HISTORY OF RHEOLOGY

Kenneth Walters
Institute of Mathematical and Physical Sciences, Aberystwyth University, Aberystwyth, UK.

Keywords: Non-Newtonian Fluid Mechanics, Computational Rheology, Molecular Modelling, Rheometry.

Contents

Summary

To many, Rheology is a relatively new science, which only really came into prominence in the second half of the 20th century. This is an oversimplification and some of the concepts encountered in rheology go back to antiquity.

In this chapter, we shall survey the way the field has developed by moving progressively through the decades (and indeed, centuries). Not surprisingly, work carried out in recent decades demands most attention.

Only major subjects are singled out for review and particular emphasis is given to the scientists (many with truly international reputations) who have graced the field and made significant contributions of lasting significance.

1. Introduction

To some, Rheology is a relatively new science, which only came into prominence following the end of the Second World War. However, in one sense, it can be considered to be a very old science, with roots in antiquity.

Notable amongst those who have (inadvertently) popularized some of the concepts which are now recognized as “rheological” are the Greek philosopher Heraclitus and the Jewish prophetess Deborah.

Interestingly, the famous dictum of the former “panta rhei” (everything flows) has been taken as the motto of the (American) Society of Rheology.

Deborah has given her name to an important non-dimensional number, which is based on an Old Testament scripture from the Book of Judges Chapter 5, verse 5: “The mountains flow before the Lord”. The basic idea is that everything flows, even the mountains, if you wait long enough! Marcus Reiner (1964) did more than anyone else to popularize these ideas and we can do no better than to quote some of his thoughts on the subject: “Deborah knew two things. First that the mountains flow, as everything flows. But, secondly, that they flowed before the Lord and not before man, for the simple reason that man in his short lifetime cannot see them flowing, while the time of observation of God is *infinite*. We may therefore well define as a non-dimensional number, the Deborah number,

$$D = \text{time of relaxation}/\text{time of observation}.$$

The difference between solids and fluids is then defined by the magnitude of D. If your time of observation is very large, or, conversely, if the time of relaxation of the material under observation is very small, you see the material flowing. On the other hand, if the time of relaxation is larger than your time of observation, the material, for all practical purposes, is a solid … . It therefore appears that the Deborah number is destined to become the fundamental number in rheology, bringing solids and fluids under a common concept. The greater the Deborah number, the more solid the material; the smaller the Deborah number the more fluid it is.”

It is readily conceded by the vast majority of workers in the field that the Deborah number concept is of significant importance in rheology.

As we shall see, other important rheological concepts were studied through the centuries and long before the formal introduction of the term Rheology in 1929. This coincided with the founding of the American Society of Rheology in Washington DC and the formal definition of Rheology is invariably associated with Professor E. C. Bingham of Lafayette College, Easton, Pa., who was one of the three organizers of the 1929 meeting, the others being Marcus Reiner of Israel (already referred to) and G. W. Scott Blair of the U.K. A convenient definition of Rheology, which would be generally accepted, is: “The science of the deformation and flow of matter”.

Figure 1. E.C.Bingham, M.Reiner and G.W.Scott Blair.

Many famous scientists can be considered to have carried out rheological research before that 1929 meeting, especially in the 19th century, but space will allow no more than a cursory mention of some of the more important developments. Any reader who is particularly interested in them is encouraged to read the extensive text, running to 250 pages, entitled "Rheology, An Historical Perspective" written by the present author in collaboration with R.I. Tanner (Tanner and Walters 1998). That text emphasizes the roles of two famous British scientists, Isaac Newton and Robert Hooke, in setting the boundaries of the modern science of Rheology.

So far as solid-like behavior is concerned, Hooke introduced his famous linear law relating stress and strain in 1678.

Nine years after the publication of Hooke's work, Newton (1687) discussed steady shear flow in a *fluid* and in the Principia is his famous hypothesis: "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". This "lack of slipperiness" is what we now call "viscosity".

The works of Hooke and Newton set the boundaries of "classical elasticity" and "fluid dynamics". However, as we shall see, Rheology goes far beyond these special cases and, by common consent, excludes them.

Usually, rheologists are concerned with materials lying between the classical extremes and a rheological glossary has emerged with such terms and expressions as "viscoelasticity" and "non-Newtonian fluid mechanics". We shall discuss these and some of the other concepts in later sections.

2. Early Departures from the Classical Extremes

The first clear experimental departure from the classical extremes introduced by Hooke and Newton is contained in the work of Wilhelm Weber on silk threads (Weber 1835, 1841). He applied a tensile load to a silk fiber and noticed an immediate (elastic) extension; this was followed by a continued slow extension with time. Removal of the load led to an immediate extension. This kind of behavior was already well known in metals, but, to Weber's surprise, it was found that the silk fiber eventually recovered its original length.

The response observed by Weber is now seen as being consistent with that expected of a *viscoelastic solid*.

So far as fluid-like materials are concerned, an influential contribution came from the pen of the famous British scientist, James Clerk Maxwell (Maxwell 1867, 1868). He put forward a (linear) equation relating stress σ and strain γ of the form:

Figure 2. James Clerk Maxwell.

$$\sigma + \lambda \frac{d\sigma}{dt} = \eta \frac{d\gamma}{dt}, \qquad (1)$$

Where t is the time, λ a time constant (known as the *relaxation time*) and η is the viscosity.

When $\lambda = 0$, we have "Newtonian" behavior and as λ becomes so large that the first term on the left-hand side of Eq. (1) can be neglected in comparison to the second, we essentially have "Hookean" elastic behavior.

Rheologists use the term "elastico-viscous liquid" or simple "elastic liquid" to describe materials that satisfy Eq. (1). This so called "Maxwell fluid" has been surprisingly influential as the years have progressed and, today, one often sees references to the UCM (Upper-Convected Maxwell) model, which is based on Eq. (1), suitably embellished with a 20th century non-linear continuum mechanics.

Equation (1) may be compared and contrasted with the simplest equation for a viscoelastic solid, named after the British scientist Lord Kelvin (see Thomson 1865, 1878) and appropriately called the Kelvin model or sometimes the Kelvin-Voigt model. This has a rheological equation of state of the form:

$$\sigma = G\gamma + \eta \frac{d\gamma}{dt}, \qquad (2)$$

Where G is a material constant.

Equations (1) and (2) set the boundaries of the research field known as "Linear Viscoelasticity". This continues to be an important area of rheological research and two issues merit our attention.

First, the simplest extension of the Maxwell Eq. (1) for an elastic liquid is provided by the so-called Jeffrey's model, with equations which are usually expressed in the form:

$$\sigma + \lambda \frac{d\sigma}{dt} = \eta \left[\frac{d\gamma}{dt} + \lambda \frac{d\gamma}{dt} \right], \qquad (3)$$

where η, λ and λ are material constants.

This model has a prominent place in the historical development of the science of rheology. For example, Jeffreys (1929) applied the equation to interpret problems associated with the earth's crust. Later, Fröhlich and Sack (1946) showed that, within the linearity constraint, a dilute suspension of elastic spheres in a viscous liquid may be expected to obey Eq. (3) and Oldroyd (1953) did the same for a dilute emulsion.

A non-linear version of Eq. (3), first introduced by Oldroyd in 1950 and called the Oldroyd B model, has had a very important influence in recent years, especially in the field of Computation Rheology (see later).

The second issue which merits attention relates to the introduction of "mechanical models" in the early years of the 20th century (see, for example, Poynting and Thomson 1902). These have proved to be a popular way of characterizing linear-viscoelastic response, without the need to go into the accompanying mathematics in detail. In these models, Hookean deformation is represented by a spring and Newtonian flow by a dashpot, and the procedure involves the association of force, extension and time in the models with stress, strain and time in the materials.

Returning briefly to the 19th century, an important and influential work of generalization, which can incorporate both solid-like and liquid-like responses, was provided by another famous scientist, Ludwig Boltzmann (see, for example, Boltzmann 1874, 1877, 1878). He introduced an *integral* constitutive equation, which generalized all previous work on non-classical materials.

Figure 3. Ludwig Boltzmann.

So, in summary, we can say that, by the turn of the 20th century, there was a general acknowledgement of the existence of materials which could not be classified as Hookean solids or Newtonian fluids. Furthermore, a general framework existed to describe the linear behavior of such materials.

-
-
-

Bibliography

Barnes H.A. and Walters K. (1985) The yield stress myth? *Rheological Acta* 24, 323-326. [A short provocative paper which questions the yield-stress concept.]

Barnes H.A. (1999) The yield stress – a review. *J. non-Newtonian Fluid Mechanics* 81, 133-178. [A comprehensive review of the yield-stress debate.]

Bingham E.C. (1922) *Fluidity and plasticity.* McGraw Hill, New York. [The introduction of the most famous equation for yield-stress materials.]

Boger D.V. (1977/78) A highly elastic constant-viscosity fluid. *J. non-Newtonian Fluid Mechanics* 3, 87-91. [The first reference to the so-called Boger fluid.]

Boger D.V. and Walters K. (1993) *Rheological Phenomena in Focus*. Elsevier. [Contains a comprehensive set of flow-visualization pictures for non-Newtonian fluids.]

Boltzmann L. (1874) Sitzber Kgl Akad Wiss Wien, Math-Naturw Classe 70, 275-306. (1877) *Sitzber Kgl Akad Wiss* Wien 76, 815-842. (1878) *Wied Ann* 5, 430-432. [A series of papers related to the famous Boltzmann integral equations for linear viscoelasticity.]

Broadbent J.M., Kaye A., Lodge A.S. and Vale D.G. (1968) Possible systematic errors in the measurement of normal stress differences in polymer solutions in steady shear flow. *Nature* 217, 55.

Coleman B.D. and Noll W. (1960) An approximate theorem for functionals with applications in continuum mechanics. *Arch. Rat. Mech. Anal.* 36, 355-370. [Derivation of the hierarchy equations for slow flow of elastic liquids.]

Crochet M.J., Davies A.R. and Walters K. (1984) *Numerical simulation of non-Newtonian flow*, Elsevier. [The first text book to be devoted to Computational Rheology.]

Doi M. and Edwards S.F. (1978) Dynamics of concentrated polymer systems Parts 1-4. J. *Chem. Soc. Faraday Trans*. 74, 1789-1801, 1802-1817, 1818-1832, 75, 38-54. (1986) *The theory of polymer dynamics*, Clarendon Press, Oxford. [Contains important work on the application of reptation ideas for polymeric systems.]

Fröhlich H. and Sack R. (1946) Theory of the rheological properties of dispersions. *Proc Roy. Soc.* A185, 415-430. [Derivation of the (linear) equations for a dilute suspension of rigid spheres in a Newtonian fluid.]

Herschel W.H. and Bulkley R. (1926) Measurement of consistency as applied to rubber benzene solutions. *Proc. Am. Assoc. Test Materials* 26, 621. [Contains an important extension to the Bingham model.]

Hooke R. (1676) *A description of helioscopes and some other instruments*. London. Printed by T.R. for John Martyn. [The introduction of the famous linear law for elastic solids – introduced as a Latin anagram!] This was followed by a more comprehensible paper in 1678 – "*De potential restitutiva"*. J.Martyn, London.

Jaumann G. (1905) Grundlagen der bewegungslehre "Springer, Leipzig (1911) *Sitz Akad Wiss Wien* 120, 385-530. [Introduction of a non-linear time derivative for non-Newtonian fluids – sometimes known as the Jaumann derivative and also the corotational derivative.]

Jeffreys H. (1929) *The earth*. Cambridge University Press. [Uses Eq. (3) in connection with problems of the earth's crust.]

Lodge A.S. (1956) A network theory of flow birefringence and stress in concentrated polymer solutions. *Trans. Faraday Soc*. 52, 120-130. [Derives constitutive equations for the so-called "rubber-like liquid".]

McLeish T.C.B. and Larson R.G. (1998) *Molecular constitutive equations for a class of branched polymers: The pom-pom polymer.* J. Rheol. 42, 81-110. [An important recent paper in polymer melt rheology.]

Maxwell J.C. (1867) P*hil. Trans. Roy. Soc*. 157, 49-88. (1868) *Phil. Mag.* 35, 129-145, 185-217. [Discusses the introduction of Eq. (1).]

Oldroyd J.G. (1950) On the formulation of rheological equations of state. *Proc. Roy. Soc.* A200, 523-541. [A very important paper on the construction of constitutive equations for elastic liquids.]

Oldroyd J.G. (1953) The elastic and viscous properties of emulsions and suspensions*. Proc. Roy. Soc*. A218, 122-132. [Derivation of the (linear) equations for dilute emulsions.]

Perera M.G.N. and Walters K. (1977) Long-range memory effects in flows involving abrupt changes in geometry. *J. non-Newtonian Fluid Mechanics* 2, 49-81, 191-204. [The first successful attempt(s) to apply (finite-difference) numerical schemes in the case of long-range memory effects and complex geometries.]

Phan Thien N. and Tanner R.I. (1977) A new constitutive equation derived from network theor*y. J. non-Newtonian Fluid Mechanics* 2, 191-204. [This paper saw the introduction of a constitutive equation which is still popular.]

Poynting J.H. and Thomson J.J. (1902) *Properties of Matter*, London: Charles Griffin and Co. Ltd. [Contains the first reference to mechanical models.]

Reiner M. (1945) A mathematical theory of dilatancy. *Amer. J. Math.* 67, 350-362. [The paper derives the equations for the so-called Reiner-Rivlin fluid.]

Reiner M. (1964) The Deborah number. *Physics Today* 17, 62. [Contains a popular introduction to the concept of the Deborah number.]

Rivlin R.S. (1948) The hydrodynamics of non-Newtonian fluids Part 1. *Proc. Roy. Soc* A193, 260-281. [The paper derives the equations for the so-called Reiner-Rivlin fluid.]

Schwedoff T. (1890) *J. Physique* [2] 9, 34-46. [Introduces Eq. (4) for materials with a yield stress.]

Tanner R.I. and Walters K. (1998) *Rheology: An historical perspective*. Elsevier. [Recommended reading for those who wish to know more about historical developments in Rheology.]

Tanner R.I. and Pipkin A.C. (1969) Intrinsic errors in pressure-hole measurements. *Trans. Soc. Rheol.* 13, 471-484. [Explains the hole-pressure error in theoretical terms.]

Thomson W. (1865) *Proc. Roy. Soc.* 14, 289-297. (1878). *Elasticity and heat in Encyclopedia Brittanica 9th Edition*. [Introduces what is often referred to as the Kelvin-Voigt model for viscoelastic solids. Thomson is better known as Lord Kelvin.]

Trouton F.T. (1906) On the coefficient of viscous traction and its relation to that of viscosity. *Proc. Roy. Soc*. 77, 426-440. [An influential paper on *extensional* flow, limited in this case to Newtonian fluids.]

Walters K. and Webster M.F. (2003) The distinctive CFD challenges of computational rheology. *Int. J. for Numerical Methods in Fluids* 43, 577-596. [An example of many of the recent reviews on developments in Computational Rheology.]

Weber W. (1835) Ann. Phys. Chem. 34, 247-257 (1841) *Ann. Phys. Chem.* 54, 1-18. [An important discovery of a viscoelastic-solid response in silk threads.]

Biographical Sketch

Professor Ken Walters was appointed Professor at the University of Wales Aberystwyth (now Aberystwyth University) in 1973. He was awarded a DSc degree in 1985. He is a former President of the British Society of Rheology and received their gold medal in 1984. He was elected a Fellow of the Royal Society in 1991 and is a Foreign Associate of the National Academy of Engineering of the United States. In 1998, he was awarded an Honorary Doctorate by the Université Joseph Fourier in France.

Professor Walters is the author of several books on rheology, rheometry and non-Newtonian fluid flow. He was Executive Editor of the Journal of Non-Newtonian Fluid Mechanics from its launch in 1976 until the publication of Volume 100 in 2002. From 1996-2000, Professor Walters was the first President of the European Society of Rheology, and from 2000-2004, he was Chairman of the International Committee on Rheology.