RHEOMETRY

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Contents

Summary

Rheology is the study of the flow of complex liquids in both simple and complex flow geometries. Whereas most flows of practical use are complex flows, it is usually not possible to perform general and quantitatively accurate measurements of the fluids' behavior in these flows due to their highly complex dynamics and kinematics. Thus, it is necessary to first study fluid behavior in simple flows for which the flow dynamics can be well established and the fluids' response studied accurately and then move up in the "scale of complexity". Rheometry is the measurement of the flow of these complex liquids in simple geometries, with the object of being able to obtain a consistent description of the rheology, in order to be better able then to understand the flow behavior in complex flows.

The main aim of this chapter is to introduce the reader to the subject of Rheometry, bring him/her up to an appreciation of the science of rheometry to a standard whereby they can choose, buy and use commercially available instruments with confidence and understanding.

1. Introduction

Rheology - in its widest and most useful sense - is the study of the flow of complex liquids in complex flow geometries [1]. Examples might range from the pulsating flow of blood in the human body, to the steady or transient flow of polymer melts in polymer-processing equipment. With all this ‘complexity’ in mind, rheometry is the measurement - hence the ‘-metry’ part of the word - of the flow of these complex liquids in simple geometries, with the object of being able to obtain a consistent description of the rheology, in order to be better able then to understand the flow behavior in complex flows. This rheological description can be obtained by applying/measuring either velocities or forces to/in the liquid in such simple geometries, which can then be converted into a fundamental form of stresses, strains and strain rates, to give an appropriate description of the liquid. Such a description would be, in its simplest form, the constant viscosity for a Newtonian liquid, but in most cases the liquid’s behavior needs far more complicated description and other parameters need to be defined and measured.

In this chapter our aim is to bring readers up to an appreciation of the science of rheometry, to a standard whereby they can choose, buy and use commercially available instruments with confidence and understanding. However, if they wish to pursue the matter to a greater depth, they are encouraged to look to more advances texts, e.g. [2, 3].

1.1. Rheometers

The scientific instruments in which rheometric measurements are performed are called rheometers [4]. They incorporate the necessary simple flow geometries described above, in which the liquid being measured is subjected to forces or movement, and from which the resulting movement or force is measured.

These are usually electro-mechanical in nature, nowadays with extensive computing facilities included to carry out the necessary control, and then the mathematical manipulation of the basic ‘raw’ data – usually force and deformation – gives the desired consistent, geometry-independent description of the rheology of the liquid being tested. The form of the mathematical manipulation for a number of situations is given below, but for most commercial rheometers this is almost always unseen by the everyday user, being embedded in the operating software of the rheometer. Also embedded and hence unseen in rheometer software are corrections to deal with the fact that the rheometer’s moving parts and the liquid being tested have an appreciable finite mass and hence significant inertial forces are produced when high speeds are involved in the flows.

Means are often incorporated into rheometers to maintain the liquid sample at any desired temperature and sometimes at a given imposed pressure.

2. Basic Definitions of Shear and Extensional Flows

Complex flows of any kind can be split up into components of shear and extensional flows, and rheometry is the search for the simple geometries described above, where either shear or extensional flows dominate. In this chapter we will deal with both these situations – first shear and then extensional flows.

In shear flows liquid elements flow *over* or *past* each other, while in extensional flow, adjacent elements flow *towards* or *away from* each other, see figure 1 for illustrations of shear and extensional deformation and flow respectively. We will now consider shear flow and later in this chapter, extensional flow.

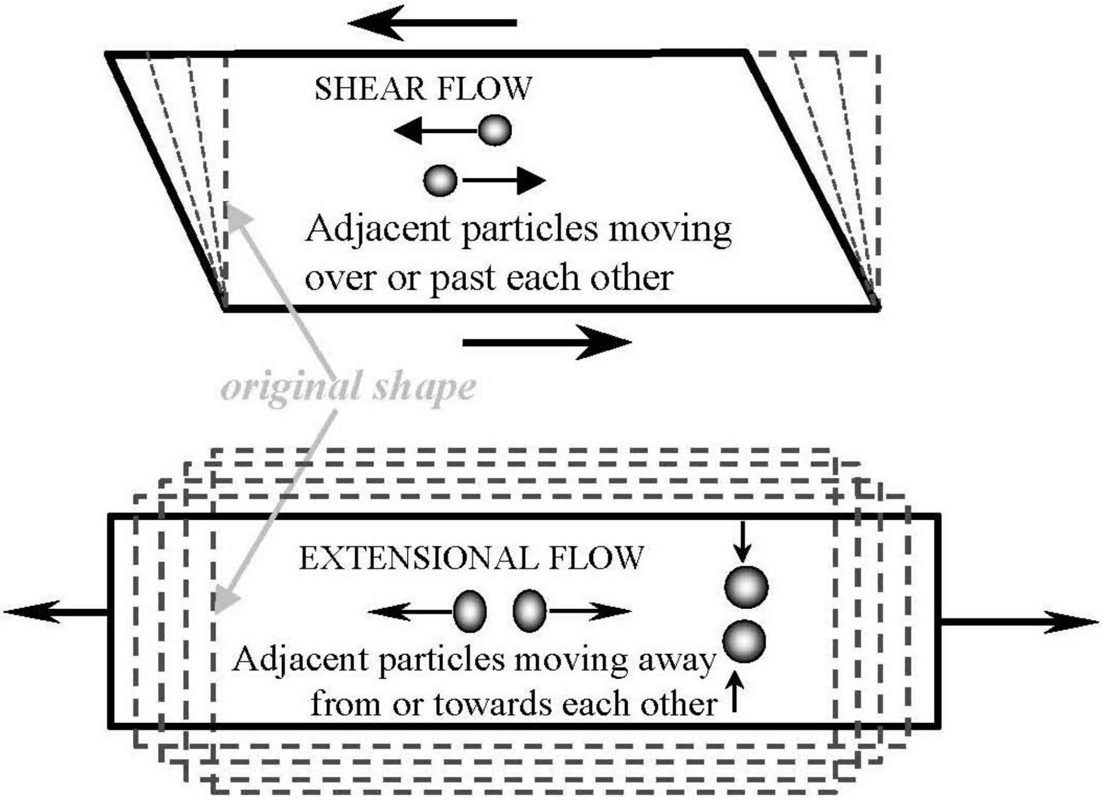

Figure 1. Particle motion in shear and extensional flows

3. Measurement of Viscosity

The simplest possible rheometric measurement is that of the shear viscosity, where the rheometer is operating as a viscometer. If the measured viscosity is constant as a function of shear stress or shear rate and viscoelastic effects are absent, then the liquid is said to be Newtonian. However, for the kind of liquids that we are interested in here, the viscosity, after being constant at low stresses/shear rates, decreases as the shear stress/shear rate increases.

3.1. The Realization of ‘Simple’ Flow Geometries in Viscosity Measurement

Viscometry is the science of the measurement of viscosity. Such viscometric measurements generally have to do with applying either a force F or a velocity V at a surface in contact with a contained test liquid. The response of this liquid to either the velocity or the force is measured at that surface or at some other nearby surface which is also in contact with the liquid. Examples of the geometries used for this purpose include tubes, parallel plates, cone-and-plate arrangements, and concentric cylinders. Sometimes artifacts arise whereby the presence of these surfaces interferes with the local liquid microstructure, giving apparent slip effects—these will be discussed in detail later.

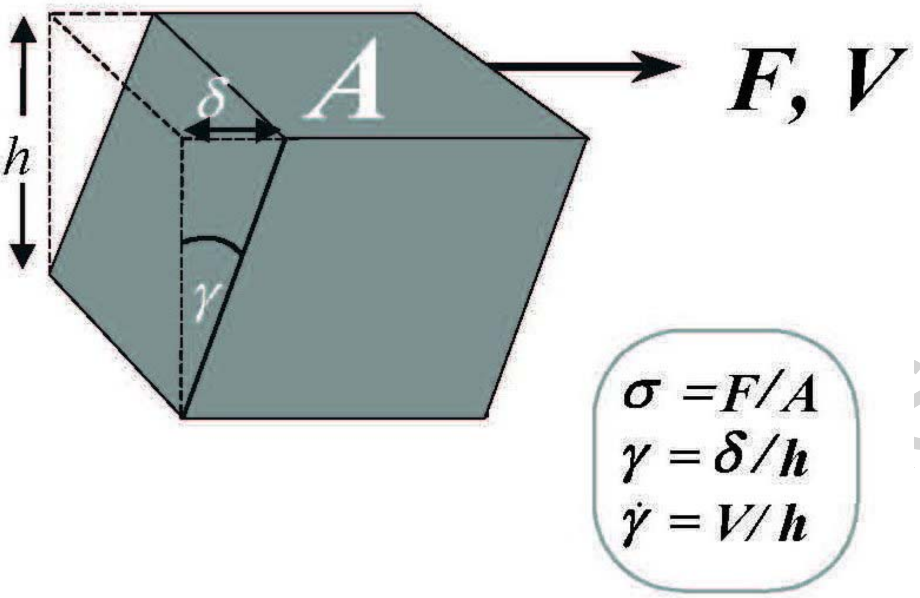

Figure 2. Definition diagram for shear flow

The aim of such viscometry is then (see Figure 2):

(a) To convert the applied force F to a representative shear stress σ, and

(b) To convert the velocity V to an equivalent shear rate $\dot{\gamma}$.

This is done using geometric constants, and is evaluated at a standard reference point such as the immediate vicinity of the tube wall or the inner cylinder or the outer edge of the cone and plate, etc. Then, for instance, the calculated shear stress σ and shear rate $\dot{\gamma}$ can be plotted as a function of one another, or else the shear stress can be divided by the shear rate to give the viscosity η.

In simple geometries the shear rate—and hence the shear stress—are the same everywhere in the liquid. Small-angle cone-and-plate and narrow-gap concentric-cylinder geometries are examples of this situation used in viscometers.

3.1.1. Small-angle Cone and Plate and Small-gap Concentric Cylinder Geometries

In these two geometries, see figure 3, the shear rate and shear stress is the same everywhere in the liquid under test.

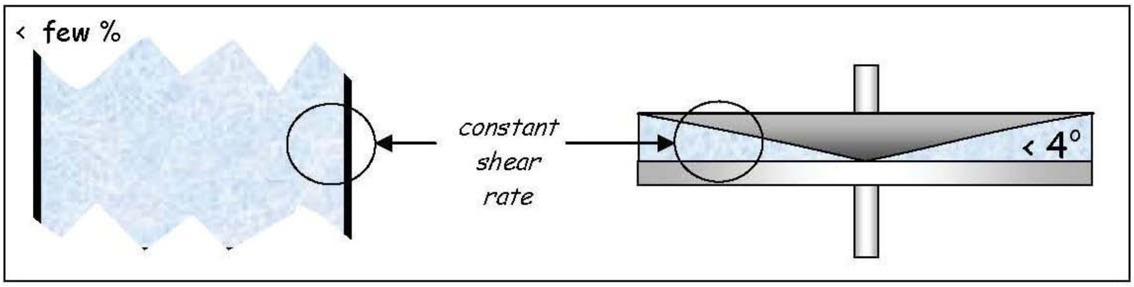

Figure 3. Two geometries where the shear rate (and shear stress) is the same everywhere in the liquid sample. Then the inner and outer cylinder - or the cone and plate - rotate relative to one another.

For these simple situations, we can write the relevant equations directly as:

(a) narrow-gap concentric cylinder:

the shear rate is given by: $$\dot{\gamma} = \frac{a_2\omega}{a_2 - a_1} \tag{1}$$

the shear stress is given by: $$\sigma = \frac{T}{2\pi a_1^2 H} \tag{2}$$

where - assuming the outer cylinder is rotating and the inner cylinder is constrained by some force-measuring device such as a spring - the inner cylinder radius is a_1, and an outer cylinder radius is a_2; ω is the rotation rate of the outer cylinder in radians per second, (ω is also equal to $2\pi f$, where f is the rotation rate in hertz, i.e., revolutions per second). The torque on the inner cylinder is T (otherwise known as the couple or moment, with units of Nm), the turning force F on the inner cylinder is given by T/a_1. Since the surface area over which the force F acts is $2\pi a_1 H$, where H is the cylinder height. The viscosity is then given by the quotient of shear stress and shear rate.

(b) small-angle cone-and-plate configuration:

the shear rate is given by: $$\dot{\gamma} = \frac{\omega}{\phi} \tag{3}$$

the shear stress is given by: $$\sigma = \frac{3T}{2\pi a^3} \tag{4}$$

where ω (as above) is the rotation rate and ϕ is the angle between the cone and plate in radians (remember 2π radians = 360°). Again the viscosity is then given by the quotient of shear stress and shear rate.

3.2. Non-simple but Manageable Viscometer Geometries

There are a number of popular viscometer geometries where the shear rate is not the same everywhere, but which are useful in that they can accommodate such realities as large particles in suspension in the liquid being tested [5]. In order to convert the basic experimental data from these non-simple geometries into unambiguous viscosity/shear-rate data, an intermediate calculation step is needed. This uses an assumption about the liquid, usually that at any particular value of shear rate, the *local* viscosity/shear-rate data can be described by a power-law-type behavior, where the slope of the log/log curve is given by n'. (For true power-law liquids, this is the same as n, the power-law index.)

Examples of this known relationship are found in –

- Flow in a wide-gap concentric-cylinder, where the *shear stress* falls off as the *inverse square* of the distance r from the centre of rotation as $T / 2H\pi r^2$.

- Flow in the parallel-plate viscometer, where the *shear rate* varies *linearly* from zero at the centre to $\alpha\omega / h$ at the edge of the plates, and

- Flow in a straight tube, where the *shear stress* varies *linearly* from zero at the centre to $Pa / 2L$ at the wall,

The following sections give the necessary equations for wide-gap concentric cylinders, the parallel-plate geometry and tubes used as viscometers. In each case the viscosity data is related to a certain shear rate calculated at some fixed point in the geometry, and n' is related to the basic measured parameters.

3.2.1. Wide-gap Concentric Cylinders

The software provided by some viscometer manufacturers for calculating viscosities in concentric-cylinder geometries only makes use of the narrow-gap approximation (you should check this in your manual). However, this only applies to gaps of at most a few percent of the outer-cylinder radius, and assumes that the shear rate and shear stress are approximately constant throughout the gap. This is not the case in many practical cases, and if for instance the inner cylinder is being rotated, the value of the shear stress decreases as the inverse square of distance from the centre of rotation as one moves away from the inner cylinder.

If non-Newtonian liquids are being measured and the narrow-gap approximation is used, the data from different-sized gaps does not coincide. However, the data can be corrected by the use of a number of lengthy analytical methods. However, a simple correction of the data can be made as follows, using an empirical correction factor worked out by the author, for the viscosity at the inner-cylinder, uncorrected shear rate:

$$\eta = \eta_{\mathrm{ng}}\left[b + n'(1-b)\right] \tag{5}$$

where η is the correct viscosity at the inner-cylinder shear rate, η_{ng} is the *calculated* viscosity based on the narrow-gap approximation, n' is the local power-law index at that shear rate at which the viscosity is being evaluated, calculated as $d \log T / d \log \omega$ where T and ω are the torque and rotational speed respectively, and, b is the gap ratio (inner-cylinder radius divided by the outer-cylinder radius). When this formula is used, data for different gap ratios, b, which would have originally appeared as a set of different curves if calculated using the narrow-gap approximation now lie on a single curve. Table 1 shows the viscosity correction factors predicted by our simple equation for a range of possible values of b and n.

Values of b	n'= 0.8	N' = 0.7	n' = 0.5
0.9	0.98	0.97	0.95
0.7	0.94	0.91	0.85
0.5	0.90	0.85	0.75

Table 1. Viscosity correction factors for non-Newtonian liquids measured in wide-gap concentric cylinder viscometers.

Complete equations for the evaluation of the viscosity in the wide-gap situation should be used for *very* shear-thinning liquids (say $n < 0.3$), i.e.

$$\dot{\gamma} = \frac{2\omega}{n(1-b^{2/n'})} , \tag{6}$$

and

$$\eta = \frac{Cn(1-b^{2/n'})}{4\pi r_{\mathrm{i}}^2 L\omega} \tag{7}$$

where

ω is the rotation rate of the inner cylinder,

C is the couple on the inner cylinder, and

r_{i} is the radius of the inner cylinder of length L.

3.2.2. The Rotating Parallel-Plate Viscometer

In a parallel-plate geometry, the upper plate is usually rotated and the couple C is like-wise measured on the upper plate (but it could be visa-versa). The shear rate varies from zero at the centre to $a\omega / h$ at the edge of the plates, where a is the plate radius, h the gap and ω the rotation rate in radians per second. The shear rate at the edge is given by

$$\dot{\gamma}_a = \frac{a\omega}{h} , \tag{8}$$

and the viscosity (evaluated at the edge shear rate $\dot{\gamma}_a$) is given by

$$\eta = \frac{3Ch}{2\pi a^4 \omega \left(1 + \frac{1}{3}\frac{d\log C}{d\log \omega}\right)}. \tag{9}$$

For a power-law liquid $d\log C/d\log$ is simply n.

3.2.3. Pipe/Tube Viscometer

Tube or pipe viscometers take many forms, but they should all be able to give the pressure-drop P as a function of flow rate Q for situations where the tube is long enough to be able to neglect entrance and end effects, say $L/a > 50$. In this case we can calculate the viscosity as a function of the wall shear rate, $\dot{\gamma}_{\mathrm{w}}$, which is given by

$$\dot{\gamma}_{\mathrm{w}} = \frac{4Q}{\pi a^3}\left(\frac{3}{4} + \frac{1}{4}\frac{d\log Q}{d\log P}\right). \tag{10}$$

The viscosity η is then given by

$$\eta = \frac{\pi a^4 P}{2QL\left(3 + \frac{d\log Q}{d\log P}\right)} \tag{11}$$

where for power-law liquids, $d\log Q/d\log P$ is simply $1/n$.

4. Viscoelastic Measurements at Small Stresses/Strains

A special case of describing the flow properties of a complex liquid is when the time or frequency response is measured without changing the ‘at-rest’ structure of the liquid. This is performed either by using small amplitude deformation or application of stress (oscillatory flow), or by the application of a small constant stress (creep). We then obtain what are called the ‘linear viscoelastic parameters’. Although strictly the geometries that should be used for this kind of testing should be limited to small-gap concentric cylinders and small-angle cone and plate, because the measurement is performed in the linear range of behavior, other geometries can easily be used and most commercial rheometers perform the calculations automatically.

This kind of testing which probes but does not change the rest relationship of the liquid is sometimes called ‘mechanical spectroscopy’, as analogous with other forms of spectroscopy, physical or chemical.

The two best-known forms of testing in the linear regime are oscillation and creep testing.

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Biographical Sketches

Howard Barnes studied Physics as an undergraduate at the University of Wales Aberystwyth, UK, and then did a PhD there with Prof. Ken Walters FRS in the Applied Mathematics department.

He then spent over 30 years at Unilever Research and Development Port Sunlight where he became a principal scientist. His particular interest is the relationship between the formulation, processing, microstructure and rheology of liquid products. He has recently retired after five years as a research professor in Industrial Rheology at Aberystwyth University. He is the author of some 80 publications in the area, and together with Professor Ken Walters and Mr John Hutton, he is a co-author of 'An

Introduction to Rheology'.

Professor Barnes has been awarded a D.Sc. and a visiting professorship from the University of Wales; prizes from the Royal Society of Chemistry and the Institution of Chemical Engineers, and an OBE from Queen Elizabeth II for 'services to science and technology'. He is a fellow of the Royal Academy of Engineering; a past president of the British Society of Rheology, and an associate member of The University of Wales Institute of Non-Newtonian Fluid Mechanics. He was the recipient of the British Society of Rheology's Annual Award, which specifically mentioned his contribution to rheology education.

João Maia was born on January 2, 1970, in Barreiro, Portugal. He has a BEng in Technological Physics Engineering obtained from the Technical University of Lisbon, Portugal (1992), a PhD in Applied Mathematics – Rheology from the University of Wales Aberystwyth, United Kingdom (1996) and an Aggregation in Polymer Science and Engineering from the University of Minho, Portugal (2007).

He was a Professor of the Department of Polymer Engineering of the University of Minho, Portugal, between 1996 and 2009 and is currently an Associate Professor at the Department of Macromolecular Science and Engineering of Case Western Reserve University, USA. He has published more than 70 papers in international peer-reviewed journals and Book chapters, has authored or co-authored 4 patents and more than 140 communications to international and national conferences, of which 14 were Plenary and/or Invited. His main fields of work are the areas of Extensional Rheometry of Polymer Melts and Rheology Applied to Materials (Polymer and Food) Processing.

Professor Maia is currently a member of the Portuguese Society of Materials, SPM, the Portuguese Society of Rheology, SPR (of which he is the Vice-President), the British Society of Rheology, BSR, the European Society of Rheology, ESR, the Society of Rheology, SoR, the American Institute of Physics; AIP, the Polymer Processing Society, PPS and the University of Wales Institute of Non-Newtonian Fluid Mechanics, UWINNFM (Associate Member).