THE FLOW CHARACTERISTICS OF
HIGHLY VISCOUS ELASTIC FLUIDS

by

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ABSTRACT

The flow properties of several polymer melts have been investigated in steady shear flow and when shear flow was applied or removed. The results have been compared with the predictions of three rheological equations of state which have been proposed to describe the behaviour of elastic fluids.

In steady shear flow the viscosity \( \eta \) and the normal stress differences \( \sigma_1 \) and \( \sigma_2 \) have been determined for two polyisobutylenes (Vistanex LM-MH and Vistanex LM-MS) and a depolymerised natural rubber (Lorival R25). There is some disagreement about the magnitude of \( \sigma_2 \) and the main objective was to determine if it was zero or not. The data were obtained from total thrust and torque measurements in a Weissenberg Rheogoniometer using cone-plate and parallel plate geometries. For the polyisobutylenes \( \sigma_2 \) was negative but small compared with \( \sigma_1 \); the ratio \( |\sigma_2/\sigma_1| \) was less than 0.3. The Lorival R25 data were not inconsistent with these conclusions.

Attempts have been made to measure stress relaxation on the cessation of shear flow and stress growth at the onset of shear flow. The measurements were carried out on the Weissenberg Rheogoniometer. For Vistanex LM-MH the form of the relaxation depended on the stiffness of the torque measuring system. This is shown to be due to ill-defined boundary conditions for transient measurements with high viscosity fluids. However reliable data could be obtained on the lower viscosity polyisobutylene (Vistanex LM-MS) provided a stiff torsion bar was used. For this material the shear stress relaxation and growth were more rapid as the shear rate increased. The normal stress transient measurements were unreliable but it appeared that relaxation and growth times for \( p_2 \) were less than for \( \sigma_1 \).
A cone-plate rheometer, which can measure the steady shear viscosity and elastic recovery of polymer melts, is described. The form of the recovery curve can also be obtained. A constant shear stress is applied to the sample and the resultant rotation and recovery when the stress is removed are measured by a capacitance technique. Data obtained on the two polyisobutylenes are reported. It is shown that the Weissenberg and Lodge theories of elastic recovery are not valid.

Die swell measurements have been carried out on an elastic fluid (Lorival R25) and a high viscosity Newtonian fluid (Paralac 385, a modified alkyd resin). The measurements were made on a capillary rheometer at shear rates below 1 sec\(^{-1}\). Both fluids showed a significant amount of die swell. For the Newtonian fluid the average die swell was 13.5% and independent of the capillary radius, viscosity and volume rate of flow. Die swell increased with shear rate for the elastic fluid but did not depend on the capillary radius, and at low shear rates was asymptotic to the Newtonian value. It is shown that the momentum balance theory of die swell is not appropriate to high viscosity fluids of any type.

The data obtained on the two polyisobutylenes have been compared with the predictions of the WJFLMB, OWFS and Kaye integral rheological equations of state. The OWFS theory is not an appropriate model for high viscosity elastic fluids such as polymer melts. It predicts elastic recovery values which are much too high and in stress growth experiments it is incapable of predicting stress overshoot which has been reported in the literature. The agreement between theory and experiment for the WJFLMB and Kaye models is reasonable for steady shear flow, stress relaxation, stress growth and total elastic recovery. However these theories do not describe the form of the recovery curve
well. Both the WJFLMB and Kaye models predict stress overshoot in stress growth experiments at high shear rates. There is some evidence that the Kaye theory might be a more useful model than the WJFLMB theory in some applications.
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1.1 Introduction

Most shaping processes in the plastics and rubber industry involve the flow of polymeric materials in the molten state. Thus a study of the rheology of polymer melts is of technological significance and should lead eventually to a better understanding of processing.

In this dissertation some of the flow properties of polymer melts are investigated and the results interpreted in terms of rheological theories. The study is confined to the behaviour of these materials in steady shear flow and to their transient responses when shear is applied or removed. Clearly this does not indicate how the materials will behave in other states of flow. However steady shear flow can be produced accurately in the laboratory and approximates closely to such practical processes as extrusion. An investigation of the properties of polymer melts in this state of flow is therefore relevant.

The fundamentals of rheology have been discussed in detail elsewhere (Lodge 1964, Middleman 1968), and we will only outline the points relevant to the present treatment. The terminology and notation used are similar to those of Lodge (1964), whose coordinate convention has been adopted where applicable.

1.2 Kinematics and Dynamics

We will assume that the materials are continuous. This implies that the derivatives of the displacements are continuous functions of the co-ordinates.
We will choose as the basic kinematical quantity the rate of
drain tensor \( \dot{e}_{ij} \). Assuming a rectangular Cartesian co-ordinate
system \( Ox_1x_2x_3 \), then the components of \( \dot{e}_{ij} \) are (Middleman 1968)

\[
\dot{e}_{ij} = \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)
\]

i, j = 1, 2, 3 \hspace{1cm} 1.1

where \( v_1, v_2, v_3 \) are the velocity components in the \( x_1, x_2 \) and \( x_3 \)
directions. The components of \( \dot{e}_{ij} \) in spherical and cylindrical
polar co-ordinates are given by Middleman (1968).

The basic dynamical variable is the stress tensor \( p_{ij} \).
The components of \( p_{ij} \) in rectangular cartesians are

\[
p_{ij} = \begin{pmatrix}
p_{11} & p_{21} & p_{31} \\
p_{12} & p_{22} & p_{32} \\
p_{13} & p_{23} & p_{33}
\end{pmatrix}
\]

1.2

where \( p_{11}, p_{22}, p_{33} \) are stresses acting normal to the surface
elements perpendicular to the \( x_1, x_2 \) and \( x_3 \) axes respectively.
\( p_{12} \) is the stress acting in the \( x_2 \) direction on the surface element
normal to the \( x_1 \) axis. \( p_{13}, p_{21}, p_{23}, p_{31} \) and \( p_{32} \) are similarly
defined. A positive \( p_{ii} \) is assumed to be a tension.

The \( p_{ii} \) are the normal stresses and the \( p_{ij} \ (i \neq j) \) are
shearing or tangential stresses. Since there will be no resultant
couple acting on the element

\[
p_{ij} = p_{ji}
\]

1.3

Thus there are only 6 independent components of the stress tensor.
Both the rate of strain tensor and the stress tensor are symmetrical.

The equation relating the kinematical state of a body at
all past times, and the dynamical quantity are Rheological Equations
of State or Constitutive Equations. These are tensor equations which
are characteristic of the material under study.
1.3 Basic Assumptions

In the present treatment we will assume that:

(i) The materials are incompressible.
(ii) The materials are isotropic in the unstressed state.
(iii) Flow is isothermal.

The compressibility of polymer melts has been investigated by Spencer & Gilmore (1950); their results indicate that it is small and the assumption given by (i) is therefore reasonable. Assumption (ii) means that the materials have no preferred direction in the unstressed state. This may not be true for solid polymers but is valid for polymer melts. Flow is a dissipative process and will not be isothermal in general. However as we shall show later temperature rises are small and isothermal flow conditions can be assumed.

1.4 Conservation Equations

The solutions to isothermal flow problems must satisfy the equations of continuity and momentum. These equations are derived from classical mechanics and reflect the principles of conservation of mass and momentum. Middleman (1968) gives the components of the equations in rectangular Cartesian, spherical polar and cylindrical polar co-ordinates.

1.5 Steady Shear Flow

For an isotropic material we need only consider flow in one direction. Assuming an orthogonal co-ordinate system $\xi_1 \: \xi_2 \: \xi_3$, then we will take the $\xi_1$ axis in the direction of flow and the $\xi_2$ axis perpendicular to the shearing surfaces. Thus a state of flow will be defined as steady shear or simple shear if the velocity
components take the form
\[ v_1 = v_1(\xi_2); \quad v_2 = v_3 = 0 \quad 1.4 \]
and
\[ \dot{e}_{ij} = G(\xi_2) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad 1.5 \]
where \( G \), the shear rate, is a scalar function of \( \xi_2 \) defined by 1.5. \( G \) will always be taken as a positive quantity.

Thus there are a family of rigid material planes, the shearing surfaces, given by \( \xi_2 = \) constant.

If we consider a rotation of the axes about \( \xi_2 \) through 180° then it follows that (Lodge 1964):
\[ p_{31} = p_{13} = p_{23} = p_{32} = 0 \quad 1.6 \]
Thus the stress tensor in simple shear flow reduces to
\[ p_{ij} = \begin{pmatrix} p_{11} & p_{21} & 0 \\ p_{21} & p_{22} & 0 \\ 0 & 0 & p_{33} \end{pmatrix} \quad 1.7 \]

Equation 1.7 represents the state of stress for an isotropic material in steady shear flow. For an incompressible material the absolute value of the normal stress will be assumed to be of no rheological significance. However the difference between the normal stresses are unaffected by the hydrostatic pressure and depend only on the rheological properties of the material. Thus there are only three stress quantities of rheological significance; two normal stress differences and a tangential stress \( p_{21} \). The normal stress differences usually considered are \((p_{11} - p_{22})\) and \((p_{22} - p_{33})\). Thus in steady shear flow the stress quantities of rheological interest are
\[
(p_{11} - p_{22}), (p_{22} - p_{33}), \quad p_{21} \quad (= p_{12}) \quad 1.8
\]
In steady shear flow the stress quantities (1.8) are
functions of the shear rate defined by

\[ P_{21} = G \eta(G) \quad 1.9 \]
\[ (P_{11} - P_{22}) = \sigma_1(G) \quad 1.10 \]
\[ (P_{22} - P_{33}) = \sigma_2(G) \quad 1.11 \]

where \( \eta, \sigma_1 \) and \( \sigma_2 \) are functions which completely describe the behaviour of the material in simple shear flow. They are called materials functions. \( \eta \) is the viscosity of the material. For a Newtonian fluid in simple shear flow \( \sigma_1 = \sigma_2 = 0 \) and \( \eta \) is a constant.

Measurements of \( \eta, \sigma_1 \) and \( \sigma_2 \) for a number of polymer melts are described in chapter 3. The material functions will also depend on temperature but this effect has not been studied in the present investigation. The transient properties of the materials when steady shear flow is applied and removed have also been investigated (chapters 4, 5 and 6) in a number of flow situations.

No attempt has been made to take into account the molecular nature of the polymers in this investigation. Instead a phenomenological approach has been adopted and the experimental results interpreted in terms of a number of continuum theories (chapter 7).
FIGURE 2.1 Viscosity versus shear rate at 230°C for various commercial thermoplastics (Pezzin 1964).

- □ general purpose polystyrene
- △ polycaprolactam
- ◊ polymethylmethacrylate
- × high impact polystyrene
2.1 Introduction

Polymer melts display both viscous and elastic responses when subjected to a specified stress history, i.e. they are elastic fluids. It is necessary, therefore, to consider both these responses if we are to understand their behaviour.

The flow properties of polymer melts will be reviewed under the following headings:

(i) Viscosity
(ii) Normal stress differences in steady shear flow
(iii) Stress relaxation and stress growth
(iv) Elastic recovery
(v) Die swell.

These are not the only important properties of polymer melts (see Lodge 1964), but they are most relevant to the present investigation since they all involve steady shear flow at some time. The flow of concentrated polymer solutions is similar and data on these systems will be cited where it is relevant.

2.2 Viscosity

The most obvious characteristic of polymer melts is that they are very viscous fluids; viscosities up to $10^7$ poise are not uncommon in some circumstances. However the viscosity of these materials is not constant but decreases as the shear rate increases. Typical viscosity-shear rate results are shown in figure 2.1 for a number of commercial plastics. We see from figure 2.1 that the rate at which the viscosity decreases with shear rate depends on the
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<th>Normal Stress Difference obtained</th>
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<tr>
<td>A Cone-plate</td>
<td>pressure distribution on plate</td>
<td>$\sigma_1 + 2\sigma_2$</td>
<td>Lodge (1964)</td>
</tr>
<tr>
<td>B Cone-plate</td>
<td>pressure on plate at rim</td>
<td>$\sigma_2$</td>
<td>White &amp; Metzner (1962)</td>
</tr>
<tr>
<td>C Cone-plate</td>
<td>total thrust exerted on plate</td>
<td>$\sigma_1$</td>
<td>Lodge (1964)</td>
</tr>
<tr>
<td>D Cone-plate</td>
<td>thrust exerted on central part of plate</td>
<td>$\sigma_1 + \beta \sigma_2$</td>
<td>Pollett (1955)</td>
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<tr>
<td>E Cone-plate with finite gap &amp; G</td>
<td>total thrust on plate as function of gap size</td>
<td>$G \frac{d\sigma_1 + \sigma_2}{dG}$</td>
<td>Jackson &amp; Kaye (1966)</td>
</tr>
<tr>
<td>F Parallel-plate</td>
<td>pressure distribution on plate</td>
<td>$\sigma_1 + \sigma_2 + G \sigma_2$</td>
<td>Lodge (1964)</td>
</tr>
<tr>
<td>G Parallel-plate</td>
<td>pressure on plate at rim</td>
<td>$\sigma_2$</td>
<td>White &amp; Metzner (1962)</td>
</tr>
<tr>
<td>H Parallel-plate</td>
<td>total thrust exerted on plate as a function of angular velocity</td>
<td>$\sigma_1 - \sigma_2$</td>
<td>White &amp; Metzner (1962)</td>
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<tr>
<td>I Coaxial cylinder (small gap)</td>
<td>difference between pressures exerted on inner &amp; outer cylinder</td>
<td>$\sigma_1$</td>
<td>Lodge (1964)</td>
</tr>
<tr>
<td>J Coaxial cylinder (large gap)</td>
<td>difference between pressures exerted on inner &amp; outer cylinders as a function of angular rotation</td>
<td>$\sigma_1$</td>
<td>White &amp; Metzner (1962)</td>
</tr>
<tr>
<td>K Axial annular flow</td>
<td>pressure difference between inner &amp; outer walls at constant axial position</td>
<td>$\sigma_2$</td>
<td>Huppler (1965)</td>
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FIGURE 2.2 Schematic representation of 'Rheological breakdown' (Pollett '1955) at shear rates $G_1$, $G_2$, and $G_3$, where $G_1 > G_2 > G_3$. 

\[ P_{21} \text{ (Arbitrary units)} \]

\[ \sigma_1 \text{ (Arbitrary units)} \]

Strain

Strain
polymer type and in all cases the viscosity tends to a constant value at low shear rates. The viscosity also depends on the molecular structure (Batchelor 1966).

2.3 Normal Stress Differences in Steady Shear Flow

The theory and assumptions underlying the techniques for measuring the normal stress differences have been reviewed by Lodge (1964) and White & Metzner (1962). A summary of the methods suggested for evaluating these quantities experimentally is given in table 2.1.

Methods have been proposed for evaluating normal stresses differences from the thrust or jet dimensions in capillary flow (White & Metzner 1962). These techniques are based on a momentum balance, which we shall see later (section 2.6) in the discussion on die swell is not applicable to polymer melts. For this reason they are not included in table 2.1 or the present discussion.

There is only a limited amount of data available in the literature on normal stress differences in polymer melts. In all cases the stresses were evaluated from measurements of total thrust (C, D, H table 2.1). This is probably because it is difficult to measure point pressures accurately in polymer melts, particularly at elevated temperatures.

The first results on polymer melts seemed to have been published by Pollett (1955). He evaluated $\sigma_1$ and $\sigma_2$ from total thrust measurements in a cone-plate rheometer (C, D), and concluded that $\sigma_2 = 0$ for a low density polyethylene at 128°C. Pollett also found at shear rates above 1 sec$^{-1}$, that $\sigma_1$ and $p_{21}$ were dependent not only on the shear rate but on the absolute magnitude of the strain. This is shown diagrammatically in figure 2.2 and is reversible on resting.
This apparent thixotropic behaviour has been referred to as 'rheological breakdown' (Pollett 1955, Cooper, Khanna & Pollett 1968), and is attributed to a structural breakdown of the polymer network. However in these experiments there was a loss of sample from the apparatus which indicates that steady shear conditions were disrupted. King (1966) noted that time dependent effects in polyethylene were accompanied by a visible break-up of the sample at the edge.

Hutton (1963) has explained the effect shown in figure 2.2 in terms of a fracture mechanism. He suggests that the fracture starts at the periphery and grows radially inwards reducing the effective area and consequently the measured stresses. This explanation is in general agreement with the observations. The structural breakdown mechanism proposed by Pollett need not be excluded entirely, but it appears to be small compared with the fracture effects.

Benbow & Howells (1961) have measured $\sigma_1$ in a cone-plate viscometer (method C) for a series of polydimethylsiloxanes. They find that $\sigma_1$ is of the same order of magnitude as $p_{21}$ and increases more rapidly with shear rate. Furthermore $\sigma_1$ tends to a square dependence on shear rate as the shear rate tends to zero. These results are consistent with King's data on polyethylene.

Meissner (1967a, 1967b) evaluated $\sigma_1$ and $\sigma_2$ for a polyethylene from total thrust in a cone-plate and parallel plate viscometer (C, H). He found that $\sigma_2 > 0$ at low shear rates and the converse at the high rates. However, these results were obtained under conditions where time effects discussed above are occurring and they may not be relevant.

Although the available information on polymer melts is limited, there is a great deal of published data on concentrated
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<tr>
<td>Pollett (1955)</td>
<td>C, D</td>
<td>low density polyethylene</td>
<td>$\sigma_2 = 0$</td>
</tr>
<tr>
<td>Meissner (1967a) (1967b)</td>
<td>C, H</td>
<td>branched polyethylene</td>
<td>$\sigma_2 &lt; 0$ for $G &lt; 0.1 \text{sec}^{-1}$ $\sigma_2 &gt; 0$ for $G &gt; 0.1 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>Greensmith &amp; Rivlin (1953)</td>
<td>F, G</td>
<td>polyisobutylene-tetratin solutions</td>
<td>$\sigma_2 &gt; 0$</td>
</tr>
<tr>
<td>Roberts (1954, 1957)</td>
<td>A, B</td>
<td>polyisobutylene-tetratin solutions</td>
<td>$\sigma_2 = 0$</td>
</tr>
<tr>
<td>Markovitz &amp; Williamson (1957)</td>
<td>A, C</td>
<td>polyisobutylene-decalin solutions</td>
<td>$\sigma_2 = 0$</td>
</tr>
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<td>Adams &amp; Lodge (1964)</td>
<td>A, B, F</td>
<td>polyisobutylene-decalin solutions</td>
<td>$\sigma_2$ from F $&gt; \sigma_2$ from B $&gt; 0$</td>
</tr>
<tr>
<td>Ginn &amp; Metzner (1965)</td>
<td>C, H</td>
<td>polyisobutylene-decalin solutions</td>
<td>$\sigma_2 &lt; 0$ for $G &lt; 7 \text{sec}^{-1}$ $\sigma_2 = 0$ for $G &gt; 7 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>Markovitz &amp; Brown (1963)</td>
<td>A, F</td>
<td>polyisobutylene-cetane solutions</td>
<td>$\sigma_2 &gt; 0$</td>
</tr>
<tr>
<td>Markovitz (1966)</td>
<td>A, F, J</td>
<td>polyisobutylene-cetane solutions</td>
<td>good agreement between methods $0 &lt; \sigma_2 &lt; 0.4\sigma_1$</td>
</tr>
<tr>
<td>Jackson &amp; Kaye (1966)</td>
<td>C, E, H</td>
<td>high molecular weight polyisobutylene in low molecular weight polyisobutylene</td>
<td>good agreement between methods $0 &gt; \sigma_2 &gt; -0.5\sigma_1$</td>
</tr>
<tr>
<td>Broadbent, Kaye, Lodge &amp; Vale, (1968)</td>
<td>A, B, C, F</td>
<td>high molecular weight polyisobutylene in low molecular weight polyisobutylene</td>
<td>results consistent $0 &gt; \sigma_2 &gt; -0.07\sigma_1$</td>
</tr>
<tr>
<td>Kotaka, Kurata &amp; Tamura (1959)</td>
<td>F, G</td>
<td>some cellulose polymers in water</td>
<td>$\sigma_2 = 0$</td>
</tr>
<tr>
<td>Huppler (1965)</td>
<td>K</td>
<td>some cellulose polymers in water</td>
<td>$\sigma_2 &gt; 0$ values from 7 to 20% of $\sigma_1$ quoted</td>
</tr>
</tbody>
</table>
polymer solutions (see Lodge 1964). Most of the techniques summarised in table 2.1 have been used to evaluate the normal stress differences in these systems.

It is generally agreed that $\sigma_1$ is of the same order as $p_{21}$ and depends on the square of shear rate (Markovitz 1966, Ginn & Metzner 1965). However, there is some disagreement about the value of $\sigma_2$; even where different workers have used the same polymer-solvent system.

A summary of the published data on $\sigma_2$ in a number of systems is shown in table 2.2. We see that there is a great deal of disagreement between different techniques and values of $\sigma_2$ from -0.5 $\sigma_1$ to +0.4 $\sigma_1$ have been reported.

Recently Broadbent, Kaye, Lodge & Vale (1968) have suggested a reason for the inconsistencies observed by Adams & Lodge (1964). They suggest that in pressure distribution apparatus the pressure tappings in the plate give rise to a systematic error in the measurements. A simple theory is proposed to take this into account and they find that the pressure arising from the hole is larger than $p_{21}$. Their data corrected for this error gave consistent results as shown in table 2.2 and the disagreement observed by Adams & Lodge (1964) was resolved. However the corrected data for $\sigma_2$ is still in disagreement with Jackson & Kaye's (1966) total thrust data on the same solution.

The errors found by Broadbent et al in pressure distribution measurements suggest that much of the data in table 2.2 may be suspect. Obviously there is a need for further data on $\sigma_2$, particularly in polymer melts.

### 2.4 Stress Relaxation and Stress Growth

When a polymer melt or solution is subjected to a certain
FIGURE 2.3 Response of various materials to shear rate history specified in top diagram.
FIGURE 2.4 Stress growth of a low density polyethylene at 114°C (Vinogradov & Belkin 1965).

\[ P_{21} \times 10^{-5} \text{ (dyn cm}^{-2}) \]

Time (sec)

- a: 0.056
- b: 0.21
- c: 0.56
- d: 2.1
flow history and then held at constant shape the stresses do not become zero instantaneously (Lodge 1964) but decreases to zero with time. This is called stress relaxation. Similarly if a constant shear rate is applied to the material at rest then the stresses do not immediately attain a steady value.

The behaviour described above is shown diagrammatically in figure 2.3, where the responses of an elastic solid and a viscous fluid are also shown for comparison. We see that the response of polymer melt is partly elastic and partly viscous and it is an example of the viscoelastic nature of the material.

Shear stress relaxation after steady shear flow at low shear rates has been studied extensively in coaxial cylinder and cone-plate viscometers (Ferry 1961, Peticolas 1961, 1963). Under these conditions the fluid viscosity was constant and the rate of relaxation independent of the applied shear rate.

Schremp, Ferry & Evans (1951) determined the effect of the steady shear rate on the shear stress relaxation properties of some polymer solutions using a coaxial cylinder apparatus. They concluded that the relaxation occurred more rapidly as the steady shear rate increased. These results were recently confirmed by Huppler et al (1967).

Vinogradov & Belkin (1965) studied the growth of the shear stress in polyethylene and polystyrene melts when a constant shear rate is applied to the fluid at rest. They found that the growth was faster as the shear rate increased. At higher shear rates the stress went through a maximum before settling to a constant value, the amount of overshoot increasing as the shear rate increased (figure 2.4). Similar results were obtained by Huppler et al (1967). Pollett (1955) and Cooper, Khanna & Pollett (1968) also observed a maximum
FIGURE 2.5 Response of various materials to shear stress history specified in top diagram.
(figure 2.2), but the stresses did not reach a constant value and the effects were much larger than observed by Vinogradov & Belkin. Pollett's results have already been discussed in section 2.3 and are possibly due to other effects.

Very few results have been published on the growth and relaxation properties of normal stresses. Freeman & Weissenberg (1948), Benbow & Howells (1961) and Huppler et al (1967) have shown that $\sigma_1$ relaxes and grows more slowly than $p_{21}$. Huppler et al also reported that the relaxation and growth of $\sigma_1$ was more rapid as the steady shear rate increased. There was also some overshoot observed at higher shear rates, but it was less than the overshoot reported for $p_{21}$.

It is generally agreed that $p_{21}$ grows and relaxes much faster than $\sigma_1$ and both stresses grow and decay faster as the shear rate is increased. Finally there is some evidence that at higher shear rates the stresses overshoot before reaching a constant value.

### 2.5 Elastic Recovery

If the shear stress is removed from a polymer melt which has been subjected to a certain flow history, the material changes shape. This behaviour is known as elastic or shear recovery. Similarly when a constant shear stress is applied to the material at rest then the shear rate does not immediately reach a steady value.

This behaviour is shown diagrammatically in figure 2.5 compared with the responses of an elastic solid and viscous fluid. We see that this behaviour is another example of the viscoelastic nature of polymer melts.

Elastic recovery following steady shear flow can be either constrained or free (Lodge 1964). In constrained recovery the boundaries are fixed so that there is no separation of the shearing surfaces.
The fluid then recovers in the opposite direction to the previous shear flow. This occurs in the conventional rotational viscometers such as the cone-plate and coaxial cylinder. The walls of the apparatus act as a constraint but one of the boundaries must be free to rotate when the stress is removed. If the fluid is unconstrained when the stress is removed recovery can take place in all co-ordinate directions; this is called free recovery.

In a constrained recovery experiment the change of shape is specified by the quantity \( \gamma_\infty \), the recoverable strain or elastic recovery. \( \gamma_\infty \) is simply the total amount of shear strain recovered.

A variety of experimental techniques have been used to measure recoverable strain. Ferry (1942), and Philippoff and his co-workers (see Philippoff 1962) used coaxial cylinder viscometers to determine the effect of shear rate. Other measurements have been carried out on polymer melts using cone-cone (Boyd 1957) cone-plate (Benbow & Howells 1961), and biconical rheometers (Rosen & Rodriguez 1965, Best & Rosen 1968). In all cases \( \gamma_\infty \) increased with shear rate.

The theories of Weissenberg (1947) and Lodge (1964) predict that \( \gamma_\infty \) is related to the steady shear flow properties of the material. The relationship takes the form

\[
\gamma_\infty = k \frac{\sigma_1}{\rho_2}
\]

where \( k = 1 \) for the Weissenberg theory and \( k = 0.5 \) for the Lodge theory.

The theories have been checked by Philippoff (1962), Benbow & Howells (1961), and Khanna & Pollett (1966). The results are conflicting. Philippoff obtained good agreement with Weissenberg's theory for a large number of polymer solutions. Benbow & Howell's results for some silicone polymers agreed with Lodge's predictions i.e. \( k = 0.5 \). However Khanna & Pollett quoted a value \( k = 0.6 \) to 0.7.
for polyethylene and plasticised polyvinylchloride. Clearly there is a need for further data to resolve these discrepancies.

The response of molten polyethylene when a constant shear stress is applied was examined by Dexter (1954). He found that the steady state conditions were reached more rapidly as the stress increased. Dexter defined a quantity called 'total elastic shear strain'. This is the intercept on the strain axis of the extrapolated straight line (steady state) portion of the strain-time plot. He found that this quantity increased with the applied stress. Kataoka (1968) found that it was equal to $\gamma_{\infty}$ at low shear stresses.

Weber & Bauer (1956) and Kapoor (1963) have demonstrated constrained recovery in capillary flow when the applied stress is removed. Because of the complex shear distribution in this geometry it is difficult to interpret these observations in terms of the recoverable shear.

It is almost impossible to carry out free recovery experimentally; the viscometer walls would have to be removed at the same time as the stress. Pollett (1958) attempted to simulate free recovery by rapidly cooling the apparatus after straining for a period to 'freeze' any strains in the sample. The 'frozen' sample was then removed and reheated to the test temperature and allowed to recover under unconstrained conditions. The sample (plasticised polyvinylchloride) expanded normal to the direction of the previous shear flow ($\xi_2$) and recovered some shape in the opposite direction to the previous shear flow ($\xi_1$). There was also some evidence for expansion in the third co-ordinate direction. These observations are consistent with Lodge's (1958) theory, and are similar to the die swell phenomenon which occurs when polymer melts are extruded. However the recovery conditions under which die swell occurs will not be completely
free and are certainly more complicated than described above.

2.6 Die Swell

A liquid jet emerging from a circular tubes changes in shape. Barus (1893) first commented on this behaviour with a material called marine glue. Later Merrington (1943) reported the results of experiments with some rubber solutions and found that the extrudate diameter was greater than the tube diameter, increasing with the rate of flow. Spencer & Dillon (1948) obtained similar results with a polystyrene melt. Similar effects occur through dies of other shapes. This expansion is called the 'Barus effect' or more usually 'die swell'. With polymer melts the expansion is large and values up to 150 - 200% have been reported by, for example, Vinogradov & Prozorovskaya (1967). Die swell is important in polymer melt extrusion where provision must be made for the expansion when dies are designed.

Barus suggested that the change in shape was due to the compressibility of the fluid. This was indicated to some extent in his viscosity results which depended on the applied pressure. If this were the sole reason large increases in volume would have to occur to account for the die swell in polymer melts, which implies high compressibility of the materials. Spencer & Gilmore (1950) showed that the compressibility of polymer melts is small and it can be neglected for practical purposes.

There is some evidence that die swell is associated with the elastic nature of polymer melts and solutions. For example, Lodge (1964) extruded a Newtonian fluid and an elastic fluid through a tube under nominally the same conditions. The fluid viscosities were similar but with the elastic fluid die swell was observed. Furthermore Rosen & Rodriguez (1965) found that die swell increased with the
elastic recovery of the material. Thus elasticity does seem to have some bearing on die swell. However we shall see later that under certain conditions die swell is obtained with Newtonian fluids, but the effect is not so pronounced.

Clegg (1958) found that the die swell of polyethylene melts at constant shear rate decreased with increasing tube length and decreasing die entry angle. Similar results were obtained by Metzner, Carley & Park (1960) and Bagley, Storey & West (1963). These observations can be explained qualitatively by a 'memory effect'. A fluid element entering the tube decreased in diameter and increased in length. At the exit an elastic liquid remembers some of its recent strain history and will tend to recover some of its original shape, i.e. die swell occurs. The amount of recovery will depend on the dwell time in the tube and the strain induced in the entry region. Thus die swell will decrease with increasing tube length and decreasing entry angle. Lodge (1964) demonstrated that this is not the complete explanation. He allowed an elastic fluid to remain in the tube for much longer than its relaxation time before extruding, and die swell was still obtained. Metzner, Carley & Park (1960) showed that if the tube is long enough die swell is independent of tube length. Some other explanation is needed in these cases.

Spencer & Dillon (1948) investigated the die swell characteristics of molten polystyrene. They suggested that die swell was a measure of the elastic strain imparted to the fluid. Applying the theory of rubber elasticity (Treloar 1958) which predicts Hooke's law in shear, they calculated a shear modulus which agreed with that obtained from molecular considerations. The agreement may be fortuitous, since rubber elasticity theory predicts, and experiments confirm, that the modulus is proportional to temperature, but the values calculated from the die swell were independent of temperature.
Bagley, Storey & West (1963) studied the effect of tube length on the die swell of a low density polyethylene. They assumed that their results could be accounted for by a memory effect arising from a typical relaxation process. An exponential relationship was assumed and an empirical equation fitted to the data. The constants in this equation are possibly related to the relaxation properties of the polymer melt in a complicated manner, but this approach does not provide any significant understanding of die swell.

McIntosh (1960) found that die swell of a carboxymethyl-cellulose solution passed through a maximum when plotted against shear stress at the wall, eventually tending to a contraction at high stresses. Middleman & Gavis (1961b) obtained similar results with some polyisobutylene solutions. No maximum has been observed for polymer melts, probably because at high shear rates melt fracture occurs (Tordella 1956) and die swell data are meaningless. The contraction is due to inertia and would occur at all shear rates if this was the only consideration (Harris 1963).

McIntosh attributed die swell to the recovery of elastic strain imparted to the fluid during its passage through the tube. Although this may be reasonable the assumed recovery mechanism is unrealistic and the subsequent theoretical analysis unsatisfactory. Since it displayed retarded elastic behaviour McIntosh used a Voigt model to interpret his results. This model is unsatisfactory as it assumes linear viscoelastic behaviour and has only one retardation time. Furthermore since shear strain in a Voigt model increases with time, the theory predicts that die swell (at constant capillary diameter and volume rate of flow) increases as the capillary length increases, contrary to all published data. This would seem to invalidate the theoretical approach of McIntosh.

The theories discussed so far have been derived empirically
and do not lead to any real understanding of die swell. They have not taken into account the normal stresses acting in a flowing polymer melt.

Gaskins & Philippoff (1959) suggested that die swell measurements would be a useful technique for determining normal stresses at high shear rates. They analysed the flow by using an energy balance approach. This was incorrect in principle since the velocity rearrangement at the tube exit is a dissipative process and this was ignored in the theoretical treatment.

Metzner et al (1961) gave an analysis of the liquid jet based on a momentum balance. Their object was to derive an expression for calculating $\sigma_1$ from the final extrudate diameter. Conversely if this approach is valid we can predict die swell from $\sigma_1$. The change in momentum flux between the tube exit and downstream where the velocity profile is flat is equated to any external forces. Since this method appears to have been rigorously developed and attracted a great deal of attention, we will discuss the theory in some detail.

Let us assume a cylindrical polar co-ordinate system $z, r, \theta$ (equivalent to $\xi_1, \xi_2$ and $\xi_3$ respectively), where $z$ is the axial co-ordinate, $r$ is the radial co-ordinate and $\theta$ is orthogonal to $r$ and $z$. The capillary axis is given by $r = 0$ and the wall $r = R$; $z = 0$ at the capillary entrance and $z = L$ at the exit. Thus $R$ and $L$ are the capillary radius and length respectively.

Neglecting surface and gravitational forces the basic equation in the axial direction is

$$\int_{0}^{R} 2\pi \rho r v^2 \, dr - \pi \rho R j^2 V_j^2 = \int_{0}^{R} 2\pi r p_{11} \, dr$$

- 17 -
where $\rho$ is the fluid density, $R_j$ is the final extrudate radius and $V_j$ is the final uniform velocity of the extrudate. $V_j$ may be eliminated by the equation of continuity

$$V_j = \frac{Q}{\pi R_j^2} \tag{2.3}$$

where $Q$ is the volume rate of flow. The atmospheric pressure in 2.2 is assumed to be zero.

Metzner assumed that steady shear flow conditions exist at the exit plane ($z = L$) thus the velocity components are

$$v_\theta = v_r = 0; \quad v_z = v_z (r) \tag{2.4}$$

The shear rate $G$ is given by (Lodge 1964)

$$G = -\frac{dv_z}{dr} \tag{2.5}$$

The integral on the left hand side of 2.2 is determined by the viscosity characteristics of the fluid. This term can be evaluated numerically, but it is more convenient to represent the shear stress - shear rate data by an empirical equation and obtain an analytical solution. Metzner chose a 'power law'

$$P_{21} = K G^N \tag{2.6}$$

where $K$ and $N$ are materials constants. $N$ is less than unity for polymer melts. The shear stress is proportional to the distance from the tube axis (Lodge 1964), thus it follows that

$$\frac{P_{21}(r)}{P_{21}(R)} = \frac{r}{R} \tag{2.7}$$

To evaluate the integral on the right hand side of 2.2 Metzner assumed that

$$\sigma_2 = 0 \tag{2.8}$$

$$P_{11} (0,L) = 0 \tag{2.9}$$

where $P_{11} (0,L)$ denotes the value of $p_{11}$ at $r = 0, z = L$. These assumptions imply that $P_{22} (R,L) = 0$ from the equations of motion (Middleman 1968). The following expression is obtained for $\sigma_1$ from
\[
\sigma_1 (R) = \frac{\rho}{N} \left( \frac{Q}{\pi R^2} \right)^2 \left[ \frac{(N+1)(1+3N)}{(1+2N)} - \frac{1}{\chi_\infty^2} \left( \frac{1+N+\ln(1/\chi_\infty)}{\ln(4Q/\pi R^3)} \right) \right]
\]

where \( \chi_\infty \) is the die swell defined by
\[
\chi_\infty = \frac{R_j}{R}
\]

Similarly the dependence of \( \sigma_1 \) on \( G \) can also be adequately represented by a power law (see data of King 1966), say
\[
\sigma_1 = AG^B
\]

where \( B \) is less than two. Thus 2.2 becomes from 2.3 to 2.9 and 2.12.

\[
\frac{1}{\chi_\infty^2} = \frac{(1+3N)}{(1+2N)} - \frac{2A(1+3N)^2 G(R)^{B-2}}{N(2N+B) \rho R^2}
\]

where
\[
G(R) = \frac{(3N+1)}{N} \frac{Q}{\pi R^3}
\]

The validity of 2.10 was checked from some earlier die swell data of Metzner, Carley & Park (1960). At a shear rate of 100 sec\(^{-1}\) equation 2.10 predicts that for a polyethylene \( \sigma_1 \) is approximately 1 dyn cm\(^{-2}\). This is several orders of magnitude lower than King (1966) reported for some typical polyethylenes at shear rates below 1 sec\(^{-1}\). Vinogradov & Prozovskaya (1967) also quote low values of \( \sigma_1 \) for some polymer melts calculated from equation 2.10. Furthermore 2.13 predicts that die swell decreases as \( G(R) \) increases, contrary to all published data on polymer melts. 2.13 also implies that there is a value of \( G(R) \) below which no real value of the extrudate radius is
obtained. This shear rate is determined by equating the terms on the right hand side of 2.13.

Since the material constants $N$, $A$ and $B$ for polymer melts are of the order of $0.75, 10^5$ dyn cm$^{-2}$ sec$^B$ and 1.5 respectively, the value of $G(R)$ before equation 2.13 can be applied is unrealistically high. For example, assuming $\rho = 1$ and $R = 0.05$ cm, then $G(R)$ must be $\sim 10^{14}$ sec$^{-1}$ before equation 2.13 predicts any real quantity for $R_j$. Clearly equations 2.10 and 2.13 cannot apply to polymer melts.

Gravity and surface tension have been ignored in equation 2.2. Gravity will be negligible in the case of horizontal jets and for vertical jets it is avoided by extruding into a liquid of the same density (Johnson & Baer 1963), with high viscosity polymer melts the effect of gravity will be negligible. Goren & Wronski (1966) showed that surface tension effects do not influence the dimensions of jets of Newtonian fluids. The neglect of surface tension and gravity in 2.2 is therefore reasonable.

The momentum balance must hold and equation 2.2 must be valid. Either the assumed initial velocity profile or the evaluation of the integral containing $p_{11}$ must be incorrect. Large errors in the assumed initial velocity profile will not alter the left hand side of 2.2 by orders of magnitude. This suggests that the evaluation of the integral containing $p_{11}$ is wrong.

The integral on the right hand side of 2.2 was evaluated using the assumptions given by 2.4, 2.8 and 2.9. These imply that $p_{22}(R,L) = 0$ from the equations of motion.

We have seen (table 2.2) that $\sigma_2$ is much smaller than $\sigma_1$ and 2.8 is therefore valid as a first approximation. However the assumption given by 2.9 seems to have been adopted arbitrarily. If
we retain the terms containing \( p_{11}(0,L) \) then equation 2.13 would read

\[
\frac{1}{\chi^2} = \frac{(1+3N)}{(1+2N)} \left\{ \frac{2N}{\rho Q^2} \sigma_1(R) + p_{22}(R,L) \right\}
\]

where \( \sigma_1(R) \) has been substituted for \( G(R) \) from 2.12.

There have been no measurements of \( p_{22}(R,L) \) reported for polymer melts so it is not known whether 2.15 is valid. Since \( B \) is approximately \( 2N \), 2.15 would be satisfied if \( p_{22}(R,L) \sim 0.5\sigma_1(R) \). These values of \( p_{22}(R,L) \) would be small and difficult to measure experimentally, particularly in polymer melts.

Sakiadis (1962) measured \( p_{22}(R,z) \) for some polymer solutions and found by extrapolation that \( p_{22}(R,L) \) is not zero. Assuming 2.4 and 2.8 Sakiadis applied a momentum balance to the jet which enabled him to calculate \( \sigma_1 \) and \( \sigma_2 \) from \( R_j \) and \( p_{22}(R,L) \). He found that \( \sigma_2 \) is much larger than \( \sigma_1 \) contrary to all published data (table 2.2).

For a Newtonian fluid 2.13 predicts that the jet will contract by 13.4%. Metzner et al (1961) found this was so with ethanol and water, they then calculated \( \sigma_1 \) from 2.10 for some polyisobutylene and carboxymethylecellulose solutions. The values obtained were consistent with results obtained by other methods and were independent of tube diameter. Apparently the method gave sensible results in these experiments which were carried out at high Reynolds numbers.

However Middleman & Gavis (1961a) and Goren & Wranski (1966) reported die swell in Newtonian fluids of the order of 10% at Reynolds numbers less than 20. At high Reynolds numbers (>150) the jets tended to contract by 13.4%. These results could be consistent with 2.15 for a Newtonian fluid \((N=1, \sigma_1(R)=0)\);
The unusual results reported by Sakiadis and the calculations with polymer melts strongly suggest that we cannot in general assume that $p_{11}(0,L)$ is zero. Lodge (1964) also maintains that this assumption is not valid. However at high Reynolds numbers (>150) it seems to give sensible results and be valid under these conditions.

Finally it has been assumed that flow is fully developed up to the exit plane (equation 2.4). This may be so at high Reynolds numbers when the jet diameter changes slowly and reaches its final diameter some distance from the tube exit (Middleman 1964). But at low Reynolds numbers the final jet diameter is reached much nearer to the tube exit (Middleman & Gavis 1961a, Middleman 1964).

Middleman & Gavis (1961a) suggest the relaxation of the velocity profile in the tube could give rise to die swell in Newtonian fluids. But they were unable to take this into account and predict the shape or final diameter of the extrudate. If profile relaxation starts in the tube prior to the exit then for elastic fluids time effects would also have to be considered (Gavis & Middleman 1963). This further complicates any subsequent analysis.

The momentum balance analysis does not seem to offer much hope of developing a theory of die swell. It is possibly valid at high Reynolds numbers, but the Reynolds number relevant to polymer melts is <<1 and it is irrelevant here. Some other method not based on inertia is likely to be more appropriate to the behaviour of low speed high viscosity fluids.

The theories discussed so far do not even permit the correct
prediction of the die swell of a Newtonian fluid. There have been two recent attempts to solve this problem.

Goren & Wronski (1966) applied a perturbation technique for large axial distances from the exit and a boundary layer method near the exit. This is an approximate method and may be valid at high Reynolds numbers where the jet decays to its final diameter some distance from its exit, but it is not appropriate to the slow flow of highly viscous fluids.

A more rigorous analysis has been given by Duda & Vrentas (1967) who used a 'Protean' co-ordinate system. In this the co-ordinate lines change shape in a manner determined by the change of extrudate dimensions. Stokes' stream function (Milne-Thompson 1960) is used as the independent variable in the radial direction and thus the free surface is defined. The theory gives a number of non-linear differential equations which must be solved subject to satisfactory boundary conditions. Solutions for high Reynolds numbers, where the equations are simplified by use of boundary layer theory, have been obtained and measurements of the jet shape are in good agreement with calculations. The more general case, where the equations are very complex, has yet to be solved.

There is no satisfactory method for calculating the shape and final diameter of low speed extrudates of any fluid. The problem is to determine the position of a free boundary, and even for a Newtonian liquid this involves the solution of a number of non-linear differential equations. One point which does not seem to have been sufficiently recognised in the literature is the discontinuity on the boundary at the exit. Inside the tube the velocity on the wall is zero, but outside the free surface has a finite velocity. There does not appear to be any convenient technique for analysing this
discontinuity.

Although the problem of die swell in Newtonian fluids is at the moment unsolved, a solution should be possible by a numerical method. Obviously this is a necessary first step before we can hope to understand the behaviour of extrudates of elastic liquids.
FIGURE 3.1 Cone-plate geometry - Spherical polar co-ordinate system
3.1 Introduction

We have seen that for isotropic, incompressible fluids in steady shear flow there are only three stress quantities of rheological interest; \( p_{21} \) (= \( p_{12} \)), \( \sigma_1 \) and \( \sigma_2 \). The techniques for measuring the tangential stress \( p_{21} \) are straightforward and well known (Wilkinson 1960). The measurements of the normal stress differences \( \sigma_1 \) and \( \sigma_2 \) are more difficult and numerous methods have been suggested; the more common techniques have been reviewed by Lodge (1964) and White & Metzner (1962) and are summarised in chapter 2.

In the present work \( p_{21} \) was evaluated from torque, and the normal stress differences from thrust measurements in a cone-plate or parallel plate rheometer. The main objective was to determine whether \( \sigma_2 \) differed significantly from zero, the value predicted by a number of rheological equations of state (Markovitz 1957). Some of the results reported in this chapter have been published elsewhere (Berry & Batchelor 1968).

3.2 Theory

The methods are based on the assumptions given in chapter 1 (section 1.3).

(i) Cone-plate rheometer

Here we consider a cone of radius \( R \) rotating about its axis, which is vertical, with a constant angular velocity \( \Omega \). The cone apex is in contact with a horizontal, stationary plate and fills the gap between the cone and plate.

We can define a spherical polar co-ordinate system \( \phi, \theta, r \) with the origin at the cone apex (figure 3.1). The cone surface is
defined by $\theta = (\pi/2 - \theta_0)$, the plate by $\theta=\pi/2$ and the axis of rotation by $\theta=0$. Thus the angle between the cone and plate is $\theta_0$. The radial co-ordinate is $r$ and $\phi$ is orthogonal to $r$ and $\theta$. $\phi$, $\theta$ and $r$ are equivalent to $\xi_1$, $\xi_2$ and $\xi_3$ respectively.

We assume that the velocity components take the form

$$\begin{align*}
v_\theta &= v_r = 0 \\
v_\phi &= r\omega(\theta) \sin \theta
\end{align*}$$

3.1

where $\omega$ is the angular velocity of the fluid at a point. Equation 3.1 satisfies the requirements that the flow is steady shear (equation 1.4). The shearing surfaces are rigid cones, $\theta = \text{constant}$, rotating with angular velocity $\omega$. The only non-zero components of the rate of strain tensor (Middleman 1968) are

$$\begin{align*}
\dot{e}_{\phi\theta} &= \dot{e}_{\theta\phi} = \sin \theta \frac{\partial}{r} \left( \frac{v_\phi}{\sin \theta} \right)
\end{align*}$$

3.2

From 1.5, 3.1 and 3.2, we obtain for the shear rate

$$G = \sin \theta \frac{d\omega}{d\theta}$$

3.3

i.e. $G$ is independent of $r$

Since the flow is symmetrical about the axis of rotation all derivatives with respect to $\phi$ are zero. Neglecting inertia and body forces the $r$-component of the momentum equation (Middleman 1968) reduces to

$$r \frac{dp_{33}}{dr} = p_{11} + p_{22} - 2p_{33}$$

3.4

$(p_{22} - p_{33})$ is independent of $r$ from 3.3, thus $dp_{33}/dr = dp_{22}/dr$ and integrating 3.4 we obtain

$$p_{22}(r) = p_{22}(R) + (p_{11} + p_{22} - 2p_{33}) \ln(r/R)$$

3.5

The total thrust $T$ on the plate is

$$T = -2\pi \int_0^R r p_{22}(r) dr - \pi R^2 p_a$$

3.6
FIGURE 3.2 Parallel plate geometry - Cylindrical polar co-ordinate system.
where $p_a$ is atmospheric pressure. Substituting for $p_{22}(r)$ from 3.5, we obtain

$$T = -\pi R^2 \left[ p_{33}(R) + p_a \right] + \frac{1}{2} \pi R^2 \sigma_1$$

where $\sigma_1$ has been written for $(p_{11} - p_{22})$. If the free surface of the fluid is part of a sphere with centre at the origin and radius $R$, then

$$p_{33}(R) + p_a = 0$$

and it follows that (Lodge 1964, Jobling & Roberts 1959)

$$\sigma_1 = \left( \frac{2T}{\pi R^2} \right)$$

Similarly $p_{21}$ can be evaluated from the torque $M$ on the plate.

$$M = 2\pi \int_0^R r^2 p_{21} \, dr$$

But $p_{21}$ is independent of $r$ from 3.3, thus

$$p_{21} = \left( \frac{3M}{2\pi R^3} \right)$$

The shear rate is usually calculated from an approximation to 3.3 given by

$$G = \frac{\Omega}{\theta_o}$$

Adams & Lodge (1964) and Walters & Waters (1968) have shown that for small values of $\theta_o$ (<10°), the error in using 3.12 to calculate the shear rate is negligible. The use of equation 3.12 is therefore justified. Thus to a good approximation the shear rate in a cone-plate rheometer is constant.

(ii) Parallel plate rheometer

In this geometry the fluid fills the gap between two concentric horizontal plates of radius $R$. One plate is stationary and the other rotates with constant angular velocity $\Omega$, the axis of rotation passes through the centre of the plates.

We can define a cylindrical polar system $r, z, \theta$ where the origin is at the centre of the lower plate (figure 3.2). The radial
co-ordinate is $r$, the vertical co-ordinate is $z$ and $\theta$ is orthogonal to $r$ and $z$. The surface of the top plate is given by $z = h$, where $h$ is the plate separation. $\theta$, $z$, $r$ are equivalent to $\xi_1$, $\xi_2$ and $\xi_3$ respectively.

We assume that the velocity components take the form

$$
\begin{align*}
\frac{\partial v_z}{\partial z} = v_r &= 0 \\
v_\theta &= \Omega r z/h
\end{align*}
$$

3.13

The only non-zero components of the rate of strain tensor are (Middleman 1968)

$$
\dot{\epsilon}_{\theta z} = \dot{\epsilon}_{z \theta} = \frac{3 v_\theta}{\partial z}
$$

3.14

From 1.5, 3.13 and 3.14, it follows that

$$
G = \frac{\Omega r}{h}
$$

3.15

Because of the symmetry about the axis of rotation we can neglect derivatives with respect to $\theta$. Neglecting inertia and body forces the $r$-component of the equations of motion (Middleman 1968) becomes

$$
\frac{r dp_{33}}{dr} = P_{11} - P_{33}
$$

3.16

Integrating

$$
P_{22}(r) = P_{33}(R) - \int_r^R \left( P_{11} - P_{33} \right) dr + \left( P_{22} - P_{33} \right)
$$

3.17

The total thrust $T$ on the plate is

$$
T = 2\pi \int_0^R r p_{22}(r) \, dr - \pi R^2 p_a
$$

3.18

Substituting for $p_{22}(r)$ from 3.17, we obtain
\[ T = \frac{2\pi}{r} \int_0^R \int_0^r \frac{\sigma_1(r)}{r} \, dr \, dr + \frac{2\pi}{r} \int_0^R \int_0^r \frac{\sigma_2(r)}{r} \, dr \, dr \]  

3.19

\[ R \]

\[ - \frac{2\pi}{r} \int_0^R r \sigma_2(r) \, dr - \pi R^2 \left[ p_{33}(R) + p_a \right] \]

3.20

where \((p_{11} - p_{22})\) and \((p_{22} - p_{33})\) have been replaced by \(\sigma_1\) and \(\sigma_2\).

Integrating by parts

\[ T = \int_0^R \pi \left\{ \sigma_1(r) - \sigma_2(r) \right\} r \, dr - \pi R^2 \left[ p_{33}(R) + p_a \right] \]

3.20

If the free surface of the fluid is part of a cylinder with centre at the origin and radius \(R\), then

\[ p_{33}(R) + p_a = 0 \]

3.21

Changing variable to \(G\) through 3.15 and differentiating 3.20 with respect to \(G(R)\), it follows that

\[ \sigma_1(R) - \sigma_2(R) = \frac{(2 + m')}{2} \left( \frac{2T}{\pi R^2} \right) \]

3.22

where

\[ m' = \frac{d \ln \left( \frac{2T}{\pi R^2} \right)}{d \ln G(R)} \]

3.23

and \(G(R)\), the shear rate at the edge of the plate, is

\[ G(R) = \Omega \, R/h \]

3.24

Equation 3.22 was derived originally by Kotaka, Kurata & Tamura (1959).

Similarly \(p_{21}\) can be obtained from the torque \(M\) on the plate as follows

\[ M = \int_0^R 2\pi r^2 p_{21}(r) \, dr \]

3.25
FIGURE 3.3 Block diagram of Weissenberg Rheogoniometer
FIGURE 3.4 Weissenberg Rheogoniometer
Changing variable to \( \alpha \) through \( 3.15 \) and differentiating with respect to \( \alpha (R) \), we obtain

\[
p_{21}(R) = \frac{(n'+3)}{3} \left( \frac{3M}{2\pi R^3} \right)
\]

where

\[
n' = \frac{d\ln \left( \frac{3M}{2\pi R^3} \right)}{d\ln \alpha (R)}
\]

From the total thrusts in the two geometries we can therefore calculate \( \alpha_1 \) and \( \alpha_2 \) as functions of \( \alpha \) (3.9 and 3.22). The torque data can be used to calculate \( p_{21} \) from 3.11 and 3.26, and so provides an internal check on the consistency of these techniques.

Two methods have been proposed for evaluating \( \alpha_2 \) from total thrust measurements in the cone and plate geometry only. Pollett (1955) suggested measuring the total thrust in the plate and on an annular guard ring, but this would be difficult experimentally. Jackson & Kaye (1967) evaluated \( \alpha_2 \) from the thrust data when the cone apex is a finite distance from the plate. The results must be extrapolated to obtain \( \alpha_2 \), requiring a great deal of data and the method is impractical. In both cases \( \alpha_1 \) was calculated according to 3.9.

3.3 Description of Apparatus

The experiments were carried out on a Weissenberg Rheogoniometer (Model R16) manufactured by Sangamo Control Ltd. (Bognor Regis). King (1964) has given a detailed description of this particular model and we will only outline the main features here.

A block diagram of the apparatus is shown in figure 3.3 and a photograph of the main part in figure 3.4. Only the motor, gearbox and associated electronic equipment have been omitted from figure 3.4. The bottom platen (1) is rotated at a synchronously controlled speed
from the motor and gearbox. The platen speed can be varied in 60 logarithmic steps from $4.74 \times 10^{-4}$ to $3.75 \times 10^2$ rev/min. The sample (2) fills the gap between the platens.

The torque developed is measured on the top platen (3) by means of a torsion bar (4). The measuring system incorporates an air bearing (5) which gives virtually frictionless angular rotation but vertical location. The top of the bar is clamped rigidly and the complete torsion head assembly (4 and 5) is mounted on the main column of the apparatus, and can be moved vertically. The rotation of the torque bar is measured by a linear transducer (6), the armature of which is bolted to a 10 cm radius arm (7) clamped to the bottom of the torque bar. The output from the transducer is fed into a transducer meter (8) and the deflection recorded on a strip recorder. The maximum angular deflection of the torsion bar is only 0.025 rad, and the use of a linear transducer to measure this is justified. Three standard bars are available giving a range of torques from approximately $10^3$ dyn cm to $2 \times 10^8$ dyn cm. The thrust generated forces the bottom platen down against the spring (9). A flexible diaphragm transmits the drive to the bottom platen but permits small vertical movements of the shaft (10). The displacement of the spring which results is detected by a transducer (11) mounted directly under the ball end of the shaft. However, if the bottom platen does move down, the shearing conditions in the sample will be altered. To overcome this the apparatus incorporates a null point servo system proposed originally by Lammiman & Roberts (1961). The signal from the transducer (11) is fed into the bridge (12) and the output is taken into a servo amplifier (13). The signal from the servo amplifier drives a servo motor (14). This servo motor, which is coupled to a micrometer (15) mounted at the free end of the spring, positions the free end of the spring to give zero deflection on the servo transducer. This technique ensures that the
required shearing conditions are maintained. The thrust can be evaluated from the displacement of the free end of the spring. This displacement is measured by a transducer (16) mounted under the micrometer and bridge (17), and the deflection is recorded on a strip recorder. The range of thrusts which can be measured with this servo system is from about $1.5 \times 10^4$ to $1.5 \times 10^8$ dyn.

In the original design the sample was controlled by an electrically heated chamber which completely surrounds the platens (18 in figure 3.4). This chamber is in two halves, each containing two heater elements embedded in an aluminium block. The total power in each block is 400 watts. The control thermocouple is embedded in one of the aluminium blocks. Originally the heaters were connected in parallel and the full power of 800 watts was switched on or off by the control system. This was unsatisfactory and the heater circuit was modified to include a series-parallel switch. In practice the heaters were connected in parallel to bring the platens to the required temperature and in series when this was attained. In spite of this modification the variation at 160°C was ± 2°C. In experiments below 40°C the heater chamber was replaced by a double walled Perspex chamber of similar shape and size. Water was pumped through the chamber from a thermostatic tank and the platen temperature could be kept constant to within 0.25°C.

The temperature is measured by a thermocouple embedded in the top platen. The system supplied was insensitive and replaced by a Scalamp Thermocouple Galvanometer (Pye Ltd.) using a copper/constantan thermocouple and an automatic compensated cold junction. The thermocouples were all calibrated against an N.P.L. calibrated thermometer.
FIGURE 3.5  Check for concentricity on bottom platen

FIGURE 3.6  Check for squareness on top platen
3.4 Method of Alignment

To achieve the assumed state of flow the platen surfaces must be perpendicular to the axis of rotation and concentric. Furthermore in cone and plate experiments the tip of the cone must just touch the surface of the plate. In practice friction between the cone tip and the plate would interfere with the measurements and is avoided by slightly truncating the cones. We must therefore ensure that the cone apex just touches the plate. Similarly in parallel plate experiments the gap must be set precisely to give the required separation.

The concentricity of the bottom platen is checked with a dial gauge in contact with the outside edge of the platen (figure 3.5). The three adjusting screws are altered until the total movement as the platen rotates is within the desired limits. Similarly we can check that the platen is perpendicular to the axis of rotation with the dial gauge in contact with the platen face near the edge. Any errors can then be corrected by the tilt screws.

The squareness of the top platen is checked and adjusted with the arrangement shown in figure 3.6. The gauge is in contact with the platen surface and the bottom platen is rotated. There is no means of correcting errors in concentricity; the main column and torsion head assembly have been preset in the factory. However we can check the accuracy of this alignment in a similar way using the dial gauge in contact with the platen edge.

The correct separation between the platens is obtained by winding the torsion head assembly (4 and 5) down until the platens are just in contact. This is indicated by a small thrust reading on the servo transducer meter. The vertical position of the top platen is given by a transducer clamped to the main column. Using this
### TABLE 3.1

<table>
<thead>
<tr>
<th>Name</th>
<th>Polymer type</th>
<th>Test temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigidex 50</td>
<td>polyethylene</td>
<td>160</td>
</tr>
<tr>
<td>Vistanex LM-MH</td>
<td>polyisobutylene</td>
<td>29.25</td>
</tr>
<tr>
<td>Vistanex LM-MS</td>
<td>polyisobutylene</td>
<td>29.25</td>
</tr>
<tr>
<td>Lorival R25</td>
<td>depolymerised natural rubber</td>
<td>23.5</td>
</tr>
</tbody>
</table>
transducer the top platen can subsequently be positioned to give the correct separation between the platens. The gap is adjusted at the test temperature.

3.5 Experimental Procedure

The materials used in the present investigation are given in table 3.1. Rigidex 50 is a typical commercial high density polyethylene which is fluid at elevated temperatures. Because of poor temperature control and possibilities of thermal degradation under these conditions it was only used in some initial checks on the apparatus. The other polymers in table 3.1 are more convenient materials to study since experiments could be carried out at or near to ambient temperatures. The polyisobutylene and Lorival R25 were therefore studied in much greater detail.

Samples of Rigidex 50 were prepared by compression moulding discs 5 cm in diameter and 0.1 cm thick. The disc was then simply inserted between the test platens. The preparation of the other samples was more difficult. A disc of material was cast in a metal ring mould on silicone impregnated paper, and allowed to degas at room temperature for several days before use. The sample was then placed in the test chamber and the release paper peeled off.

After the sample was inserted the gap was closed to the correct separation and brought to the test temperature. Any excess material was removed with a spatula. Stresses introduced into the material during the filling operation were allowed to relax before experiments commenced. With Rigidex 50 experiments were started within 15 minutes of inserting the sample between the platens, and stopped after approximately 60 minutes to avoid errors due to heat degradation. The polyisobutylene and Lorival R25 were left to relax overnight and there was no necessity to complete the experiments...
**TABLE 3.2**

**Cone dimensions**

<table>
<thead>
<tr>
<th>$\theta_0$ (deg)</th>
<th>Truncation (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Loughborough</td>
</tr>
<tr>
<td></td>
<td>Loughborough</td>
</tr>
<tr>
<td>1.92</td>
<td>0.0079</td>
</tr>
<tr>
<td>3.96</td>
<td>0.0160</td>
</tr>
<tr>
<td>6.02</td>
<td>0.0295</td>
</tr>
</tbody>
</table>
Measurements were carried out in each sense of rotation at any particular angular velocity and the mean of the force readings calculated.

The dimensions of the platens used were measured at Loughborough University (Department of Industrial Engineering & Management). The results for the cones are shown in table 3.2 with the values quoted by the manufacturer.

The cone angles are all within 0.03° of the manufacturer's specification, but there is a marked discrepancy in the values found for the truncation. At Loughborough two different techniques were used to measure the truncation and the agreement between them was good. Thus it would appear that the manufacturer's values for the gap setting are incorrect.

The plates used were flat to within ±0.00025 cm, and the diameter of all platens used was 5 cm.

The majority of experiments were carried out using the truncation specified by the manufacturer. Errors due to this incorrect gap setting will be discussed later.

3.6 Experimental Errors

There are several possible sources of error which can arise in rotational viscometers:

(i) Inertial effects.

(ii) Temperature rise due to shear heating

(iii) Misalignment of platens

(iv) Incorrect gap setting

(v) Axial movement of rotating member

The effect of these errors on thrust and torque data is
is discussed below. In particular (i), (iii), (iv) and (v) will affect normal stress measurements (Adams & Lodge 1964).

(i) Inertial effects

In the theory presented in section 3.2 inertial effects were neglected. In cone-plate and parallel plate experiments inertia will produce a slow circulatory flow radially out on the moving platen and towards the axis on the fixed platen. A pressure gradient will also be developed radially on the platens. Thus the assumed velocity distributions (equations 3.1 and 3.13) will be incorrect and the expressions for calculating the stresses may be in error. To determine if inertial effects are significant we need only make an approximate analysis; ignoring the circulatory flow and calculating the pressure distribution for a Newtonian fluid. The analysis is analogous to the method used by Greensmith & Rivlin (1953).

If the inertial terms are retained, then for the parallel plate geometry the r-component of the equations of motion becomes for a Newtonian fluid (Aris 1962).

\[ \frac{dp_{33}}{dr} = - \frac{\rho v_\theta^2}{r} \]  \hspace{1cm} 3.28

where \( \rho \) is the fluid density. If we replace the inertial term \( (\rho v_\theta^2/r) \) at each point by the value averaged over the gap at constant \( r \), then from 3.13 and 3.28 it follows that

\[ \frac{dp_{33}}{dr} = - \frac{\rho \Omega^2 r}{3} \]  \hspace{1cm} 3.29

Integrating

\[ p_{33}(r) = p_{33}(R) - \frac{\rho \Omega^2}{6} [r^2 - R^2] \]  \hspace{1cm} 3.30
FIGURE 3.7 Effect of gap setting in parallel plate experiments - Vistanex LM-MH, 29.25°C. Top - thrust; bottom - torque.

G(R) sec⁻¹

○ 0.0906
△ 0.0572
□ 0.0287
The total thrust on the plate $T^1$ due to inertia is

$$T^1 = - \int_0^R 2\pi r p_{22}(r) + \pi R^2 p_a$$  \hspace{1cm} 3.31

but $p_{22} = p_{33}$ for a Newtonian fluid, thus from 3.21, 3.30 and 3.31 we obtain

$$T^1 = - \rho \frac{\Omega^2 R^4}{12}$$  \hspace{1cm} 3.32

i.e. a negative thrust is generated.

Similarly equation 3.32 can be shown to apply to the cone-plate system if the inertial forces are averaged with respect to gap angle $\theta$ at constant $r$.

The thrusts due to inertia calculated from 3.32 in the present experiments will be $< 0.5$ dyn. This is negligible compared with the thrusts due to normal stresses and can be neglected.

Furthermore in parallel plate experiments the thrust at constant $G(R)$ will depend on gap setting $(h)$ if inertia is significant.

Some thrust and torque results obtained with Vistanex LM-MH at 29.25°C using three different gap settings (0.136, 0.108 and 0.0861 cm) are shown in figure 3.7. Two independent samples were studied at gap settings of 0.136 and 0.108 cm and the mean value at each shear rate is reported. Only one sample was studied at the other gap setting. Figure 3.7 indicates that the results are independent of gap setting. Student's $t$-test (Brownlee 1949) was applied to all the data and confirmed that there was no significant difference between the results at the various gap settings and we can assume that inertial effects are negligible.
TABLE 3.3

Temperature rise due to shear heating

<table>
<thead>
<tr>
<th>Material</th>
<th>G (Sec(^{-1}))</th>
<th>ΔT (°C/Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vistanex LM-MH</td>
<td>0.229</td>
<td>1.55 × 10(^{-3})</td>
</tr>
<tr>
<td>Lorival R25</td>
<td>0.229</td>
<td>1.44 × 10(^{-4})</td>
</tr>
<tr>
<td>Rigidex 50</td>
<td>0.572</td>
<td>7.22 × 10(^{-4})</td>
</tr>
</tbody>
</table>
The neglect of inertial terms in the theory given in section 3.2 is therefore justified. However they may be significant in low viscosity fluids at high speeds of rotation.

(ii) Temperature rise due to shear heating

Viscous flow is a dissipative process and energy will be converted into heat. This will result in a temperature rise in the sample which might produce errors in the measurements. To calculate the approximate temperature rise due to shear heating we will assume that there is no heat loss from the sample. Clearly this will overestimate shear heating effects since there will be some heat loss. However it will indicate if shear heating is likely to be significant.

The temperature rise per sec of shearing (\( \Delta T \)) is given by:

\[
\Delta T = \frac{p_{21} G}{\rho C_p}
\]

where \( C_p \) is the specific heat of the polymer melt.

Typical results for the materials used in the present experiments are given in table 3.3 for the highest shear rate likely to be encountered. The specific heat and density of the polymers were obtained from Brandrup & Immergut (1966).

In practice the rise will be much smaller than shown in table 3.3 but the results do show that shear heating effects are small and can be neglected.

(iii) Misalignment of the platens

The platens must be perpendicular to the axis of rotation and concentric if the assumed state of flow is to be maintained. If the platens are not parallel convergent flow is produced in one half of the gap and divergent flow in the other half. This would give
rise to a pressure distribution on the plate even for Newtonian fluids, but the total thrust would be zero (Adams & Lodge 1964). The situation with elastic fluids is probably more complicated because of relaxation effects. Blyler & Kurtz (1967) have shown that when the platens are not concentric the deformation produced is oscillatory. Thus errors in alignment could effect the measurements.

The manufacturer claims that the maximum tilt between the platens during rotation should be <0.0002 rad, and the maximum concentricity error, as measured by method given earlier, should be <0.0025 cm of total movement on each platen. A tedious trial and error procedure is normally required to adjust the platens to within these limits.

The effect of small alignment errors was investigated by offsetting the tilt and concentricity in a series of experiments with Rigidex 50. Results were obtained at the correct setting (manufacturer's specification), with the maximum tilt between the platens set at 0.0009 rad and with a maximum concentricity error of 0.018 cm (equivalent to 0.009 cm total movement on each platen). Student's t-test was applied to the data and indicated no significant effect due to misalignment. It is straightforward to adjust the platens so that the concentricity error is less than 0.005 cm on each platen and the maximum tilt is 0.0004 rad. These errors are not significant and this accuracy of alignment was subsequently adopted.

(iv) Errors in gap setting

The gap between the platens can be adjusted to within 1% of the required value and errors of this magnitude are unlikely to affect the measurements. However most of the cone-plate data were
obtained using the separation specified by the manufacturer which we have seen is incorrect. To establish if this affected the results, the gap was varied in a series of experiments using the cone giving a gap angle of 3.93°.

Experiments were carried out with a Vistanex LM-MS at 29.25°C using four different gap settings from 0.0208 to 0.0132 cm. This variation in gap setting is greater than the errors indicated in table 3.2 for all the cones. The same sample was used throughout and the cone lowered by about 0.025 cm at the end of each series of experiments.

The sets of data were compared in turn with the data obtained at a gap setting of 0.0160 cm, the correct setting according to measurements carried out at Loughborough University. Student's t-test showed, with one exception, that there was no significant effect due to gap setting. The exception was the P_{21} data for 0.0132 cm; this was significantly higher. However P_{21} was <5% higher in this case and no other experiments have been carried out at this gap setting. The σ_{1} data for this gap setting are in good agreement.

Thus it seems that errors due to incorrect gap setting are negligible. All other cone-plate results were obtained using the gap setting specified by the manufacturer and the results will not be affected.

(v) Axial movement of rotating shaft

The deflection of the normal force spring, and hence the bottom platen, was monitored as the platen rotated without a sample. There was some evidence of a small periodic axial movement of the shaft. The amplitude of this axial displacement was ~ 10^{-6} cm and occurred twice a revolution.
Any axial movement of the shaft will produce a periodic component of flow in the radial direction and hence a periodic pressure will be exerted on the bottom platen. To determine whether such pressures would influence the measurements we can make an approximate calculation assuming a Newtonian fluid.

If the platens are separating at a velocity $u$, then continuity requires that

$$\pi r^2 u = \int_0^h 2\pi \nu r \, dz$$

3.34

Since $h \ll R$, it is reasonable to assume that the distribution of $\nu_r$ across the gap, is the same as would be obtained for the flow of a Newtonian fluid in an infinitely wide parallel slit, i.e. $\nu_r$ is a parabolic function of $z$. Thus from 3.34 and the equations of motion for a Newtonian fluid (Aris 1962) it follows that

$$\frac{\partial p_{22}}{\partial r} = -\frac{6\eta u r}{h^3}$$

3.35

Integrating

$$p_{22}(r) = p_{22}(R) + \frac{3\eta u}{h^3} \left( R^2 - r^2 \right)$$

3.36

Thus the total thrust on the plate $T_{ax}$ is

$$T_{ax} = -\frac{3\pi \eta u R^4}{2h^3}$$

3.37

Similarly for the cone-plate geometry with a small gap angle, we can assume that equation 3.35 is valid. Substituting for $h = R_0$

in 3.35, we find

$$\frac{\partial p_{22}}{\partial r} = -\frac{6\eta u}{r^2 R_0^3}$$

3.38
### TABLE 3.4

**Thrusts due to axial movement**

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$\theta_o$ or $h$</th>
<th>Maximum $T_{ax}$ (dyn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cone-plate</td>
<td>1.92°</td>
<td>4918</td>
</tr>
<tr>
<td>cone-plate</td>
<td>3.93°</td>
<td>573</td>
</tr>
<tr>
<td>cone-plate</td>
<td>6.0°</td>
<td>161</td>
</tr>
<tr>
<td>parallel plate</td>
<td>0.0861 cm</td>
<td>1130</td>
</tr>
<tr>
<td>parallel plate</td>
<td>0.108 cm</td>
<td>574</td>
</tr>
<tr>
<td>parallel plate</td>
<td>0.136 cm</td>
<td>287</td>
</tr>
</tbody>
</table>
and the thrust on the plate is

$$ T_{\text{ax}} = -\frac{6\pi \eta u R}{\omega^3} \quad 3.39 $$

To estimate the order of magnitude of $T_{\text{ax}}$ we will treat the axial movement independently of any flow due to rotation. This is justified since we only wish to see if small axial movements could produce large thrusts with high viscosity fluids.

Let us assume that $u$ is a result of a sinusoidal axial movement of amplitude $\Delta h$ occurring twice every revolution. The maximum value of $u$ will be $2\Delta h$. The maximum thrusts have been calculated using values relevant to the present apparatus; $\Delta h = 10^{-6}$ cm, $\Omega = 0.0375$ rev/min and $\eta = 5 \times 10^5$ poise. The results calculated from equations 3.37 and 3.39 are shown in table 3.4 for the geometries used in the present study.

Table 3.4 indicates that thrusts developed as a result of any axial movement will only be significant with the smallest gap angle ($1.92^\circ$). In all other cases these thrusts will be less than the variation in the thrust during an experiment. The difficulties in obtaining reliable data with a gap angle of $1.92^\circ$ are discussed later.

3.7 Experimental Results

Of the materials described in table 3.1, only depolymerized natural rubber and the polyisobutlenes were studied in detail using the parallel plate and cone-plate geometries. Since the experimental details were slightly different for the three materials they will be discussed in turn.

The shear rate at the free boundary $G(R)$ in parallel plate experiments is determined by (a) the radius of the plates, (b) the
FIGURE 3.8 Lorival R25, 23.5°C - Parallel plate torque data.

- h (cm)
  - 0.102
  - 0.0762
  - 0.0635

--- 95% confidence limits
speed of rotation and (c) the spacing between the plates. In the present experiments only the last two were varied.

(i) Depolymerized Natural Rubber (Lorival R25)

The experiments were carried out at room temperature. Torque and thrust readings were obtained in each geometry as a function of the speed of rotation, with a platen temperature of 23.5 ± 0.5°C. For the cone-plate measurements the cone giving a gap angle of 3.93° was used and three independent samples were studied. The gap between the plates in the parallel plate measurements were set at 0.0635, 0.0762 and 0.102 cm in successive experiments. One sample was studied at the first setting and two at each of the other settings. The range of shear rate covered was about 0.02 to 0.3 sec⁻¹.

The parallel plate torque results are shown in figure 3.8, and we see that \((3M/2\pi R^3)\) is a function of \(G(R)\) only, as demanded by the theory. Each point in this figure is the mean value obtained at that peripheral shear rate. Using logarithmic coordinates a second order polynomial was fitted to the data by least squares, the curve (solid line) and 95% confidence limits (broken line) are shown in figure 3.8. Details and the technique for curve fitting and calculating confidence limits are discussed by Plackett (1960). The equation of the line is

\[
\log(3M/2\pi R^3) = 4.464 + 0.8218 \log G(R) - 0.03545 [\log G(R)]^2 \quad 3.40
\]

\(n'\) (equation 3.27) was evaluated from equation 3.40 by differentiation and \(p_{21}(R)\) calculated from 3.26. The value of \(p_{21}\) obtained as a function of shear rate is given by the solid line
FIGURE 3.9  Lorival R25, 23.5°C - Comparison of cone-plate and parallel plate

\[ \Delta \text{ cone plate} \quad \text{--- parallel plate} \]
FIGURE 3.10 Lorival R25, 23.5°C - Thrust data

\[ \frac{2T}{\pi R^2} \text{(dyn cm}^{-2}) \]

\[ \log_{10}(2T/\pi R^2) \]

\[ \log_{10}(G(R) \text{ (sec}^{-1}) \]

\[ h \text{ (cm)} \]

- □ 0.102
- ○ 0.0762
- △ 0.0635

---

95% confidence limits
FIGURE 3.11 Lorival R25, 23.5°C - Normal stress differences

- \( \sigma_1 \)
- \( (\sigma_1 - \sigma_2) \)
in figure 3.9. The points are the average value obtained at each shear rate in the cone-plate system, where $p_{21}$ was calculated from equation 3.11. The scatter of the parallel plate data is indicated by the confidence limits in figure 3.8. The 95% confidence limits of the cone-plate results expressed as a percentage of the mean values are between 6 and 9%. Thus, though there is some scatter the agreement between the 2 geometries is reasonable.

The thrust data from the parallel plate experiments show more scatter (figure 3.10) but $(2T/πR^2)$ depends only on $G(R)$. As before a second order polynomial was fitted to the data and the 95% confidence limits calculated. These are shown in figure 3.10 as solid and broken lines respectively. The equation of the line is

$$\log \left(\frac{2T}{\pi R^2}\right) = 4.609 + 1.534 \log G(R) + 0.1549 \left[\log G(R)\right]^2 \text{ 3.41}$$

Equation 3.41 was differentiated to give $m'$ (equation 3.23) and $(\sigma_1 - \sigma_2)$ was calculated from 3.22.

The dependence of $(\sigma_1 - \sigma_2)$ on shear rate is shown in figure 3.11, the scatter in the data is indicated by the confidence limits in figure 3.10. The mean values of $\sigma_1$, obtained in the cone-plate experiments are also given in figure 3.11, the scatter in this data is also large, the 95% confidence limits are ± 5 to 17% of the mean values.

The results indicate that $\sigma_2$ is negligible compared with $\sigma_1$, but there is a tendency for $\sigma_1$ to fall below $(\sigma_1 - \sigma_2)$ at lower shear rates. However, the scatter is large, the differences if real are small, and we cannot conclude that there is any significant difference between the results i.e. that $\sigma_2 \neq 0$. 

- 44 -
The results for \( \sigma_2 \) were not conclusive and clearly a more rigorous statistical experimental design was needed. Since thrust was found to be more sensitive to temperature variations than torque, we can attribute some of the scatter in figure 3.10 to poor temperature control under ambient conditions. The measurements with the polyisobutylenes were, therefore, carried out at 29.25°C which gave better temperature control (± 0.25°C). Since \( \sigma_2 \) is evaluated from the difference between thrust results obtained in cone-plate and parallel plate geometries, the data should be obtained at the same values of shear rate. This was achieved in the polyisobutylene experiments by adjusting the spacing in parallel plate experiments so that the peripheral shear rates corresponded to the cone-plate shear rate.

(ii) Vistanex LM-MH

For the parallel plate experiments three gap settings were used, 0.136, 0.108 and 0.0861 cm. Two independent samples were studied at the first two spacings and one sample at the third. For the cone-plate measurements the cone giving a gap angle of 3.93° was used and four independent samples were studied. The difference between the peripheral shear rates in the parallel plate system at the settings above and the cone-plate shear rates was <1%. The range of shear rates covered was 0.0181 to 0.228 sec\(^{-1}\).

The parallel plate data must be differentiated to give \((\sigma_1-\sigma_2)\) and \(p_{21}\) as functions of the shear rate, (equations 3.22, 3.23, 3.26 and 3.27) and since graphical techniques are unreliable a numerical method was used, movable strip differentiation (Hershey et al 1967). A low order polynomial is fitted to an odd number of points centred on the point required and the function differentiated
FIGURE 3.12  Vistanex LM-MH, 29.25°C - Comparison of cone-plate and parallel plate

- cone-plate
- parallel plate
analytically to give the slope. The 95% confidence limits are a convenient estimate of the error in the slope and these were also calculated. Each set of data was processed by this method. This technique is discussed in detail in Appendix A.

Good results were obtained using either the 5 or 7 point formula for both the thrust and torque data. The confidence limits on the 7 point formula were usually smaller, and the derivatives tended to be smoother, so these were used to calculate the slopes.

Second order polynomials gave an adequate fit to the log \( \log \frac{3M}{2 \pi R^3} \) versus log \( G(R) \) results over 7 points and these were used to calculate \( n' \), which decreased from about 0.9 to 0.6 as the shear rate increased and the 95% confidence limits were all <±0.1. An error of 0.1 in the slope only affects the calculated value of \( p_{21} \) by 3% and the use of this method to calculate \( n' \) is justified.

The mean values of \( p_{21} \) in the parallel plate geometry calculated from equation 3.26 are shown in figure 3.12 as a function of shear rate (solid line). The points in this figure are the mean values obtained from cone-plate measurements where \( p_{21} \) was calculated from 3.9. The agreement between the two geometries is excellent.

The log \( 2T/\pi R^2 \) - log \( G(R) \) results were adequately represented by linear plots over 7 points and these were used to estimate \( m' \) (equation 3.23). \( m' \) decreased from about 1.8 to 1.5 over the range of shear rates studied and the 95% confidence limits were all <±0.12. This error in \( m' \) would alter the calculated value of \( (\sigma_1-\sigma_2) \) by only 2% and was therefore neglected in the subsequent statistical analysis. Since the scatter in the original data is about ±10% we are justified in ignoring any error in \( m' \).
FIGURE 3.13 Vistanex LM-MH, 29.25°C - Normal stress differences

- \( \sigma_1 \)
- \( (\sigma_1 - \sigma_2) \)
### TABLE 3.5

**Vistanex LM-MH, 29.25°C. - Normal stress differences**

<table>
<thead>
<tr>
<th>G(sec(^{-1}))</th>
<th>Normal Stress Difference (\times 10^{-3}) dyn cm(^{-2})</th>
<th>(\sigma_2)</th>
<th>95% Confidence Limits (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\sigma_1)</td>
<td>((\sigma_1 - \sigma_2))</td>
<td>(\sigma_1)</td>
</tr>
<tr>
<td>0.0181</td>
<td>1.99</td>
<td>2.09</td>
<td>0.05</td>
</tr>
<tr>
<td>0.0228</td>
<td>2.94</td>
<td>3.25</td>
<td>0.105</td>
</tr>
<tr>
<td>0.0288</td>
<td>4.26</td>
<td>4.99</td>
<td>0.171</td>
</tr>
<tr>
<td>0.0362</td>
<td>6.49</td>
<td>7.20</td>
<td>0.109</td>
</tr>
<tr>
<td>0.0455</td>
<td>9.63</td>
<td>10.5</td>
<td>0.090</td>
</tr>
<tr>
<td>0.0572</td>
<td>13.9</td>
<td>16.2</td>
<td>0.165</td>
</tr>
<tr>
<td>0.0721</td>
<td>20.5</td>
<td>22.7</td>
<td>0.107</td>
</tr>
<tr>
<td>0.0908</td>
<td>28.2</td>
<td>33.8</td>
<td>0.199</td>
</tr>
<tr>
<td>0.114</td>
<td>39.1</td>
<td>46.9</td>
<td>0.199</td>
</tr>
<tr>
<td>0.144</td>
<td>56.1</td>
<td>67.7</td>
<td>0.207</td>
</tr>
<tr>
<td>0.181</td>
<td>77.4</td>
<td>94.7</td>
<td>0.224</td>
</tr>
<tr>
<td>0.228</td>
<td>109.0</td>
<td>131.0</td>
<td>0.297</td>
</tr>
</tbody>
</table>

\(^a\) Expressed as percentage of mean value

\(b\) Only 2 results
\( \sigma_1 - \sigma_2 \) was then calculated from equation 3.22.

\( \sigma_1 - \sigma_2 \) is shown in figure 3.13 as a function of shear rate with the value of \( \sigma_1 \) obtained from cone-plate measurements using equation 3.5. Each point in figure 3.13 is the mean value obtained at that particular shear rate. The data are also given in table 3.5 with their 95% confidence limits. Although there is some overlap in the confidence limits the cone-plate results are consistently lower than the parallel plate results which infers that \( \sigma_2 < 0 \). Students t-test was applied to the data shown in table 3.5 to see if the differences were real and the analysis indicated that the differences are statistically significant. We can, therefore, conclude that \( \sigma_2 \) is negative. Also we see from table 3.5 that the ratio \( \sigma_2/\sigma_1 \) increases as the shear rate increases.

Lodge (1964) showed that the assumed state of flow in the cone-plate geometry does not satisfy the equations of motion, but is compatible in parallel plate experiments. The results obtained for \( p_{21} \) in the two geometries were however consistent which suggests that the assumed flow in cone-plate experiments, (equation 3.1), is a reasonable approximation.

Walters & Waters (1968) showed theoretically that the equations of motion are satisfied if there is also a radial component of flow, called secondary flow. Giesekus (1965) showed that these secondary flows exists in practice. Since one platen is rotating the path of a fluid particle is helical and not circular as assumed in the earlier theoretical analysis.

Markovitz (1957), Jobling & Roberts (1959) and Adams & Lodge (1964) measured the pressure distribution developed on the plate with some polymer solutions using small gap angles \((< 4°)\).
TABLE 3.6

Typical thrust results with 1.92° gap - Vistanex LM-MS, 29.25°C.

<table>
<thead>
<tr>
<th>G (sec⁻¹)</th>
<th>Ω (rev/min)</th>
<th>Thrust x 10⁻⁵ (dyn)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Max</td>
</tr>
<tr>
<td>0.0589</td>
<td>0.0188</td>
<td>0.995</td>
</tr>
<tr>
<td>0.0933</td>
<td>0.0298</td>
<td>1.99</td>
</tr>
<tr>
<td>0.148</td>
<td>0.0474</td>
<td>3.83</td>
</tr>
</tbody>
</table>
Their results are consistent with equation 3.1. Apparently secondary flows were too weak to be detected in these experiments. Walters & Waters (1968) also showed that secondary flow is small in steady shear experiments with small gap angles and will depend on the cone angle.

Clearly some secondary flow is essential to satisfy the equations of motion but its effect appears to be small and depends on cone angle. Its effect was examined with Vistanex LM-MS at 29.25°C using three cones of varying gap angles; 1.92°, 3.93° and 6° (table 3.2).

(iii) Vistanex LM-MS

Three independent samples were studied for each cone over a range of shear rates. For the 3.93° and 6° experiments the stresses were calculated in the usual way from the mean of readings in each sense of rotation. The interpretation of results with the 1.92° gap was not straightforward. The torque readings were normal but the thrust readings showed a slow oscillation. The period of the oscillation was half of a revolution of the platen and its amplitude was significant (table 3.6).

We have seen that there is an inherent periodic axial movement of the rotating member in the instrument occurring twice every revolution, which could produce significant periodic thrusts for Newtonian fluids in small gap angles. The amplitudes of the oscillations shown in table 3.6 are of the same order as the estimated value for a Newtonian fluid of similar viscosity in the same geometry (table 3.4). We can, therefore, attribute the behaviour shown in table 3.6 to axial movement.

It was assumed that this oscillation was superimposed on the thrust developed in steady rotation. The values of σ₁ were
FIGURE 3.14 Vistanex LM-MS, 29.25°C - Effect of cone angle

\[ p_{21} \quad \sigma_1 \]

\[ \theta_0 \text{ (deg)} \]

- □ 6.0
- ○ 3.93
- △ 1.92
FIGURE 3.15 Vistanex LM-MS, 29.25°C - Comparison of cone-plate and parallel plate

- ○ cone-plate
- — parallel plate
FIGURE 3.16 Vistanex LM-MS, 29.25°C - Normal stress differences

- $\sigma_1$
- $(\sigma_1 - \sigma_2)$

Graph showing Normal Stress Difference (dyn cm$^{-2}$) vs. $G$ (sec$^{-1}$) with log-log scales.
TABLE 3.7

Vistanex LM-MS, 29.25°C. - Normal stress differences

<table>
<thead>
<tr>
<th>G (sec⁻¹)</th>
<th>Normal Stress Difference x 10⁻³ (dyn cm⁻²)</th>
<th>( \sigma_1 )</th>
<th>(( \sigma_1 - \sigma_2 ))</th>
<th>( \frac{\sigma_2}{\sigma_1} )</th>
<th>95% Confidence Limits ( a )</th>
<th>( \sigma_1 )</th>
<th>(( \sigma_1 - \sigma_2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0362</td>
<td>3.34</td>
<td>4.01</td>
<td>0.201</td>
<td>9.2</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0455</td>
<td>4.99</td>
<td>5.52</td>
<td>0.106</td>
<td>12.9</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0572</td>
<td>7.17</td>
<td>8.14</td>
<td>0.135</td>
<td>12.7</td>
<td>4.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0721</td>
<td>10.5</td>
<td>11.7</td>
<td>0.114</td>
<td>7.0</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0908</td>
<td>15.7</td>
<td>17.3</td>
<td>0.102</td>
<td>7.7</td>
<td>5.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.114</td>
<td>22.8</td>
<td>25.3</td>
<td>0.110</td>
<td>10.3</td>
<td>9.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.144</td>
<td>33.1</td>
<td>37.0</td>
<td>0.116</td>
<td>8.4</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.181</td>
<td>45.2</td>
<td>51.1</td>
<td>0.131</td>
<td>10.4</td>
<td>5.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.228</td>
<td>61.3</td>
<td>70.6</td>
<td>0.152</td>
<td>22.5</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Expressed as percentage of mean value
therefore calculated from the average of the maximum and minimum thrusts in each sense of rotation.

The results of the experiments with the different cones are shown in figure 3.14. In spite of the uncertain nature of the 1.92° results the agreement for both $\sigma_1$ and $p_{21}$ is good. It appears that secondary flow effects were negligible in these experiments and we were justified in using equations 3.9 and 3.11 to calculate $\sigma_1$ and $p_{21}$.

Parallel plate data was also obtained on Vistanex LM-MS at the gap settings used for Vistanex LM-MH. The test temperature was the same as in the cone-plate experiments (29.25°C). Two independent samples were studied at each gap setting and as before results were independent of gap setting.

The results were processed by the procedure used for Vistanex LM-MH. The values of $p_{21}$ obtained in the geometries are shown in figure 3.15. The line represents the mean values of the parallel plate data and each point the value obtained in the cone-plate using the 3.93° gap angle. The agreement between the two sets of data is excellent.

The normal stress differences ($\sigma_1-\sigma_2$) and $\sigma_1$ are shown in figure 3.16 where each point is the mean value at the shear rate. The data are also shown in table 3.7 with their 95% confidence limits. Students t-test was applied to the data and indicated that $\sigma_2 < 0$ consistent with the previous results on the higher viscosity Vistanex LM-MH. The ratio $\sigma_2/\sigma_1$ is lower in this case and does not seem to depend on the shear rate.

The cone-plate results shown in table 3.7 were obtained from fewer measurements than the parallel plate data, which explains the difference in the confidence limits.
FIGURE 3.17 Vistanex LM-MH, 29.25°C - Parallel plate boundary conditions at free surface
3.8 Discussion

In the theoretical analysis of these experiments we assumed that the shape of the free boundary is defined by the co-ordinate system. Thus, for the cone-plate geometry we assume that the free boundary is part of a sphere and in the parallel plate part of a cylinder. In practice this is not so, since surface tension effects produce a surface which is concave. The effect of this departure from ideal conditions was checked in a series of experiments using parallel plate geometry. The gap between the plates was altered so that the shape of the free boundary was convex, flat (ideal) and concave in turn (figure 3.17). Obviously the top two profiles are unstable and will tend to a concave profile in time, however some spot checks could be carried out with the boundaries shown in figure 3.17. The measured thrusts and torques did not depend on the shape of the boundary but only on G(R). The precise configuration of the free boundary is not therefore important.

Pollett and his co-workers (see Cooper, Khanna, & Pollett 1968) have reported that the continuous shearing of polymer melts resulted in rheological breakdown. The stresses did not reach a constant value but after passing through a maximum at about 10 strain units decayed rapidly with the applied strain, and in some cases fell to less than 50% of the maximum value.

No evidence was found of such gross change in the stresses with time under normal conditions. However, at shear rates above 0.3 sec\(^{-1}\) there was a fall in the stresses similar to that reported by Pollett, but this was always accompanied with a break up of the flow pattern at the edge; an effect also noted by Hutton (1963) who attributed this to a fracture mechanism. As this shear rate was
FIGURE 3.18 Vistanex LM-MS, 29.25°C - Viscosity and $\frac{\sigma_1}{G^2}$ as a function of $G$
approached measurements were made alternately at the high and at a low reference shear rate. The stresses at the reference shear rate only changed significantly when there was evidence of a disturbance in the flow pattern at the boundary. Possibly some of Pollett's results are due to this, certainly in an early paper (Pollett 1955) he mentions pushing the melt into the test chamber with a hot spatula!

Because of the uncertain boundary conditions which exist at the higher shear rates it is not possible to obtain reliable results. The present results are therefore limited to shear rates below 0.3 sec\(^{-1}\) and time dependent effects were not important.

The flow properties in steady shear flow are completely characterised by the three material functions \(\eta, \sigma_1\) and \(\sigma_2\). These functions have been evaluated from torque and thrust measurements in cone-plate and parallel plate geometries. The torque in the two geometries both give \(\eta\) and so provides a convenient check on the consistency of the method. The disadvantage of this technique is that \(\sigma_2\) was evaluated from the difference between two measured quantities of similar magnitude. Thus, we can only say that the polyisobutylene results indicate that \(\sigma_2\) differs significantly from zero, is negative and less than 30\% of \(\sigma_1\). The values of \(\sigma_2\) for Lorival R25 are less certain but not inconsistent with the polyisobutylene data.

For all three materials \(\sigma_1\) increased with shear rate faster than \(p_{21}\) and tended to vary linearly with \(G^2\) at low shear rates, while the viscosity \(\eta\) tended to a constant. This is indicated in figure 3.18 for Vistanex LM-MS and we also see that \(\eta\) and the quantity \((\sigma_1/G^2)\) decreased as the shear rate \(G\) increased. The other materials behaved similarly and the results are in agreement with
other published data on polymer melts (Benbow & Howells 1961, King 1966).

The results reported above will be compared with the predictions of a number of rheological equations of state in chapter 7.
4.1 Introduction

The transient responses of elastic fluids when shear flow is applied or removed provide a further check on the validity of the various rheological equations of state. Two techniques are usually considered; (i) a step stress function is applied and the strain measured as a function of time, e.g. shear recovery, or (ii) a step velocity function is applied and the stresses measured as a function of time, e.g. stress relaxation.

Attempts to determine the responses of two polymer melts to (ii) are described in this chapter. Some of the results reported here have been published elsewhere (Batchelor, Berry & Horsfall 1969). Later we will describe shear recovery measurements.

4.2 Theory

Assuming a rectangular Cartesian co-ordinate system \( x_1 \), \( x_2 \), \( x_3 \) (equivalent to \( \xi_1 \), \( \xi_2 \) and \( \xi_3 \) respectively), then we will consider the responses of the material to the following velocity distributions:

\[
\begin{align*}
v_1 &= Gx_2 [1 - H(t)] ; \\
v_2 &= v_3 = 0
\end{align*}
\]
\[ \tag{4.1} \]
\[
\begin{align*}
v_1 &= Gx_2 H(t) \\
v_2 &= v_3 = 0
\end{align*}
\]
\[ \tag{4.2} \]

Where \( G \) is the steady state shear rate, \( t \) is the time and \( H(t) \) is the Heaviside function defined by

\[
H(t) = \begin{cases} 
0 & t < 0 \\
1 & t \geq 0 
\end{cases}
\]  \[ \tag{4.3} \]

Thus 4.1 and 4.2 correspond to stress relaxation and stress growth experiments respectively.

For \( t \geq 0 \) the stresses will be denoted by \( p_{21}(t) \) and \( \sigma_1(t) \). Thus \( p_{21}(\infty) \) and \( \sigma_1(\infty) \) are the steady state stresses in growth experiments, and \( p_{21}(0) \) and \( \sigma_1(0) \) are the steady state
The cone-plate viscometer is a convenient apparatus for carrying out the experiments since the shear rate is constant throughout the sample and the conditions specified by equations 4.1 and 4.2 can, in principle, be achieved. The basic assumptions and theory of this instrument have been discussed previously (chapter 3).

4.3. Experimental Procedure

The experiments were carried out on the rheogoniometer described in the previous chapter. A cone-plate geometry giving a gap angle of 3.93° was used in all experiments. The diameter of the platens was 5 cm.

The experimental materials were the two polyisobutylenes described in the previous chapter (Vistanex LM-MH and Vistanex LM-MS) and a low conversion alkyd resin Paralac 385 (ICI Ltd., Dyestuffs Division). The polyisobutylene samples were prepared and inserted between the platens by the technique described in chapter 3. Paralac 385 was heated to about 90°C and simply poured onto the bottom platen.

The output signals from the torque and thrust transducers were passed through a filter network to remove high frequency noise, and then displayed on an ultraviolet recorder (SE 2005 S.E. Laboratories). There were a number of difficulties which occurred during the experiments, associated with:

(i) The drive system

(ii) Specification of the boundary conditions

(iii) The measurement of the relaxation and growth of $\sigma_i$

These affect both relaxation and growth experiments but we will only consider their influence on relaxation. Similar arguments will apply to growth measurements.
FIGURE 4.1 Drive-brake system in the rheogoniometer
FIGURE 4.2 Arrangement for determining spindle rotation
FIGURE 4.3 Normal rotation of switch
(i) **Drive system**

The drive is transmitted to the bottom platen through a clutch disc held in contact with the driving plate by an electromagnetic coil (figure 4.1). The brake is applied by a similar plate attached to the body of the apparatus. Brake or drive is obtained by energising the respective coil. The manufacturer claims that stopping and starting occurs in less than 10 ms.

Some preliminary measurements were made to check the operation of the brake-drive system using Vistanex LM-MH as the test material at 29.25°C. Only torque was recorded in these experiments.

The sample was deformed at a shear rate of about $10^{-2}$ sec$^{-1}$ until steady state conditions were attained. The brake was then applied and the torque recorded as a function of time. The relaxation traces were not reproducible under nominally the same conditions, and this seemed to be connected with the method of operating the brake-drive switch. Since no irregularity could be seen in the drive the brake-drive operation was examined electronically.

Relays were connected across the coils and set to operate the event marker on the ultraviolet recorder. This was to determine precisely when one coil energised and the other de-energised. The rotation of the spindle was monitored with the arrangement shown in figure 4.2, where the transducer body was clamped in a stand resting on the base of the rheogoniometer. The outputs from this transducer and the torque transducer were displayed simultaneously on the recorder. In this way we could determine what happened to the torque and rotation when the brake was applied.

When no special care was taken to operate the brake-drive rotary switch, the result shown in figure 4.3 was obtained. There
FIGURE 4.4 Very slow rotation of switch
FIGURE 4.5 Relaxation using toggle switch
was a time delay of 70 ms between disengaging the clutch and applying the brake. During this period the rate of rotation increased, consistent with the observed rise in torque. Obviously figure 4.3 does not represent relaxation from steady flow conditions.

There is a general tendency to use more care and turn the rotary switch slowly. The result of this is shown in figure 4.4. The interval when the bottom platen was neither driven nor braked increased and the effect on the torque was more severe. There was a dead spot when neither coil was energised which could be held indefinitely.

The rotary brake-drive switch was replaced by a toggle switch giving the result shown in figure 4.5. The changeover was too fast to detect and the traces were independent of the method of operation. There was still a slight disturbance, marked 'A' in figure 4.5. This is believed to be due to mechanical vibration which is transmitted to the torque bar. Reducing the voltage to the coils or the distance between the brake and drive plate had no effect. Braking was sluggish if the voltage dropped, and the distance between the plates is critically adjusted to avoid friction in the drive position.

The disturbance was small and most of the curve could be interpreted satisfactorily. However during the first few milliseconds the data are uncertain. All the subsequent results were obtained with the toggle switch.

(ii) Boundary conditions for stress relaxation

The velocity distribution is assumed to be given by 4.1, thus the sample should be held between fixed boundaries during a
FIGURE 4.6 Rheogoniometer torsion head
FIGURE 4.7 Stress relaxation of Vistanex LM-MH at 29.25°C, steady shear rate = 0.00229 sec\(^{-1}\) -- Effect of torsion bar.

<table>
<thead>
<tr>
<th>Diameter of bar (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
</tr>
<tr>
<td>0.25</td>
</tr>
<tr>
<td>0.35</td>
</tr>
</tbody>
</table>
relaxation experiment. In the rheogoniometer the torque is calculated from the deflection of a calibrated torsion bar, which is coupled to the top platen (figure 4.6). In steady shear flow the bar is deflected from its null position by an amount depending on the melt viscosity, shear rate and bar stiffness. When flow ceases the bar returns to its null position. Thus the sample during relaxation is not constrained between fixed boundaries and the condition specified by 4.1 is not achieved. The trace recorded is the deflection of the bar from the null position. The fixed points are the top of the torsion bar and the bottom platen, in practice the interaction of the material and the measuring system is measured.

The effect of these unsatisfactory boundary conditions was studied with Vistanex LM-MH using the three standard torsion bars. The relative stiffness of these bars is 1:17:58. The fluid viscosity at the test temperature (29.25°C) was about $6.90 \times 10^{-5}$ poise at the steady shear rate of $0.00229 \text{ sec}^{-1}$. The results are shown in figure 4.7. The inconsistency of these curves show that the interaction between the melt and the measuring system is significant and reliable relaxation data cannot be obtained.

The torsion bar is coupled to the platens to produce a Maxwell element. For a Newtonian fluid we should observe a 'relaxation' effect which can be predicted from the fluid viscosity and the torsion bar stiffness. The predicted curve for a Newtonian fluid is (Horsfall 1969):

$$\frac{p_{21}(t)}{p_{21}(0)} = \exp \left(- \frac{2\pi t}{\delta_0}\right)$$

4.4
FIGURE 4.8 Viscosity of Paralac 385
FIGURE 4.9 Stress relaxation of Paralac 385 — Comparison of theory and experiment

- Theory
- .54°C, steady shear rate = 0.00723 sec\(^{-1}\)
- 38.5°C, steady shear rate = 0.114 sec\(^{-1}\)
Figure 4.10 Stress relaxation of Vistanex LM-MS at 29.25°C, steady shear rate = 0.0229 sec\(^{-1}\) — Effect of torsion bar

\[
\frac{p_{21}(t)}{p_{21}(0)}
\]

Time (sec)

<table>
<thead>
<tr>
<th>Diameter of bar (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
</tr>
<tr>
<td>0.25 and 0.35</td>
</tr>
</tbody>
</table>
where $\lambda$ is the length of the torque arm, $\delta_0$ is the deflection of the arm from its null position in steady flow and $\Omega$ is the angular velocity of the bottom platen in steady flow.

Paralac 385 is a convenient material for testing the validity of 4.4. Horsfall (1969) has shown that it is a high viscosity Newtonian fluid over a wide range of shear rates and temperatures. The viscosity - shear rate characteristics of Paralac 385 obtained at a series of temperatures are shown in figure 4.8.

No normal stresses were detected in these experiments. Relaxation experiments were carried out at 38.5°C and 54°C following steady flow at shear rates of 0.00723 and 0.114 sec$^{-1}$ respectively. The 0.25" torsion bar was used which has a stiffness of $1.45 \times 10^8$ dyn cm radian$^{-1}$. The results are plotted in figure 4.9 with the predicted curve calculated from equation 4.4. The agreement between experiment and theory is good.

Newtonian fluids should relax instantaneously and the results in figure 4.9 indicate the significance of the interaction between the material and the measuring system. The magnitude of these effects will, from equation 4.4, depend on the melt viscosity and the torsion bar stiffness. Huppler et al (1967) reported that the effects described above were negligible for low viscosity fluids (<500 poise) and concluded that reliable transient data could be obtained with the rheogoniometer.

The experiments were repeated with a lower viscosity polymer melt (Vistanex LM-MS) to see if reliable results could be obtained. The low shear rate viscosity of this melt was about $4.75 \times 10^5$ poise at 29.25°C. Typical results obtained with the standard torque bars are shown in figure 4.10. The data with the 0.25" and 0.35" diameter bars now coincide, but the results with the 0.125" diameter bar are
FIGURE 4.11 Relaxation of $\sigma_1$ and $P_{21}$ for Vistanex LM-MS at 29.25°C, steady shear rate = 0.144 sec$^{-1}$.

- $P_{21}$
- $\sigma_1$
- response of servo system
significant difference. Thus errors due to unsatisfactory boundary conditions seem to be negligible provided a stiff torsion bar is used. The properties of Vistanex LM-MS were studied in detail using the 0.35" diameter torsion bar.

(iii) Measurement of the relaxation of $\sigma_1$

The servo method for determining thrust introduces a number of uncertainties. The response of the servo is not known or easy to assess and the servo drifts steadily so that thrust data are less reliable and more scattered than torque data. Also the gain setting on the servo amplifier is critical and its effect difficult to determine. Thus the $\sigma_1$ relaxation data are less reliable than the $p_{21}$ relaxation data.

The response of the servo mechanism was checked using a method described by Huppler et al (1967). Paralac 385 was inserted between the cone and plate and the temperature maintained at 54°C. The viscosity of Paralac 385 at this temperature is approximately the same as Vistanex LM-MS at 29.25°C. Weights were suspended from an arm clamped to the bottom platen to give thrust readings equivalent to the steady flow values of $\sigma_1$ for Vistanex LM-MS at 29.25°C. The weights were removed and the decay of the thrust noted.

A typical result is shown in figure 4.11. The servo system overshoots by a large amount before settling to a steady value. The growth behaviour was similar and there did not seem to be any dependence on the applied load. A typical relaxation curve for Vistanex LM-MS at 29.25°C is shown for comparison; this was obtained in the normal way following shear flow. Obviously the servo response affected this result and not much significance can be attached to any
FIGURE 4.12 Stress relaxation of Vistanex LM-MS at 29.25°C —
Effect of steady shear rate.

<table>
<thead>
<tr>
<th>G (sec⁻¹)</th>
<th>0.144</th>
<th>0.0362</th>
<th>0.00572</th>
</tr>
</thead>
</table>

\[
\frac{p_{21}(t)}{p_{21}(0)}
\]
FIGURE 4.13 Stress growth of Vistanex LM-MS at 29.25°C — Effect of steady shear rate

\[ G \ (\text{sec}^{-1}) \]

- \[ 0.144 \]
- \[ 0.0362 \]
normal stress relaxation data.

4.4 Experimental Results

Only the results obtained with Vistanex LM-MS will be discussed since these are the only ones likely to be reliable. Experiments were carried out over a range of shear rates from 0.00572 to 0.144 sec\(^{-1}\) at 29.25°C. Normal stress relaxation data were also obtained but, as we have seen, were not reliable.

The effect of the steady shear rate on the relaxation of \(p_{21}\) is shown in figure 4.12. The stress decays monotonically to zero and relaxes faster as the steady shear rate \(G\) increases. However the range of \(G\) covered was not large enough to be conclusive. These results are in tentative agreement with the findings of Huppler et al (1967).

Similarly the growth time of \(p_{21}\) was reduced slightly as the applied shear rate increased (figure 4.13). No evidence was found of the overshoot at higher shear rates reported by Huppler et al (1967) and Vinogradov & Belkin (1965). Possibly the conditions were not reached where overshoot can occur.

The relaxation of \(\sigma_1\) is shown in figure 4.11 compared with the relaxation of \(p_{21}\). Obviously the uncertainties discussed earlier are included in figure 4.11, but it does indicate that \(\sigma_1\) decays more slowly than \(p_{21}\). Similarly the growth of \(\sigma_1\) was slower than \(p_{21}\). Benbow & Howells (1961) have found similar behaviour with some polydimethylsiloxanes. We cannot make any comment about the effect of \(G\) on the relaxation and growth of \(\sigma_1\) since the data are scattered, cover a limited range of shear rates and are not reliable.

4.5 Discussion

With high viscosity polymer melts it may not be possible to
obtain reliable relaxation and growth data with the rheogoniometer. Experiments with torque bars of varying stiffness should indicate the magnitude of the interaction between the material and measuring system. With Vistanex LM-MH this was significant and the data were not reliable. Possibly data could be obtained with torsion bars of varying stiffness and the results extrapolated to infinite stiffness; however extrapolation may be uncertain and require a large number of results to be successful. For example, extrapolation of the data in figure 4.7 is unlikely to be practical.

The results with Vistanex LM-MS suggest that reliable data can be obtained on lower viscosity materials provided a stiff torsion bar is used. In practice there will be a limit to the stiffness that can be tolerated by the deflection that can be accurately measured.

Because of the servo method for measuring thrust the \( \sigma_1 \) relaxation growth results are unreliable, but it is possible to conclude that \( \sigma_1 \) relaxes and grows much slower than \( p_{21} \).

Although the results have been obtained on the rheogoniometer, the findings are relevant to any investigation of transient behaviour where similar techniques are used to measure torque. Other published data on polymer melts, (e.g. Peticolas 1963) may not be free of the effects discussed earlier.
5.1 Introduction

In the previous chapter the measurement of stress relaxation following steady shear flow was discussed. We saw that reliable data cannot always be obtained with high viscosity melts because of the nature of the method of measuring stress. Transient measurements on elastic liquids are useful for checking rheological equations of state, and in some cases is the only method of distinguishing between the theories (Huppler et al 1967).

The measurement of shear recovery when an applied stress is removed, is unambiguous but does not seem to have attracted as much interest as stress relaxation or stress growth. In some published papers (e.g. Kotaka et al 1959) shear recovery values are quoted which have been derived from some other measurement assuming a particular theory to be valid. In this chapter results of recovery measurements on two polyisobutylenes are reported. The data were obtained on a cone-plate viscometer.

5.2 Theory

We will consider the response of the material to the following shear stress history

\[ p_{21}(t) = p_{21}(0) [1 - H(t)] \]  

where \( H(t) \) is the Heaviside function (equation 4.3).

Thus for time \( t < 0 \) the conditions are steady shear flow at a constant shear stress of \( p_{21}(0) \). The stress is removed at \( t=0 \) and an elastic fluid recovers in the opposite direction to the previous shear flow. The behaviour of the material can be characterised by the shear strain recovered \( \gamma(t) \), at time \( t \).
FIGURE 5.1 Scale diagram of cone-plate viscometer
FIGURE 5.2 Cone-plate viscometer
In a cone-plate viscometer \( \gamma(t) \) is given by

\[
\gamma(t) = \left[ \phi(t) - \phi(0) \right] / \theta_0
\]

where \( \phi(t) \) and \( \phi(0) \) are the angular positions of the rotating member at \( t \) and \( t=0 \), measured from some origin, and \( \theta_0 \) is the gap angle. The total recovery \( \gamma_\infty \) as \( t \to \infty \) is:

\[
\gamma_\infty = \left[ \phi(\infty) - \phi(0) \right] / \theta_0
\]

\( \gamma_\infty \) is usually called the recoverable strain or elastic recovery. For a Newtonian fluid

\[
\gamma(t) = \gamma_\infty = 0
\]

The cone-plate viscometer is a convenient apparatus for measuring \( \gamma(t) \) and \( \gamma_\infty \) since a homogeneous shear stress is applied to the sample and the condition specified by 5.1 can, in principle, be achieved. The basic assumptions and theory of this viscometer have been discussed previously (chapter 3).

5.3 Description of Apparatus

The apparatus is based on a cone-plate viscometer used by Benbow & Howells (1961) for studying the viscosity and recovery properties of some polymer melts. A constant shear stress \( \sigma_{21} \) is applied to the cone by weights on a cord wound around a pulley attached to the rotating shaft. The resultant rotation and recovery when the load is removed are measured by some suitable device.

A scale diagram of the apparatus is shown in figure 5.1 and a photograph in figure 5.2. The rotating shaft (2) is mounted in two angle contact bearings (4) (SKF ENIO; 10 x 28 x 8 mm) separated by an accurately machined spacer (3). This spacer determines the separation of the inner races and lips on the bearing cover plates locate the outer races. The pulley assembly (1) is bolted to the shaft. The axial movement of the shaft is negligible but it can rotate freely. The bearings are mounted in two circular plates (20) which are bolted
to three support pillars (22). These pillars are fixed to a heavy triangular base to give stability to the apparatus. The torque is applied by hanging weights on a cord wound round the pulley (1) and over an external pulley.

The cone holder (6) is silver soldered to the shaft and the cone is attached by three counter-sunk Allen screws which pass through hollow bolts at the locating holes (5). The hollow bolts are used to adjust the tilt of the cone. This method of attaching and adjusting the cones is the same as used in the rheogoniometer, and the cones designed for the rheogoniometer can be used in this apparatus without modification. In practice a Tufnol block was inserted between the cone and (6) to reduce heat losses from the sample. There was no direct electrical path between the cone and the rest of the apparatus.

The bottom platen consists of a large stainless steel circular plate (7) with a raised central portion of 5 cm diameter, which defines the lower boundary of the fluid under test. (7) is bolted to a brass plate (8), which is channelled so that a liquid from a thermostatic tank can be circulated to control the sample temperature. The whole assembly is braised to the bottom shaft (9).

The shaft (9) sits on the spindle of a micrometer (17), which defines the vertical position of the bottom platen. A ball bearing head, not shown in figure 5.1, is attached to the end of the micrometer spindle giving a point contact with the shaft. The micrometer is clamped at (16) to the housing (15) which is bolted to a circular plate (21) and hence to the supporting pillars. The bottom shaft is contained in the holder (11) which is bolted to (15). The micrometer spindle moves the complete bottom platen assembly (7,8,9) to the required vertical position and the platen can then be clamped (10).
The sample temperature is controlled by circulating water through (8) from an external thermostatic tank. The temperature is measured by a copper constantan thermocouple in the bottom platen and is read off on a Scalamp Thermocouple Galvanometer (Pye Ltd.). The thermostatic bath is controlled by a Tempette unit (Tecan Ltd.). The overall temperature variation was checked by thermocouples in the sample close to the cone and plate surfaces. These showed that the overall variation in the sample temperature was ±0.25°C at 30°C.

5.4 Method of Alignment

The technique for adjusting the platens so that they are concentric and perpendicular to the axis of rotation is similar to the procedure described for the rheogoniometer. The concentricity of the bottom platen is adjusted by 4 screws (14) and the squareness by jack screws (12). When the adjustment is complete the bottom platen assembly is locked (13). It is more convenient to set up the cone in a lathe before assembly, but the alignment was rechecked when it was assembled. The platens were set up to the same accuracy as in the rheogoniometer, i.e. maximum error of concentricity on each platen <0.005 cm and maximum tilt between platens <0.0004 rad.

Since the cone is truncated the bottom platen must be adjusted so that the cone apex touches the plate. This is achieved by adjusting the micrometer until the cone and plate touch, which is indicated by electrical contact. The micrometer setting is taken, and subsequently the bottom platen can be adjusted to give the required separation when a sample is placed between the platens.

In practice, with a sample between the gap, the micrometer tended to slip in its housing. The final adjustment was therefore made by setting the gap at the periphery to the correct amount using a cathetometer. The gap can be set to within 1% of the required value.
FIGURE 5.3 Schematic diagram of measuring system
5.5 Measurement of Rotation

The rotation of the cone is measured by a capacitance technique. The pulley assembly (1) is profiled near the circumference on the top surface in a series of saw teeth. A probe (18) is brought in close proximity with this profiled face and the capacitance between this face and the probe is measured on a capacitance bridge. As the cone rotates the distance between the probe and profiled face alters and the resulting change in capacity can be recorded by some suitable method. The test face on (1) is profiled in 7 section; 4 of 22.5°, 2 of 90° and 1 of 180°. The distance between the probe and profiled face over each section is proportional to the angle of rotation and the total change in each section is 0.0254 cm. Another probe (19) is positioned close to the bottom surface to compensate for any axial movement. A schematic plan of the arrangement of probes and surface cam is shown in figure 5.3.

The probes are standard equipment manufactured by Wayne Kerr Ltd. (Type MC1). The sensing area consists of an inner electrode (0.36 cm diameter) and a guard ring which are separated by an insulating sleeve. The sensor is flat and its overall diameter is 0.51 cm. The probes are used with a transducer bridge (Type TE 2000 Wayne Kerr Ltd.) and the distance between the sensor and a flat parallel surface is measured directly on a linear scale. In the present case the test surface is not parallel to the probe but since the probes are calibrated directly against angular movement this does not matter.

The transducer bridge can give continuous readings of the sum or difference of the distances measured by two separate probes.
FIGURE 5.4 Resistance network between capacitance bridge and UV recorder
Angular Deflection \((\text{rad} \times 10^3)\)

UV Recorder Reading

**FIGURE 5.5** Calibration curves for most sensitive ranges.

- \(r_2\) (ohm)
  - O 1000
  - △ 2000
Thus to compensate for any axial movement we can add the distances measured by probes (18) and (19) and in effect measure the change in thickness of the face cam as the shaft rotates.

The output from the transducer bridge is passed through a resistance network and is displayed on an ultra-violet recorder (SEL Type 2005). The circuit between the bridge and recorder is shown in figure 5.4. The zero is set on the recorder by adjusting $r_1$. The required sensitivity is obtained by $r_2$, and $r_3$ is the galvanometer damping resistance. The zero is adjusted so that the working range is near the centre of any profiled section.

5.6 Calibration of Probe

The measuring system is calibrated by an optical lever. A small mirror attached to the rotating shaft reflects the light from a galvanometer lamp onto a scale one meter from the axis of rotation.

Typical calibration curves obtained on the most sensitive ranges used are shown in figure 5.5 for one of the 22.5° sections. The linearity is good and we can discriminate on the most sensitive range to better than $\pm 2.5 \times 10^{-4}$ rad, which for a cone giving a 3.93° gap angle is equivalent to $\pm 3.64 \times 10^{-3}$ strain units. The calibration curves were linear for all ranges tested up to a full scale deflection of 0.25 rad, which was the least sensitive range used.

5.7 Experimental Procedure

Two bulk polyisobutylene, Vistanex LM-MH and Vistanex LM-MS, were used in this investigation. The properties of these materials have been studied in some detail earlier in the rheogoniometer (chapters 3 and 4). The method of sample preparation and the procedure for inserting the material between the platens was the same.
TABLE 5.1

Cone dimensions

<table>
<thead>
<tr>
<th>Gap angle $\theta_0$ (deg)</th>
<th>Cone radius $R$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>1.25</td>
</tr>
<tr>
<td>3.93</td>
<td>2.5</td>
</tr>
<tr>
<td>6.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>
FIGURE 5.6 Vistanex LM-MS, 29.25°C — Typical recovery trace; \( p_{21}(0) = 3.75 \times 10^4 \text{ dyn cm}^{-2} \), \( R=2.5 \text{ cm} \), \( \theta_o = 3.93^\circ \)
as described in the earlier experiments and, as before the test
temperature was 29.25 ± 0.25°C. The data reported here were obtained
with three cones, whose dimensions are given in table 5.1.

The probe was calibrated before and after a series of
measurements to check that there was no drift in the electronics.
The slope of the calibration curves altered by less than 1% in all
cases. For steady state measurements the value of $r_2$ (figure 5.4)
was chosen so that the full-scale deflection on the recorder was
$\sim 0.25$ rad. Two sensitivities were used for recovery measurements,
giving full-scale deflections of about 0.02 and 0.04 rad.

The stress was applied manually by hanging a weight on the
end of a cord wound round the pulley assembly and then over an external
pulley. The shear rate in steady state measurements was determined
from the slope of the angular displacement - time graph displayed on
the recorder. To measure recovery the weight was removed after a
given amount of strain, and the amount of recovery determined from the
recorder trace. A typical trace is shown in figure 5.6, which also
indicates the recoverable strain $\gamma_\infty$. This method of removing the stress
seemed to be satisfactory and the results were independent of the
operator.

5.8 Experimental Errors

The main sources of error which can arise in cone-plate
viscometry have been discussed in chapter 3. Since the present
apparatus was adjusted to the same accuracy as the rheogoniometer it
is unlikely that alignment errors etc. will affect results. However,
there are two other possible sources of error which can effect
recovery results:

(i) Inertia of the apparatus

(ii) Friction in the bearings
(i) **Effect of inertia**

We have already seen that inertial effects in the fluid are not significant. However when the stress is removed there will be a tendency for the platen to continue rotating due to the inertia of the apparatus, e.g. in the spindle, pulley assembly, cone etc. We can calculate this overshoot for a Newtonian fluid which should give some indication of the effect of inertia in the recovery measurements.

When the stress is removed, we obtain for a Newtonian fluid

\[ M_i \frac{d\omega^1}{dt} = -M \]  \hspace{1cm} 5.5

where \( M_i \) is the moment of inertia of the system, \( M \) is the torque in the fluid and \( \omega^1 \) is the angular velocity of the rotating platen at time \( t \). \( M \) can be calculated from the viscosity of the fluid.

\[ M = \frac{2\pi R^3 \eta \omega^1}{3\Theta_0} \]  \hspace{1cm} 5.6

If the stress is removed at \( t=0 \), then substituting 5.5 in 5.6 and integrating with boundary conditions \( \omega^1 = \Omega \) at \( t=0 \), we obtain

\[ \omega^1 = \Omega \exp \left( -\frac{Et}{M_i} \right) \]  \hspace{1cm} 5.7

where

\[ E = \frac{2\pi R^3 \eta}{3\Theta_0} \]  \hspace{1cm} 5.8

and \( \Omega \) is the angular velocity of the rotating platen during the previous steady shear flow. Integrating 5.7 we finally obtain

\[ \phi(t) - \phi(0) = \frac{\Omega M_i}{E} \left[ 1 - \exp \left( -\frac{Et}{M_i} \right) \right] \]  \hspace{1cm} 5.9
FIGURE 5.7 Typical trace with high viscosity

Newtonian fluid (Paralac 385 57°C)

$P_{21}(\omega) = 7.5 \times 10^4 \text{ dyn cm}^{-2}$, $R = 2.5 \text{ cm}$, $\theta_0 = 3.93^\circ$
FIGURE 5.8 Vistanex LM-MS, 29.25°C — Effect of cone dimensions

<table>
<thead>
<tr>
<th>θ_0 (deg)</th>
<th>R (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>1.25</td>
</tr>
<tr>
<td>6.0</td>
<td>2.5</td>
</tr>
<tr>
<td>3.93</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Thus \([\phi(t) - \phi(0)]\) is the amount of overshoot at time \(t\) when the stress is removed. The value of \(E/M_j\) was between \(10^3\) and \(10^6\) sec\(^{-1}\) in the present experiments and the amount of overshoot calculated from 5.9 as \(t \to \infty\) was <4×10\(^{-5}\) rad. Thus inertia effects are unlikely to be significant and can be neglected. This was confirmed by an experiment with a high viscosity Newtonian fluid (Paralac 385). The viscosity of this fluid was \(2.1\times10^5\) poise at 57°C which is of the same order as the viscosity of the polyisobutylenes and the applied stress was \(7.50\times10^4\) dyn cm\(^{-2}\). We can see from figure 5.7 that there was no measurable overshoot when the stress was removed.

(ii) Friction in the bearings

This was estimated by determining the torque which must be applied to rotate the cone when no sample was present. The torque was approximately \(2.5\times10^3\) dyn cm and was independent of the axial thrusts, which were applied by dead loads to represent the effect of normal stresses. Since the lowest torque applied in the present experiments was \(1.25\times10^5\) dyn cm friction in the bearings is unlikely to affect the steady state results.

It is difficult to assess the effect of friction in the bearings on recovery measurements. However, if recovery data are independent of the cone dimensions it seems reasonable to assume that any errors caused by friction in the bearings are negligible. Experiments have been carried out with Vistanex LM-MS at 29.25°C using the cones in table 5.1. We see from figure 5.8 that the recovery results were independent of cone angle and cone radius, which suggests that errors due to friction in the bearings can be neglected. All the subsequent data reported in this chapter were obtained using the 2.5 cm radius cone giving a gap angle of 3.93°.
FIGURE 5.9 Vistunex LM-MH, 29.25°C – Comparison of rheogoniometer and shear recovery apparatus.

- □ shear recovery apparatus
- O rheogoniometer
FIGURE 5.10 Vistanex LM-MS, 29.25°C — Comparison of rheogoniometer and shear recovery apparatus

- ○ rheogoniometer
- □ shear recovery apparatus
FIGURE 5.11 Vistanex LM-MS, 29.25°C. — Effect of applied strain

\[ P_{21}(o) \times 10^{-4} \text{ dyn cm}^{-2} \]

- ○ 1.50
- □ 3.75
- △ 6.00
5.9 Experimental Results

The steady state shear rates were measured in one series of experiments on each material to ensure that the results were consistent with the rheogoniometer. The sample was sheared for 10 units of strain before the angular displacement was recorded as a function of time. A linear plot was obtained and the shear rate \( \dot{\gamma} \) was calculated from the slope. Data were obtained over a range of applied stress \( p_{21}(0) \), from \( 1.50 \times 10^4 \) to \( 7.50 \times 10^4 \) dyn cm\(^{-2}\) for Vistanex LM-MS and \( 3.00 \times 10^4 \) to \( 1.05 \times 10^5 \) dyn cm\(^{-2}\) for Vistanex LM-MH. The results for the two materials are shown in figures 5.9 and 5.10 compared with the rheogoniometer data. Each point represents the average of the values obtained in each sense of rotation. The agreement between the two rheometers is good for both materials.

We have assumed in 5.1 that before the stress is removed, i.e. for \( t<0 \), the flow is steady shear and has been maintained for an infinite time. Thus the measured values of \( \gamma_\infty \) should be independent of the previous shear history. This can be checked by measuring the recovery as a function of the applied strain at constant \( p_{21}(0) \). The applied strain was varied from 5 to 45 with Vistanex LM-MS at three different stress levels. The results are shown in figure 5.11 and we see that \( \gamma_\infty \) is independent of the applied strain. All subsequent data reported were obtained at an applied strain of 10 and we can assume that equation 5.1 is valid.

The shear recovery of the polyisobutylenes was measured over the same range of shear stresses as the steady state measurements shown in figures 5.9 and 5.10. At any particular shear stress \( \gamma_\infty \) was calculated from the mean of the values obtained in each sense of rotation. Three independent samples were studied for each material over the complete range of shear stresses.
FIGURE 5.12 Vistanex LM-MS, 29·25°C — Shear recovery as a function of steady shear stress

- Experimental
- Weissenberg theory
- Lodge theory
FIGURE 5.13  Vistamex LM-MH, 29.25°C — Shear recovery as a function of the steady shear stress

- Experimental
- Weissenberg theory
- Lodge theory
FIGURE 5.14 Polyisobutylene melts, 29.25°C — Shear recovery as a function of $\sigma_1/p_{21}$

- Vistanex LM-MS
- Vistanex LM-MH
The results for the materials are shown in figures 5.12 and 5.13. The recoverable strain increases and the gradient \( [\partial \gamma_\infty / \partial \sigma_{21}(0)] \) decreases as the applied stress increases. These results are consistent with other published data on polymer melts (Best & Rosen 1968, Benbow & Howells 1961).

According to the theories of Weissenberg (1947) and Lodge (1964) \( \gamma_\infty \) is related to the steady shear flow properties of the fluid as follows:

\[
\text{Weissenberg} \quad \gamma_\infty = \sigma_1 / \sigma_{21} \quad 5.10 \\
\text{Lodge} \quad \gamma_\infty = \sigma_1 / 2\sigma_{21} \quad 5.11
\]

These theories differ by a factor of two and this has been an issue of some controversy (see Bogue & Doughty 1966). Benbow & Howells' (1961) data on some polydimethylsiloxanes are in reasonable agreement with equation 5.11 but for a large number of polymer solutions Philippoff (1962) reported that equation 5.10 was more appropriate.

Using the data from chapter 3 we are able to compare the predictions of these theories with the experimental results. The predictions are also shown in figures 5.12 and 5.13 and we see that neither theory is appropriate, but the experimental data are closer to Lodge's theory.

We have plotted \( \gamma_\infty \) versus \( \sigma_1 / \sigma_{21} \) for both materials in figure 5.14. The recovery values are the mean at that particular shear rate and the \( (\sigma_1 / \sigma_{21}) \) values were interpolated from the steady state data. We see that there is some evidence that \( \gamma_\infty \) is a linear function of \( (\sigma_1 / \sigma_{21}) \) which is the same for both materials. The line in figure 5.14 is represented approximately by

\[
\gamma_\infty = 0.6 \sigma_1 / \sigma_{21} \quad 5.12
\]

This is close to the relationship reported by Khanna & Pollett (1965) for some polyvinylchloride compounds.
FIGURE 5.15 Vistanex LM-MS, 29.25°C — Recovery curves

\[ p_{21}(o) \times 10^{-4} \text{ dyn cm}^{-2} \]

- □ 1.50
- △ 3.75
- ○ 6.00
FIGURE 5.16 Vistanex LM-MS, 29.25°C – Normalised recovery curves

\[ \frac{y(t)}{y_\infty} \times 10^{-4} \text{ dyn cm}^{-2} \]

- \( \triangle \) 1.50
- \( \square \) 3.75
- \( \bigcirc \) 6.00
The complete recovery curve was also obtained for Vistanex LM-MS at three values of $p_{21}(0)$. These are shown in figure 5.15 where each point is the average of the strain $\gamma(t)$ in both senses of rotation. Initially the recovery is rapid but slows down and is complete in about 60 seconds. These results are very similar to those published by Rosen & Rodriguez (1965). The recovery curves were normalised and we see from figure 5.16 that the plot of $\gamma(t)/\gamma_\infty$ against $t$ is independent of the steady shear stress $p_{21}(0)$.

5.10 Discussion

We have seen that reliable data can be obtained on the apparatus described earlier and have reported data obtained on two polymer melts. The results are consistent with the published data on other polymer melts but are not consistent with Philippoff's measurements on polymer solutions. This may indicate that the flow mechanisms of polymer melts and concentrated polymer solutions are different. There is strong evidence that the recovery is a function of the stresses in steady shear flow.

The expected recovery for a number of theories has been calculated. The results described above will be evaluated in terms of these theories later, in chapter 7.
Chapter 6
DIE SWELL OF ELASTIC AND VISCOS FLUIDS

6.1 Introduction

Although die swell in polymer melts has been thought to be associated with normal stresses (Lodge 1964, Metzner et al 1960), no measurements of these phenomena have been reported at the same shear rates. Die swell data have all been obtained at typical extrusion shear rates (>10 sec⁻¹), but we have seen that reliable normal stress data cannot be obtained much above 1 sec⁻¹. Clearly measurements of die swell at much lower shear rates are needed.

Die swell has also been observed in Newtonian fluids under certain conditions (Middleman & Gavis 1961a). However these observations were made on low viscosity fluids (<10 poise) at Reynolds numbers >2. The Reynolds number appropriate to polymer melt processing is <<1 and a comparison with these previous results is irrelevant. It is necessary to determine the die swell properties of a polymer melt and a Newtonian fluid of similar viscosity under the same flow conditions.

In this chapter the results of die swell measurements carried out in capillary flow on a polymer melt and a Newtonian fluid of similar viscosity are reported. The measurements were made at shear rates below 1 sec⁻¹.

6.2 Theory of the Capillary Rheometer

In this type of rheometer the fluid is forced through a circular capillary of radius R and length L. The force can be applied by a piston or gas pressure.

We will assume a cylindrical co-ordinate system, z, r, θ, where z is the axial co-ordinate, r is the radial co-ordinate and θ
FIGURE 6.1 Capillary flow geometry — Cylindrical polar co-ordinate system.
is orthogonal to \( z \) and \( r \) (figure 6.1). \( z, r \) and \( \theta \) are equivalent to \( \xi_1, \xi_2 \) and \( \xi_3 \) respectively. The capillary axis is defined by \( r = 0 \) and the wall by \( r = R; \ z = 0 \) at the capillary entrance and \( z = L \) at the exit.

We will assume that the velocity components are

\[
v_z = v_z(r); \ v_r = v_\theta = 0 \tag{6.1}
\]

and there is no slip at the wall, i.e.

\[
v_z(R) = 0 \tag{6.2}
\]

Equation 6.1 satisfies the conditions that the flow is steady shear. Lodge (1964) has shown that the above assumptions are compatible with the equations of motion provided that

\[
\frac{dp_{22}}{dz} = \text{constant} \tag{6.3}
\]

Equation 6.3 can be checked in principle from measurements of \( p_{22}(R) \) at various \( z \). In practice this is never done.

Using 6.1 to 6.3 we can show from the rate of strain tensor and the equations of motion (Middleman 1968) that

\[
G = - \frac{dv_z}{dr} \tag{6.4}
\]

and

\[
p_{21}(r) = - \frac{dp_{22}}{dz} \frac{r}{2} \tag{6.5}
\]

Thus \( p_{21} \) varies linearly with \( r \) and is a maximum at the wall given by

\[
p_{21}(R) = - \frac{dp_{22}}{dz} \frac{R}{2} \tag{6.6}
\]

The volume rate of flow \( Q \) is

\[
Q = \int_{0}^{R} 2\pi r v_z \, dr \tag{6.7}
\]
Since the flow is steady state, $p_{21}$ is a function of $G$ only and we can write

$$G = f(p_{21}) \quad 6.8$$

Thus from 6.4 to 6.8 we obtain after integration and changing the variable to $p_{21}$.

$$\int_{0}^{p_{21}(R)} (Q/\pi R^3) = p_{21}(R)^3 \int_{0}^{p_{21}} p_{21}^2 f(p_{21}) \, dp_{21} \quad 6.9$$

Thus $(Q/\pi R^3)$ is a unique function of $p_{21}(R)$. Differentiating 6.9 we obtain

$$G(R) = \left(3n' + 1 \right) \left( \frac{Q}{\pi R^3} \right) \quad 6.10$$

where

$$n' = \frac{d \ln p_{21}(R)}{d \ln (Q/\pi R^3)} \quad 6.11$$

Equation 6.10 was derived originally by Rabinowitsch (1929).

Thus from measurements of $p_{22}(R)$ at various z and the volume rate of flow Q, we can obtain $p_{21}$ as a function of G. In practice the total pressure drop across the capillary ($\Delta P$) is measured and $p_{21}(R)$ calculated from

$$p_{21}(R) = \frac{\Delta P R}{2L} \quad 6.12$$

Errors in using 6.12 to calculate $p_{21}(R)$ will be discussed later.

We will define the die swell $\chi_\infty$ as follows

$$\chi_\infty = \frac{R_j}{R} \quad 6.13$$

where $R_j$ is the final constant radius of the extrudate.

6.3 Description of the Apparatus

The viscometer is based on a design by Atkinson &
FIGURE 6.2 Capillary rheometer
FIGURE 6.3 Scale diagram of capillary rheometer
Nancarrow (1949) and is intended for use with the Hounsfield Tensometer (Tensometer Ltd.). A general view of the apparatus and a scale diagram of the viscometer are given in figures 6.2 and 6.3. The tensometer which is usually used horizontally, was mounted vertically to simplify the measurements of die swell.

The piston (1) forces the fluid under test (3), which is contained in the barrel (2), through a capillary (4). The tensometer can only apply a tensile force and this is converted to a compression by the arrangement shown in figure 6.4. The barrel is mounted on the lower plate (5 figure 6.4) and the piston under the upper plate (6). The cross member (7) is connected to the load measuring system and (8) is attached to the cross head and hence the drive.

The barrel consists of two brass sections silver soldered together. Each section is hollowed out so that a suitable fluid can be pumped through the barrel from a thermostat bath.

The capillaries are stainless steel tubing (Accles & Pollock Ltd.) inserted in a brass sleeve to give rigidity. They are attached to the viscometer and held in place by the screwed collar (9 figure 6.3) and are jacketed to provide a means of temperature control. The tubes protrude about 0.2 cm from the exit to make the observations of the extrudate easier.

The piston is driven at a preselected speed by a constant speed motor via a system of pulleys. The speed can be varied in five equal logarithmic steps from about 0.0025 cm/min to 0.08 cm/min; these low piston speeds are necessary to achieve the required low shear rates. The operating screw which drives the cross head was badly worn in parts and in practice slight variations in speeds
occurred. However the speed did remain constant long enough to make measurements. The screw was replaced for later experiments and gave constant and reproducible speeds at each setting.

The load on the piston was measured by a proof ring transducer (10 figure 6.2). This is a modification to the system supplied with the tensometer. The piston speed was determined by a displacement transducer (11) mounted on the compression arrangement. Both transducers and their associated bridges were supplied by BPA Electronics Ltd.. The output from each bridge was displayed simultaneously on an ultraviolet recorder (SE Laboratories Ltd.) and the piston speed determined from the displacement-time trace.

The proof ring which was calibrated by dead weights, covered a range of piston loads from 1 to 250 lb. The displacement transducer was calibrated against a micrometer in a special jig. Total piston movements of up to 0.5 cm could be detected without repositioning the transducer.

The sample temperature was controlled by pumping water or paraffin oil through the barrel and capillary jacket from a thermostatic tank. Water was used at ambient temperatures and paraffin above 50°C. The tank was controlled by a Tempette unit (Tecam Ltd.) The temperature was determined from thermocouples embedded in the barrel and in the capillary close to the exit. The variation during a run was about ±0.5°C at 23.5°C, at higher temperatures the variation was much larger; ±1.5°C at 60°C.

To minimise friction between the piston and barrel wall the former was relieved along most of its length. In addition the internal diameter of the barrel (1.275 cm) was marginally greater than the maximum piston diameter of 1.270 cm. Thus there was some
<table>
<thead>
<tr>
<th>Capillary</th>
<th>Diameter (cm)</th>
<th>Length/Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.252 ± 0.002</td>
<td>77.4</td>
</tr>
<tr>
<td>A2</td>
<td>0.252 ± 0.002</td>
<td>58.1</td>
</tr>
<tr>
<td>B1</td>
<td>0.195 ± 0.002</td>
<td>76.1</td>
</tr>
<tr>
<td>C1</td>
<td>0.134 ± 0.004</td>
<td>75.8</td>
</tr>
</tbody>
</table>
FIGURE 6.5 Steady shear flow data obtained on rheogoniometer

- p21 Paralac 385, 60°C
- p21 Paralac 385, 65°C
- p21 Lorival R25, 23.5°C
- σ1 Lorival R25, 23.5°C
leakage flow past the piston; errors due to this are discussed later. The piston is a sloppy fit in (6) (figure 6.4) so that in operation it is self aligning.

The dimensions of the capillaries used in the present investigation are given in table 6.1. The diameters were determined from the mean of two measurements made at each end of the capillary with a microscope.

6.4 Experimental Procedure

The two materials studied were a modified alkyd resin (Paralac 385) and a depolymerised natural rubber (Lorival R25). We have seen in previous chapters that Lorival R25 displays large normal stresses whereas Paralac 385 does not; it is a Newtonian fluid. The experimental conditions were chosen so that the materials had similar viscosities (~10^5 poise). The steady shear flow data obtained on the rheogoniometer are shown in figure 6.5.

The barrel was filled with material and left for several hours at the test temperature to allow entrapped air to escape before the drive was applied. A small quantity of pigment was incorporated into the Paralac 385 to make the extrudate visible. This had no effect on the flow properties of the material.

To eliminate the effect of gravity the melts were extruded into an optical cell containing a liquid of the same density as the material under test. A mixture of methanol and water was used for the Lorival R25 experiments and glycerol for the Paralac 385 experiments.

The effect of viscosity was studied with Paralac 385 by carrying out experiments at 60°C and 65°C, which altered the viscosity by a factor of three. The extrudate was maintained at these temperatures by radiation from a 100 watt bulb. This crude
arrangement was adequate for these experiments as the overall control of temperature was only \(\pm 1.5^\circ\text{C}\). It is not possible to improve the temperature control at elevated temperatures with the present apparatus. The test temperature in the Lorival R25 experiments was \(23.5 \pm 0.5^\circ\text{C}\).

When the load and piston speed reached steady values the diameter of the extrudate was measured with a travelling microscope at various distances from the tube exit up to 2 cm. In any particular run four measurements were made at each point and the average value of the extrudate diameter at that point calculated. Measurements were made over a range of piston speeds using three different radius capillaries; 0.126, 0.0975 and 0.067 cm (table 6.1).

6.5 Experimental Errors

There are two main sources of error which can arise in capillary flow measurements

(i) End effects

(ii) Shear heating effects

(i) End effects

Ideally \(p_{21}(R)\) should be calculated from equation 6.5, but measurements of \(p_{22}(R)\) are difficult to make. Usually the total pressure drop is measured and \(p_{21}(R)\) calculated from equation 6.12. However there are a number of sources of energy loss and \(\Delta P\) must be corrected to take these into account. They arise from kinetic energy in the issuing stream, leakage flow past the piston, and viscous and elastic behaviour when the fluid converges or diverges at the ends of the capillary.
Table 6.2

Effect of L/R on die swell of Lorival R25

<table>
<thead>
<tr>
<th>Capillary</th>
<th>L/R</th>
<th>(4Q/\pi R^3)</th>
<th>Extruder diam* (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>134.8</td>
<td>0.131</td>
<td>0.302</td>
</tr>
<tr>
<td>A1</td>
<td>134.8</td>
<td>0.0677</td>
<td>0.298</td>
</tr>
<tr>
<td>A2</td>
<td>116.2</td>
<td>0.126</td>
<td>0.304</td>
</tr>
<tr>
<td>A2</td>
<td>116.2</td>
<td>0.0642</td>
<td>0.294</td>
</tr>
</tbody>
</table>

* Average value for distances >0.4 cm from capillary exit.
End effects can be accounted for by including an effective length $\xi R$ in equation 6.12, where $\xi$ is the end correction which depends on the shear rate. $p_{21}(R)$ is then given by

$$p_{21}(R) = \frac{\Delta P R}{2(L + \xi R)}$$  \hspace{1cm} \text{6.14}

Bagley (1957) and Metzner et al (1960) have applied equation 6.14 successfully to polymer melts to calculate values of $p_{21}(R)$ which were found to be independent of geometry. $p_{21}(R)$ is, therefore, obtained from measurements of $\Delta P$ at constant $(Q/\pi R^3)$ for various $L/R$.

Merz & Colwell (1958) showed that provided $L/R$ is larger than 120, end effects can be neglected for polymer melts, i.e. $\xi$ is insignificant. Thus end effects are likely to be small in the present experiments and $p_{21}(R)$ can be calculated from equation 6.12.

Die swell also depends on the $L/R$ ratio (Bagley et al 1963) and on the geometry of the die entry (Metzner et al 1960). These effects can be attributed to elastic effects in the die entry region which decay during the passage of the melt through the capillary. However at large $L/R$ ratios the die swell is independent of tube length (Bagley et al 1963, Metzner et al 1960). The effect of $L/R$ was checked with Lorival R25 using capillaries A1 and A2 (table 6.1). We see from table 6.2 that the die swell was independent of $L/R$. Since $L/R \geq 116$ in the present experiments we can neglect entrance effects in the die swell measurements.

(ii) Temperature rise due to shear heating

The maximum possible mean temperature rise due to shear heating can be estimated by assuming there is no heat loss from the sample. This will overestimate the effect but should indicate if shear heating is significant. The temperature rise $\Delta T$ is given by
FIGURE 6.6 Lorival R25, 23.5°C – $p_{21}(R)$ as a function of $(4Q/\pi R^3)$

<table>
<thead>
<tr>
<th>$R$ (cm)</th>
<th>0.126</th>
<th>0.067</th>
<th>0.0975</th>
</tr>
</thead>
</table>

$3 \times 10^3$ to $3 \times 10^5$

$10^{-2}$ to $10^0$

$4Q/\pi R^3$ (sec$^{-1}$)
FIGURE 6.7 Lorival R25, 23.5°C — Comparison of cone-plate and capillary rheometers

- □ cone-plate (rheogoniometer)
- ○ capillary
\[ \Delta T = \Delta P / \rho C_p \]  

where \( \rho \) is the fluid density and \( C_p \) is the specific heat of the material. For Lorival R25 at \( G(R) = 1 \) sec\(^{-1} \) and \( L/R = 160 \); then \( \Delta P \sim 10^7 \) dyn cm\(^{-2} \) and we find from equation 6.15 that \( \Delta T \) is approximately 0.5°C. The specific heat and density of the polymer were obtained from Brandrup & Immergut (1966). In practice the temperature rise will be much less than 0.5°C and we can assume that shear heating effects are negligible in the present experiments.

6.6 Experimental Results

The pressure and piston speed were recorded in a series of experiments with Lorival R25 to ensure that the apparatus gave results consistent with those obtained on the rheogoniometer. As predicted by the theory (equation 6.9) \( p_{21}(R) \) is a unique function of \( Q / \pi R^3 \) (figure 6.6). This implies that slip at the wall is negligible (Oldroyd 1958). The shear rate at the wall \( G(R) \) was, therefore, calculated from equation 6.10. To obtain \( n' \) (equation 6.11) a second order polynomial was fitted to the \( \log (Q / \pi R^3) - \log (\Delta P / RL) \) data by least squares and the function differentiated analytically. The dependence of \( p_{21} \) on \( G \) is shown in figure 6.7. The cone-plate results obtained on the rheogoniometer are also shown and the agreement between the results obtained with the two geometries is good.

Die swell measurements were made on each material. Capillaries A1, B1 and C1 (table 6.1) were used for the Lorival R25 experiments and A2, B1 and C1 for the Paralac 385 experiments. Some attempt was made to obtain data with Paralac 385 using A1 but it was abandoned because of poor temperature control obtained with this very long die. The load readings were not recorded during the die swell measurements.
Die swell as a function of shear rate

**FIGURE 6.8** Lorival R25 and Paralac 385 — Die swell as a function of shear rate
The extrudate diameter reached a constant value at about 3R from the exit of the capillary. The die swell was therefore determined for each run from the mean value of the measured diameter for distances from the capillary exit greater than 3R.

The results are shown in figure 6.8 and we see that both the elastic (Lorival R25) and the viscous (Paralac 385) fluids show a significant amount of die swell. The average die swell for Paralac 385 was 13.5% and independent of the capillary radius, viscosity and volume rate of flow. For the elastic fluid die swell increased with shear rate but was independent of the tube radius. These results agree with Vinogradov & Prozorovskaya's (1964, 1967) observations on polystyrene and polypropylene. At low shear rates the die swell for the elastic fluid appeared to be asymptotic to the Newtonian result.

6.7 Discussion

The normal stress difference $\sigma_1$ was calculated from the die swell data for Lorival R25 by the momentum balance method (chapter 2, equation 2.13). The values of $\sigma_1$ obtained were more than seven orders of magnitude lower than the results obtained from the rheogoniometer measurements reported in chapter 3. Clearly, as we have already seen in chapter 2, the momentum balance approach to die swell is not appropriate to polymer melts.

It has been confirmed that high viscosity Newtonian fluids exhibit a significant amount of die swell at low shear rates. The average die swell of 13.5% is higher than has been previously reported (Middleman & Gavis 1961a, Goren & Wronski 1966), but the present data were obtained at much lower Reynolds numbers ($<10^{-7}$).
There are, therefore, two contributions to the die swell of polymer melts. The first is associated with a viscous effect and superimposed on this is an effect due to the elastic nature of polymer melts.
7.1 Introduction

Extensive reviews of rheological equations of state have been published by Markovitz (1957), Bogue & Doughty (1966) and Spriggs, Huppler & Bird (1966). In Spriggs et al's excellent review 20 different models are tabulated in uniform notation and compared in a number of flow situations. We will not, therefore, attempt to give a comprehensive appraisal of all the theories but pick the most promising models from the literature. In assessing the theories the previous authors have relied mostly on polymer solution data. There have been few attempts to test models using data on high viscosity polymer melts in a number of flow situations.

The main requirements of a rheological equation of state to describe polymer melt behaviour are

(i) It should be a tensor equation.
(ii) The theory must predict variable viscosity, normal stress differences, stress relaxation and growth, shear recovery and dynamic behaviour.
(iii) It should preferably have some molecular basis.
(iv) The model should be explicit and contain a small number of constants which can be obtained from simple laboratory experiments. This is so that the models have some hope of being applied in engineering applications such as polymer processing.
(v) No physically impossible situations should arise.

Obviously not all theories will meet all these requirements. However the model we are looking for should be realistic yet
mathematically tractable if it is to be of any use in engineering applications.

7.2 Classification of Theories

Any classification of theories is arbitrary since some models are special cases of others (Bogue & Doughty 1966). However we can classify them according to the form they are conventionally used into those involving

(i) a time derivative of stress,
(ii) an integral of the strain or rate of strain history,
(iii) some simple function between the stress and strain or rate of strain.

The third type may be useful in some steady flow situations but they do not predict transient behaviour and we will not consider this class of theory any further.

The models involving time derivatives of the stress have been inspired mainly by the pioneering work of Oldroyd (1950) and the integral equations are a development of Lodge's (1956) network theory of flow.

Models involving a time derivative of the stress are unattractive for a number of reasons (Tanner 1968, White 1968). Firstly equations explicit in stress are preferable since once the kinematics are prescribed the stress can be readily calculated. This seems more practical than calculating the strains from the stress since even in instances where one component of the stress tensor is known, we may not know the other components, e.g. shear recovery. Tanner & Simmons (1967) also found that instabilities occurred when the solution of problems using a differential model were attempted
on a computer. Since the trend will be to put rheological models on computers — in some cases this may offer the only hope of a solution — this is another reason for using integral equations. Finally integral models have largely developed from the theory of Lodge (1956) which is a molecular approach based on the successful theory of rubber elasticity. Thus we will restrict our attention to a number of integral theories using a common notation.

7.3 Description of Theories

To simplify the mathematics the theories will be expressed in a common notation using a Cartesian co-ordinate system $Ox_1 \ x_2 \ x_3$.

Lodge (1956, 1964) proposed a network theory of flow for polymer systems based on the kinetic theory of rubber elasticity. This theory, which describes qualitatively many of the features of polymer melt behaviour, is the basis for a number of rheological models and is a useful starting point.

Lodge assumes that the network junctions in the model have a finite lifetime but the concentration of junctions of a given age is constant. The proposed constitutive equation is

$$P_{ij} = -p\delta_{ij} + \int_{-\infty}^{t} \phi(t-t') C_{ij} \, dt' \quad 7.1$$

where $P_{ij}$ is the stress tensor, $p$ an arbitrary hydrostatic pressure and $\delta_{ij}$ the unit tensor. $C_{ij}$ is the Finger strain tensor whose components are given by

$$C_{ij} = \left( \begin{array}{cc} \frac{\partial x_i}{\partial x_{k'}} & \frac{\partial x_j}{\partial x_{k'}} \end{array} \right) \quad 7.2$$

where $x_i$ are the co-ordinates of a particle at current time, $t$ and $x_i'$ are the co-ordinates at some past time $t'$. $\phi$ is a function of the
elapsed time \((t-t')\) and can be interpreted as the 'junction age distribution function'. We can assume that older states are less important than newer states and thus \(\phi\) is a decreasing function of \((t-t')\).

Thus the stress is postulated to depend on the history of the strain and \(\phi\) is commonly called the **memory function**.

Equation 7.1 predicts qualitatively all the general features of polymer melt flow, e.g. stress relaxation, normal stress differences, shear recovery etc. However it incorrectly predicts that the viscosity and \((\sigma_1/G^2)\) are independent of shear rate. It also predicts that \(\sigma_2=0\) and while this is a good approximation in some cases it is not true in general.

A model similar to (7.1) has also been proposed by Fredricksen (1962)

\[
P_{ij} = -p\delta_{ij} - \int_{-\infty}^{t} \mu(t-t') \frac{\partial C_{ij}}{\partial t'} \, dt' \quad 7.3
\]

where \(\mu\) is the memory function. This model appears to have been inspired by Oldroyd (1950 equation 57). Equation 7.3 predicts the same behaviour as 7.1 and therefore suffers from the same disadvantages.

Lodge (see Spriggs et al 1966) suggested that a more useful model would be obtained if the memory function included a dependence on an invariant of the rate of strain tensor \(\dot{C}_{ij}\). He suggested an equation of the form

\[
P_{ij} = -p\delta_{ij} + \int_{-\infty}^{t} \phi(t-t', I_2(t')) \left[ (1+\varepsilon) C_{ij} + \varepsilon C_{ij}^{-1} \right] \, dt' \quad 7.4
\]
Where $I_2$ is the second invariant of the rate of strain tensor defined by

$$I_2 = \varepsilon_{ij} \cdot \varepsilon_{ij} \quad 7.5$$

$c$ is a constant and $C_{ij}^{-1}$ is the Cauchy-Green strain tensor whose components are

$$C_{ij}^{-1} = \left( \frac{\partial x_k'}{\partial x_i} \cdot \frac{\partial x_k'}{\partial x_j} \right) \quad 7.6$$

The term in $C_{ij}^{-1}$ is due to Ward & Jenkins (1958) and allows for non-zero values of $\sigma_2$. MacDonald & Bird (1966) proposed the following form for the memory function.

$$\phi[t-t', I_2(t')] = \left[ \frac{\eta_0}{n_1^{\infty}} \lambda_n \right] \sum_{n=1}^{\infty} \frac{\exp[-(t-t')/\lambda_n]}{\lambda_n(1+\frac{1}{2}I_2(t')c^2\lambda_n^2)} \quad 7.7$$

where $\eta_0$ is the zero shear rate viscosity, the $\lambda_n$ are time constants and $c$ is a constant. The $\lambda_n$ are related to a master constant $\lambda$ by

$$\lambda_n = \frac{\lambda}{n^\alpha} \quad 7.8$$

where $\alpha$ is a constant.

The model given by equations 7.4, 7.7 and 7.8 is known as the WJFLMB theory and contains 5 constants, $\eta_0$, $c$, $\lambda$, $\alpha$ and $c$.

The choice for $\lambda_n$ (equation 7.8) was guided by the molecular theory of Rouse (1953). In Spriggs et al's (1966) excellent review this theory appeared to be the most successful for describing the flow behaviour of polymer solutions. It has not been applied to data on high viscosity polymer melts.

In the same way that the WJFLMB model developed from Lodge's 1956 theory (equation 7.1), 7.3 has been extended to give the OWFS model (Sprigg's et al 1966).
The proposed equation is

\[
P_{ij} = -p\delta_{ij} - \int_{-\infty}^{t} \mu[t-t', I_2(t')] \left[ (1+\varepsilon')^2 \frac{\partial C_{ij}}{\partial t'} + \frac{\varepsilon}{2} \frac{\partial C_{ij}^{-1}}{\partial t'} \right] \, dt'  
\]

where \( \mu \) is given by

\[
\mu[t-t', I_2(t')] = \left( \frac{\eta_0}{\sum_{n=1}^{\infty} \lambda_n} \right) \sum_{n=1}^{\infty} \exp \left[ -\frac{(t-t')/\lambda_n}{1+\frac{1}{2}I_2(t')c^2\lambda_n^2} \right] 
\]

and the \( \lambda_n \) are defined by 7.8. This model contains the same 5 constants \( \eta_0, c, \lambda, \alpha, \varepsilon \) as the WJFLMB theory.

Kaye (1962) proposed an extension to Lodge's 1956 model similar to Rivlin's (1956) extension of theory of rubber elasticity. The equation takes the form

\[
P_{ij} = -p\delta_{ij} + 2 \int_{-\infty}^{t} \left\{ \frac{\partial U}{\partial J_1} C_{ij} - \frac{\partial U}{\partial J_2} C_{ij}^{-1} \right\} \, dt'  
\]

where \( J_1, J_2 \) are invariants of \( C_{ij} \) defined by

\[
J_1 = C_{ii} \\
J_2 = \frac{1}{2} \left[ (C_{ii})^2 - C_{ij} C_{ij} \right] 
\]

and \( U \) is a scalar function of \( J_1, J_2 \) and \( (t-t') \).

An identical expression to (7.11) was published separately by Bernstein, Kearsley & Zapas (1964) and this model is sometimes known as the BKZ theory. However we shall refer to it as the Kaye model.

Equation (7.11) is equivalent to considering the memory function in equation 7.4 to be a function of the strain invariants
J_1 and J_2 instead of the rate of strain invariant I_2.

Zapas (1966) has considered some forms for U but they do not appear to be very useful and do not give explicit solutions even in steady shear flow. Bogue & Doughty (1966) postulated the following form for U

\[
\frac{\partial U}{\partial J_1} = \frac{1}{4} \sum_{m=1}^{\infty} Q_m \exp \left[ -s/\lambda_m - b(J_1 - 3)^{1/2} \right] \left[ \frac{1 + b(J_1 - 3)^{1/2}}{\lambda_m s} \right]
\]

where \( Q_m, \lambda_m \) and b are constants and

\[
s = (t-t')
\]

A similar expression to 7.13 exists for \( \frac{\partial U}{\partial J_2} \).

The \( Q_m \) and \( \lambda_m \) are not interrelated and this can lead to a large number of constants. We might relate these to some master constants as in the WJFLMB and OWFS models. We, therefore, propose the following for U

\[
\frac{\partial U}{\partial J_1} = \frac{1}{4} \left( \frac{\eta_0}{\sum_{m=1}^{\infty} \lambda_m} \right) \sum_{m=1}^{\infty} \exp \left[ -s/\lambda_m - b(J_1 - 3)^{1/2} \right] \left[ \frac{1 + b(J_1 - 3)^{1/2}}{\lambda_m s} \right]
\]

\[
\frac{\partial U}{\partial J_2} = \frac{\varepsilon}{4} \left( \frac{\eta_0}{\sum_{m=1}^{\infty} \lambda_m} \right) \sum_{m=1}^{\infty} \exp \left[ -s/\lambda_m - b(J_2 - 3)^{1/2} \right] \left[ \frac{1 + b(J_2 - 3)^{1/2}}{\lambda_m s} \right]
\]

Where \( \eta_0 \) is the zero shear rate viscosity and the \( \lambda_m \) are related to \( \lambda \) by

\[
\lambda_m = \frac{\lambda}{m^a}
\]

where a is a constant

Thus like the WJFLMB and OWFS models there are 5 constants; \( a, \lambda, b, \eta_0, \varepsilon \). Similar models to equation 7.11 have been
considered by White (1968), while Bogue (1966) has discussed integral equations similar to the WJFLMB model but with the time constants depending on the mean shear rate over the past history. This form becomes rather clumsy and can lead to a large number of independent constants.

Thus we have three integral theories - WJFLMB, OWFS and Kaye - which we will compare with the experimental data obtained in the previous chapters. The models differ slightly but all contain integrals over the past time which are weighted so that old events are less important.

7.4 Comparison of Theories with Experimental Data

The theories were evaluated using the data for the two polyisobutylene's reported in chapters 3, 4 and 5. The model parameters were estimated from the steady shear flow results and then used to predict the behaviour in stress relaxation, stress growth and shear recovery. Thus the transient experiments are completely independent tests of the validity of the various theories.

The calculations were all carried out on an Atlas computer (University of London). To simplify the notation we will assume subsequently that

\[ \sum_{n} = \sum_{n=1}^{\infty} \]

7.17

(i) Steady shear flow

The kinematic equations are

\[
\begin{align*}
    x_1 &= x_1' + G(t-t') x_2' \\
    x_2 &= x_2' ; x_3 &= x_3' \\
    \text{and} \quad I_2(t') &= 2G^2
\end{align*}
\]

7.18
where $G$ is the steady shear rate. Evaluating $C_{ij}$ and $C_{ij}^{-1}$ from 7.2 and 7.6 we find from 7.12 that

$$J_1 = J_2 = 3 + G^2(t-t')^2$$ 7.19

**WJFLMB Theory:**

Substituting from above in the constitutive equation for this model (equations 7.4, 7.7 and 7.8) changing variable to $s$ (equation 7.14), we obtain

$$P_{21} = \eta_0 GZ(\alpha)^{-1} \sum_n n^\alpha / (n^{2\alpha} + c^2 \lambda^2 G^2)$$ 7.20

$$\sigma_1 = 2\eta_0 \lambda^2 G^2 Z(\alpha)^{-1} \sum_n 1 / (n^{2\alpha} + c^2 \lambda^2 G^2)$$ 7.21

$$\sigma_2 / \sigma_1 = \varepsilon / 2$$ 7.22

where $Z(\alpha)$ is the Riemann zeta function

$$Z(\alpha) = \sum_{n} 1/n^\alpha$$ 7.23

**OWFS Theory:**

We can show that this model (equations 7.9 and 7.10) gives identical results to the WJFLMB predictions

**Kaye Theory:**

By substituting for $J_1$, $J_2$, $C_{ij}$ and $C_{ij}^{-1}$ from 7.2, 7.6 and 7.12 in the constitutive equation (7.11, 7.15 and 7.16), we obtain

$$P_{21} = \eta_0 GZ(\alpha)^{-1} \sum_m 1 / (m^\alpha + bG\lambda)$$ 7.24

$$\sigma_1 = 2\lambda \eta_0 G^2 Z(\alpha)^{-1} \sum_m 1 / (m^\alpha + bG\lambda)^2$$ 7.25

$$\sigma_2 / \sigma_1 = \varepsilon / 2$$ 7.26
FIGURE 7.1 WJFLMB/OWFS Theories — Typical master curves in steady shear flow

\[ \left( \frac{q}{2 \lambda G^2 \eta_0} \right) \times 10^2 \text{ or } (\eta/\eta_0) \]
### TABLE 7.1

Model constants

<table>
<thead>
<tr>
<th></th>
<th>Vistanex LM-MS</th>
<th>Vistanex LM-MH</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_0 ) (poise)</td>
<td>( 4.74 \times 10^5 )</td>
<td>( 6.9 \times 10^5 )</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>-0.26</td>
<td>-0.32</td>
</tr>
<tr>
<td>WJFLMB/OWFS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha )</td>
<td>3.5</td>
<td>2.5</td>
</tr>
<tr>
<td>( c )</td>
<td>0.66</td>
<td>0.875</td>
</tr>
<tr>
<td>( \lambda ) (Sec)</td>
<td>2.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Kaye</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a )</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>( b )</td>
<td>0.4</td>
<td>0.48</td>
</tr>
<tr>
<td>( \lambda ) (Sec)</td>
<td>2.5</td>
<td>3.75</td>
</tr>
</tbody>
</table>
FIGURE 7.2 Vistanex LM-MH, 29·25°C – Comparison of steady shear data with WJFLMB/OWFS theories

<table>
<thead>
<tr>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_{21}$</td>
<td>○</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>□</td>
</tr>
</tbody>
</table>
FIGURE 7.3 Vistanex LM-MH, 29.25°C — Comparison of steady shear data with Kaye theory

<table>
<thead>
<tr>
<th></th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_1$</td>
<td></td>
<td>○</td>
</tr>
<tr>
<td>$P_{21}$</td>
<td></td>
<td>□</td>
</tr>
</tbody>
</table>
FIGURE 7.4 Vistanex LM-MS, 29.25°C – Comparison of steady shear data with WJFLMB/OWFS theories

<table>
<thead>
<tr>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>P21</td>
<td>⭕</td>
</tr>
<tr>
<td>σ1</td>
<td>⭕</td>
</tr>
</tbody>
</table>
FIGURE 7.5  Vistanex LM-MS, 29·25°C — Comparison of steady shear data with Kaye theory

<table>
<thead>
<tr>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>P21</td>
<td>O</td>
</tr>
<tr>
<td>a1</td>
<td>□</td>
</tr>
</tbody>
</table>
The procedure for estimating the model constants in the WJFLMB/OWFS theories was as follows:

(a) The viscosity of the fluid at low shear rates was approximately constant and this value was taken as $\eta_0$.

(b) A series of master curves were prepared for various $\alpha$ (figure 7.1).

(c) $\alpha$ and $\alpha\lambda$ were then determined by shifting the experimental log ($\eta/\eta_0$) - log $G$ curves along the shear rate axis until they coincided with one of the viscosity master curves.

(d) Similarly $\lambda$ was determined by shifting the experimental log ($\sigma_1/G^2$) - log $G$ curve along the ($\sigma_1/G^2$) axis until it coincided with a normal stress master curve.

(e) $\epsilon$ was calculated from the average value of $(\sigma_2/\sigma_1)$.

For the master curves shown in figure 7.1 the infinite series in equations 7.20 and 7.21 were truncated at $n=50$. This is justified since preliminary calculations showed that there was <0.001% difference between using 50 or 200 terms.

The constants in the Kaye model were obtained by an identical procedure.

The constants obtained for the two polyisobutylenes are shown in table 7.1. Using these values the theoretical curves are compared with the experimental data in figures 7.2 to 7.5.

The $p_21$ data are fitted quite well for the models and the fit of the $\sigma_1$ data, although it is not so good, is reasonable. There does not appear to be much difference between the WJFLMB/OWFS and Kaye theories in this flow situation.

The main weakness of these models in steady shear flow is that the curve of $p_21$ versus $G$ is related to the slope of $\sigma_1$ versus
G. In addition the ratio $\sigma_2/\sigma_1$ is required to be a constant which, considering the accuracy of the $\sigma_2$ data, is probably adequate as a first approximation.

(ii) **Stress relaxation**

Assuming that steady shear flow is stopped at $t=0$, then we wish to calculate how the stresses vary with time for $t>0$. The kinematic equations are given by

\[
\begin{align*}
    x_1 &= x_1' - \cdot Gx_2't' \\
    x_2 &= x_2' \quad ; \quad x_3 = x_3' \quad \text{for } t'<0<0t \\
    I_2 &= 2G^2 \\
    x_1 &= x_1' \quad ; \quad I_2 = 0 \quad \text{for } 0t'$t
\end{align*}
\]

where $G$ is the steady state shear rate. Evaluating $J_1$ and $J_2$ from 7.2, 7.6, 7.12, 7.27 and 7.28, we find

\[
\begin{align*}
    J_1 &= J_2 = 3 + G^2t'^2 \quad \text{for } t'<0 \\
    &= 3 \quad \text{for } t'\geq0 \\
\end{align*}
\]

Thus:

\[
\begin{align*}
    |(J_2 - 3)^{\frac{1}{2}}| &= -Gt' \quad \text{for } t'<0 \\
    &= 0 \quad \text{for } t'\geq0 \\
\end{align*}
\]

Substituting 7.27 to 7.30 in the constitutive equations (7.4, 7.7, 7.8 to 7.11, 7.15, 7.16) changing variable to $s$ and integrating, we obtain the following predictions for stress relaxation

OWFS/WJFLMB Theories:

These are identical in stress relaxation

\[
\begin{align*}
    \frac{p_{21}(t)}{p_{21}(0)} &= \sum_n n^\alpha \exp(-t/\lambda_n)/(n^{2\alpha} + G^2c^2\lambda^2) \\
    &= \sum_n n^\alpha/(n^{2\alpha} + G^2c^2\lambda^2) \\
\end{align*}
\]

- 95 -
\[
\sigma_1(t) = \sum_n \exp(-t/\lambda_n)/(n^2 + G^2c^2\lambda^2) \\
\sigma_1(o) = \sum_n 1/(n^2 + G^2c^2\lambda^2)
\]

Kaye Theory:

\[
P_{21}(t) = \sum_m \exp(-t/\lambda_m) (1-bGt)/(ma + bG\lambda) \\
P_{21}(o) = \sum_m 1/(ma + bG\lambda)
\]

\[
+ \sum_m \exp(bGt)bGt^2\lambda^{-1} E_1[t\lambda^{-1}(ma + bG\lambda)] \\
\sum_m 1/(ma + bG\lambda)
\]

\[
\sigma_1(t) = \frac{\sum_m \exp(-t/\lambda_m) (bGt^2\lambda^{-1}ma + b^2G^2t^2 - bGt^2)/2}{\sum_m 2/(ma + bG\lambda)^2} \\
\sigma_1(o) = \frac{\sum_m \exp(bGt)bGt^3\lambda^{-2} E_1[t\lambda^{-1}(ma + bG\lambda)]}{\sum_m 2/(ma + bG\lambda)^2}
\]

where

\[
E_1[x] = \int_x^\infty \frac{\exp(-t)}{t} \, dt
\]

\[7.35\]

\(p_{21}(t), \sigma_1(t)\) are the stress values for \(t>0\). \(p_{21}(o)\) and \(\sigma_1(o)\) are steady state stresses at a shear rate of \(G\).

A number of theoretical relaxation curves have been calculated from equations 7.31 to 7.34 for steady shear rates from 0.00572 to 14.4 sec\(^{-1}\). We have seen in chapter 4 that only the Vistanex LM-MS data for stress relaxation and stress growth were reliable; the calculations were therefore carried out using the model constants for this material (table 7.1). As for the steady shear rate predictions, the calculations were stopped at \(n\) or \(m = 50\).

\(E_1[x]\) (equation 7.35), which appears in the Kaye model predictions,
FIGURE 7.6 Stress relaxation of Vistanex LM-MS, 29·25°C
- Comparison of theory and experiment, steady shear rate = 0·144 sec^{-1}
was calculated using a polynomial approximation given by Abramowitz & Stegun (1965 p.231). The error in the approximation is stated to be $< 2 \times 10^{-7}$.

The theories predict that

(a) $P_{21}$ relaxes faster than $\sigma_1$

(b) There is very little change in the rate of stress relaxation ($<1\%$) for values of $G$ less than about 1 sec$^{-1}$, but above 1 sec$^{-1}$ the stresses relax more rapidly as $G$ increases.

These points agree qualitatively with the results reported in chapter 4 and other published data (Benbow & Howells 1961, Huppler et al 1967).

We have seen in chapter 4 that the $\sigma_1$ relaxation data are unreliable and we can only compare quantitatively the prediction of $P_{21}$ with experiment. This is shown in figure 7.6 for a steady shear rate of 0.144 sec$^{-1}$. Only results at this shear rate are shown because the experimental data cover the range of 0.00572 to 0.144 sec$^{-1}$ and there is little effect due to shear rate under these conditions.

The agreement between theory and experiment is fair but the observed relaxation is faster initially than predicted by the models. This is consistent with Huppler et al's (1967) data at low shear rates. There does not seem to be much difference between the OWFS/WJFLMB and Kaye theories; the relaxation of the OWFS/WJFLMB models are more rapid initially and vice versa at longer times for all shear rates. Huppler's results at higher shear rates do indicate that the OWFS/WJFLMB theoretical relaxation is too rapid initially and possibly the Kaye model would fit their results better under these conditions.
(iii) Stress growth

We assume that shear flow is applied to \( t=0 \), and the problem is to calculate the growth of the stresses as a function of time. The kinematic equations are

\[
\begin{align*}
x_1 &= x_1' + Gx_2't \\
x_2 &= x_2' ; x_3 = x_3' & \text{for } t'<0<t \tag{7.36} \\
I_2 &= o
\end{align*}
\]

\[
\begin{align*}
x_1 &= x_1' + Gx_2'(t-t') \\
x_2 &= x_2' ; x_3 = x_3' & \text{for } 0\leq t'<t \tag{7.37} \\
I_2 &= 2G^2
\end{align*}
\]

Evaluating \( J_1 \) and \( J_2 \) we obtain

\[
\begin{align*}
J_1 &= J_2 = 3 + G^2t^2 & \text{for } t'<0<t \tag{7.38} \\
&= 3 + G^2(t-t')^2 & \text{for } 0\leq t'<t
\end{align*}
\]

Thus

\[
\begin{align*}
| (J_1 - 3)^{\frac{1}{2}} | &= Gt & \text{for } t'<0 \tag{7.39} \\
&= G(t-t') & \text{for } t\geq 0
\end{align*}
\]

Substituting 7.33 to 7.36 in the rheological equations of state and integrating as before, the following predictions for stress growth.

OWFS Theory:

\[
\begin{align*}
p_{21}(t) &= 1 - \sum_n n^n \exp(-t/\lambda_n)/(n^{2\alpha} + G^2\lambda^2) \\
p_{21}(\infty) &= \frac{\sum_n n^\alpha/(n^{2\alpha} + G^2\lambda^2)}{\sum_n 1/(n^{2\alpha} + G^2\lambda^2)} \tag{7.40} \\
\dot{\sigma}_1(t) &= 1 - \sum_n n^n \exp(-t/\lambda_n)t\lambda^{-1}/(n^{2\alpha} + G^2\lambda^2) \\
\dot{\sigma}_1(\infty) &= \frac{\sum_n 1/(n^{2\alpha} + G^2\lambda^2)}{\sum_n \exp(-t/\lambda_n)/(n^{2\alpha} + G^2\lambda^2)} \tag{7.41}
\end{align*}
\]
7.42 \[ P_{21}(t) = 1 - \sum_{n} \frac{n^\alpha \exp(-t/\lambda_n)}{(n^{2\alpha} + G^2c^2\lambda^2)} \]

\[ P_{21}(\infty) = \sum_{n} \frac{n^\alpha}{(n^{2\alpha} + G^2c^2\lambda^2)} + \sum_{n} \frac{G^2c^2\lambda t \exp(-t/\lambda_n)}{(n^{2\alpha} + G^2c^2\lambda^2)} \]

\[ \sigma_1(t) = 1 - \sum_{n} \frac{n^\alpha t \lambda^{-1} \exp(-t/\lambda_n)}{(n^{2\alpha} + G^2c^2\lambda^2)} \]

\[ \sigma_1(\infty) = \sum_{n} \frac{1}{(n^{2\alpha} + G^2c^2\lambda^2)} \]

\[ \frac{\left(1 - \frac{G^2c^2t^2}{2}\right)}{\sum_{n} 1/(n^{2\alpha} + G^2c^2\lambda^2)} \]

7.44 \[ P_{21}(t) = 1 - \sum_{m} \frac{\exp(-bGt) \exp(-t/\lambda_m)}{(m^\alpha + bG\lambda)} \]

\[ P_{21}(\infty) = \sum_{m} \frac{1}{(m^\alpha + bG\lambda)} + \sum_{m} \frac{\exp(-bGt) bGt^2 \lambda^{-1} E_1[t/\lambda_m]}{(m^\alpha + bG\lambda)} \]

\[ \sigma_1(t) = 1 - \sum_{m} \frac{\exp(-bGt) \exp(-t/\lambda_m) [t \lambda^{-1} (m^\alpha + bG\lambda) + 1]}{(m^\alpha + bG\lambda)^2} \]

\[ \sigma_1(\infty) = \sum_{m} \frac{1}{(m^\alpha + bG\lambda)^2} + \sum_{m} \frac{\exp(-bGt) bGt^3 \lambda^{-2} E_1[t/\lambda_m]}{2(m^\alpha + bG\lambda)^2} \]

7.45

where \( P_{21}(\infty) \) and \( \sigma_1(\infty) \) are the steady state values of the stresses.

Theoretical stress growth curves were calculated for the same steady shear rates as for the stress relaxation curves discussed.
FIGURE 7.7 Stress growth of Vistanex LM-MS, 29.25°C — Comparison of theory and experiment, steady shear rate = 0.144 sec$^{-1}$
FIGURE 7.8 Theoretical stress growth curves, steady shear rate = 1.44 sec$^{-1}$
earlier. The models predict that $p_{21}$ reaches a steady value quicker than $\sigma_1$, qualitatively in agreement with the Vistanex LM-MS data and other published results (Huppler et al 1967, Benbow & Howells 1961).

At shear rates < about 1 sec$^{-1}$ the models give similar predictions, which are in reasonable agreement with experimental data (figure 7.7). The OWFS prediction is not shown in figure 7.7 but it is within 1% of the WJFLMB curve at these low shear rates. There is very little effect due to shear rate under these conditions, experimentally or theoretically.

As the shear rate increases there is a marked difference in the predictions of the three models. At shear rates above about 1 sec$^{-1}$ the modified Kaye and WJFLMB models predict that the stresses overshoot before reaching a steady value. No overshoot is predicted by the OWFS model. The predictions for a steady shear rate of 1.44 sec$^{-1}$ are shown in figure 7.8, and we also see that the WJFLMB model predicts a much larger overshoot than the modified Kaye model.

The data reported in chapter 4 did not exhibit any overshoot but the results are restricted to shear rates < 1 sec$^{-1}$. Vinogradov & Belkin (1965) reported overshoot in polystyrene and polyethylene melts and Huppler et al (1967) reported similar behaviour for a number of polymer solutions at high shear rates.

The amount of overshoot predicted by the Kaye and WJFLMB models increases as the shear rate increased and the time at which the stresses reach a maximum decreases. These points are qualitatively in agreement with the published data.

Huppler found that the predicted overshoot for the WJFLMB model was much larger than observed experimentally. The modified Kaye theory would seem to fit their data better in this respect. The OWFS model is clearly unsuitable since it does not predict any overshoot.
(iv) Constrained shear recovery

Let us assume that steady shear flow has been applied for a very long time and is removed at \( t = 0 \), thus

\[
\begin{align*}
P_{21} & = \text{constant} = P_{21}(G) \quad \text{for } t < 0 \\
P_{21} & = 0 \quad \text{for } t \geq 0
\end{align*}
\]

where \( G \) is the steady shear rate (for \( t < 0 \)).

The problem is to calculate the recovery as a function of time. We assume that the system is constrained so that only simple shear recovery occurs, i.e. in the \( x_1 \) co-ordinate direction. The kinematic description is

\[
\begin{align*}
x_1 & = x_1' + [\gamma(t) - Gt'] x_2'' \\
x_2 & = x_2' ; x_3 = x_3' \\
I_2(t') & = 2G^2 \\
x_1 & = x_1' + [\gamma(t) - \gamma(t')] x_2'' \\
x_2 & = x_2' ; x_3 = x_3' \\
I_2(t') & = 2 \left[ \frac{\partial \gamma(t')}{\partial t'} \right]^2
\end{align*}
\]

where \( \gamma(t) \) is the strain recovered at \( t \). The total elastic recovery \( \gamma_\infty \) is given by

\[
\gamma_\infty = \gamma(t) \quad \text{as } t \rightarrow \infty
\]

Substituting from 7.46 and 7.47 in the constitutive equation for the WJPLMB model we obtain

\[
0 = \int_0^\infty \sum_n \frac{\exp[-(t-t')/\lambda_n] \left[ \gamma(t) - Gt' \right]}{\lambda_n (1 + G^2c^2\lambda_n^2)} dt' + \int_0^\infty \sum_n \frac{\exp[-(t-t')/\lambda_n] \left[ \gamma(t) - \gamma(t') \right]}{\lambda_n (1 + D^2c^2\lambda_n^2)} dt'
\]

- 101 -
where
\[ D^2 = \left[ \frac{\partial^2 \gamma(t')}{\partial t'^2} \right]^2 \]  
\[ \text{7.51} \]

The second integral cannot be solved analytically since \( \gamma(t') \) is unknown. However by substituting for \( t' \) from 7.14, the first integral can be evaluated; 7.50 becomes

\[ 0 = G \sum_n \frac{n^\alpha \exp(-t/\lambda_n)}{(n^2 + G^2c^2\lambda^2)} + \gamma(t) \sum_n \frac{n^{2\alpha} \exp(-t/\lambda_n)}{(n^2 + G^2c^2\lambda^2)} \]
\[ + \int \sum_n \frac{\exp\left[-(t-t')/\lambda_n\right]\left[\gamma(t) - \gamma(t')\right]}{\left(1 + D^2c^2\lambda_n^2\right)} dt' \]
\[ \text{7.52} \]

Similarly for the OWFS model we obtain

\[ 0 = G \sum_n \frac{n^\alpha \exp(-t/\lambda_n)}{(n^2 + G^2c^2\lambda^2)} + \int \sum_n \frac{\exp\left[-(t-t')/\lambda_n\right]D dt'}{\left(1 + D^2c^2\lambda_n^2\right)} \]
\[ \text{7.53} \]

The solution for the Kaye model is more complicated since we do not know \( | (J_1 - 3)^\frac{1}{2} | \) for \( t' \leq \delta \). Evaluating \( J_1 \) and \( J_2 \) we find

\[ J_1 = J_2 = 3 + \left[ \gamma(t) - \frac{Gt'}{2} \right]^2 \text{ for } -\infty < t' < \infty \]
\[ J_1 = J_2 = 3 + \left[ \gamma(t) - \gamma(t') \right]^2 \text{ for } t > t' \geq 0 \]
\[ t^* = \frac{Gt - \gamma(t)}{G} \]
\[ \text{7.54} \]
\[ \text{7.55} \]
\[ \text{7.56} \]

Then from 7.54 and 7.56

\[ | (J_1 - 3)^\frac{1}{2} | = \frac{Gt^* + G(t-t')}{t-t^*} \text{ for } -\infty < t' < t-t^* \]
\[ | (J_1 - 3)^\frac{1}{2} | = \frac{Gt^* - G(t-t')}{o > t' \geq t-t^*} \]
\[ \text{7.57} \]
Since \( \gamma(t') \) is negative and decreases with \( t \)
\[
| (J - 3)^{\frac{1}{2}} | = \gamma(t') - \gamma(t) \quad \text{for } 0 \leq t' < t \quad 7.58
\]
Substituting 7.46 to 7.48, 7.57 and 7.58 in the constitutive equation for the Kaye model we obtain
\[
0 = \int_{t-t^*}^{t} \sum_{m} G \exp(-bGt) \exp \left[-\frac{1-bG\lambda_m}{\lambda_m} \right] \left[ 1 - \frac{bG+bGt^*}{s} \right] (s-t^*) \, dt'
\]
\[
+ \int_{t^*}^{\infty} \sum_{m} G \exp(bGt) \exp \left[-\frac{1-bG\lambda_m}{\lambda_m} \right] \left[ 1 + \frac{bG-bGt^*}{s} \right] (s-t^*) \, dt'
\]
\[
+ \int_{0}^{\infty} \sum_{m} \exp \left[-\frac{s + b[\gamma(t) - \gamma(t')]}{\lambda_m} \right] \left[ 1 - \frac{b[\gamma(t) - \gamma(t')]}{s} \right] \frac{[\gamma(t) - \gamma(t')] \, dt'}{[\gamma(t) - \gamma(t')]}
\]
where \( s \) is given by 7.14. The last integral cannot be solved analytically. However the other integrals can be solved by substituting for \( t' \) from 7.14; equation 7.59 then becomes.
\[
0 = G \sum_{m} \exp \left[-\frac{t^*}{\lambda_m} \right] \lambda \left[ \frac{(1-bGt^*)}{(m^a+bG\lambda)} - \frac{(1+bGt^*)}{(m^a-bG\lambda)} \right]
\]
\[
+ G \exp[-D\gamma(t)] \sum_{m} \exp(-t/\lambda_m) \left[ \frac{t-t^* + \lambda(1+bGt^*)}{(m^a+bG\lambda)} \right]
\]
\[
+ (Gt^*)^2 b \exp(bGt^*) \sum_{m} E_1 \left[ t^* \lambda^{-1}(m^a+bG\lambda) \right]
\]
\[
- (Gt^*)^2 b \exp(bGt^*) \sum_{m} B
\]
\[
+ \int \sum_{m} \exp \left[ -s/\lambda_{m}^{b} [\gamma(t)-\gamma(t')] \right] \left[ \frac{1 - b[\gamma(t)-\gamma(t')]}{\lambda_{m}^{s}} \right] [\gamma(t)-\gamma(t')] dt'
\]

where the \( B_{m} \) are given by

\[
B_{m} = E_{1} \left[ t^{\lambda^{-1}} (m^{\theta}-b_{m}\lambda) \right] - E_{1} \left[ t^{\lambda^{-1}} (m^{\theta}-b_{m}\lambda) \right] \quad \text{for} \quad (m^{\theta}-b_{m}\lambda) > 0
\]
\[
B_{m} = \ln \left( t^{*}/t \right) \quad \text{for} \quad (m^{\theta}-b_{m}\lambda) = 0
\]
\[
B_{m} = \ln \left( t^{*}/t \right) + \sum_{n} \frac{(t^{*n} - t^{n})}{n \ln \left[ \lambda/(m^{\theta}-b_{m}\lambda) \right]} \quad \text{for} \quad (m^{\theta}-b_{m}\lambda) < 0
\]

To calculate the model predictions it is necessary to solve 7.52, 7.53 and 7.60 for \( \gamma(t) \), which cannot be done analytically. However, by solving the integrals in these equations numerically we can obtain \( \gamma(t) \) by an iterative process. The integrals were solved by the trapezium rule and we assume, therefore, that 7.52, 7.53, and 7.60 can be approximated by

**WJFLMB Theory:**

\[
0 = \gamma(t) \sum_{n} \exp \left(-t/\lambda_{n}\right) \frac{n^{2\alpha}/(n^{2\alpha}+G^{2}c^{2}2^{\lambda^{2}})}{n^{2\alpha}+G^{2}c^{2}2^{\lambda^{2}}}
\]
\[
+ GL \sum_{n} \exp \left(-t/\lambda_{n}\right) \frac{n^{\alpha}/(n^{2\alpha}+G^{2}c^{2}2^{\lambda^{2}})}{n^{2\alpha}+G^{2}c^{2}2^{\lambda^{2}}}
\]
\[
+ \sum_{k} \sum_{\lambda_{n}} \exp \left[ -(t_{k} - \bar{t}_{j})/\lambda_{n} \right] \frac{[\gamma(t_{k}) - \bar{\gamma}_{j}(t')] \Delta t_{j}}{\lambda_{n} \left( 1+D_{j}^{2} c^{2} \lambda_{n}^{2} \right)}
\]

**OWFS Theory:**

\[
0 = GL \sum_{n} \frac{n^{\alpha} \exp(-t/\lambda_{n})/(n^{2\alpha} + G^{2}c^{2}2^{\lambda^{2}})}{n^{2\alpha} + G^{2}c^{2}2^{\lambda^{2}}}
\]
\[ + \sum_{j=1}^{k} \sum_{n} \exp \left\{ -(t_k - t_j)/\lambda_n \right\} \frac{D_j \Delta t_j}{(1 + D_j^2 c^2 \lambda_n^2)} \] 7.63

Kaye Theory:

\[ 0 = G \lambda \sum_{m} \exp \left\{ -t^*/\lambda_m \right\} \left[ \frac{1-bGt^*}{(m^a+bG\lambda)} - \frac{1+bGt^*}{(m^a-bG\lambda)} \right] \]

\[ + G \exp \left\{ bY(t) \right\} \sum_{m} \exp(-t/\lambda_m) \left[ \frac{t-t^* + \lambda(1+bGt^*)}{(m^a - bG\lambda)} \right] \]

\[ - (Gt^*)^2 b \exp(-bGt^*) \sum_{m} B_m \]

\[ + (Gt^*)^2 b \exp(bGt^*) \sum_{m} E[ t^* \lambda_m^{-1} / (m^a + bG\lambda) ] \]

\[ + \sum_{m} \sum_{j=1}^{k} \exp \left[ -(t_k - \bar{t}_j) + b [Y(t_k) - \bar{Y}_j(t')] \right] \frac{1 - b [Y(t_k) - \bar{Y}_j(t')] \left[ Y(t_k) - \bar{Y}_j(t') \right]}{\lambda_m (t_k - \bar{t}_j)} \Delta t_j \] 7.64

where

\[ \Delta t_j = t_j - t_{j-1} = (k^*)^{j-1} \Delta t_1 \] 7.65

\[ t_k = t = \sum_{j=1}^{k} \Delta t_j \] 7.66

\[ \bar{t}_j = (t_j + t_{j-1})/2 \] 7.67

\[ \bar{D}_j = [Y(t_j) - Y(t_{j-1})] / \Delta t_j \] 7.68

\[ \bar{Y}_j(t') = [Y(t_j) + Y(t_{j+1})] / 2 \] 7.69

and \( k^* \) is a constant.

The \( B_m \) in 7.64 are evaluated from 7.61 depending on the
value of \((m^a - bG\lambda)\). If we take small increments of time, \(\gamma(t)\) can be evaluated at each increment by some iteration process. Since the recovery curve approximates to an exponential it seems reasonable to use time increments which increase with \(t\) to reduce the amount of computation. Thus usually \(k^*\) (equation 7.65) will be \(> 1\).

The calculation proceeds as follows

(a) \(\Delta t_1, k^*, G\) and a maximum time of \(t\) are specified

(b) \(t_1\) and \(\bar{t}_1\) are calculated from 7.66 and 7.67

(c) \(\gamma(t_1)\), is found from 7.62 to 7.64 by an iterative process suggested by Horsfall (1969). The method is based on the secant technique (Ralston 1965) and is written as a standard subroutine. The programme must be supplied with two trial values of \(\gamma(t_1)\) to start the iteration. These were chosen to be near zero and a value larger than we would expect. \(\bar{D}_1\) and \(\bar{\gamma}_1(t')\) were calculated from 7.68 and 7.69 using the most up to date estimate of \(\gamma(t_1)\) (N.B. \(\gamma(t_0) = 0\)).

The iteration stopped at some specified convergence criterion, in this case if the modulus of the left hand side in equations 7.62 to 7.64 was \(< 10^{-7}\).

(d) \(t_2, \bar{t}_2\) are calculated and the process repeated.

Thus in general for \(\gamma(t_k)\) we proceed as follows

(e) Calculated \(\Delta t_k, \bar{t}_k, t_k\) from 7.65 to 7.67

(f) Find \(\gamma(t_k)\) by the iterative process described above, using the current estimate of \(\gamma(t_k)\) to calculate \(\bar{D}_k\) and \(\bar{\gamma}_k(t')\) at each iteration. For \(\bar{D}_k\) and \(\bar{\gamma}_j(t')\), where \(j < k\), the values of \(\gamma(t_j)\) previously calculated are used.

(g) The procedure was repeated until \(t_k\) reached the specified maximum \(t\). This was chosen by trial and error so that \(\gamma(t_k)\) was independent of time, i.e. to within 0.2% of \(\gamma(t_{k-1})\). Thus it is
TABLE 7.2

Kaye's theory - Effect of $k^*$ and $\Delta t_1$ on recovery calculations

<table>
<thead>
<tr>
<th>$G$ (sec$^{-1}$)</th>
<th>$k^*$</th>
<th>$\Delta t_1/k^*$ (sec)</th>
<th>$\gamma_\infty$</th>
<th>Material constants (see table 7.1)</th>
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<tbody>
<tr>
<td>0.05</td>
<td>2.0</td>
<td>0.005</td>
<td>0.11784</td>
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<tr>
<td></td>
<td></td>
<td>0.0025</td>
<td>0.11801</td>
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<td></td>
<td></td>
<td>0.00125</td>
<td>0.11801</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>2.0</td>
<td>0.005</td>
<td>0.42833</td>
<td>Vistanex LM-MS</td>
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<td>0.42925</td>
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</tr>
<tr>
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<td>0.00125</td>
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</tr>
<tr>
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<td>1.5</td>
<td>0.00125</td>
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<td>0.68936</td>
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TABLE 7.3

WJFLMB theory - Effect of $k^*$ and $\Delta t_1$ on recovery calculations

<table>
<thead>
<tr>
<th>$G$ (sec$^{-1}$)</th>
<th>$k^*$</th>
<th>$\Delta t_1/k^*$ (sec)</th>
<th>$\gamma_\infty$</th>
<th>Material constants (see table 7.1)</th>
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<tbody>
<tr>
<td>0.05</td>
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<td>0.15450</td>
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<tr>
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<td>2.0</td>
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<td>0.15818</td>
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<td>0.25</td>
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TABLE 7.4

OWFS theory - Effect of k* and Δt₁ on recovery calculations

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<tr>
<th>G (sec⁻¹)</th>
<th>k*</th>
<th>Δt₁/k* (sec)</th>
<th>Y∞</th>
<th>Material constants (see table 7.1)</th>
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</thead>
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<td>0.22212</td>
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<td>2.0</td>
<td>0.0006</td>
<td>0.22396</td>
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</tr>
<tr>
<td></td>
<td>1.6</td>
<td>0.0006</td>
<td>0.22349</td>
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</tr>
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<td>0.22294</td>
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</tr>
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<td>1.0399</td>
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<td>0.0012</td>
<td>1.0431</td>
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<td>2.0</td>
<td>0.0006</td>
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</tr>
<tr>
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<td>0.0006</td>
<td>1.0269</td>
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<tr>
<td></td>
<td>1.5</td>
<td>0.0006</td>
<td>1.0178</td>
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</table>
FIGURE 7.9 Shear recovery of Vistanex LM-MH, 29.25°C
- Comparison of experiment and theory

\[ G \text{ (sec}^{-1}) \]

---

- Kaye
- WJFLMB
- OWFS
- Δ Experiment
FIGURE 7.10 Shear recovery of Vistanex LM-MS, 29.25°C
Comparison of experiment and theory

Δ Experiment
--- OWFS
--- Kaye
--- WJFLMB
reasonable to assume that $\gamma(t_{k})$ for the maximum $t$ is a good estimate of $\gamma_\infty$. The highest value of $t$ needed was \~20 seconds.

The infinite series in 7.62 to 7.64 were terminated at $n$ or $m = 50$ as before. Similarly terms containing $E_1 (x)$ in 7.64 were neglected for $x \geq 50$. A few calculations where terms in $E_1 (x)$ were neglected for $x \geq 100$ showed that this last assumption is reasonable; the differences were not noticed to five significant digits.

The accuracy of the numerical integration was checked using different values of $\Delta t_1/k^*$ and $k^*$. Typical results for the Kaye theory are given in table 7.2, which shows that there is less than 1% difference between the values of $\gamma_\infty$ obtained for the various $t_1$ and $k^*$. Since a high value of $k^*$ is preferred to minimize computer time, all the other results for the Kaye theory reported here were obtained using $k^* = 2$ and $t_1 = 0.0025$ sec. Recovery curves were calculated for various values of $G$ from 0.03 to 0.25 sec$^{-1}$, using the material constants in table 7.1.

The effects of $k^*$ and $\Delta t_1$ on the results for the WJFLMB and OWFS theories are shown in tables 7.3 and 7.4. Clearly a lower value of $k^*$ is needed for the WJFLMB theory to give the same order of convergence as the Kaye model. Similarly it is necessary to use a lower value of $\Delta t_1$ and $k^*$ for the OWFS model. The results subsequently reported were obtained using $k^* = 1.6$, $\Delta t_1/k^* = 0.00125$ sec for the WJFLMB theory, and $k^* = 1.6$, $\Delta t_1/k^* = 0.0006$ sec for the OWFS theory.

The predictions of the three models for $\gamma_\infty$ are compared with the experimental data in figures 7.9 and 7.10. The OWFS model generally predicts values which are higher than the experimental data, particularly at high shear rates where they differ by a factor of two. Also the slope...
FIGURE 7.11 Shear recovery curve for Vistanex LM-MS, 29.25°C

- Comparison with theory

- Experiment
- Kaye
- WJFLAB
\[ \partial \gamma / \partial G \] for this model increases as \( G \) increases contrary to the experimental results.

However for the Kaye and WJFLMB theories the agreement between experiment and theory is much better. We see that the theoretical recovery is lower than the observed recovery at low shear rates and vice versa at the higher shear rates. This is similar to the discrepancy between the theoretical and experimental \( \sigma_1 \) data (figures 7.2 to 7.5). Possibly if the normal stress steady state data are fitted better the elastic recovery prediction may also be improved. The results indicate that there is little to choose between the WJFLMB and Kaye models for predicting total elastic recovery \( \gamma_e \).

The expression for the Kaye model (equation 7.64) is more complicated than the other models but less computer time was needed since a larger time increment could be used for the same accuracy. This is possibly because the OWFS and WJFLMB models contain time derivatives of the strain. Numerical differentiation is notoriously susceptible to errors and we might expect to use very small time increments to get an accurate estimate of a gradient.

The predicted curves for the Kaye and WJFLMB theories are compared with experiment in figure 7.11. The models predict a much faster recovery than is observed experimentally: the WJFLMB model is closer to the data than the Kaye model. Both theories predict that the recovery is slower as \( G \) increases. However the effect is very small at the shear rates investigated. We saw earlier (chapter 5) that \( G \) did not have a significant effect on the experimental recovery curves.

There does not appear to be a unique theoretical relationship for all \( G \) between \( \gamma_e \) and the ratio of the stresses \( \sigma_1 / p_{21} \) in shear flow. It depends on the magnitude of the model constants. However as
G tended to zero the Kaye and the WJFLMB models tended to the Lodge (1964) prediction i.e.

\[ \gamma_\infty = \sigma_1/2p_{21} \]  

Also as the shear rate increased the predicted \( \gamma_\infty \) is larger than given by 7.70 for the kaye theory and lower for the WJFLMB theory. We saw in chapter 5 that experimentally there did appear to be a relation between \( \gamma_\infty \) and \( \sigma_1/p_{21} \) and the value of \( \gamma_\infty \) was found to be greater than predicted by the Lodge theory.

There is a reasonable agreement between experiment and the Kaye and WJFLMB theories for the total recovery \( \gamma_\infty \). This is encouraging but neither model describes the recovery curve adequately. The OWFS model is not suitable for describing this experiment.

7.5 Discussion

In steady shear flow there is little to choose between the models. Their main weakness is that the slope of the \( \sigma_1 - G \) curve is rigidly related to the \( p_{21} - G \) curve and hence to one material constant '\( a \)' (WJFLMB/OWFS) or '\( a \)' (Kaye). Thus we obtained a good fit to the viscosity data but the predicted slope of \( \sigma_1 \) versus \( G \) was too steep. Another deficiency of the theories in steady shear flow is that the ratio \( \sigma_2/\sigma_1 \) is constant. This could be avoided by replacing \( \varepsilon \) in the WJFLMB/OWFS models by some scalar function of \( I_2 \) and changing the dependence of \( U \) on \( J_2 \) in the Kaye theory. The present and other published data are not precise enough to suggest the form for these functions and any modification at this time would seem unnecessary.

There is little to choose between the theories in stress relaxation or stress growth at low shear rates. The agreement between
theory and experiment is fair. However, in stress growth experiments at shear rates >1 sec\(^{-1}\), the models behave differently. The WJFLMB and Kaye theories predict that the stresses overshoot; the OWFS model does not. The amount of overshoot is much higher for the WJFLMB model. Thus this experiment would seem to be an excellent method for distinguishing between theories. Unfortunately the present data are limited to shear rates below 1 sec\(^{-1}\) and we could not determine whether the melts exhibit overshoot. However, there is ample evidence (Vinogradov & Belkin 1965, Huppler et al 1967) that overshoot occurs in polymer melts and solutions at higher shear rates. The OWFS model is therefore unsuitable.

Huppler reported that the overshoot predicted by the WJFLMB theory was much larger than occurred experimentally. The Kaye model would probably describe this experiment better.

For the total elastic recovery \(\gamma_\infty\) the predictions of the Kaye and WJFLMB theories are in reasonable agreement with experiment but the prediction of the OWFS model is much too high. The recovery curve is, however, not described very well by any of the models; the WJFLMB theory is the nearest.

Clearly the OWFS theory is not a suitable model for polymer melts. The WJFLMB and Kaye constitutive equations look more promising but it is not possible to decide at this stage which is better. They would appear to be capable of some modification to improve on the weaknesses described earlier. The WJFLMB model looks less mathematically complicated in the simple flows we have considered. However, in the iterative calculations (recovery) the Kaye model did appear to converge more rapidly. This may be an important point to consider in the choice of the most suitable rheological equation of state.
Total thrust and torque measurements in cone-plate and parallel plate rheometers are useful techniques for determining \( \eta, \sigma_1 \) and \( \sigma_2 \) for polymer melts in steady shear flow. Data are presented at shear rates from 0.01 to 0.3 sec\(^{-1}\) for two polyisobutlenes and a depolymerised natural rubber.

A statistical analysis of the polyisobutylene results indicates that \( \sigma_2 \) is significantly different from zero, is negative and the ratio \( |\sigma_2/\sigma_1| \) is less than 0.3. The data for depolymerised natural rubber are not inconsistent with these conclusions. \( \eta \) and the quantity \( \sigma_1/G^2 \) decrease as the shear rate increases but tend to a constant value at low shear rates.

It is not always possible to obtain reliable stress relaxation and stress growth data on rotational viscometers such as the Weissenberg Rheogoniometer. Experiments with Vistanex LM-MH and Paralac 385 confirmed that interaction between the fluid under test and the measuring system can be significant for high viscosity fluids. The results reported for Vistanex LM-MS however, indicate that reliable data can be obtained on lower viscosity fluids if a stiff torsion bar is used. For this material \( P_{21} \) grows and relaxes faster as the steady shear rate increases.

The normal stress relaxation and growth data are unreliable but there is some evidence that \( \sigma_1 \) relaxes and grows more slowly than \( P_{21} \).

Shear recovery results are reported for the two polyisobutlenes over a range of steady shear stresses from \( 1.5 \times 10^4 \) to \( 1.05 \times 10^5 \) dyn cm\(^{-2}\). The total recovery \( \gamma_\infty \) increases as the steady shear stress increases.
but the rate of recovery is independent of the applied stress.

The recovery data have been compared with the values calculated from the steady shear flow stresses according to the theories of Lodge and Weissenberg. Neither theory is appropriate but the experimental points are closer to Lodge's theory.

The recovery data for both materials reduce to a single curve if $\gamma^*$ is plotted against $\sigma_1/p_{21}$.

It has been confirmed that a Newtonian fluid exhibits die swell at low shear rates. The average die swell is 13.5%, and is independent of capillary radius, volume rate of flow and viscosity.

For a high viscosity elastic fluid die swell increases with shear rate but is independent of capillary radius. At low shear rates the die swell is asymptotic to the Newtonian value.

It is shown that the momentum balance theory, which relates $\sigma_1$ to die swell is not appropriate to highly viscous fluids of any type.

The predictions of three integral rheological equations of state — OWFS, WJFLMB and Kaye — have been compared with the experimental data obtained on the polyisobutylenes. Many of the features of the flow behaviour of elastic fluids are described by the WJFLMB and Kaye theories, but the OWFS theory is deficient on several points and it is not a suitable model.

There is very little difference between the WJFLMB and Kaye models when they are compared with the polyisobutylene data. The agreement between the experiment and theory in steady flow, stress relaxation, stress growth and total shear recovery is reasonable, but neither theory describes the form of the recovery curve satisfactorily. The Kaye theory would seem to fit other published data on stress
growth better than the WJFLMB theory.

The major disadvantages of the theories are that the slopes of the $p_{21}$ versus $\gamma_\infty$ and $\sigma_1$ versus $G$ curves are related to the slope of the $\eta$ versus $G$ curve. Also $\sigma_2/\sigma_1$ is required to be a constant, but this is not a serious limitation.

In the iterative calculations for recovery the Kaye model converged more rapidly than the WJFLMB model and less computer time was used. This may be a significant point in favour of the Kaye type of theory, which contains terms in strain and invariants of strain only, over the WJFLMB type of theory, which contain terms in strain and invariants of the rate of strain.

Clearly further experimental results are required to establish which type of rheological equation of state is a suitable model to describe the flow properties of high viscosity elastic fluids. Both the WJFLMB and Kaye theories are useful starting points and appear to be capable of some modification to improve on some of their deficiencies.
APPENDIX A

Differentiation of Experimental Data

The method is based on the movable strip technique discussed by Hershey, Zakin & Simha (1967). The slope is estimated by fitting a low order polynomial to an odd number of data points centred on the point required, and differentiating the function analytically. The procedure must be modified at the ends of the tabulated data. Since there are several errors in Hershey et al's paper, e.g. equations 24, 25 and 32 are wrong, we will outline the method in some detail. The notation used in this appendix is independent of the rest of the thesis.

We will assume that the data are represented by:

$$y_i = \sum_{j=0}^{m} a_j x_i^j + e_i$$  \hspace{1cm} A.1

Where $x_i$ is the independent variable, $y_i$ is the observed value of the dependent variable, the $a_j$ are unknown coefficients in the polynomial and $e_i$ is the error. We will assume that all the error is in the dependent variable $y_i$.

The $a_j$ are evaluated by least squares analysis giving the following set of simultaneous equations written in matrix notation (Plackett 1960):

$$(A) = (X'X)^{-1} (X'Y)$$  \hspace{1cm} A.2

Where $(A)$ is the column vector with elements $a_j$; $(X'X)$ and $(X'Y)$ are defined by:

$$(X'X) = \begin{bmatrix} N' & \sum x_i & \sum x_i^2 & \ldots & \sum x_i^m \\ \sum x_i & \sum x_i^2 & \sum x_i^3 & \ldots & \sum x_i^{m+1} \\ \sum x_i^2 & \sum x_i^3 & \sum x_i^4 & \ldots & \sum x_i^{m+2} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \sum x_i^m & \sum x_i^{m+1} & \sum x_i^{m+2} & \ldots & \sum x_i^{2m} \end{bmatrix}$$  \hspace{1cm} A.3
where \( N' \) is the number of data points in the strip.

Thus the \( a_j \) are readily obtained from A.2 provided we can invert \((X'X)\). The gradient is then calculated from

\[
\frac{dy}{dx} = \sum_{j=1}^{m} j a_j x_i^{j-1} \tag{A.5}
\]

Initially we must determine \( N' \) and the degree of polynomial \( m \) which adequately represents the observations.

**Estimation of \( m \)**

This is estimated by an analysis of variance (Plackett 1960). We calculate the sum of squared residuals \( R_u \) for each value of \( u = 1, 2, 3, \ldots \) etc., and the variance ratio \( F_u \) for testing the hypothesis \( a_u = 0 \). \( R_u \) and \( F_u \) are evaluated from

\[
R_u = \sum_{i=1}^{N'} \left( y_i - \sum_{j=0}^{u} a_j x_i^j \right)^2 \tag{A.6}
\]

\[
F_u = \frac{(R_{u=1} - R_u) (N' - u - 1)}{R_u} \tag{A.7}
\]

If \( F_u \) is less than the \( F \)-distribution with 1 and \((N'-u-1)\) degrees of freedom at some appropriate probability level, \( 0.05 \) is convenient, then \( a_u x_i^u \) need not be included in A.1. Thus \( m = (u-1) \) is an adequate fit to the data. This analysis of variance must be applied at all
points to ensure that all portions of the data are well represented by the value of \( m \) finally selected.

**Estimation of \( N' \)**

The number of points \( N' \) to include in the strip cannot be decided by any known statistical test. Repeating the calculations with various \( N' \) and deciding the best value by inspection seems to be the only method, unless there is prior knowledge about the relationship between \( x \) and \( y \). Good results have been obtained with \( N' = 7 \) (Zakin et al 1966) and \( N' = 5 \) (Hershey et al 1967), but each set of data must be examined individually.

**Error in Calculated Slope**

The 95% confidence limits are a convenient estimate of the error in the slope. These are given by (Graybill 1961):

\[
\pm t_{0.05} \left\{ \left( g'(x) (X'X)^{-1} g(x) \sigma^2 \right)^{\frac{1}{2}} \right\}
\]

Where \( g(x) \) is the column vector defined by:

\[
g(x) = \begin{bmatrix} 0 \\ 1 \\ 2x \\ 3x^2 \\ \vdots \\ mx^{m-1} \end{bmatrix}
\]

\( g'(x) \) is the transpose of \( g(x) \) and \( \sigma^2 \), the variance, is calculated from

\[
\sigma^2 = R_m / (N' - m - 1)
\]

\( t_{0.05} \) is the appropriate Student's t-distribution for \( (N'-m-1) \) degrees of freedom.
Procedure at the ends of the data

We can only use the method described above for points which are at least \((N'-1)/2\) intervals from the ends of the tabulated data. For the other points the slope is calculated from the polynomial fitted at \((N'-1)/2\) intervals from the ends of the data. The confidence limit is calculated from A.8 in the usual way. The errors at these end points will tend to be larger.

Numerical Technique

The problem was programmed for the Atlas computer (University of London) using Fortran V language. The simultaneous equations (A.2) were solved by Gauss elimination with pivotal interchange (Bickley & Thompson 1964), and the slope and confidence limits evaluated from A.5 and A.8. The calculations were in single precision arithmetic, i.e. 11 digits.
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### LIST OF SYMBOLS

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<th>Symbol</th>
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<td>a</td>
<td>Constant in Kaye theory</td>
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<tr>
<td>B</td>
<td>Exponent in power law (equation 2.12)</td>
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<td>$B_m$</td>
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<tr>
<td>b</td>
<td>Constant in Kaye theory</td>
</tr>
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<td>$C_p$</td>
<td>Specific heat</td>
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<td>$C_{ij}$</td>
<td>Finger strain tensor (equation 7.2)</td>
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</tr>
<tr>
<td>$\dot{e}<em>{11}$, $\dot{e}</em>{12}$, $\dot{e}_{13}$</td>
<td>Components of rate of strain tensor in Cartesian co-ordinates and co-ordinate system $\xi_1$, $\xi_2$, $\xi_3$.</td>
</tr>
<tr>
<td>$\dot{e}<em>{\phi\phi}$, $\dot{e}</em>{\phi\theta}$, $\dot{e}_{\phi\tau}$</td>
<td>Components of rate of strain tensor in spherical polar co-ordinates.</td>
</tr>
<tr>
<td>$\dot{e}<em>{\theta\theta}$, $\dot{e}</em>{\theta\zeta}$, $\dot{e}_{\theta\tau}$</td>
<td>Components of rate of strain tensor in cylindrical polar co-ordinates.</td>
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<tr>
<td>G</td>
<td>Shear rate</td>
</tr>
<tr>
<td>$H(t)$</td>
<td>Heaviside function (equation 4.3)</td>
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<tr>
<td>h</td>
<td>Separation between plates in parallel plate rheometer</td>
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<tr>
<td>$I_2$</td>
<td>Second invariant of rate of strain tensor (equation 7.5)</td>
</tr>
<tr>
<td>$J_1$, $J_2$</td>
<td>Invariants of $C_{ij}$ (equation 7.12)</td>
</tr>
<tr>
<td>K</td>
<td>Constant in power law (equation 2.6)</td>
</tr>
<tr>
<td>k</td>
<td>Constant in equation 2.1</td>
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</table>
$k^*$ Constant in equation 7.65
L Length of a capillary
£ Length of a torque arm
M Total torque on the plate of a cone-plate or parallel plate rheometer.
Mi Moment of inertia
m' Defined by equation 3.23
N Exponent in power law (equation 2.6)
n' Defined by equation 3.27 or 6.11
p Arbitrary hydrostatic pressure
$p_a$ Atmospheric pressure
$P_{ij}$ Stress tensor
$P_{11}, P_{12}, P_{13}$ Components of stress tensor
Q Volume rate of flow
Qm Constants in Bogue-Doughty theory
R Radius of plate, cone or capillary
Rf Final radius of extrudate issuing from capillary
r, θ, z Cylindrical polar co-ordinates
r, θ, φ Spherical polar co-ordinates
s t-t' Thrust exerted on rheogoniometer platens due to normal stress effect
T Thrust exerted on rheogoniometer platens due to inertia
$T_1$ Thrust exerted on rheogoniometer platens due to axial movement of rotating member.
t Present time
t' Past time
t* Time defined by equation 7.56
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \bar{t}_j )</td>
<td>Time defined by equation 7.67</td>
</tr>
<tr>
<td>( t_k )</td>
<td>Time defined by equation 7.66</td>
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<tr>
<td>( U )</td>
<td>Function in Kaye theory</td>
</tr>
<tr>
<td>( u )</td>
<td>Axial movement of rotating member in rheogoniometer</td>
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<tr>
<td>( V_j )</td>
<td>Final velocity of the extrudate issuing from a capillary</td>
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<tr>
<td>( v_1, v_2, v_3 )</td>
<td>Components of velocity in Cartesian co-ordinates  and co-ordinate system ( \xi_1, \xi_2, \xi_3 ).</td>
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<tr>
<td>( v_r, v_\theta, v_z )</td>
<td>Components of velocity in cylindrical polar co-ordinates</td>
</tr>
<tr>
<td>( v_r, v_\theta, v_\phi )</td>
<td>Components of velocity in spherical polar co-ordinates</td>
</tr>
<tr>
<td>( x_1, x_2, x_3 )</td>
<td>Cartesian co-ordinate system</td>
</tr>
<tr>
<td>( x'_1, x'_2, x'_3 )</td>
<td>Cartesian co-ordinates at past time ( t' )</td>
</tr>
<tr>
<td>( Z(x) )</td>
<td>Riemann zeta function (equation 7.23)</td>
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<tr>
<td>( \alpha )</td>
<td>Constant in WJFLMB and OWFS theories</td>
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<tr>
<td>( \gamma(t) )</td>
<td>Shear strain recovered at time ( t )</td>
</tr>
<tr>
<td>( \gamma_\infty )</td>
<td>Total shear strain recovered</td>
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<tr>
<td>( \bar{V}_j(t') )</td>
<td>Defined by equation 7.69</td>
</tr>
<tr>
<td>( \Delta h )</td>
<td>Axial movement</td>
</tr>
<tr>
<td>( \Delta P )</td>
<td>Pressure drop across capillary</td>
</tr>
<tr>
<td>( \Delta t_j )</td>
<td>Time increment, defined by equation 7.65.</td>
</tr>
<tr>
<td>( \Delta T )</td>
<td>Temperature rise due to shear heating (equations 3.33 and 6.15).</td>
</tr>
<tr>
<td>( \delta_{ij} )</td>
<td>Unit tensor ( (= 1 ) if ( i=j ), ( = 0 ) if ( i \neq j ) )</td>
</tr>
<tr>
<td>( \delta_0 )</td>
<td>Deflection of torque arm from its null position</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>Constant in WJFLMB, OWFS and Kaye theories</td>
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<tr>
<td>( \zeta )</td>
<td>End correction in capillary flow</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Viscosity</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>$\eta_0$</td>
<td>Viscosity at zero shear rate</td>
</tr>
<tr>
<td>$\theta_0$</td>
<td>Gap angle in cone-plate rheometer</td>
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<td>$\lambda$</td>
<td>Time constant in WJFLMB, OWFS and Kaye theories</td>
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<tr>
<td>$\lambda_m$</td>
<td>Time constant defined by 7.16</td>
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<td>$\lambda_n$</td>
<td>Time constant defined by 7.8</td>
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<td>$\mu$</td>
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<tr>
<td>$\xi_1, \xi_2, \xi_3$</td>
<td>An orthogonal co-ordinate system</td>
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<tr>
<td>$\rho$</td>
<td>Density</td>
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<tr>
<td>$\sigma_1$</td>
<td>$(P_{11} - P_{22})$</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>$(P_{22} - P_{33})$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Memory function in WJFLMB and Lodge theories</td>
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<tr>
<td>$\chi_\infty$</td>
<td>Die swell ($= R_j/R$)</td>
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<tr>
<td>$\Omega$</td>
<td>Angular velocity of the rotating member of a cone-plate or parallel plate rheometer in steady shear flow</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular velocity at a point</td>
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<tr>
<td>$\omega^1$</td>
<td>Angular velocity due to the inertia of rotating member of a constant stress cone-plate rheometer in a transient experiment.</td>
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