

2nd Edition

# Rheology for Chemists

## An Introduction

Jim W Goodwin and Roy W Hughes



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# **Rheology for Chemists**

## **An Introduction**

### **2nd Edition**

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# Preface

## PREFACE TO THE 1ST EDITION

Everyday we are all concerned with the rheological response of a variety of materials because we have to pour, spread or reshape them. Hopefully it will be in a peaceful situation such as when we are standing on the seashore with water lapping around our feet as they gently sink into the sand and not in the situation where flows are produced by erupting volcanoes. That rheological behaviour is fundamental to our existence is clear from the way our blood flows to our very conception where the way that the flow properties of polyelectrolyte gels change with pH is a critical factor.

In the workplace, many chemists have the problem of formulating materials into a convenient form. Although we could use as an example foods, pharmaceuticals, or cleaning materials let us consider a decorative paint as an example that serves to illustrate the range of responses that we demand. The function of a paint is twofold. We wish to apply a polymer film to protect the surface that we are painting and secondly, it is a carrier for pigments to give a decorative finish. In the can we wish the pigment particles to remain suspended and to this end we produce a weak gel. A by-product of this is the nondrip behaviour. On application it must easily “thin” to be readily laid on, then we have the problem of levelling and runs prior to drying. The former is driven by surface-tension forces whilst the latter is the response to gravitational forces on the film. Hence, we require the gelation to start to reoccur but at a rate where sufficient levelling will take place. So what exactly are we asking this material to do? Firstly, it should be a soft solid that melts when we apply a force with a brush or roller, and then it must resolidify at a controlled rate. How do we achieve this? Well, not by magic, but by chemistry. We control the interactions between the molecules and the particles in the paint so that the best structure and diffusional timescales for our purposes are produced. It is the purpose of this book to clarify this process. Not just with paint of course but with any formulation.

The excitement in the study of rheology is in seeing how the timescales are so important, in seeing how our materials behave and for the chemist it is rewarding to see how the controlling factor is the same intermolecular forces that we have been trained to manipulate. Now we will have to work in terms of

stresses and strains and use some simple algebra in order to enable us to describe or predict behaviour. As this is an introductory text, derivations will only be given where they are straightforward and provide greater understanding. For more complex results, the important relationship is given and the enthusiast can find more detail from the appropriate references. The algebra is simply a compact shorthand notation that enables us to summarise the behaviour; much more important is the understanding of the mechanisms involved as it is this that gives one the “feel” for a subject. It is this that we wish to promote and to this end we restrict ourselves to the simple experiments that we would normally carry out in the laboratory and do not tackle the complex flows that may be important for engineering applications.

The format of the book is very straightforward. The subject with essential terminology is introduced in the first chapter. The following two chapters develop the ideas for the limiting behaviour, *i.e.* when we are not too concerned with the timescales. The next two chapters develop these ideas further as the temporal behaviour comes to the fore. Finally, we move into nonlinear behaviour. Most readers will feel right at home here as we discuss the types of experiment that they are carrying out everyday. Our aim is that every chapter should be as self-contained as possible and so we revisit basic ideas and extend them where necessary with the intention that the depth of understanding increases as the reader progresses through the book. Above all, we are interested in how atoms and molecules interact to control the handling properties of materials. Many of the systems of importance to the chemist are polymeric and particulate, and discussion of these takes up the lion’s share of the volume, but it is the same forces that occur between simple molecules that we must consider in these cases too. Few undergraduate or graduate programmes have much if any discussion of rheology, polymers and colloids and we see this volume as the starting point for repairing this omission.

Jim Goodwin, Roy Hughes  
November 1999

## PREFACE TO THE 2ND EDITION

Since the publication of the 1<sup>st</sup> edition of *Rheology for Chemists*, system dimensions have become an important topic and there has been a very large expansion of publications on subjects such as microfluidics and nanoparticle systems. With decreasing size, the range and magnitude of interparticle forces become increasingly important as the separation distances frequently fall within the same range. This brings into sharp focus much of the text as we have stressed the importance of the microstructural aspects throughout the volume.

Another major change in the rheological scene since we started preparing the first edition has been the maturing of the instrumentation market. The expectation is now to be able to carry out rheological measurements as routinely and

easily as using any of the general analytical instruments. However, the interpretation of the data still requires more manipulation than, for example, calculating the relative composition of a material from an FTIR spectra. Hence, the basic toolbox provided by this volume is an important aid in handling the data successfully.

Jim Goodwin, Roy Hughes  
May 2007

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## CHAPTER 1

# Introduction

The study of rheology is the study of the deformation of matter resulting from the application of a force. The type of deformation depends on the state of matter; for example, gases and liquids will flow when a force is applied, whilst solids will deform by a fixed amount and we expect them to regain their shape when the force is removed. In other words we are studying the “*handling properties of materials*”. This immediately reminds us that we must consider solutions and dispersions and not simply pure materials. In fact, the utility of many of the materials we make use of every day is due to their rheological behaviour and many chemists are formulating materials to have a particular range of textures, flow properties, *etc.* or are endeavouring to control transport properties in a manufacturing plant. Interest in the textures of materials, such as say a chocolate mousse or a shower gel, may be of professional interest to the chemist in addition to natural curiosity. How do we describe these quantitatively? What measurements should we make? What is the chemistry underlying the texture so that we may control it? All these questions make us focus on rheology.

The aim of this text is to enable the reader to gain an understanding of the physical origins of viscosity, elasticity, and viscoelasticity. The route that we shall follow will be to introduce the key concepts through physical ideas and analogues that are familiar to chemists and biologists. Ideas from chemical kinetics, infrared, and microwave spectroscopy are invariably covered in some depth in many science courses and so should aid the understanding of rheological processes. The mathematical content will be kept to the minimum necessary to give us a quantitative description of a process, and we have taken care to make any manipulations as transparent as possible.

There are two important underlying ideas that we shall return to throughout this work. Firstly, we should be aware that intermolecular forces control the way our materials behave. This is where the chemical nature is controlling the physical response. The second is the importance of the timescale of our observations, and here we may observe quite different physical responses when our experiments are carried out at different timescales. The link between the two arises through the *structure* that is the consequence of the forces and the timescale for changes by microstructural motion resulting from thermal or

mechanical energy. What is so exciting about rheology is the insights that we gain into the origins of the behaviour of such a wide variety of systems in our everyday mechanical world.

## 1.1 DEFINITIONS

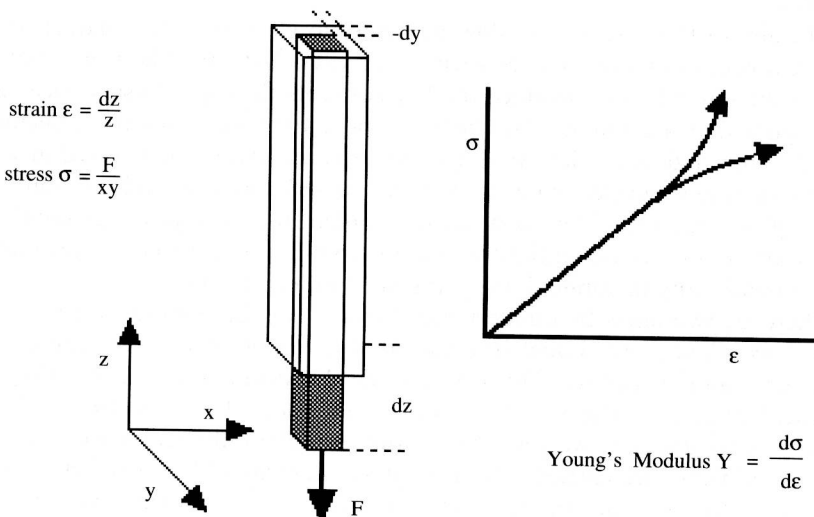
### 1.1.1 Stress and Strain

The *stress* is simply defined as the force divided by the area over which it is applied. Pressure is a *compressive bulk stress*. When we hang a weight on a wire, we are applying an *extensional stress* and, when we slide a piece of paper over a gummed surface to reach the correct position, we are applying a *shear stress*. We shall focus more strongly on this latter stress as most of our instruments are designed around this format. The units of stress are Pascals.

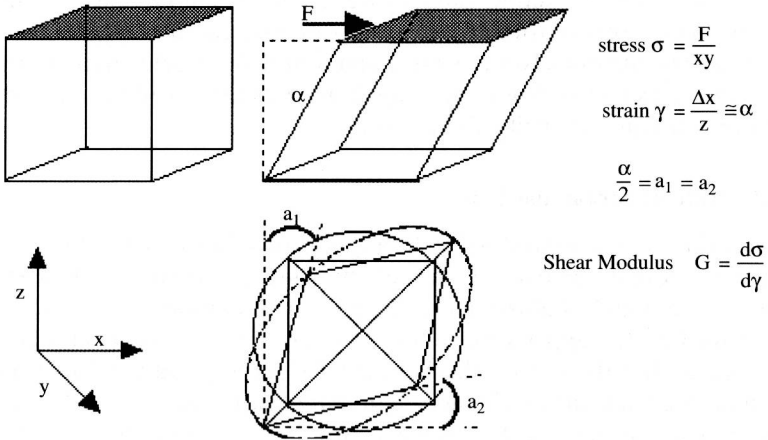
When a stress is applied to a material, a deformation will be the result. In order to make calculations tractable, we define the *strain* as the relative deformation, that is, the deformation per unit length. The length that we use is the one over which the deformation occurs. This is illustrated in Figures 1.1 and 1.2.

There are several features of note in Figures 1.1 and 1.2:

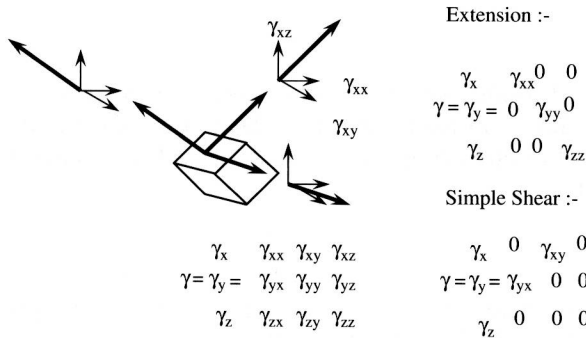
1. The elastic modulus is constant at small stresses and strains. This linearity gives us Hooke's law,<sup>1</sup> which states that the stress is directly proportional to the strain.
2. The shear strain, produced by the application of a shear stress  $\sigma$ , is illustrated in Figure 1.2. The lower section of the figure shows the general case where there is no rotation of the principal axes of strain. These are



**Figure 1.1** Extensional strain at constant volume  $\epsilon = \gamma_{zz} = (\gamma_{xx} + \gamma_{yy})$ .



**Figure 1.2** Shear strain  $\gamma = \gamma_{xz} = \gamma_{zx}$ .



**Figure 1.3** Strain and stress are tensors.

simply the diagonals of the material element, one of which shortens whilst the other lengthens. We will see later how this leads to compressive and extensional forces on pairs of particles as they collide in a flowing system.

3. At high stresses and strains, nonlinearity is observed. Strain hardening (an increasing modulus with increasing strain up to fracture) is normally observed with polymeric networks. Strain softening is observed with some metals and colloids until yield is observed.
4. We should recognise that stress and strain are tensor quantities and not scalars. This will not present any difficulties in this text but we should bear it in mind as the consequences can be dramatic and can be useful. To illustrate the mathematical problem, we can think what happens when we apply a strain to an element of our material. The strain is made up of three orthogonal components that can be further subdivided into components, each of which are lined up with our axes. This is shown in Figure 1.3.

Figures 1.2 and 1.3 show how if we apply a simple shear strain,  $\gamma$ , in our rheometer this is formally made up of two equal components,  $\gamma_{xy}$  and  $\gamma_{yx}$ . By restricting ourselves to simple and well-defined deformations and flows, *i.e.* simple viscometric flows, most algebraic difficulties will be avoided but the exciting consequences will still be seen.

### 1.1.2 Rate of Strain and Flow

When a fluid system is studied by the application of a stress, motion is produced until the stress is removed. Consider two surfaces separated by a small gap containing a liquid as illustrated in Figure 1.4. A constant shear stress must be maintained on the upper surface for it to move at a constant velocity,  $u$ . If we can assume that there is no slip between the surface and the liquid, there is a continuous change in velocity across the *small* gap to zero at the lower surface. Now, in each second the displacement produced is  $x$  and the strain is:

$$\gamma = x/z \quad (1.1)$$

and as  $u = \frac{dx}{dt}$ , we can write the *rate of strain* as:

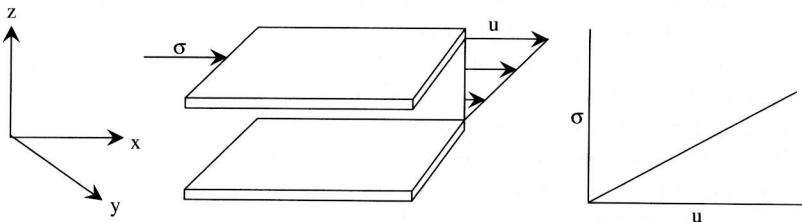
$$\frac{d\gamma}{dt} = \frac{u}{z} \quad (1.2)$$

The terms *rate of strain*, *velocity gradient*, *shear rate* are all used synonymously and Newton's dot is normally used to indicate the differential operator with respect to time. For large gaps the rate of strain will vary across the gap and so we should write:

$$\dot{\gamma} = \frac{du}{dz} \quad (1.3)$$

When the plot of shear stress *versus* shear rate is linear, the liquid behaviour is simple and the liquid is Newtonian<sup>2</sup> with the coefficient of viscosity,  $\eta$ , being the proportionality constant.

When a flow is used that causes an extension of a liquid, the resistance to this motion arises from the *extensional viscosity*,  $\eta_e$ , and the extension rate is  $\dot{\epsilon}$ . Extensional flows require an acceleration of the fluid as it thins and so *steady flows are never achieved* and this means that the microstructural time-scale is particularly important. Many practical applications involve extensional flows, frequently with a shear component. For example, spraying, spreading,



**Figure 1.4** A velocity gradient produced when a fluid is sheared.

and roller coating are common ways to apply products from the food, pharmaceutical, paint and printing industries. Although the analysis may be carried out as if the materials are continua with uniform properties, the control comes from an understanding of the role of molecular architecture and forces.

## 1.2 SIMPLE CONSTITUTIVE EQUATIONS

### 1.2.1 Linear and Nonlinear Behaviour

It is a simple matter to write down an algebraic relationship that describes the simpler forms of rheological behaviour. For example:

for a Hookean solid

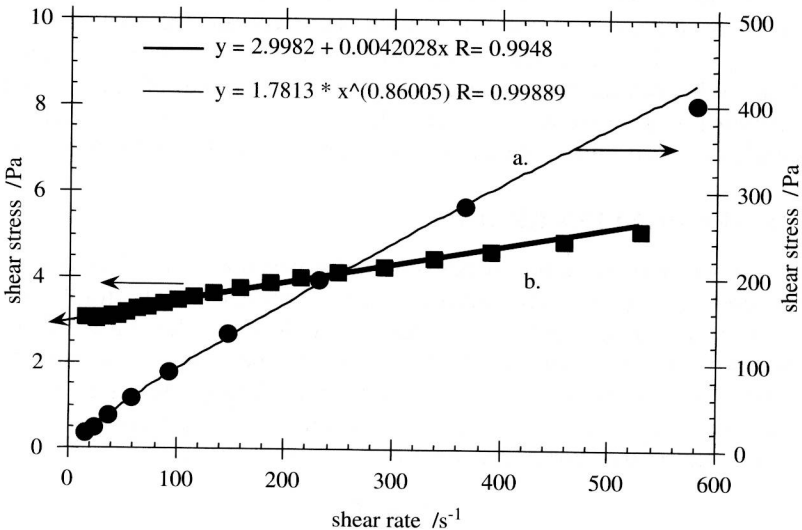
$$\sigma = G\gamma \quad (1.4)$$

and a Newtonian liquid

$$\sigma = \eta\dot{\gamma} \quad (1.5)$$

These equations should fully describe the stress–strain–time relationship for the materials over the full range of response. However, the range over which such *linear* behaviour is observed is invariably limited. Usually large stresses and strains or short times bring deviations from eqns (1.4) or (1.5).

As the behaviour becomes more complicated more parameters are required to fit the experimental curves. To illustrate this, consider two common equations used to describe shear-thinning behaviour observed in viscometers. Figure 1.5 shows these two responses.



**Figure 1.5** (a) Power-law behaviour from a 12% poly(vinylpyrrolidone) solution; (b) Bingham plastic behaviour from a 14%w/v sodium kaolinite dispersion.



Figure 1.5(a) shows a steady shear-thinning response and the experimental points can be fitted to a simple equation:

$$\sigma = A_c \dot{\gamma}^n \quad (1.6)$$

where the two fitting parameters are  $A_c$ , the “consistency”, and  $n$ , the “power-law index”. This equation is often presented in its viscosity form:

$$\eta = A_c \dot{\gamma}^{n-1} \quad (1.7)$$

Figure 1.5(b) shows the behaviour of a “Bingham plastic” and the fitting equation is:

$$\sigma = \eta_p \dot{\gamma} + \sigma_B \quad (1.8)$$

Here, the fitting parameters are the slope of the line, (the plastic viscosity,  $\eta_p$ ) and the Bingham or dynamic yield stress, (the intercept,  $\sigma_B$ ). Other constitutive equations will be introduced later in this volume as appropriate.

## 1.2.2 Using Constitutive Equations

The first use that we can make of our constitutive equations is to fit and smooth our data and so enable us to discuss experimental errors. However, in doing this we have the material parameters from the model. Of course it is these that we need to record on our data sheets as they will enable us to reproduce the experimental curves and we will be able to compare the values from batch to batch of a product or reformulation. This ability to collapse more or less complicated curves down to a few numbers is of great value whether we are engaged in production of, the application of, or research into materials.

The corollary is that we should always keep in mind the experimental range. Extrapolation outside that range is unwise. This will become particularly clear when we discuss the yield phenomenon – an area of wide interest in many practical situations. Whatever the origins claimed for these models, they all really stem from the phenomenological study of our materials and so our choice of which one to use should be based on the maximum utility and simplicity for the job in hand.

## 1.3 DIMENSIONLESS GROUPS

An everyday task in our laboratories is to make measurements of some property as a function of one or more parameters and express our data graphically, or more compactly as an algebraic equation. To understand the relationships that we are exploring, it is useful to express our data as quantities that do not change when the units of measurement change. This immediately enables us to “scale” the response. Let us take as an example the effect of temperature on reaction rate. The well-known Arrhenius equation gives us the variation:

$$k_r = A \exp(-E_a/RT) \quad (1.9)$$

Here  $k_r$  is the rate of a reaction measured at temperature  $T$ .  $E_a$  is the activation energy and  $R$  is the gas constant. Now  $RT$  is the value of thermal