CHAPTER 1

INTRODUCTION

1.1 What is rheology?

The term 'Rheology' * was invented by Professor Bingham of Lafayette College, Indiana, on the advice of a colleague, the Professor of Classics. It means *the study of the deformation and flow of matter*. This definition was accepted when the American Society of Rheology was founded in 1929. That first meeting heard papers on the properties and behaviour of such widely differing materials as asphalt, lubricants, paints, plastics and rubber, which gives some idea of the scope of the subject and also the numerous scientific disciplines which are likely to be involved. Nowadays, the scope is even wider. Significant advances have been made in biorheology, in polymer rheology and in suspension rheology. There has also been a significant appreciation of the importance of rheology in the chemical processing industries. Opportunities no doubt exist for more extensive applications of rheology in the biotechnological industries. There are now national Societies of Rheology in many countries. The British Society of Rheology, for example, has over 600 members made up of scientists from widely differing backgrounds, including mathematics, physics, engineering and physical chemistry. In many ways, rheology has come of age.

1.2 Historical perspective

In 1678, Robert Hooke developed his *"True Theory of Elasticity"*. He proposed that "the power of any spring is in the same proportion with the tension thereof", i.e. *if you double the tension you double the extension*. This forms the basic premise behind the theory of classical (infinitesimal-strain) elasticity.

At the other end of the spectrum, Isaac Newton gave attention to liquids and in the *"Principia"* published in 1687 there appears the following hypothesis associated with the steady simple shearing flow shown in Fig. 1.1: "The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another".

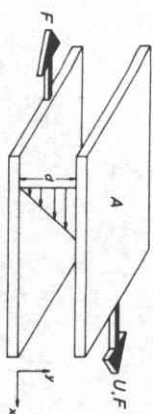* Definitions of terms in single quotation marks are included in the Glossary.

1

Fig. 1.1 Showing two parallel planes, each of area A, at $y = 0$ and $y = d$, the intervening space being filled with sheared liquid. The upper plane moves with relative velocity U and the lengths of the arrows between the planes are proportional to the local velocity v_x in the liquid.

This lack of slipperiness is what we now call 'viscosity'. It is synonymous with "internal friction" and is a measure of "resistance to flow". The force per unit area required to produce the motion is F/A and is denoted by σ and is proportional to the 'velocity gradient' (or 'shear rate') U/d, i.e. *if you double the force you double the velocity gradient*. The constant of proportionality η is called the coefficient of viscosity, i.e.

$$\sigma = \eta U/d. \qquad (1.1)$$

(It is usual to write $\dot{\gamma}$ for the shear rate U/d; see the Glossary.)

Glycerine and water are common liquids that obey Newton's postulate. For glycerine, the viscosity in SI units is of the order of 1 Pa.s, whereas the viscosity of water is about 1 mPa.s, i.e. one thousand times less viscous.

Now although Newton introduced his ideas in 1687, it was not until the nineteenth century that Navier and Stokes independently developed a consistent three-dimensional theory for what is now called a Newtonian viscous liquid. The governing equations for such a fluid are called the Navier–Stokes equations.

For the simple shear illustrated in Fig. 1.1, a 'shear stress' σ results in 'flow'. In the case of a Newtonian liquid, the flow persists as long as the stress is applied. In contrast, for a Hookean solid, a shear stress σ applied to the surface $y = d$ results in an instantaneous deformation as shown in Fig. 1.2. Once the deformed state is reached there is no further movement, but the deformed state persists as long as the stress is applied.

The angle γ is called the 'strain' and the relevant 'constitutive equation' is

$$\sigma = G\gamma, \qquad (1.2)$$

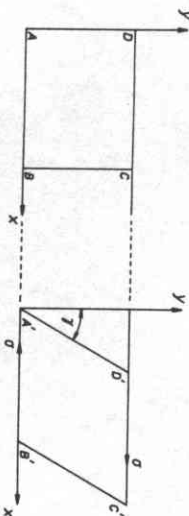where G is referred to as the 'rigidity modulus'.

Fig. 1.2 The result of the application of a shear stress σ to a block of Hookean solid (shown in section). On the application of the stress the material section $ABCD$ is deformed and becomes $A'B'C'D'$.

Three hundred years ago everything may have appeared deceptively simple to Hooke and Newton, and indeed for two centuries everyone was satisfied with Hooke's Law for solids and Newton's Law for liquids. In the case of liquids, Newton's law was known to work well for some common liquids and people probably assumed that it was a universal law like his more famous laws about gravitation and motion. It was in the nineteenth century that scientists began to have doubts (see the review article by Markovitz (1968) for fuller details). In 1835, Wilhelm Weber carried out experiments on silk threads and found out that they were not perfectly elastic. "A longitudinal load", he wrote, "produced an immediate extension. This was followed by a further lengthening with time. On removal of the load an immediate contraction took place, followed by a gradual further decrease in length until the original length was reached". Here we have a solid-like material, whose behaviour cannot be described by Hooke's law alone. There are elements of flow in the described deformation pattern, which are clearly associated more with a liquid-like response. We shall later introduce the term 'viscoelasticity' to describe such behaviour.

So far as fluid-like materials are concerned, an influential contribution came in 1867 from a paper entitled "On the dynamical theory of gases" which appeared in the "Encyclopaedia Britannica". The author was James Clerk Maxwell. The paper proposed a mathematical model for a fluid possessing some elastic properties (see §3.3).

The definition of rheology already given would allow a study of the behaviour of all matter, including the classical extremes of Hookean elastic solids and Newtonian viscous liquids. However, these classical extremes are invariably viewed as being outside the scope of rheology. So, for example, Newtonian fluid mechanics based on the Navier–Stokes equations is not regarded as a branch of rheology and neither is classical elasticity theory. The over-riding concern is therefore with materials between these classical extremes, like Weber's silk threads and Maxwell's elastic fluids.

Returning to the historical perspective, we remark that the early decades of the twentieth century saw only the occasional study of rheological interest and, in general terms, one has to wait until the second World War to see rheology emerging as a force to be reckoned with. Materials used in flamethrowers were found to be viscoelastic and this fact generated its fair share of original research during the War. Since that time, interest in the subject has mushroomed, with the emergence of the synthetic-fibre and plastics-processing industries, to say nothing of the appearance of liquid detergents, multigrade oils, non-drip paints and contact adhesives. There have been important developments in the pharmaceutical and food industries and modern medical research involves an important component of biorheology. The manufacture of materials by the biotechnological route requires a good understanding of the rheology involved. All these developments and materials help to illustrate the substantial relevance of rheology to life in the second half of the twentieth century.

1.3 The importance of non-linearity

So far we have considered elastic behaviour and viscous behaviour in terms of the laws of Hooke and Newton. These are linear laws, which assume direct proportionality between stress and strain, or strain rate, whatever the stress. Further, by implication, the viscoelastic behaviour so far considered is also linear. Within this linear framework, a wide range of rheological behaviour can be accommodated. However, this framework is very restrictive. The range of stress over which materials behave linearly is invariably limited, and the limit can be quite low. In other words, material properties such as rigidity modulus and viscosity can change with the applied stress, and the stress need not be high. The change can occur either instantaneously or over a long period of time, and it can appear as either an increase or a decrease of the material parameter.

A common example of non-linearity is known as 'shear-thinning' (cf. §2.3.2). This is a reduction of the viscosity with increasing rate of shear in steady flow. The toothpaste which sits apparently unmoving on the bristles of the toothbrush is easily squeezed from the toothpaste tube—a familiar example of shear-thinning. The viscosity changes occur almost instantaneously in toothpaste. For an example of shear-thinning which does not occur instantaneously we look to non-drip paint. To the observer equipped with no more than a paintbrush the slow recovery of viscosity is particularly noticeable. The special term for time-dependent shear-thinning followed by recovery is 'thixotropy', and non-drip paint can be described as thixotropic. Shear-thinning is just one manifestation of non-linear behaviour, many others could be cited, and we shall see during the course of this book that it is difficult to make much headway in the understanding of rheology without an appreciation of the general importance of non-linearity.

1.4 Solids and liquids

It should now be clear that the concepts of elasticity and viscosity need to be qualified since real materials can be made to display either property or a combination of both simultaneously. Which property dominates, and what the values of the parameters are, depend on the stress and the duration of application of the stress. The reader will now ask what effect these ideas will have on the even more primitive concepts of solids and liquids. The answer is that in a detailed discussion of real materials these too will need to be qualified. When we look around at home, in the laboratory, or on the factory floor, we recognise solids or liquids by their response to low stresses, usually determined by gravitational forces, and over a human, everyday time-scale, usually no more than a few minutes or less than a few seconds. However, if we apply a very wide range of stress over a very wide spectrum of time, or frequency, using rheological apparatus, we are able to observe liquid-like properties in solids and solid-like properties in liquids. It follows therefore that difficulties can, and do, arise when an attempt is made to label a given material as a

solid or a liquid. In fact, we can go further and point to inadequacies even when qualifying terms are used. For example, the term plastic–rigid solid used in structural engineering to denote a material which is rigid (inelastic) below a 'yield stress' and yielding indefinitely above this stress, is a good approximation for a structural component of a steel bridge but it is nevertheless still limited as a description for steel. It is much more fruitful to classify rheological behaviour. Then it will be possible to include a given material in more than one of these classifications depending on the experimental conditions.

A great advantage of this procedure is that it allows for the mathematical description of rheology as the mathematics of a set of behaviours rather than of a set of materials. The mathematics then leads to the proper definition of rheological parameters and therefore to their proper measurement (see also §3.1).

To illustrate these ideas, let us take as an example, the silicone material that is nicknamed "Bouncing Putty". It is very viscous but it will eventually find its own level when placed in a container—given sufficient time. However, as its name suggests, a ball of it will also bounce when dropped on the floor. It is not difficult to conclude that in a slow flow process, occurring over a long time scale, the putty behaves like a liquid—it finds its own level slowly. Also when it is extended slowly it shows ductile fracture—a liquid characteristic. However, when the putty is extended quickly, i.e. on a shorter time scale, it shows brittle fracture—a solid characteristic. Under the severe and sudden deformation experienced as the putty strikes the ground, it bounces—another solid characteristic. Thus, a given material can behave like a solid or a liquid depending on the time scale of the deformation process.

The scaling of time in rheology is achieved by means of the 'Deborah number', which was defined by Professor Marcus Reiner, and may be introduced as follows.

Anyone with a knowledge of the QWERTY keyboard will know that any book on *rheology* has at least one incorrect reference to *theology*. (Hopefully, the present book is an exception!). However, this is not to say that there is no connection between the two. In the fifth chapter of the book of Judges in the Old Testament, Deborah is reported to have declared, "The mountains flowed before the Lord...". On the basis of this reference, Professor Reiner, one of the founders of the modern science of rheology, called his dimensionless group the Deborah number D_e. The idea is that *everything flows if you wait long enough*, even the mountains!

$$D_e = \tau / T,$$

$$(1.3)$$

where T is a characteristic time of the deformation process being observed and τ is a characteristic time of the material. The time τ is infinite for a Hookean elastic solid and zero for a Newtonian viscous liquid. In fact, for water in the liquid state τ is typically 10^{-12} s whilst for lubricating oils as they pass through the high pressures encountered between contacting pairs of gear teeth τ can be of the order of 10^{-6} s

and for polymer melts at the temperatures used in plastics processing τ may be as high as a few seconds. There are therefore situations in which these liquids depart from purely viscous behaviour and also show elastic properties.

High Deborah numbers correspond to solid-like behaviour and low Deborah numbers to liquid-like behaviour. A material can therefore appear solid-like either because it has a very long characteristic time or because the deformation process we are using to study it is very fast. Thus, even mobile liquids with low characteristic times can behave like elastic solids in a very fast deformation process. This sometimes happens when lubricating oils pass through gears.

Notwithstanding our stated decision to concentrate on material *behaviour*, it may still be helpful to attempt definitions of precisely what we mean by *solid* and *liquid*, since we do have recourse to refer to such expressions in this book. Accordingly, we define a solid as *a material that will not continuously change its shape when subjected to a given stress*, i.e. for a given stress there will be a fixed final deformation, which may or may not be reached instantaneously on application of the stress. This liquid as *a material that will continuously change its shape (i.e. will flow) when subjected to a given stress, irrespective of how small that stress may be*.

The term 'viscoelasticity' is used to describe behaviour which falls between the classical extremes of Hookean elastic response and Newtonian viscous behaviour. In terms of ideal material response, a solid material with viscoelasticity is invariably called a 'viscoelastic solid' in the literature. In the case of liquids, there is more ambiguity so far as terminology is concerned. The terms 'viscoelastic liquid', 'elastico-viscous liquid', 'elastic liquid' are all used to describe a liquid showing viscoelastic properties. In recent years, the term 'memory fluid' has also been used in this connection. In this book, we shall frequently use the simple term elastic liquid.

Liquids whose behaviour cannot be described on the basis of the Navier–Stokes equations are called 'non-Newtonian liquids'. Such liquids may or may not possess viscoelastic properties. This means that all viscoelastic liquids are non-Newtonian, but the converse is not true: not all non-Newtonian liquids are viscoelastic.

1.5 Rheology is a difficult subject

By common consent, rheology is a difficult subject. This is certainly the usual perception of the newcomer to the field. Various reasons may be put forward to explain this view. For example, the subject is interdisciplinary and most scientists and engineers have to move away from a possibly restricted expertise and develop a broader scientific approach. The theoretician with a background in continuum mechanics needs to develop an appreciation of certain aspects of physical chemistry, statistical mechanics and other disciplines related to microrheological studies to fully appreciate the breadth of present-day rheological knowledge. Even more daunting, perhaps, is the need for non-mathematicians to come to terms with at least some aspects of non-trivial mathematics. A cursory glance at most text books

on rheology would soon convince the uninitiated of this. Admittedly, the apparent need of a working knowledge of such subjects as *functional analysis* and *general tensor analysis* is probably overstated, but there is no doubting the requirement of some working knowledge of modern mathematics. This book is an *introduction* to rheology and our stated aim is to explain any mathematical complication to the nonspecialist. We have tried to keep to this aim throughout most of the book (until Chapter 8, which is written for the more mathematically minded reader).

At this point, we need to justify the introduction of the indicial notation, which is an essential mathematical tool in the development of the subject. The concept of pressure as a (normal) force per unit area is widely accepted and understood; it is taken for granted, for example, by TV weather forecasters who are happy to display isobars on their weather maps. Pressure is viewed in these contexts as a scalar quantity, but the move to a more sophisticated (tensor) framework is necessary when viscosity and other rheological concepts are introduced.

We consider a small plane surface of area Δs drawn in a deforming medium (Fig. 1.3).

Let n_x, n_y and n_z represent the components of the unit normal vector to the surface in the x, y, z directions, respectively. These define the orientation of Δs in space. The normal points in the direction of the +ve side of the surface. We say that the material on the +ve side of the surface exerts a force with components $F_x^{(n)}$ Δs, $F_y^{(n)}$ Δs, $F_z^{(n)}$ Δs on the material on the –ve side, it being implicitly assumed that the area Δs is small enough for the 'stress' components $F_x^{(n)}$, $F_y^{(n)}$, $F_z^{(n)}$ to be regarded as constant over the small surface Δs. A more convenient notation is to replace these components by the stress components σ_{nx}, σ_{ny}, σ_{nz}, the first index referring to the *orientation* of the plane surface and the second to the direction of the stress. Our sign convention, which is universally accepted, except by Bird et al. (1987(a) and (b)), is that a positive σ_{zz} (and similarly σ_{yy} and σ_{xx}) is a tension. Components σ_{xx}, σ_{yy} and σ_{zz} are termed 'normal stresses' and σ_{xx}, σ_{xy} etc. are called 'shear stresses'. It may be formally shown that $\sigma_{xy} = \sigma_{yx}$, $\sigma_{xz} = \sigma_{zx}$ and $\sigma_{yz} = \sigma_{zy}$ (see, for example Schowalter 1978, p. 44).

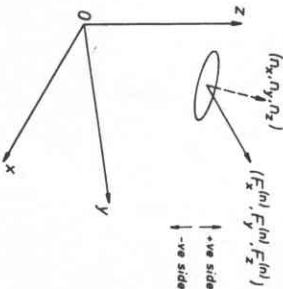Figure 1.4 may be helpful to the newcomer to continuum mechanics to explain

Fig. 1.3 The mutually perpendicular axes 0x, 0y, 0z are used to define the position and orientation of the small area Δs and the force on it.
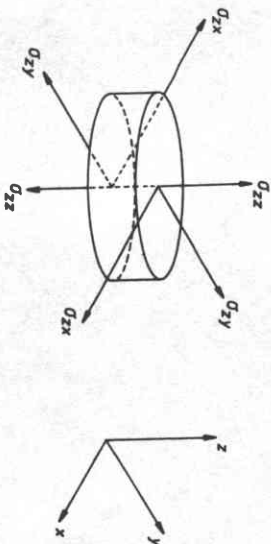
Fig. 1.4 The components of stress on the plane surfaces of a volume element of a deforming medium.

the relevance of the indicial notation. The figure contains a schematic representation of the stress components on the plane surfaces of a small volume which forms part of a general continuum. The stresses shown are those acting *on* the small volume *due* to the surrounding material.

The need for an indicial notation is immediately illustrated by a more detailed consideration of the steady simple-shear flow associated with Newton's postulate (Fig. 1.1), which we can conveniently express in the mathematical form:

$$v_x = \dot{\gamma} y, \quad v_y = v_z = 0, \tag{1.4}$$

where v_x, v_y, v_z are the velocity components in the x, y and z directions, respectively, and $\dot{\gamma}$ is the (constant) shear rate. In the case of a Newtonian liquid, the stress distribution for such a flow can be written in the form

$$\sigma_{yx} = \eta\dot{\gamma}, \quad \sigma_{xz} = \sigma_{yz} = 0, \quad \sigma_{xx} - \sigma_{yy} = 0, \quad \sigma_{yy} - \sigma_{zz} = 0, \tag{1.5}$$

and here there would be little purpose in considering anything other than the shear stress σ_{yx} which we wrote as σ in eqn. (1.1). Note that it is usual to work in terms of normal stress *differences* rather than the normal stresses themselves, since the latter are arbitrary to the extent of an added isotropic pressure in the case of incompressible liquids and we would need to replace (1.5) by

$$\left.\begin{aligned} \sigma_{yx} &= \eta\dot{\gamma}, \quad \sigma_{xz} = \sigma_{yz} = 0, \\ \sigma_{xx} &= -p, \quad \sigma_{yy} = -p, \quad \sigma_{zz} = -p, \end{aligned}\right\} \tag{1.6}$$

where p is an arbitrary isotropic pressure. There is clearly merit in using (1.5) rather than (1.6) since the need to introduce p is avoided (see also Dealy 1982, p. 8).

For elastic liquids, we shall see in later chapters that the stress distribution is more complicated, requiring us to modify (1.5) in the following manner:

$$\left.\begin{aligned} \sigma_{yx} &= \eta(\dot{\gamma})\dot{\gamma}, \quad \sigma_{xz} = \sigma_{yz} = 0, \\ \sigma_{xx} - \sigma_{yy} &= N_1(\dot{\gamma}), \quad \sigma_{yy} - \sigma_{zz} = N_2(\dot{\gamma}), \end{aligned}\right\} \tag{1.7}$$

where it is now necessary to allow the viscosity to vary with shear rate, written mathematically as the function $\eta(\dot{\gamma})$, and to allow the normal stresses to be non-zero and also functions of $\dot{\gamma}$. Here the so called normal stress differences N_1 and N_2 are of significant importance and it is difficult to see how they could be conveniently introduced without an indicial notation*. Such a notation is therefore not an optional extra for mathematically-minded researchers but an absolute necessity. Having said that, we console ourselves with the promise that this represents the only major mathematical difficulty we shall meet until we tackle the notoriously difficult subject of constitutive equations in Chapter 8.

1.6 Components of rheological research

Rheology is studied by both university researchers and industrialists. The former may have esoteric as well as practical reasons for doing so, but the industrialist, for obvious reasons, is driven by a more pragmatic motivation. But, whatever the background or motivation, workers in rheology are forced to become conversant with certain well-defined sub-areas of interest which are detailed below. These are (i) rheometry; (ii) constitutive equations; (iii) measurement of flow behaviour in complex (non-rheometric) complex geometries; (iv) calculation of behaviour in complex flows.

1.6.1 Rheometry

In 'rheometry', materials are investigated in simple flows like the steady simple-shear flow already discussed. It is an important component of rheological research. Small-amplitude oscillatory-shear flow (§3.5) and extensional flow (Chapter 5) are also important.

The motivation for any rheometrical study is often the hope that observed behaviour in industrial situations can be correlated with some easily measured rheometrical function. Rheometry is therefore of potential importance in assessing the usefulness of any proposed constitutive model for the test material, whether this is based on molecular or continuum ideas. Indirectly, therefore, rheometry may be relevant in industrial process modelling. This will be especially so in future when the full potential of *computational fluid dynamics* using large computers is realized within a rheological context.

A number of detailed texts dealing specifically with rheometry are available. These range from the "How to" books of Walters (1975) and Whorlow (1980) to the "Why?" books of Walters (1980) and Dealy (1982). Also, most of the standard texts

---

* By common convention N_1 is called the first normal stress difference and N_2 the second normal stress difference. However, the terms "primary" and "secondary" are also used. In some texts N_1 is defined as $\sigma_{xx} - \sigma_{zz}$, whilst N_2 remains as $\sigma_{yy} - \sigma_{zz}$.

on rheology contain a significant element of rheometry, most notably Lodge (1964, 1974), Bird et al. (1987(a) and (b)), Schowalter (1978), Tanner (1985) and Janeschitz-Kriegl (1983). This last text also considers 'flow birefringence', which will not be discussed in detail in the present book (see also Doi and Edwards 1986, §4.7).

1.6.2 Constitutive equations

Constitutive equations (or rheological equations of state) are equations relating suitably defined stress and deformation variables. Equation (1.1) is a simple example of the relevant constitutive law for the Newtonian viscous liquid.

Constitutive equations may be derived from a microrheological standpoint, where the molecular structure is taken into account explicitly. For example, the solvent and polymer molecules in a polymer solution are seen as distinct entities. In recent years there have been many significant advances in microrheological studies. Here, there is no direct appeal to the individual microscopic components, and, for example, a polymer solution is treated as a homogeneous continuum.

The basic discussion in Chapter 8 will be based on the principles of *continuum mechanics*. No attempt will be made to give an all-embracing discourse on this difficult subject, but it is at least hoped to point the interested and suitably equipped reader in the right direction. Certainly, an attempt will be made to assess the status of the more popular constitutive models that have appeared in the literature, whether these arise from microscopic or macroscopic considerations.

1.6.3 Complex flows of elastic liquids

The flows used in rheometry, like the viscometric flow shown in Fig. 1.1, are generally regarded as being *simple* in a rheological sense. By implication, all other flows are considered to be *complex*. Paradoxically, complex flows can sometimes occur in what appear to be simple geometrical arrangements, e.g. flow into an abrupt contraction (see §5.4.6). The complexity in the flow usually arises from the coexistence of shear and extensional components; sometimes with the added complication of inertia. Fortunately, in many cases, complex flows can be dealt with by using various numerical techniques and computers.

The experimental and theoretical study of the behaviour of elastic liquids in complex flows is generating a significant amount of research at the present time. In this book, these areas will not be discussed in detail: they are considered in depth in recent review articles by Boger (1987) and Walters (1985); and the important subject of the *numerical simulation* of non-Newtonian flow is covered by the text of Crochet, Davies and Walters (1984).

CHAPTER 2

VISCOSITY

2.1 Introduction

In this chapter we give detailed attention to the steady shear viscosity which was introduced in Chapter 1. Such a study is appropriate, since viscosity is traditionally regarded as a most important material property and any practical study requiring a knowledge of material response would automatically turn to the viscosity in the first instance.

The concept of viscosity was introduced in §1.2 through Newton's postulate, in which the shear stress σ was related to the velocity gradient, or shear rate $\dot{\gamma}$, through the equation

$$\sigma = \eta\dot{\gamma}, \qquad (2.1)$$

where η is the shear viscosity. Table 2.1 is an approximate guide to the range of viscosities of familiar materials at room temperature and pressure. Most of the examples shown exhibit Newtonian behaviour under normal circumstances, by which we mean that η is independent of shear rate for the shear rates of interest.

For Newtonian liquids, η is sometimes called the coefficient of viscosity but it is now more commonly referred to simply as *the viscosity*. Such a terminology is helpful within the context of rheology, since, for most liquids, η is not a *coefficient*,

TABLE 2.1
The viscosity of some familiar materials at room temperature

Liquid	Approximate viscosity (Pa.s)
Glass	10^{40}
Molten glass (500 °C)	10^{12}
Bitumen	10^{8}
Molten polymers	10^{3}
Golden syrup	10^{2}
Liquid honey	10^{1}
Glycerol	10^{0}
Olive oil	10^{-1}
Bicycle oil	10^{-2}
Water	10^{-3}
Air	10^{-5}

but a *function* of the shear rate $\dot{\gamma}$. We define the function $\eta(\dot{\gamma})$ as the 'shear viscosity' or simply viscosity, although in the literature it is often referred to as the 'apparent viscosity' or sometimes as the shear-dependent viscosity. An instrument designed to measure viscosity is called a 'viscometer'. A viscometer is a special type of 'rheometer' (defined as an instrument for measuring rheological properties) which is limited to the measurement of viscosity.

The current SI unit of viscosity is the Pascal-second which is abbreviated to Pa.s. Formerly, the widely used unit of viscosity in the cgs system was the Poise, which is smaller than the Pa.s by a factor of 10. Thus, for example, the viscosity of water at 20.2 °C is 1 mPa.s (milli-Pascal second) and was 1 cP (centipoise).

In the following discussion we give a general indication of the relevance of viscosity to a number of practical situations; we discuss its measurement using various viscometers; we also study its variation with such experimental conditions as shear rate, time of shearing, temperature and pressure.

2.2 Practical ranges of variables which affect viscosity

The viscosity of real materials can be significantly affected by such variables as shear rate, temperature, pressure and time of shearing, and it is clearly important for us to to highlight the way viscosity depends on such variables. To facilitate this, we first give a brief account of viscosity changes observed over practical ranges of interest of the main variables concerned, before considering in depth the shear rate, which from the rheological point of view, is the most important influence on viscosity.

2.2.1 *Variation with shear rate*

Table 2.2 shows the approximate magnitude of the shear rates encountered in a number of industrial and everyday situations in which viscosity is important and therefore needs to be measured. The approximate shear rate involved in any operation can be estimated by dividing the average velocity of the flowing liquid by a characteristic dimension of the geometry in which it is flowing (e.g. the radius of a tube or the thickness of a sheared layer). As we see from Table 2.2, such calculations for a number of important applications give an enormous range, covering 13 orders of magnitude form 10^{-6} to 10^{7} s^{-1}. Viscometers can now be purchased to measure viscosity over this entire range, but at least three different instruments would be required for the purpose.

In view of Table 2.2, it is clear that the shear-rate dependence of viscosity is an important consideration and, from a practical standpoint, it is as well to have the particular application firmly in mind before investing in a commercial viscometer. We shall return to the shear-rate dependence of viscosity in §2.3.

2.2.2 *Variation with temperature*

So far as temperature is concerned, for most industrial applications involving aqueous systems, interest is confined to 0 to 100°C. Lubricating oils and greases are

TABLE 2.2
Shear rates typical of some familiar materials and processes

Situation	Typical range of shear rates (s^{-1})	Application
Sedimentation of fine powders in a suspending liquid	10^{-6}–10^{-4}	Medicines, paints
Levelling due to surface tension	10^{-2}–10^{-1}	Paints, printing inks
Draining under gravity	10^{-1}–10^{1}	Painting and coating. Toilet bleaches
Extruders	10^{0}–10^{2}	Polymers
Chewing and swallowing	10^{1}–10^{2}	Foods
Dip coating	10^{1}–10^{2}	Paints, confectionary
Mixing and stirring	10^{1}–10^{3}	Manufacturing liquids
Pipe flow	10^{0}–10^{3}	Pumping, Blood flow
Spraying and brushing	10^{3}–10^{4}	Spray-drying, painting, fuel atomization
Rubbing	10^{4}–10^{5}	Application of creams and lotions to the skin
Milling pigments in fluid bases	10^{3}–10^{5}	Paints, printing inks
High speed coating	10^{5}–10^{6}	Paper
Lubrication	10^{3}–10^{7}	Gasoline engines

used from about −50°C to 300°C. Polymer melts are usually handled in the range 150°C to 300°C, whilst molten glass is processed at a little above 500°C.

Most of the available laboratory viscometers have facilities for testing in the range −50°C to 150°C using an external temperature controller and a circulating fluid or an immersion bath. At higher temperatures, air baths are used.

The viscosity of Newtonian liquids decreases with increase in temperature, approximately according to the Arrhenius relationship:

$$\eta = Ae^{-B/T} ,\qquad (2.2)$$

where T is the absolute temperature and A and B are constants of the liquid. In general, for Newtonian liquids, the greater the viscosity, the stronger is the temperature dependence. Figure 2.1 shows this trend for a number of lubricating oil fractions.

The strong temperature dependence of viscosity is such that, to produce accurate results, great care has to be taken with temperature control in viscometry. For instance, the temperature sensitivity for water is 3% per °C at room temperature, so that ±1% accuracy requires the sample temperature to be maintained to within ±0.3°C. For liquids of higher viscosity, given their stronger viscosity dependence on temperature, even greater care has to be taken.
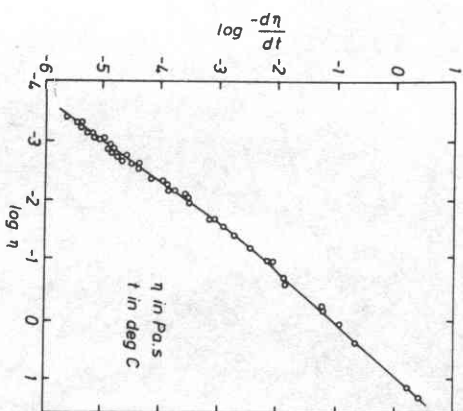
Fig. 2.1. Logarithm of viscosity/temperature derivative versus logarithm of viscosity for various lubricating oil fractions (Cameron 1966, p. 27).

It is important to note that it is not sufficient in viscometry to simply maintain control of the thermostat temperature; the act of shearing itself generates heat within the liquid and may thus change the temperature enough to decrease the viscosity, unless steps are taken to remove the heat generated. The rate of energy dissipation per unit volume of the sheared liquid is the product of the shear stress and shear rate or, equivalently, the product of the viscosity and the square of the shear rate.

Another important factor is clearly the rate of heat extraction, which in viscometry depends on two things. First, the kind of apparatus: in one class the test liquid flows through and out of the apparatus whilst, in the other, test liquid is permanently contained within the apparatus. In the first case, for instance in slits and capillaries, the liquid flow itself convects some of the heat away. On the other hand, in instruments like the concentric cylinder and cone-and-plate viscometers, the conduction of heat to the surfaces is the only significant heat-transfer process.

Secondly, heat extraction depends on the dimensions of the viscometers: for slits and capillaries the channel width is the controlling parameter, whilst for concentric cylinders and cone-and-plate devices, the gap width is important. It is desirable that these widths be made as small as possible.

2.2.3 *Variation with pressure*

The viscosity of liquids increases exponentially with isotropic pressure. Water below 30°C is the only exception, in which case it is found that the viscosity first decreases before eventually increasing exponentially. The changes are quite small for pressures differing from atmospheric pressure by about one bar. Therefore, for most practical purposes, the pressure effect is ignored by viscometer users. There
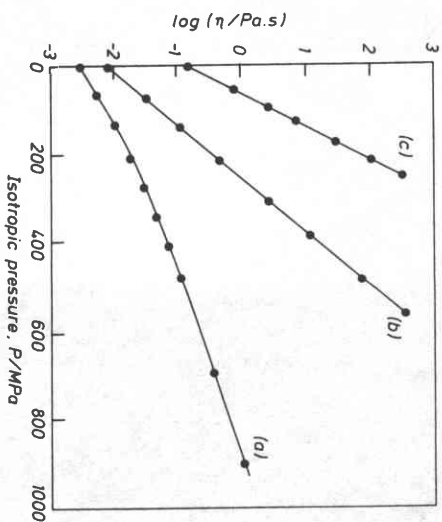
Fig. 2.2. Variation of viscosity with pressure: (a) Di-(2-ethylhexyl) sebacate; (b) Naphthenic mineral oil at 210°F; (c) Naphthenic mineral oil at 100°F. (Taken from Hutton 1980.)

are, however, situations where this would not be justified. For example, the oil industry requires measurements of the viscosity of lubricants and drilling fluids at elevated pressures. The pressures experienced by lubricants in gears can often exceed 1 GPa, whilst oil-well drilling muds have to operate at depths where the pressure is about 20 MPa. Some examples of the effect of pressure on lubricants is given in Fig. 2.2 where it can be seen that a viscosity rise of four orders of magnitude can occur for a pressure rise from atmospheric to 0.5 GPa.

2.3 **The shear-dependent viscosity of non-Newtonian liquids**

2.3.1 *Definition of Newtonian behaviour*

Since we shall concentrate on *non-Newtonian* viscosity behaviour in this section, it is important that we first emphasize what Newtonian behaviour is, in the context of the shear viscosity.

Newtonian behaviour in experiments conducted at constant temperature and pressure has the following characteristics:

(i) The only stress generated in simple shear flow is the shear stress σ, the two normal stress differences being zero.

(ii) The shear viscosity does not vary with shear rate.

(iii) The viscosity is constant with respect to the time of shearing and the stress in the liquid falls to zero immediately the shearing is stopped. In any subsequent

shearing, however long the period of resting between measurements, the viscosity is as previously measured.

(iv) The viscosities measured in different types of deformation are always in simple proportion to one another, so, for example, the viscosity measured in a uniaxial extensional flow is always three times the value measured in simple shear flow (cf. §5.3).

A liquid showing any deviation from the above behaviour is non-Newtonian.

2.3.2 The shear-thinning non-Newtonian liquid

As soon as viscometers became available to investigate the influence of shear rate on viscosity, workers found departure from Newtonian behaviour for many materials such as dispersions, emulsions and polymer solutions. In the vast majority of cases, the viscosity was found to decrease with increase in shear rate, giving rise to what is now generally called 'shear-thinning' behaviour although the terms temporary viscosity loss and 'pseudoplasticity' have also been employed.*

We shall see that there are cases (albeit few in number) where the viscosity increases with shear rate. Such behaviour is generally called 'shear-thickening' although the term 'dilatancy' has also been used.

For shear-thinning materials, the general shape of the curve representing the variation of viscosity with shear stress is shown in Fig. 2.3. The corresponding graphs of shear stress against shear rate and viscosity against shear rate are also given.

The curves indicate that in the limit of very low shear rates (or stresses) the viscosity is constant, whilst in the limit of high shear rates (or stresses) the viscosity is again constant, but at a lower level. These two extremes are sometimes known as the lower and upper Newtonian regions, respectively, the *lower* and *upper* referring to the *shear rate* and not the viscosity. The terms "first Newtonian region" and "second Newtonian region" have also been used to describe the two regions where the viscosity reaches constant values. The higher constant value is called the "zero-shear viscosity".

Note that the liquid of Fig. 2.3 does not show 'yield stress' behaviour although if the experimental range had been 10^4 s^{-1} to 10^{-1} s^{-1} (which is quite a wide range) an interpretation of the modified Fig. 2.3(b) might draw that conclusion. In Fig. 2.3(b) we have included so-called 'Bingham' plastic behaviour for comparison purposes. By definition, Bingham plastics will not flow until a critical yield stress σ_y is exceeded. Also, by implication, the viscosity is infinite at zero shear rate and there is no question of a first Newtonian region in this case.

There is no doubt that the concept of yield stress can be helpful in some practical situations, but the question of whether or not a yield stress exists or whether all non-Newtonian materials will exhibit a finite zero-shear viscosity becomes of more

* The German word is "strukturviscosität" which is literally translated as *structural viscosity*; and is not a very good description of shear-thinning.

(a)
Viscosity, η /Pa.s vs Shear stress σ /Pa

(b)
Shear stress, σ/Pa vs Shear rate, γ̇ /s⁻¹

(c)
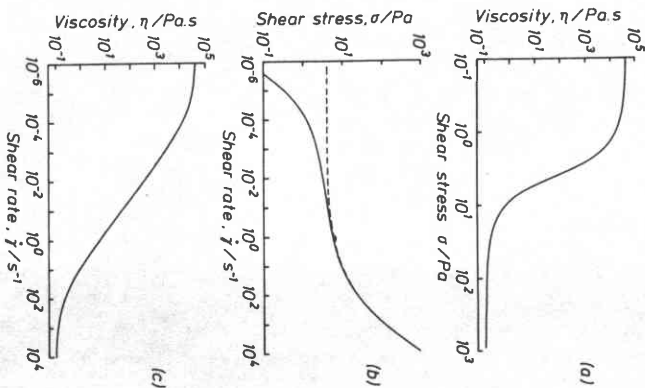Viscosity, η /Pa.s vs Shear rate, γ̇ /s⁻¹

Fig. 2.3. Typical behaviour of a non-Newtonian liquid showing the interrelation between the different parameters. The same experimental data are used in each curve. (a) Viscosity versus shear stress. Notice how fast the viscosity changes with shear stress in the middle of the graph; (b) Shear stress versus shear rate. Notice that, in the middle of the graph, the stress changes very slowly with increasing shear rate. The dotted line represents ideal yield-stress (or Bingham plastic) behaviour; (c) Viscosity versus shear rate. Notice the wide range of shear rates needed to traverse the entire flow curve.

than esoteric interest as the range and sophistication of modern constant-stress viscometers make it possible to study the very low shear-rate region of the viscosity curve with some degree of precision (cf. Barnes and Walters 1985). We simply remark here that for dilute solutions and suspensions, there is no doubt that flow occurs at the smallest stresses: the liquid surface levels out under gravity and there is no yield stress. For more concentrated systems, particularly for such materials as gels, lubricating greases, ice cream, margarine and stiff pastes, there is understandable doubt as to whether or not a yield stress exists. It is easy to accept that a lump of one of these materials will never level out under its own weight. Nevertheless there is a growing body of experimental evidence to suggest that even concentrated systems flow in the limit of very low stresses. These materials appear not to flow merely because the zero shear viscosity is so high. If the viscosity is 10^{10} Pa.s it would take years for even the slightest flow to be detected visually!

The main factor which now enables us to explore with confidence the very low shear-rate part of the viscosity curve is the availability, on a commercial basis, of

constant stress viscometers of the Deer type (Davis et al. 1968). Before this development, emphasis was laid on the production of constant shear-rate viscometers such as the Ferranti-Shirley cone-and-plate viscometer. This latter machine has a range of about 20 to 20,000 s^{-1}, whilst the Haake version has a range of about 1 to 1000 s^{-1}, in both cases a 10^3-fold range. The Umsttter capillary viscometer, an earlier development, with a choice of capillaries, provides a 10^6-fold range. Such instruments are suitable for the middle and upper regions of the general flow curve but they are not suitable for the resolution of the low shear-rate region. To do this, researchers used creep tests (§3.7.1) and devices like the plastometer (see, for example, Sherman, 1970, p 59), but there was no overlap between results from these instruments and those from the constant shear-rate devices. Hence the low shear-rate region could never be unequivocally linked with the high shear-rate region. This situation has now changed and the overlap has already been achieved for a number of materials.

Equations that predict the shape of the general flow curve need at least four parameters. One such is the Cross (1965) equation given by

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{(1 + (K\dot{\gamma})^m)},$$ (2.2a)

or, what is equivalent,

$$\frac{\eta_0 - \eta}{\eta_0 - \eta_\infty} = (K\dot{\gamma})^m,$$ (2.2b)

where η_0 and η_∞ refer to the asymptotic values of viscosity at very low and very high shear rates respectively, K is a constant parameter with the dimension of time and m is a dimensionless constant.

A popular alternative to the Cross model is the model due to Carreau (1972)

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{(1 + (K\dot{\gamma})^2)^{m/2}},$$ (2.3)

where K_1 and m_1 have a similar significance to the K and m of the Cross model.

By way of illustration, we give examples in Fig. 2.4 of the applicability of the Cross model to a number of selected materials.

It is informative to make certain approximations to the Cross model, because, in so doing, we can introduce a number of other popular and widely used viscosity models. * For example, for $\eta \ll \eta_0$ and $\eta \gg \eta_\infty$, the Cross model reduces to

$$\eta = \frac{\eta_0}{(K\dot{\gamma})^m},$$ (2.4)

---

* We have used shear *rate* as the independent variable. However, we could equally well have employed the shear *stress* in this connection, with, for instance, the so-called Ellis model as the equivalent of the Cross model.
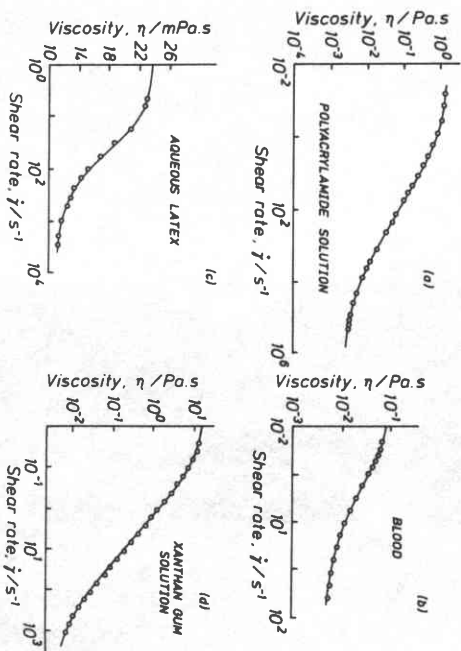
Fig. 2.4. Examples of the applicability of the Cross equation (eqn. (2.2a)): (a) 0.4% aqueous solution of polyacrylamide. Data from Boger (1977(b)). The solid line represents the Cross equation with $\eta_0 = 1.82$ Pa.s, $\eta_\infty = 2.6$ mPa.s, $K = 1.5$ s, and $m = 0.60$; (b) Blood (normal human, $Hb = 37\%$). Data from Mills et al. (1980). The solid line represents the Cross equation with $\eta_0 = 125$ mPa.s, $\eta_\infty = 5$ mPa.s, $K = 52.5$ s and $m = 0.715$; (c) Aqueous dispersion of polymer latex spheres. Data from Quemada (1978). The solid line represents the Cross equation with $\eta_0 = 24$ mPa.s, $\eta_\infty = 11$ mPa.s, $K = 0.018$ s and $m = 1.0$; (d) 0.35% aqueous solution of Xanthan gum. Data from Whitcomb and Macosko (1978). The solid line represents the Cross equation with $\eta_0 = 15$ Pa.s, $\eta_\infty = 5$ mPa.s, $K = 10$ s, $m = 0.80$.

which, with a simple redefinition of parameters can be written

$$\eta = K_2\dot{\gamma}^{n-1}.$$ (2.5)

This is the well known 'power-law' model and n is called the power-law index. K_2 is called the 'consistency' (with the strange units of Pa.s^n).

Further, if $\eta \ll \eta_0$, we have

$$\eta = \eta_\infty + \frac{\eta_0}{(K\dot{\gamma})^m},$$ (2.6)

which can be rewritten as

$$\eta = \eta_\infty + K_2\dot{\gamma}^{n-1}.$$ (2.7)

This is called the *Sisko* (1958) *model*. If n is set equal to zero in the Sisko model, we obtain

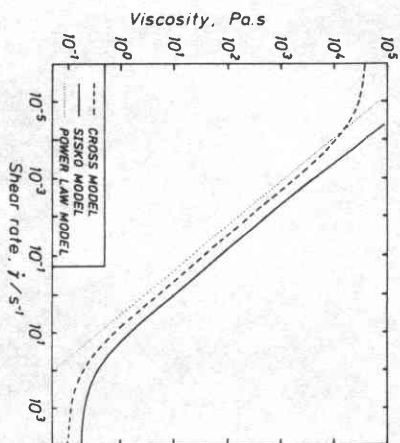$$\eta = \eta_\infty + \frac{K_2}{\dot{\gamma}},$$ (2.8a)

Fig. 2.5 Typical viscosity/shear rate graphs obtained using the Cross, power-law and Sisko models. Data for the Cross equation curve are the same as used in Fig. 2.3. The other curves represent the same data but have been shifted for clarity.

which, with a simple redefinition of parameters can be written

$$\sigma = \sigma_y + \eta_p \dot\gamma, \qquad (2.8b)$$

where σ_y is the yield stress and η_p the plastic viscosity (both constant). This is the *Bingham model* equation.

The derived equations apply over limited parts of the flow curve. Figure 2.5 illustrates how the power-law fits only near the central region whilst the Sisko model fits in the mid-to-high shear-rate range.

The Bingham equation describes the shear stress/shear rate behaviour of many shear-thinning materials at low shear rates, but only over a one-decade range (approximately) of shear rate. Figures 2.6(a) and (b) show the Bingham plot for a synthetic latex, over two different shear-rate ranges. Although the curves fit the Bingham equation to characterize viscosity behaviour is unreliable in this case. However, the concept of yield stress is sometimes a very good approximation for practical purposes, such as in characterizing the ability of a grease to resist slumping in a roller bearing. Conditions under which this approximation is valid are that the local value of n is small (say < 0.2) and the ratio η_0/η_∞ is very large (say $> 10^9$).

The Bingham-type extrapolation of results obtained with a laboratory viscometer to give a yield stress has been used to predict the size of solid particles that could be permanently suspended in a gelled liquid. This procedure rarely works in practice for thickened aqueous systems because the liquid flows, albeit slowly, at stresses below this stress. The use of η_0 and Stokes' drag law gives a better prediction of the settling rate. Obviously, if this rate can be made sufficiently small the suspension becomes "non-settling" for practical purposes.
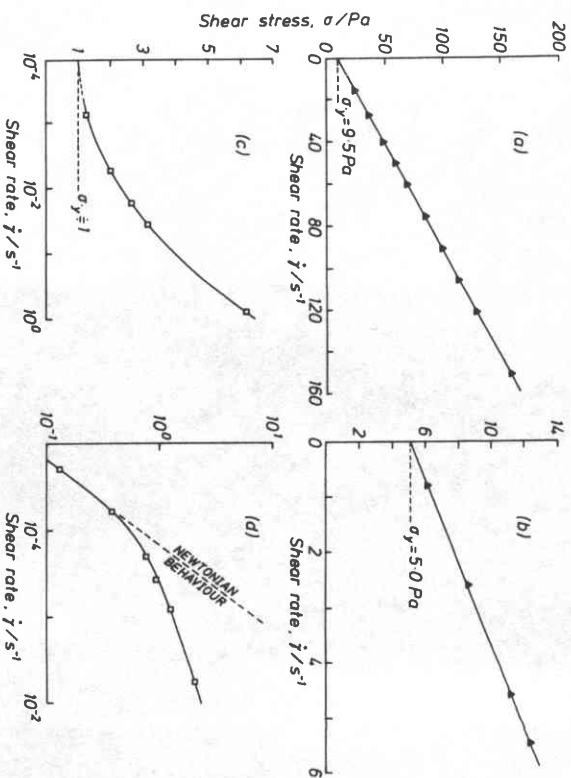
Fig. 2.6. Flow curves for a synthetic latex (taken from Barnes and Walters 1985): (a and b) Bingham plots over two different ranges of shear rate, showing two different intercepts; (c) Semi-logarithmic plot of data obtained at much lower shear rates, showing yet another intercept; (d) Logarithmic plot of data at the lowest obtainable shear rates, showing no yield-stress behaviour; (e) The whole of the experimental data plotted as viscosity versus shear rate on logarithmic scales.
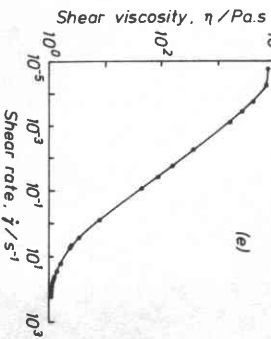
The power-law model of eqn. (2.5) fits the experimental results for many materials over two or three decades of shear rate, making it more versatile than the Bingham model. It is used extensively to describe the non-Newtonian flow properties of liquids in theoretical analyses as well as in practical engineering applications. However, care should be taken in the use of the model when employed outside the range of the data used to define it. Table 2.3 contains typical values for the power-law parameters for a selection of well-known non-Newtonian materials. The power-law model fails at high shear rates, where the viscosity must ulti-

TABLE 2.3
Typical power-law parameters of a selection of well-known materials for a particular range of shear rates.

Material	K_2(Pa.s^n)	n	Shear rate range (s^{-1})
Ball-point pen ink	10	0.85	10^0–10^3
Fabric conditioner	10	0.6	10^0–10^2
Polymer melt	10000	0.6	10^2–10^4
Molten chocolate	50	0.5	10^{-1}–10
Synovial fluid	0.5	0.4	10^{-1}–10^2
Toothpaste	300	0.3	10^0–10^3
Skin cream	250	0.1	10^0–10^2
Lubricating grease	1000	0.1	10^{-1}–10^2

mately approach a constant value; in other words, the local value of n must ultimately approach unity. This failure of the power-law model can be rectified by the use of the Sisko model, which was originally proposed for high shear-rate measurements on lubricating greases. Examples of the usefulness of the Sisko model in describing the flow properties of shear-thinning materials over four or five decades of shear rate are given in Fig. 2.7.

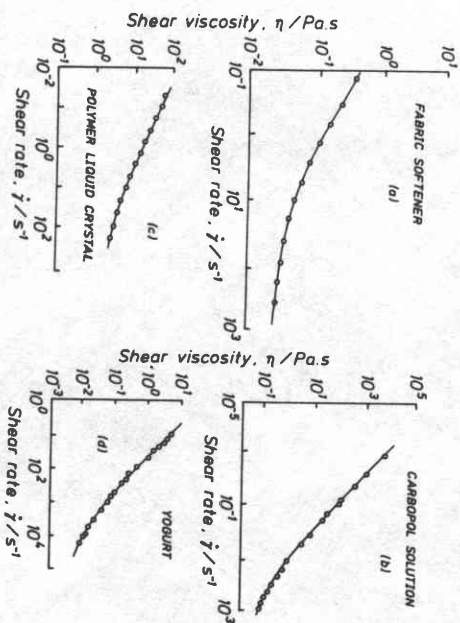Attempts have been made to derive the various viscosity laws discussed in this

Fig. 2.7. Examples of the applicability of the Sisko model (eqn. (2.7)): (a) Commercial fabric softener. Data obtained by Barnes (unpublished). The solid line represents the Sisko model with $\eta_\infty = 24$ mPa.s, $K_2 = 0.11$ Pa.s^n and $n = 0.4$; (b) 1% aqueous solution of Carbopol. Data obtained by Barnes (unpublished). The solid line represents the Sisko model with $\eta_\infty = 0.08$ Pa.s, $K_2 = 8.2$ Pa.s^n and $n = 0.066$; (c) 40% Racemic poly-γ-benzyl glutamate polymer liquid crystal. Data points obtained from Onogi and Asada (1980). The solid line represents the Sisko model with $\eta_\infty = 1.25$ Pa.s, $K_2 = 15.5$ Pa.s^n, $n = 0.5$; (d) Commercial yogurt. Data points obtained from deKee et al. (1980). The solid line represents the Sisko model with $\eta_\infty = 4$ mPa.s, $K_2 = 34$ Pa.s^n and $n = 0.1$.

section from microstructural considerations. However, these laws must be seen as being basically empirical in nature and arising from curve-fitting exercises.

2.3.3 The shear-thickening non-Newtonian liquid

It is possible that the very act of deforming a material can cause rearrangement of its microstructure such that the resistance to flow increases with shear rate. Typical examples of the shear-thickening phenomenon are given in Fig. 2.8. It will be observed that the shear-thickening region extends over only about a decade of shear rate. In this region, the power-law model can usually be fitted to the data with a value of n greater than unity.

In almost all known cases of shear-thickening, there is a region of shear-thinning at lower shear rates.
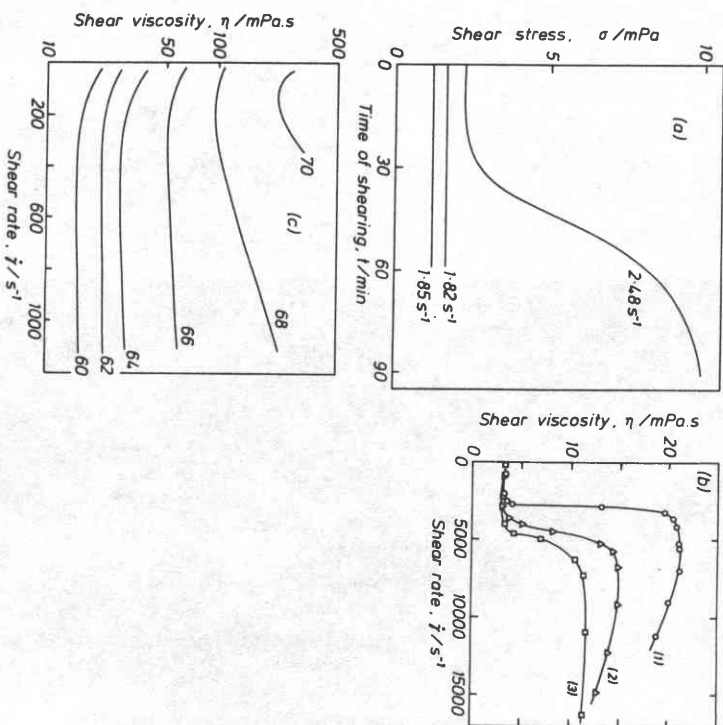

Fig. 2.8. Examples of shear-thickening behaviour: (a) Surfactant solution. CTA-sal. solution at 25°C, showing a time-effect (taken from Gravsholt 1979); (b) Polymer solution. Solution of anti-misting polymer in aircraft jet fuel, showing the effect of photodegradation during (1) 1 day, (2) 15 days, (3) 30 days exposure to daylight at room temperature (taken from Matthys and Sabersky 1987); (c) Aqueous suspensions of solid particles. Deflocculated clay slurries showing the effect of concentration of solids. The parameter is the %w/w concentration (taken from Beazley 1980).

2.3.4 Time effects in non-Newtonian liquids

We have so far assumed by implication that a given shear rate results in a corresponding shear stress, whose value does not change so long as the value of the shear rate is maintained. This is often not the case. The measured shear stress, and hence the viscosity, can either increase or decrease with time of shearing. Such changes can be reversible or irreversible.

According to the accepted definition, a gradual decrease of the viscosity under shear stress followed by a gradual recovery of structure when the stress is removed is called 'thixotropy'. The opposite type of behaviour, involving a gradual increase in viscosity, under stress, followed by recovery, is called 'negative thixotropy' or 'anti-thixotropy'. A useful review of the subject of time effects is provided by Mewis (1979).

Thixotropy usually occurs in circumstances where the liquid is shear-thinning (in the sense that viscosity levels decrease with increasing shear rate, other things being equal). In the same way, anti-thixotropy is usually associated with shear-thickening behaviour. The way that either phenomenon manifests itself depends on the type of test being undertaken. Figure 2.9 shows the behaviour to be expected from relatively inelastic colloidal materials in two kinds of test: the first involving step changes in applied shear rate or shear stress and the second being a loop test with the shear
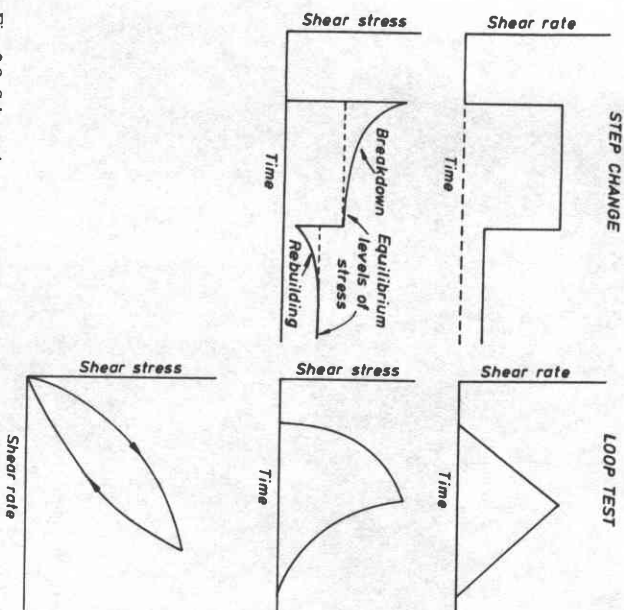

Fig. 2.9 Schematic representation of the response of an inelastic thixotropic material to two shear-rate histories.

rate increased continuously and linearly in time from zero to some maximum value and then decreased to zero in the same way.

If highly elastic colloidal liquids are subjected to such tests, the picture is more complicated, since there are contributions to the stress growth and decay from viscoelasticity.

The occurrence of thixotropy implies that the flow history must be taken into account when making predictions of flow behaviour. For instance, flow of a thixotropic material down a long pipe is complicated by the fact that the viscosity may change with distance down the pipe.

2.3.5 Temperature effects in two-phase non-Newtonian liquids

In the simplest case, the change of viscosity with temperature in two-phase liquids is merely a reflection of the change in viscosity of the continuous phase. Thus some aqueous systems at room temperature have the temperature sensitivity of water, i.e. 3% per °C. In other cases, however, the behaviour is more complicated. In dispersions, the suspended phase may go through a melting point. This will result in a sudden and larger-than-expected decrease of viscosity. In those dispersions, for which the viscosity levels arise largely from the temperature-sensitive colloidal interactions between the particles, the temperature coefficient will be different from that of the continuous phase. For detergent-based liquids, small changes in temperature can result in phase changes which may increase or decrease the viscosity dramatically.

In polymeric systems, the solubility of the polymer can increase or decrease with temperature, depending on the system. The coiled chain structure may become more open, resulting in an increase in resistance to flow. This is the basis of certain polymer-thickened multigrade oils designed to maintain good lubrication at high temperatures by partially offsetting the decrease in viscosity with temperature of the base oil (see also §6.11.2).

2.4 Viscometers for measuring shear viscosity

2.4.1 General considerations

Accuracy of measurement is an important issue in viscometry. In this connection, we note that it is possible in principle to calibrate an instrument in terms of speed, geometry and sensitivity. However, it is more usual to rely on the use of standardized Newtonian liquids (usually oils) of known viscosity. Variation of the molecular weight of the oils allows a wide range of viscosities to be covered. These oils are chemically stable and are not very volatile. They themselves are calibrated using glass capillary viscometers and these viscometers are, in turn, calibrated using the internationally accepted standard figure for the viscosity of water (1.002 mPa.s at 20.00 °C, this value being uncertain to ±0.25%). Bearing in mind the accumulated errors in either the direct or comparative measurements, the everyday measurement of viscosity must obviously be worse than the 0.25% mentioned above. In fact for mechanical instruments, accuracies of ten times this figure are more realistic.

2.3.4 Time effects in non-Newtonian liquids

We have so far assumed by implication that a given shear rate results in a corresponding shear stress, whose value does not change so long as the value of the shear rate is maintained. This is often not the case. The measured shear stress, and hence the viscosity, can either increase or decrease with time of shearing. Such changes can be reversible or irreversible.

According to the accepted definition, a gradual decrease of the viscosity under shear stress followed by a gradual recovery of structure when the stress is removed is called 'thixotropy'. The opposite type of behaviour, involving a gradual increase in viscosity, under stress, followed by recovery, is called 'negative thixotropy' or 'anti-thixotropy'. A useful review of the subject of time effects is provided by Mewis (1979).

Thixotropy usually occurs in circumstances where the liquid is shear-thinning (in the sense that viscosity levels decrease with increasing shear rate, other things being equal). In the same way, anti-thixotropy is usually associated with shear-thickening behaviour. The way that either phenomenon manifests itself depends on the type of test being undertaken. Figure 2.9 shows the behaviour to be expected from relatively inelastic colloidal materials in two kinds of test: the first involving step changes in applied shear rate or shear stress and the second being a loop test with the shear
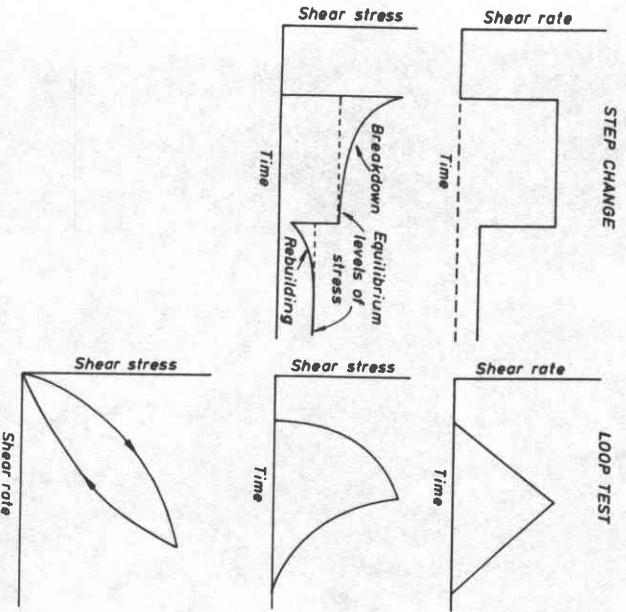

Fig. 2.9. Schematic representation of the response of an inelastic thixotropic material to two shear-rate histories.

rate increased continuously and linearly in time from zero to some maximum value and then decreased to zero in the same way.

If highly elastic colloidal liquids are subjected to such tests, the picture is more complicated, since there are contributions to the stress growth and decay from viscoelasticity.

The occurrence of thixotropy implies that the flow history must be taken into account when making predictions of flow behaviour. For instance, flow of a thixotropic material down a long pipe is complicated by the fact that the viscosity may change with distance down the pipe.

2.3.5 Temperature effects in two-phase non-Newtonian liquids

In the simplest case, the change of viscosity with temperature in two-phase liquids is merely a reflection of the change in viscosity of the continuous phase. Thus some aqueous systems at room temperature have the temperature sensitivity of water, i.e. 3% per °C. In other cases, however, the behaviour is more complicated. In dispersions, the suspended phase may go through a melting point. This will result in a sudden and larger-than-expected decrease of viscosity. In those dispersions, for which the viscosity levels arise largely from the temperature-sensitive colloidal interactions between the particles, the temperature coefficient will be different from that of the continuous phase. For detergent-based liquids, small changes in temperature can result in phase changes which may increase or decrease the viscosity dramatically.

In polymeric systems, the solubility of the polymer can increase or decrease with temperature, depending on the system. The coiled chain structure may become more open, resulting in an increase in resistance to flow. This is the basis of certain polymer-thickened multigrade oils designed to maintain good lubrication at high temperatures by partially offsetting the decrease in viscosity with temperature of the base oil (see also §6.11.2).

2.4 Viscometers for measuring shear viscosity

2.4.1 General considerations

Accuracy of measurement is an important issue in viscometry. In this connection, we note that it is possible in principle to calibrate an instrument in terms of speed, geometry and sensitivity. However, it is more usual to rely on the use of standardized Newtonian liquids (usually oils) of known viscosity. Variation of the molecular weight of the oils allows a wide range of viscosities to be covered. These oils are chemically stable and are not very volatile. They themselves are calibrated using glass capillary viscometers and these viscometers are, in turn, calibrated using the internationally accepted standard figure for the viscosity of water (1.002 mPa.s at 20.00 °C, this value being uncertain to ±0.25%). Bearing in mind the accumulated errors in either the direct or comparative measurements, the everyday measurement of viscosity must obviously be worse than the 0.25% mentioned above. In fact for mechanical instruments, accuracies of ten times this figure are more realistic.
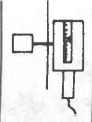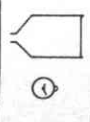
VISCOMETER TYPE	VARIABLES TO CHANGE	MEASUREMENT	CONVENIENCE	ROBUSTNESS
	BOB SPEED AND DIAMETER	COUPLE	**	*
	EXIT TUBE DIAMETER	EFFLUX TIME	**	**
	BALL SIZE	VELOCITY	**	**

g. 2.10. Examples of industrial viscometers with complicated flow fields, including star-ratings for venience and robustness.

4.2 Industrial shop-floor instruments

Some viscometers used in industry have complicated flow and stress fields, though their operation is simple. In the case of Newtonian liquids, the use of such instruments does not present significant problems, since the instruments can be calibrated with a standard liquid. However, for non-Newtonian liquids, complicated theoretical derivations are required to produce viscosity information, and in some cases no amount of mathematical complication can generate consistent viscosity data (see, for example, Walters and Barnes 1980).

Three broad types of industrial viscometer can be identified (Fig. 2.10). The first type comprises rotational devices, such as the Brookfield viscometer. There is some type of consistent interpretation of data from such instruments (cf. Williams 1979). The second type of instrument involves what we might loosely call "flow through constrictions" and is typified by the Ford-cup arrangement. Lastly, we have those that involve, in some sense, flow around obstructions such as in the Glen Creston falling-ball instrument (see, for example, van Wazer et al. 1963). Rising-bubble techniques can also be included in this third category.

For all the shop-floor viscometers, great care must be exercised in applying formulae designed for Newtonian liquids to the non-Newtonian case.

4.3 Rotational instruments; general comments

Many types of viscometer rely on rotational motion to achieve a simple shearing ow. For such instruments, the means of inducing the flow are two-fold: one can ther drive one member and measure the resulting couple or else apply a couple id measure the subsequent rotation rate. Both methods were well established fore the first World War, the former being introduced by Couette in 1888 and the tter by Searle in 1912.

There are two ways that the rotation can be applied and the couple measured: e first is to drive one member and measure the couple on the *same* member, whilst e other method is to drive one member and measure the couple on the *other*. In

modern viscometers, the first method is employed in the Haake, Contraves, Ferranti-Shirley and Brookfield instruments; the second method is used in the Weissenberg and Rheometrics rheogoniometers.

For couple-driven instruments, the couple is applied to one member and its rate of rotation is measured. In Searle's original design, the couple was applied with weights and pulleys. In modern developments, such as in the Deer constant-stress instrument, an electrical drag-cup motor is used to produce the couple. The couples that can be applied by the commercial constant stress instruments are in the range 10^{-6} to 10^{-2} Nm; the shear rates that can be measured are in the range 10^{-6} to 10^3 s^{-1}, depending of course on the physical dimensions of the instruments and the viscosity of the material. The lowest shear rates in this range are equivalent to one complete revolution every two years; nevertheless it is often possible to take steady-state measurements in less than an hour.

As with all viscometers, it is important to check the calibration and zeroing from time to time using calibrated Newtonian oils, with viscosities within the range of those being measured.

2.4.4 The narrow-gap concentric-cylinder viscometer

If the gap between two concentric cylinders is small enough and the cylinders are in relative rotation, the test liquid enclosed in the gap experiences an almost constant shear rate. Specifically, if the radii of the outer and inner cylinders are r_o and r_1, respectively, and the angular velocity of the inner is Ω_1, (the other being stationary) the shear rate $\dot\gamma$ is given by

$$\dot\gamma = \frac{r_o\Omega_1}{r_o - r_1}.$$ (2.9)

For the gap to be classed as "narrow" and the above approximation to be valid to within a few percent, the ratio of r_1 to r_o must be greater than 0.97.

If the couple on the cylinders is C, the shear stress in the liquid is given by

$$\sigma = \frac{C}{2\pi r_o^2 L},$$ (2.10)

and from (2.9) and (2.10), we see that the viscosity is given by

$$\eta = \frac{C(r_o - r_1)}{2\pi r_o^3 \Omega_1 L},$$ (2.11)

where L is the effective immersed length of the liquid being sheared. This would be the real immersed length, l, if there were no end effects. However, end effects are likely to occur if due consideration is not given to the different shearing conditions which may exist in any liquid covering the ends of the cylinders

One way to proceed is to carry out experiments at various immersed lengths, l, keeping the rotational rate constant. The extrapolation of a plot of C against l then gives the correction which must be added to the real immersed length to provide the value of the effective immersed length L. In practice, most commercial viscometer manufacturers arrange the dimensions of the cylinders such that the ratio of the depth of liquid to the gap between the cylinders is in excess of 100. Under these circumstances the end correction is negligible.

The interaction of one end of the cylinder with the bottom of the containing outer cylinder is often minimized by having a recess in the bottom of the inner cylinder so that air is entrapped when the viscometer is filled, prior to making measurements. Alternatively, the shape of the end of the cylinder can be chosen as a cone. In operation, the tip of the cone just touches the bottom of the outer cylinder container. The cone angle (equal to $\tan^{-1}[(r_o - r_i)/r_o]$) is such that the shear rate in the liquid trapped between the cone and the bottom is the same as that in the liquid between the cylinders. This arrangement is called the Mooney system, after its inventor.

2.4.5 The wide-gap concentric-cylinder viscometer

The limitations of very narrow gaps in the concentric-cylinder viscometer are associated with the problems of achieving parallel alignment and the difficulty of coping with suspensions containing large particles. For these reasons, in many commercial viscometers the ratio of the cylinder radii is less than that stated in §2.4.4: thus some manipulation of the data is necessary to produce the correct viscosity. This is a nontrivial operation and has been studied in detail by Krieger and Maron (1954). Progress can be readily made if it is assumed that the shear stress/shear rate relationship over the interval of shear rate in the gap can be described by the power-law model of eqn. (2.5). The shear rate in the liquid at the inner cylinder is then given by

$$\dot{\gamma} = \frac{2\Omega_i}{n(1 - b^{2/n})},$$ \hfill (2.12)

where b is the ratio of the inner to outer radius (i.e. $b = r_i/r_o$). Note that the shear rate is now dependent on the properties of the test liquid, unlike the narrow-gap instrument.

The shear stress in the liquid at the inner cylinder is given by

$$\sigma = \frac{C}{2\pi r_i^2 L}.$$ \hfill (2.13)

The value of n can be determined by plotting C versus Ω, on a double-logarithmic ... ... the slope at the value of Ω, under consideration.
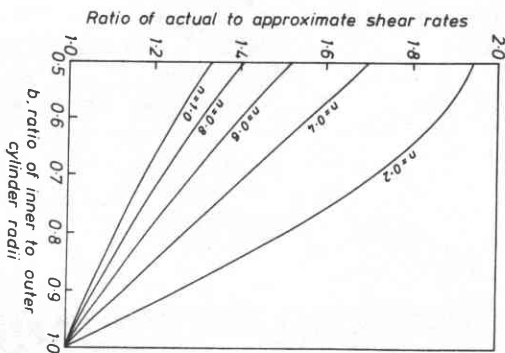
Fig. 2.11. Ratio of actual (eqn. 2.12) to approximate (eqn. 2.9) shear rates at the rotating cylinder as a function of the ratio of the inner to the outer cylinder radii, with n the power law index as parameter.

The viscosity (measured at the inner-cylinder shear rate) is given by

$$\eta = \frac{Cn(1 - b^{2/n})}{4\pi r_i^2 L \Omega_i}.$$ \hfill (2.14)

The error involved in employing the narrow-gap approximation instead of the wide-gap expression, eqn. (2.14), is shown in Fig. 2.11. Clearly, using values of $b < 0.97$ gives unacceptable error when the liquid is shear-thinning ($n < 1$).

The lower limit of shear rate achievable in a rotational viscometer is obviously governed by the drive system. The upper limit, however, is usually controlled by the test liquid. One limit is the occurrence of viscous heating of such a degree that reliable correction cannot be made. However, there are other possible limitations. Depending on which of the cylinders is rotating, at a critical speed the simple circumferential streamline flow breaks down, either with the appearance of steady (Taylor) vortices or turbulence. Since both of these flows require more energy than streamline flow, the viscosity of the liquid *apparently* increases. In practical terms, for most commercial viscometers, it is advisable to consider the possibility of such disturbances occurring if the viscosity to be measured is less than about 10 mPa.s.

2.4.6 Cylinder rotating in a large volume of liquid

If we take the wide-gap Couette geometry to the extreme with the radius of the outer cylinder approaching infinity, the factor $(1 - b^{2/n})$ in (2.12) and (2.14)
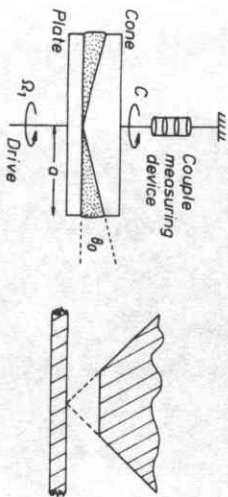
Fig. 2.12. The cone-and-plate viscometer. Cross-sectional diagram of one possible configuration, viz. cone on top, rotating plate and couple measured on the cone. The inset shows the form of truncation used in many instruments.

approaches unity. For a power-law liquid, the values of the shear rate and shear stress in the liquid at the rotating cylinder of radius r_1 are then given by

$$\dot{\gamma} = 2\Omega_1/n \quad (2.15)$$

and

$$\sigma = \frac{C}{2\pi r_1^2 L}. \quad (2.16)$$

Again, at any particular value of Ω_1, n can be calculated as the local value of $d(\ln C)/d(\ln \Omega_1)$. These equations are applicable to viscometers of the Brookfield type in which a rotating bob is immersed in a beaker of liquid. The technique is restricted to moderately low shear rates: 0.1 s^{-1} to 10 s^{-1} is a typical range.

2.4.7 The cone-and-plate viscometer

In the cone-and-plate geometry shown in Fig. 2.12, the shear rate is very nearly the same everywhere in the liquid provided the gap angle θ_0 is small (see Chapter 4 for the details). The shear rate in the liquid is given by

$$\dot{\gamma} = \Omega_1/\theta_0, \quad (2.17)$$

where Ω_1 is the angular velocity of the rotating platten. Note that the shear rate does not depend on the properties of the liquid.

The shear stress (measured via the couple C on the cone) is given by

$$\sigma = \frac{3C}{2\pi a^3}, \quad (2.18)$$

where a is the radius of the cone. Thus the viscosity is given by

$$\eta = \frac{3C\theta_0}{2\pi a^3 \Omega_1}. \quad (2.19)$$

If the liquid under investigation has a low viscosity, high rotational speeds are

often necessary to produce torques large enough to be measured accurately. However, under these circumstances, 'secondary flows' may arise (see, for example, Walters 1975). The secondary flow absorbs extra energy, thus increasing the couple, which the unwary may mistakenly associate with shear-thickening. Cheng (1968) has provided an empirical formula which goes some way towards dealing with the problem.

All cone-and-plate instruments allow the cone to be moved away from the plate to facilitate sample changing. It is very important that the cone and plate be reset so that the tip of the cone lies in the surface of the plate. For a 1° gap angle and a cone radius of 50 mm, every 10 μm of error in the axial separation produces an additional 1% error in the shear rate.

To avoid error in contacting the cone tip (which might become worn) and the plate (which might become indented), the cone is often truncated by a small amount. In this case, it is necessary to set the virtual tip in the surface of the plate as shown in Fig. 2.12 (b). A truncated cone also facilitates tests on suspensions.

2.4.8 The parallel-plate viscometer

For torsional flow between parallel plates (see Fig. 2.13) the shear rate at the rim ($r = a$) is given by

$$\dot{\gamma}_a = a\Omega_1/h. \quad (2.20)$$

It is this shear rate that finds its way into the interpretation of experimental data for torsional flow. It can be shown (Walters 1975, p. 52) that the viscosity is given by

$$\eta = \frac{3Ch}{2\pi a^4 \Omega_1\left(1 + \frac{1}{3}\frac{d\ln C}{d\ln \Omega_1}\right)}, \quad (2.21)$$

where C is the couple on one of the plates. For power-law models, eqn. (2.21) becomes

$$\eta = \frac{3Ch}{2\pi a^4 \Omega_1\left(1 + \frac{n}{3}\right)}. \quad (2.22)$$
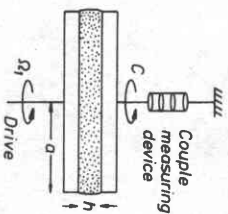

Fig. 2.13. Cross-sectional diagram of the torsional parallel-plate viscometer.

It will be noticed from eqn. (2.20) that the rim shear rate may be changed by adjusting either the speed Ω, or the gap h.

In the torsional-balance rheometer, an adaptation of the parallel-plate viscometer (see Chapter 4 for the details), shear rates in the 10^4 to 10^5 s^{-1} range have been attained.

2.4.9 Capillary viscometer

If a Newtonian liquid flows down a straight circular tube of radius a at a volume flowrate Q (see Fig. 2.14), the pressure gradient generated along it (dP/dl) is given by the Poiseuille equation:

$$\frac{dP}{dl} = \frac{8Q\eta}{\pi a^4}. \tag{2.23}$$

In this situation, the shear stress in the liquid varies linearly from $(a/2)(dP/dl)$ at the capillary wall to zero at the centre line. For Newtonian liquids, the shear rate varies similarly from $4Q/(\pi a^3)$ in the immediate vicinity of the wall to zero at the centreline. If, however, the viscosity varies with shear rate the situation is more complex. Progress can be made by concentrating on flow near the wall. Analysis shows (cf. Walters 1975, Chapter 5) that for a non-Newtonian liquid, the shear rate at the wall is modified to

$$\dot{\gamma}_w = \frac{4Q}{\pi a^3}\left(\frac{3}{4} + \frac{1}{4}\frac{d\ln Q}{d\ln \sigma_w}\right), \tag{2.24}$$

whilst the shear stress at the wall σ_w, is unchanged at $(a/2)(dP/dl)$. The bracketed term in (2.24) is called the Rabinowitsch correction. Then finally

$$\eta(\dot{\gamma}_w) = \frac{\sigma_w}{\dot{\gamma}_w} = \frac{\pi a^4(dP/dl)}{8Q\left(\frac{3}{4} + \frac{1}{4}\frac{d\ln Q}{d\ln \sigma_w}\right)}. \tag{2.25}$$

When shear-thinning liquids are being tested, $d(\ln Q)/d(\ln \sigma_w)$ is greater than 1 and for power-law liquids is equal to $1/n$. Since n can be as low as 0.2, the contribution
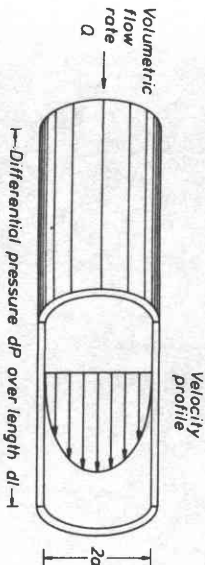

Fig. 2.14. Cutaway diagram of laminar Newtonian flow in a straight circular capillary tube.

Volumetric flow rate Q — Velocity profile — $2a$ — Differential pressure dP over length dl

of the $d(\ln Q)/d(\ln \sigma_w)$ factor to the bracketed term can be highly significant in determining the true wall shear rate.

Care has to be taken in defining and measuring the pressure gradient dP/dl. If the pressure in the external reservoir supplying the capillary and the receiving vessel are measured, then, unless the ratio of tube length to radius is very large (>100), allowance must be made for entrance and exit effects. These arise from the following sources for all types of liquid:

(i) Viscous and inertial losses in the converging stream up to the entrance.

(ii) Redistribution of the entrance velocities to achieve the steady state velocity profile within the tube.

(iii) Similar effects to the above at the exit.

Formulae exist which account for these effects for Newtonian liquids, (i) and (iii) being associated with the names of Hagenbach and Couette (see, for example Kestin et al. 1973). However, these effects are small if the ratio of tube length to radius is 100 or more.

The main end effects can be avoided if at various points on the tube wall, well away from the ends, the pressures are measured by holes connected to absolute or differential pressure transducers. Any error arising from the flow of the liquid past the holes in the tube wall (see §4.4.1.II) is cancelled out when identical holes are used and the pressure gradient alone is required.

It is not often convenient to drill pressure-tappings, and a lengthy experimental programme may then be necessary to determine the type-(i) errors in terms of an equivalent pressure-drop and type-(ii) errors in terms of an extra length of tube. The experiments required can be deduced from the theoretical treatment of Kestin et al. (1973) and a recent application of them has been published by Galvin et al. (1981). If the liquid is highly elastic, an additional entrance and exit pressure drop arises from the elasticity. The so-called Bagley correction then allows an estimate of the elastic properties to be calculated. It is also used to provide an estimate of the extensional viscosity of the liquid (see §5.4.6).

Before leaving the discussion of the capillary viscometer, it is of interest to study the pressure-gradient/flow-rate relationship for the power-law model (2.5):

$$\frac{dP}{dl} = \frac{2K_2}{a}\left[\frac{(3n+1)Q}{\pi a^3}\right]^n. \tag{2.26}$$

From this equation we see the effect of changes in such variables as pipe radius. For Newtonian liquids, the pressure drop for a given flow rate is proportional to the fourth power of the radius, but this is changed if the liquid is shear-thinning. For instance, if $n = \frac{1}{3}$, the pressure drop is proportional to the square of the radius. This is clearly important in any scale-up of pipe flow from pilot plant to factory operation.
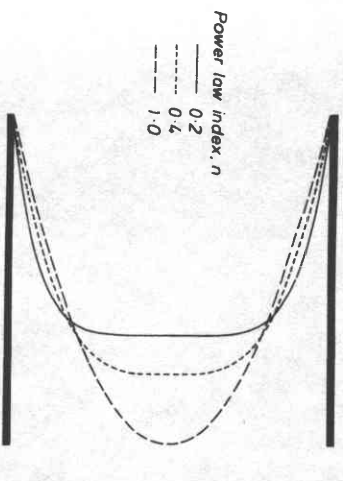
Power law index, n
—— 0·2
----- 0·4
— — 1·0

Fig. 2.15. The velocity profiles for the laminar flow of power-law liquids in a straight circular pipe, calculated for the same volumetric throughput. Note the increase in the wall shear rate and the increasingly plug-like nature of the flow as n decreases.

The velocity profile in pipe flow is parabolic for Newtonian liquids. For power-law liquids this is modified to

$$v(r) = \frac{Q(3n+1)}{\pi a^2(n+1)}\left(1 - \left(\frac{r}{a}\right)^{(n+1)/n}\right).$$ (2.27)

Figure 2.15 shows the effect of progressively decreasing the power-law index, i.e. increasing the degree of shear thinning. We see the increasing plug-like nature of the flow with, effectively, only a thin layer near the wall being sheared. This has important consequences in heat-transfer applications, where heating or cooling is applied to the liquid from the outside of the pipe. The overall heat transfer is partly controlled by the shear rate in the liquid near the pipe wall. For a power-law liquid, this shear rate is changed from the Newtonian value by a factor $[3 + (1/n)]/4$. This means that heat transfer is increased for shear-thinning liquids ($n < 1$) and decreased for shear-thickening liquids ($n > 1$), but the former is the larger effect.

2.4.10 Slit viscometer

Flow under an applied pressure gradient between two parallel stationary walls is known as slit flow. It is a two-dimensional analogue of capillary flow. The governing equations for slit flow are (cf. Walters 1975, Chapter 5)

$$\sigma_w = \frac{h}{2}\frac{dP}{dl}$$ (2.28)

and

$$\dot{\gamma}_w = \frac{2Q}{bh^2}\left(2 + \frac{d\ln Q}{d\ln\sigma_w}\right).$$ (2.29)

where h is the slit height and b is the slit width, Q is the flow rate and dP/dl is the pressure gradient.

Slit flow forms the basis of the viscometer version of the Lodge stressmeter. The stressmeter is described more fully in Chapter 4. The viscometer version differs from that discussed in §4.4.3 in that the transducer T_1 in Fig. 4.13 is unnecessary and is replaced by a solid wall. The instrument has the advantage that shear rates in excess of 10^6 s^{-1} can be achieved with little interference from viscous heating.

2.4.11 On-line measurements

It is frequently necessary to monitor the viscosity of a liquid "on line" in a number of applications, particularly when the constitution or temperature of the liquid is likely to change. Of the viscometers described in this chapter, the capillary viscometer and the concentric-cylinder viscometer are those most conveniently adapted for such a purpose. For the former, for example, the capillary can be installed directly in series with the flow: the method has attractive features, but its successful application to non-Newtonian liquids is non-trivial.

Care must be taken with the on-line concentric-cylinder apparatus, since the interpretation of data from the resulting helical flow is not easy.

Other on-line methods involve obstacles in the flow channel: for example, a float in a vertical tapered tube, as in the Rotameter, will arrive at an equilibrium position in the tube depending on the precise geometry, the rate of flow, the viscosity and the weight of the obstacle. The parallel-plate viscometer has also been adapted for on-line measurement (see, for example, Noltingk 1975).