{12} & 0 \\ p_{12} & p_{22} & 0 \\ 0 & 0 & p_{33} \end{pmatrix} \tag{3.153}$$

where p_{12} is known and equal to σ and $p_{11} - p_{33}$ and $p_{22} - p_{33}$ are to be determined. We consider the special case when Ω is given by (2.6), i.e.,

$$\Omega = S_{10}'(J_1-3) + S_{01}'(J_2-3) \tag{3.154}$$

From (3.149) we find

$$\sigma = \int_{-\infty}^{0} 2F(t)\left\{S'_{10}(t-t') + S'_{01}(t-t')\right\}dt' + \int_{0}^{t} 2\left\{F(t) - F(t')\right\}\left\{S'_{10}(t-t') + S'_{01}(t-t')\right\}dt' \tag{3.155}$$

This is an integral equation for F(t). We note that $t \to o_+$ $F(t) \to F(o)$, where

$$\sigma = F(o)\int_{-\infty}^{0} 2\{S'_{10}(o-t') + S'_{01}(o-t')\}dt' \tag{3.156}$$

or from (2.7) and (2.8),

$$\sigma = F(o)\{N'_0 + M'_0\} \tag{3.157}$$

$$F(o) = \frac{\sigma}{N'_0 + M'_0} \neq 0 \tag{3.158}$$

Physically there is an instantaneous shear of amount F(o) the instant the shear stress is applied. Following Lodge (1958 B) we find that (3.155) has an asymptotic solution for large t of the form

$$F(t) \sim F(o)\left\{\frac{N'_0 + M'_0}{N'_1 + M'_1} \cdot t + \frac{(N'_0 + M'_0)(N'_2 + M'_2)}{2(N'_1 + M'_1)^2}\right\} \tag{3.159}$$

and we note that the shear rate $\frac{dF(t)}{dt}$, for large t is given by

$$\frac{dF(t)}{dt} = F(o)\frac{(N'_0 + M'_0)}{(N'_1 + M'_1)} \tag{3.160}$$

or, using (3.158),

$$\frac{dF}{dt} = \frac{\sigma}{N'_1 + M'_1} = G \quad \text{say} \tag{3.161}$$

This of course is the steady value we would expect from (2.3). From (3.149) we find

$$p_{11}-p_{33} = \int_{-\infty}^{0} 2\, S'_{10}(t-t')\, F^2(t)dt' + \int_{0}^{t} 2\, S'_{10}(t-t')\{F(t) - F(t')\}^2 dt' \tag{3.162}$$

$$p_{33}-p_{22} = \int_{-\infty}^{0} 2\, S'_{10}(t-t')F^2(t)dt' + \int_{0}^{t} 2\, S'_{01}(t-t')\{F(t) - F(t')\}^2 dt' \tag{3.163}$$

and hence

$$p_{11}-p_{33} = \frac{G^2N_0'(N_1' + M_1')^2}{(N_0' + M_0')^2} \qquad \text{as } t \to o_+ \tag{3.164}$$

$$p_{11}-p_{33} = G^2N_2' \qquad \text{as } t \to \infty \tag{3.165}$$

$$p_{33}-p_{22} = \frac{G^2M_0'\{N_1' + M_1'\}^2}{\{N_0' + M_0'\}^2} \qquad \text{as } t \to o_+ \tag{3.166}$$

$$p_{33}-p_{22} = G^2M_2' \qquad \text{as } t \to \infty \tag{3.167}$$

These results are plotted in Fig. IV. It will be noted that γ_1, the extrapolated value of the asymptotic form of F(t) at t = o, i.e.

$$\gamma_1 = \frac{G(N_2' + M_2')}{2(N_1' + M_1')} \tag{3.168}$$

is probably more easily measured experimentally than F(o).

2) Removal of shear stress from a constrained system

Consider a system in which a constant shear stress σ has been applied for a very long time and is suddenly removed at time t = o. The system is constrained so that only a simple shear recovery is possible. That is, we must have

$$\begin{aligned} p_{12} &= \sigma \quad t < o \\ p_{12} &= o \quad t > o \end{aligned} \tag{3.169}$$

and therefore, since the constant stress has been maintained for a very long time, we have

$$\underline{\underline{A}} = \begin{pmatrix} 1 & -Gt & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad t < o \tag{3.170}$$

$$\underline{\underline{A}} = \begin{pmatrix} 1 & -F^*(t) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad t > o \tag{3.171}$$

where $F^*(t)$ is to be determined. We find, from (3.14), that for t > o,

$$\underline{\underline{P}} - p\underline{\underline{I}} = \int_{-\infty}^{0} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'<o} \begin{pmatrix} 1+(F^*-Gt')^2 & F^*-Gt' & 0 \\ F^*-Gt' & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt'$$

$$+ \int_{0}^{t} 2\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'>o} \begin{pmatrix} 1+(F^*-F^{*\prime})^2 & (F^*-F^{*\prime}) & 0 \\ (F^*-F^{*\prime}) & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt'$$

$$- \int_{-\infty}^{0} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'<o} \begin{pmatrix} 1 & -(F^*-Gt') & 0 \\ -(F^*-Gt') & 1+(F^*-Gt')^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt'$$

$$- \int_{0}^{t} 2\left(\frac{\partial\Omega}{\partial J_2}\right)_{t'>o} \begin{pmatrix} 1 & -(F^*-F^{*\prime}) & 0 \\ -(F^*-F^{*\prime}) & 1+(F^*-F^{*\prime})^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt' \qquad (3.172)$$

where $F^* = F^*(t)$ $\qquad F^{*\prime} = F^*(t')$

$$\begin{aligned} t > o \quad t' < o \quad J_1 = J_2 = \{F^* - Gt'\}^2 + 3 \\ t > o \quad t' > o \quad J_1 = J_2 = \{F^* - F^{*\prime}\}^2 + 3 \end{aligned} \qquad (3.173)$$

and $\left(\frac{\partial\Omega}{\partial J_1}\right)_{t'<o}$, etc., have their usual meanings.

For $t > o$ we have

$$\underline{\underline{P}} = \begin{pmatrix} p_{11} & 0 & 0 \\ 0 & p_{22} & 0 \\ 0 & 0 & p_{33} \end{pmatrix} \qquad (3.174)$$

where p_{11}, p_{22}, p_{33} are to be determined. Again, considering the special case when Ω takes the form (2.6), we find that $F^*(t)$ is determined by

$$0 = \int_{-\infty}^{0} 2(F^*-Gt')\left\{S_{10}'(t-t') + S_{01}'(t-t')\right\}dt' + \int_{0}^{t} 2(F^*-F^{*\prime})\left\{S_{10}'(t-t')+S_{01}'(t-t')\right\}dt' \qquad (3.175)$$

and it can be shown that

$$F^*(o) = \frac{-\sigma}{(N_0' + M_0')} = \frac{-G(N_1' + M_1')}{N_0' + M_0'} \qquad (3.176)$$

and, the total recovery, γ_1^*, is

$$F^{*}(\infty) = \gamma_1^{*} = -\frac{G(N_2' + M_2')}{2(N_1' + M_1')} \tag{3.177}$$

From (3.172) we see that $p_{11} - p_{33}$ and $p_{22} - p_{33}$ are determined by

$$p_{11} - p_{33} = \int_{-\infty}^{0} 2\, S_{10}'(t-t')\left\{F^{*}(t) - Gt'\right\}^2 dt' + \int_{0}^{t} 2\, S_{10}'(t-t')\left\{F^{*}(t) - F^{*}(t')\right\}^2 dt' \tag{3.178}$$

$$p_{33} - p_{22} = \int_{-\infty}^{0} 2\, S_{01}'(t-t')\left\{F^{*}(t) - Gt'\right\}^2 dt' + \int_{0}^{t} 2\, S_{01}'(t-t')\left\{F^{*}(t) - F^{*}(t')\right\}^2 dt' \tag{3.179}$$

The instantaneous change in $p_{11} - p_{33}$, when the stress is removed, is found by taking $\mathrm{Lt}\; t \to 0_+$

$$\underset{t \to 0_+}{\mathrm{Lt}} (p_{11} - p_{33}) = G^2 N_2' - \frac{G^2(M_1' + N_1')}{(N_0' + M_0')^2}\left\{N_0' N_1' + 2M_0' N_1' - M_1' N_0'\right\} \tag{3.180}$$

$$\underset{t \to 0_+}{\mathrm{Lt}} (p_{33} - p_{22}) = G^2 M_2' - \frac{G^2(M_1' + N_1')}{(N_0' + M_0')^2}\left\{M_1' M_0' + 2N_0' M_1' - M_0' N_1'\right\} \tag{3.181}$$

We note that the instantaneous change in the normal force is not necessarily the same for the sudden removal of shear stress as for the sudden application of shear stress. Lodge, using $\Omega = S_{10}'(t-t')\{J_1 - 3\}$, found these instantaneous changes to be the same.

i) Discussion

It was pointed out in CoA Note 134 that equations of state may be divided into two classes; those which have as their basis microrheology (that is a description of the macroscopic rheological properties of a material in terms of microscopic elements which may even be molecular) and those which are purely phenomenological. It is possible to subdivide both these types into two categories; the first we shall call the strain history type and the second the point derivative type. In the point derivative type of equation of state the stress at the current time t at a given particle is a polynomial function of the matrices representing the rate of strain tensor, 2nd rate of strain tensor, etc., where the rate of strain and its derivatives are evaluated at the current time and at the given particle. A typical example of this type of equation of state is the Stokesian fluid defined by

$$p_{ij} = p\delta_{ij} + \mu A_{ij}^{(1)} + \nu A_{ik}^{(1)} A_{kj}^{(1)} \tag{3.182}$$

where

$$A^{(1)}_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \tag{3.183}$$

and v_i is the velocity of the particle at x_i and time t.

The equations of state discussed in this paper and that of Lodge (1956) are of the strain history type. That is, the stress is a function of all the strains between any time t′ in the past and the current time t. It should be possible to relate these two types of equations of state.

This Note discusses transient behaviour in liquids whose flow properties are governed by an equation of state (3.3) which is of the strain history type. In order to simplify the mathematics we have considered only homogeneous deformations, and it has been necessary to assume that we may ignore inertial effects. The most useful deformation to study is, of course, shear flow, since in general this is the deformation most often found in practice.

Two major differences between Newtonian and non-Newtonian fluids are that, even in the absence of inertial forces, non-Newtonian fluids usually show elastic effects and stress relaxation effects. In this Note it has been shown that, by considering the variation of stress on changing the deformation, the equation of state (3.3) predicts stress relaxation effects and, by considering the change in deformation on rapidly altering the stress, the equation of state also predicts elastic effects.

Moreover, by considering special systems, it is shown that the elastic effect may be divided into two parts; an instantaneous deformation followed by a time-dependent deformation. These deformations may be compared with experiment. Pollett (1958) has in fact measured the total elastic recovery in polyvinyl chloride melts when a shear flow is suddenly stopped. The elastic properties of the fluids obeying the point derivative type of equation of state are discussed by Ericksen (1960). While he is able to give a mathematical justification for calling the fluid described by such an equation of state elastic, it is difficult to interpret his results in terms of the deformation one would obtain if the stress produced by a given deformation were suddenly removed. The strain history equations of state are, in this sense, more useful in describing elastic effects.

Since, in a physical system, inertia is always present, in practice it will never be possible to produce an instantaneous elastic recovery, although the recovery may be so rapid initially that it may be possible experimentally to identify the first recovery with the instantaneous recovery of the theory. Although in designing a physical experiment some effort may be made to keep the deformation homogeneous, in general the deformation will be inhomogeneous. The problem of predicting the deformation on the sudden change of the boundary conditions becomes very difficult and in fact a deformation which is a continuous function of position may not exist - see Lodge (1958) for example.

However, if experiments could be interpreted in terms of the theory, and this is possible with well-designed experiments, stress relaxation and elastic recovery experiments would be invaluable in defining the form of Ω in equation (3.3). An examination of equations (2.3), (2.4) and (2.5) of Part II shows that even if all the stresses needed to maintain a state of simple shear flow (or an equivalent shear flow) are measured for all shear rates, then these measurements are not sufficient to define Ω completely. However, it has been pointed out in this Note that stress relaxation experiments do give sufficient information. Most experiments in this field have investigated the steady state behaviour of non-Newtonian fluids. Experiments on stress relaxation and elastic recovery are needed. A further Note will deal with the interpretation of the existing experimental results in terms of this equation of state.

References

1. Ciferri, A. and Flory, P.J. — J. Appl. Phys., Vol. 30, 1959, p. 1498.
2. Ericksen, J.L. — The behaviour of certain visco-elastic materials in laminar shearing motions. In Bergen, E., Ed. Viscoelasticity - phenomenological aspects. Academic Press, 1960.
3. Lodge, A.S. — Trans. Faraday Soc. Vol. 52, 1956, p. 120.
4. Lodge, A.S. — A theory of elastic recovery in concentrated solutions of elastomers. In Mason, P. and Wookey, N., Eds. Rheology of elastomers. Pergamon Press, 1958.
5. Lodge, A.S. — Rheologica Acta. Band 1, 1958 B, p. 158.
6. Lodge, A.S. — Colloque International de Rheologie. Paris, 1960.
7. Pollett, W.F.O. — Rheologica Acta. Band 1, 1958, p. 257.

APPENDIX I

To prove that a homogeneous deformation can be represented by $A_{ij}x_j = A'_{ij}\, x'_j$

Consider a transformation which transforms the point x_i into X_i, the origin being fixed. The most general transformation which converts planes into planes is

$$x_1 = \frac{a_{11}X_1 + a_{12}X_2 + a_{13}X_3}{b_1X_1 + b_2X_2 + b_3X_3 + e} \qquad x_2 = \frac{a_{21}X_1 + a_{22}X_2 + a_{23}X_3}{b_1X_1 + b_2X_2 + b_3X_3 + e} \quad \text{etc.} \tag{A1}$$

Consider a set of planes defined by

$$P_1x_1 + P_2x_2 + P_3x_3 = Q \tag{A2}$$

where P_i is fixed and Q varies. Substituting, we get

$$X_1\,(a_{11}P_1 + a_{21}P_2 + a_{31}P_3 - Qb_1) + X_2\,(a_{12}P_1 + a_{22}P_2 + a_{32}P_3 - Qb_2) + X_3\,(a_{13}P_1 + a_{23}P_2 + a_{33}P_3 - Qb_3) = Qe \tag{A3}$$

If the transformed set of planes is to remain a set of parallel planes as Q varies, we must have the coefficients of X_i constant. That is,

$$b_1 = b_2 = b_3 = 0$$

The transformation has become

$$x_i = \mu_{ij}\, X_j \qquad \mu_{ij} = \frac{a_{ij}}{e} \tag{A4}$$

Now we consider a transformation in which a particle at x_i^o at times t_o is continuously deformed into the point x_i at t. Hence,

$$x_i^o = \mu_{ij}(t_o,t)x_j \tag{A5}$$

and if x'_i is the position at t′,

$$x_i^o = \mu_{ij}(t_o,t')x'_j \tag{A6}$$

whence,

$$\mu_{ij}(t_o,t')x'_j = \mu_{ij}(t_o,t)x_j \tag{A7}$$

Now, in the fluids we consider, there is no preferred configuration so $\mu_{ij}(t,t_o)$ is not a function of any special t_o, so that

$$\mu_{ij}(t)x_j = \mu_{ij}(t')x'_j \tag{A8}$$

and in the original notation,

$$A_{ij}\, x_j = A'_{ij}\, x'_j \tag{A9}$$

APPENDIX II

The thixotropic properties of the liquid with an equation of state in which $\Omega = S'_{10}(J_1-3) + S'_{01}(J_2-3)$

The shear stress as a function of time, when a simple shear flow is started at $t = o$ in a liquid which has been at rest for all $t < o$, is given by equation (3.51).

Using $\Omega = S'_{10}(J_1-3) + S'_{01}(J_2-3)$, where $S'_{10}(t-t')$ and $S'_{01}(t-t')$ are positive for all $(t-t') > o$, we find

$$(p_{12})_T = \int_{-\infty}^{o} t' G\, S'_{10}(t-t')dt' + \int_{-\infty}^{o} t' G\, S'_{01}(t-t')dt' \tag{A10}$$

and obviously p_{12} is monotonic in t if $(p_{12})_T$ is monotonic in t. But

$$(p_{12})_T = -G\int_t^{\infty}(\tau-t)\{S'_{10}(\tau) + S'_{01}(\tau)\}d\tau \text{ when } \tau = t-t' \tag{A11}$$

$$\frac{d(p_{12})_T}{dt} = G\int_t^{\infty}\{S'_{10}(\tau) + S'_{01}(\tau)\}d\tau \tag{A12}$$

and, since S'_{10} and S'_{01} are positive for all τ, the right hand side is positive for all t. Hence $(p_{12})_T$, and therefore p_{12} are monotonic and any liquid obeying the equation of state where Ω is given by (2.6) can show only negative thixotropy.

APPENDIX III

On the solution of

$$\underline{\underline{P}}' - p\underline{\underline{I}} = \underline{\underline{A}}_o^{-1}\, \tilde{\underline{\underline{A}}}_o^{-1}\, N'_o - \tilde{\underline{\underline{A}}}_o\, \underline{\underline{A}}_o\, M'_o$$

This equation for $\underline{\underline{A}}_o$, the instantaneous deformation when a simple shear flow is suddenly applied, may be solved (at least numerically) in the following manner.

Let

$$\underline{\underline{X}} = \underline{\underline{\tilde{A}}}_o \underline{\underline{A}}_o \qquad \text{(A13)}$$

then

$$\underline{\underline{X}}^{-1} = \underline{\underline{A}}_o^{-1} \underline{\underline{\tilde{A}}}_o^{-1} \qquad \text{(A14)}$$

and hence

$$\underline{\underline{P}}' = p\underline{\underline{I}} + N_o' \underline{\underline{X}}^{-1} - M_o' \underline{\underline{X}} \qquad \text{(A15)}$$

but if $\underline{\underline{X}}$ is diagonal so is $\underline{\underline{P}}'$. Hence if the principal values of $\underline{\underline{P}}$ are τ_1, τ_2, τ_3 and those of $\underline{\underline{X}}$ are x_1, x_2, x_3, we have

$$\tau_i = p + N_o' x_i - \frac{M_o'}{x_i} \qquad i = 1, 2, 3 \qquad \text{(A16)}$$

subject to det $\underline{\underline{X}} = 1$ (A17)

or $x_1 x_2 x_3 = 1$

where

$$\underline{\underline{L}}\,\underline{\underline{P}}'\,\underline{\underline{\tilde{L}}} = \text{diag}(\tau_1, \tau_2, \tau_3) \qquad \text{(A18)}$$

$$\underline{\underline{L}}\,\underline{\underline{X}}\,\underline{\underline{\tilde{L}}} = \text{diag}(x_1, x_2, x_3) \qquad \text{(A19)}$$

$\underline{\underline{L}}$ being the orthogonal transformation which diagonalized $\underline{\underline{P}}'$. Since $\underline{\underline{P}}'$ is known $\underline{\underline{L}}'$ and τ_i can be found. From equation (A16) and (A17), x_i can be determined. Equation (A19) enables $\underline{\underline{X}}$ to be found.

APPENDIX IV

On the roots of

$$r^6 + r^4 \left\{\frac{N_2' G^2}{N_o'}\right\} - r^2 \left\{\frac{N_1'^2 G^2}{N_o'^2}\right\} - 1$$

Let

$$r^2 = x \qquad \text{(A 20)}$$

$$\frac{N_2' G^2}{N_o'} = \alpha \qquad \text{(A21)}$$

$$\frac{N_2'^2 G^2}{N_o'^2} = \beta > o \tag{A22}$$

Then if

$$f(x) = x^3 + \alpha x^2 - \beta x - 1 \tag{A23}$$

We now see that

$$f(o) = -1$$
$$f(\infty) = +\infty$$

and hence there are either one or three real positive roots.

Now

$$f'(x) = 3x^2 + 2\alpha x - \beta \tag{A24}$$

The turning points are given by

$$f'(x) = o \tag{A25}$$

or

$$3x = -\alpha \pm \sqrt{\alpha^2 + 3\beta^2} \tag{A26}$$

and hence the turning values are given by one negative and one positive value of x. The positive value corresponds to a minimum of f(x) and there is therefore only one real positive root of

$$f(x) = o \tag{A27}$$

Moreover,

$$f(1) = \alpha - \beta$$
$$= \frac{1}{N_o'^2}\left\{N_2' N_o' - N_1'^2\right\}G^2 \tag{A28}$$

If $N_2'N_o' - N_1'^2 > o$ then the positive root of $f(x) = o$ lies between 0 and 1
If $N_2'N_o' - N_1'^2 < o$ then the positive root of $f(x) = o$ is greater than one.

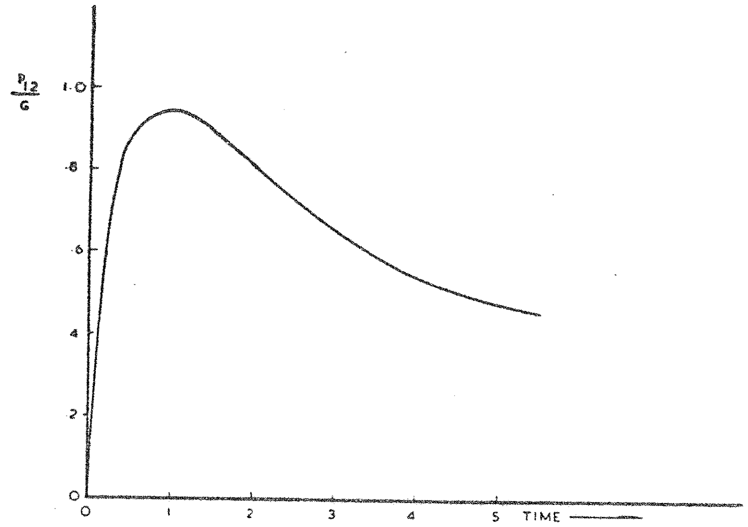

FIG. 1 GRAPH OF VISCOSITY AS A FUNCTION OF TIME FOR A LIQUID FOR WHICH $2\frac{\partial\Omega}{\partial J_1} = Me^{-mt} - (J_1 - 3)Ne^{-nt}$ AND $\frac{\partial\Omega}{\partial J_2} = 0$

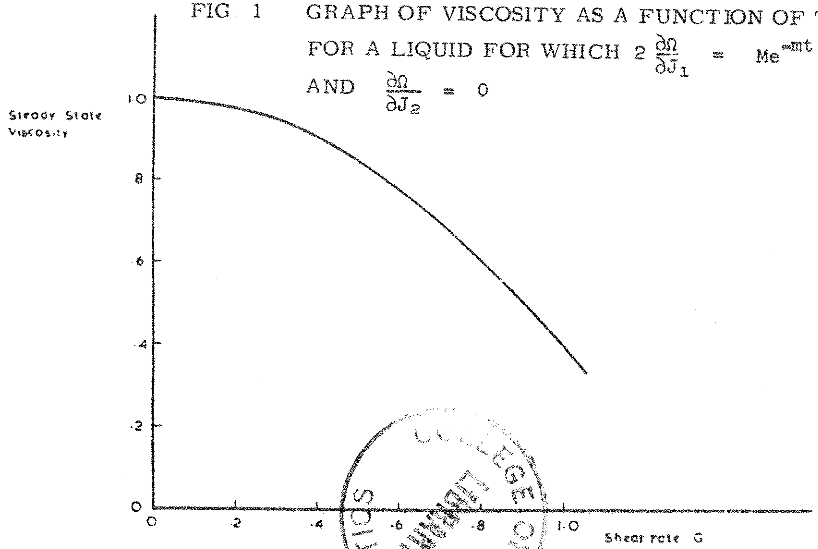

FIG. II GRAPH OF STEADY STATE VISCOSITY AS A FUNCTION OF SHEAR RATE FOR A LIQUID FOR WHICH

$$2\frac{\partial\Omega}{\partial J_1} = Me^{-mt} - (J_1 - 3)Ne^{-nt} \qquad \frac{\partial\Omega}{\partial J_2} = 0$$

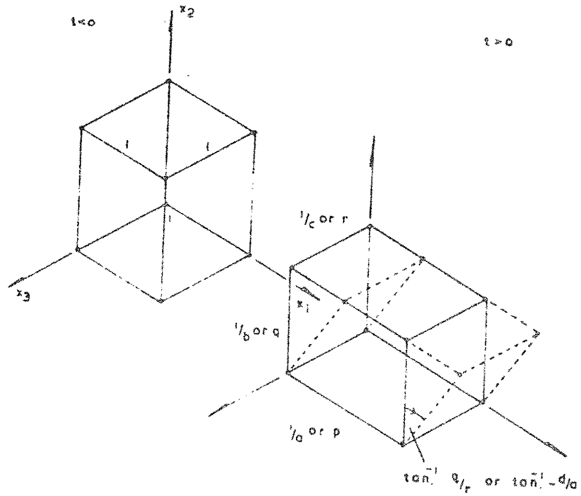

FIG. III DIAGRAM OF THE INSTANTANEOUS CHANGE IN DEFORMATION ON SUDDENLY REMOVING (OR APPLYING) THE STRESS NEEDED TO MAINTAIN SIMPLE SHEAR FLOW.

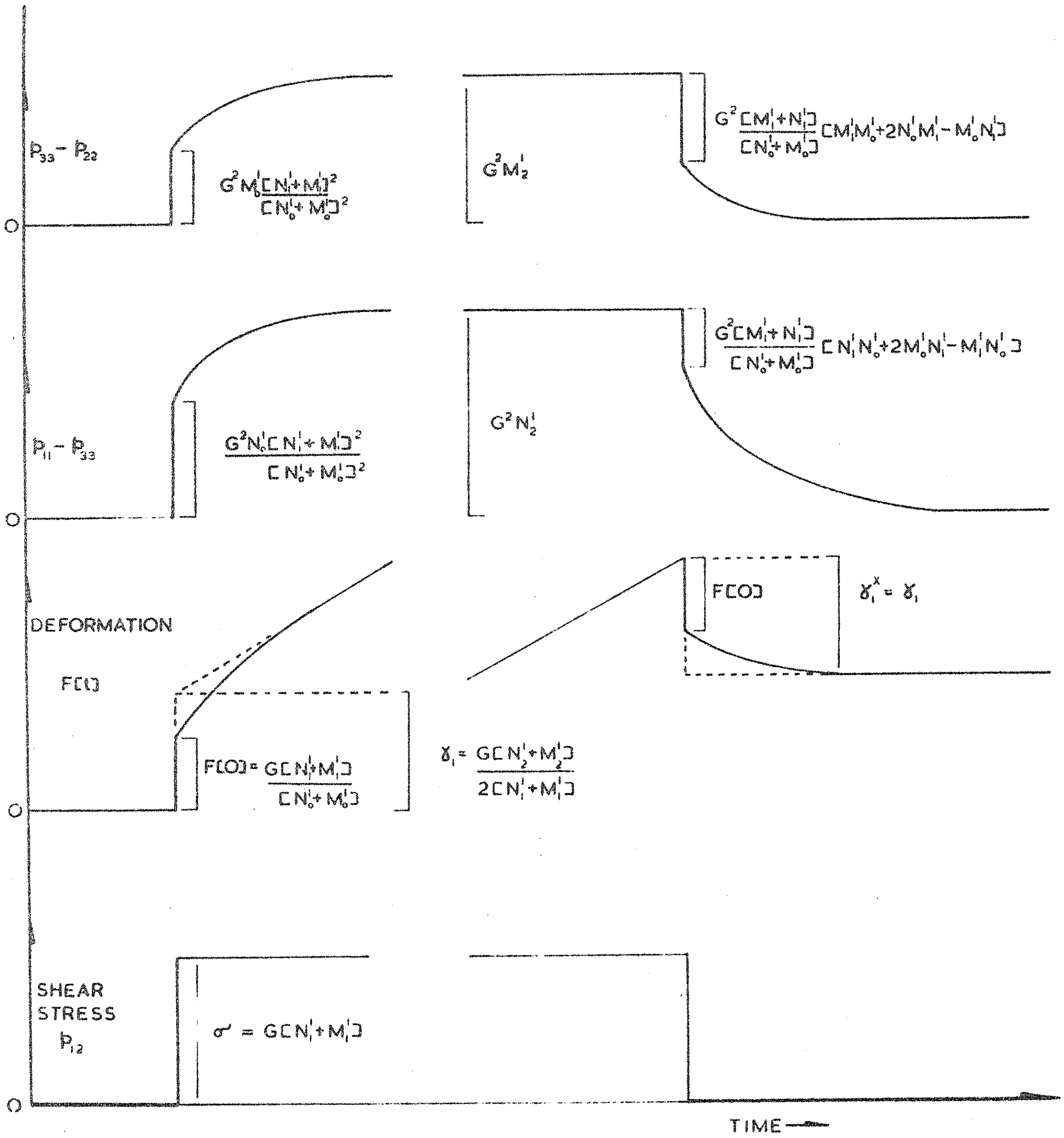

FIG. IV. CONSTRAINED SHEAR FLOW. BEHAVIOUR OF THE DEFORMATION AND STRESS FOR THE SUDDEN APPLICATION AND SUDDEN REMOVAL OF A CONSTANT SHEAR STRESS