

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,¹ which states that the stress is directly proportional to the strain.
2. The shear strain, produced by the application of a shear stress σ , 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

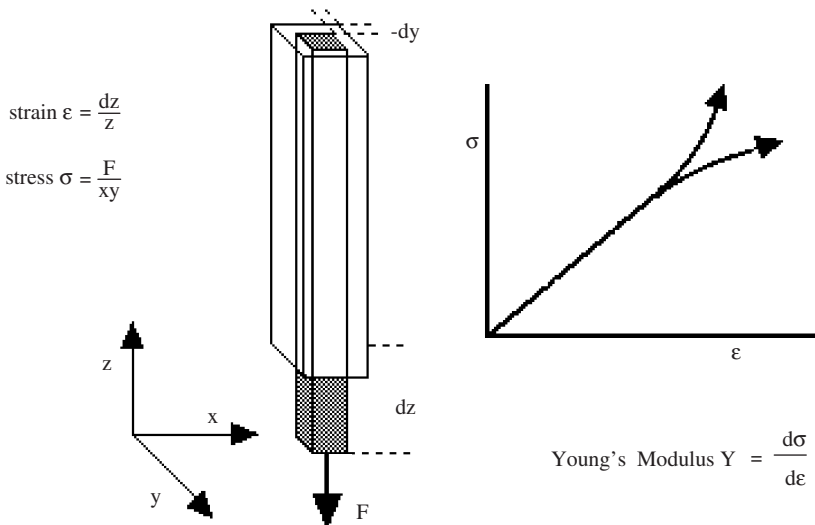


Figure 1.1 Extensional strain at constant volume $\epsilon = \gamma_{zz} = (\gamma_{xx} + \gamma_{yy})$.

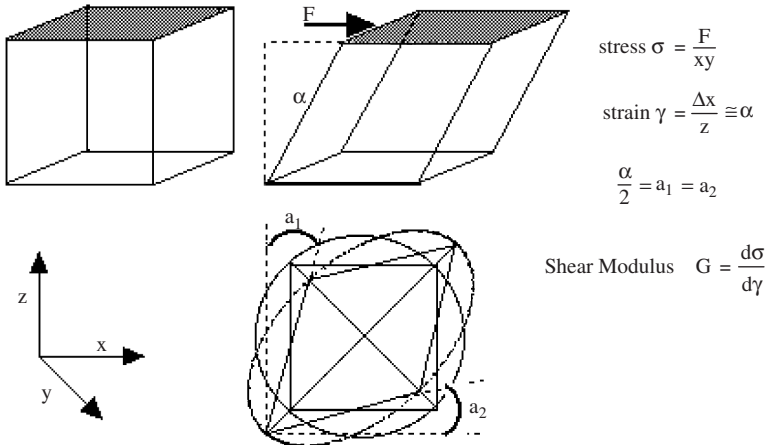


Figure 1.2 Shear strain $\gamma = \gamma_{xz} = \gamma_{zx}$.

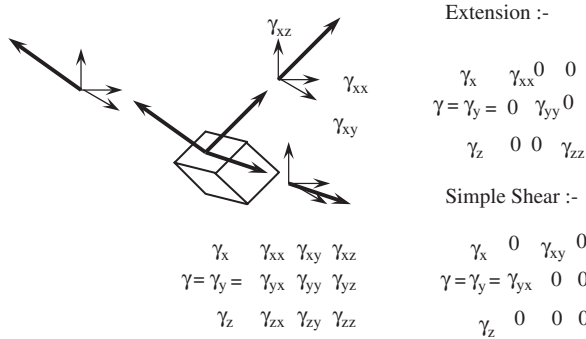


Figure 1.3 Strain and stress are tensors.

- 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, γ , in our rheometer this is formally made up of two equal components, γ_{xy} and γ_{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 Newtonian² with the coefficient of viscosity, η , 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*, η_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,

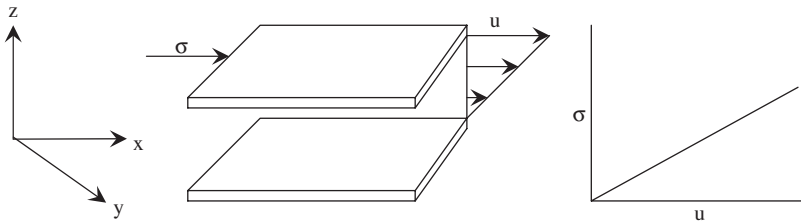


Figure 1.4 A velocity gradient produced when a fluid is sheared.

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

$$\sigma = G\gamma \tag{1.4}$$

and a Newtonian liquid

$$\sigma = \eta\dot{\gamma} \tag{1.5}$$

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.

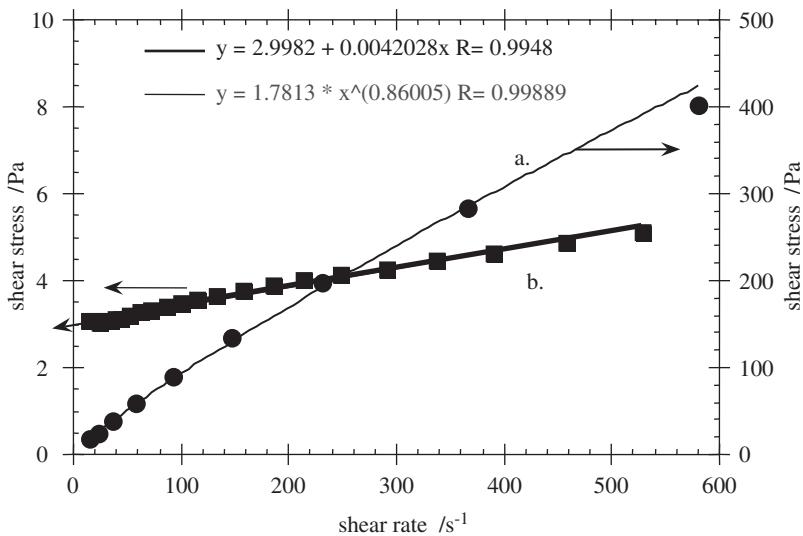


Figure 1.5 (a) Power-law behaviour from a 12% poly(vinylpyrrolidone) solution; (b) Bingham plastic behaviour from a 14%w/v sodium kaolinite dispersion.

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, η_p) and the Bingham or dynamic yield stress, (the intercept, σ_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

energy and so the magnitude of the dimensionless group, (E_a/RT) , immediately gives us a feel as to the importance of the activation process. For example, if $E_a \ll RT$, then the activation process will not slow the reaction rate significantly from the fastest possible rate A . On the other hand, if $E_a \gg RT$, then the reaction rate will be very much slower than A . Mechanistically this reminds us of the Boltzmann energy distribution and stochastic processes. The dimensionless group, (E_a/RT) , is known as the ‘‘Arrhenius group’’.

Another example from chemical kinetics can be seen in the rate equation for first-order reactions. Here, the equation relating the concentration of a species A at time t , $[A](t)$ to the reaction time and the initial concentration, $[A](0)$ is:

$$[A](t) = [A](0) \exp(-k_r t) \quad (1.10)$$

The rate coefficient, k_r , has units of t^{-1} and so can equally well be thought of in terms of the characteristic time for the reaction to take place. Hence if $k_r t \gg 1$, the reaction will be a long way towards completion, whereas if $k_r t \ll 1$, very little change will have occurred. Equation (1.10) describes the decay of radioactive elements and $1/k_r$ could be considered as the characteristic time for the *relaxation* of the element from its active to its nonactive state.

1.3.1 The Deborah Number

Maxwell introduced the idea of viscous flow being the manifestation of the decay of elastically stored energy. If we follow this concept through we will see how a dimensionless group, the Deborah number, D_e , arises naturally. Let us consider a piece of matter in which all the molecules or particles (either small or large, it makes no difference) have had time to diffuse to some low energy state. Now, if we *instantaneously* strain (deform) the material, we will store energy because the *structure* is perturbed and the molecules are in a higher-energy state. As we hold the matter in this new shape, we find it becomes easier as the molecules diffuse until an equivalent low-energy state to the initial one has been achieved although the original shape has been lost, *i.e.* viscous flow has occurred. We can define the characteristic time for this process to occur as the *stress relaxation time*, τ , of the material. Now the Deborah number is³:

$$D_e = \frac{\tau}{t} \quad (1.11)$$

The relaxation of the stress resulting from a step strain can be observed experimentally and we see that it is the result of diffusive motion of the microstructural elements. Although we can have a mechanistic picture, what does this mean in terms of our measurements? We have the very striking result that our material classification must depend on the time t , *i.e.* the experimental or *observation* time. Hence, we can usefully classify material behaviour into *three* categories:

$$\begin{array}{lll} D_e \gg 1 & D_e \sim O(1) & D_e \ll 1 \\ \text{solid-like} & \text{viscoelastic} & \text{liquid-like} \end{array}$$

The most frequently quoted example to illustrate this behaviour is the children's toy "Silly Putty" which is a poly(dimethyl siloxane) polymer. Pulled rapidly it shows brittle fracture like any solid and if pulled slowly it flows as a liquid. The relaxation time for this material is ~ 1 s. After $t = 5\tau$ the stress will have fallen to 0.7% of its initial value so the material will have effectively "forgotten" its original shape. That is one could describe it as having a "memory" of around 5 s (about that of a mackerel!). Many other materials in common use have relaxation times within an order of magnitude or so of 1 s. Thickened detergents, personal care products and latex paints provide examples. It is of course no coincidence and this timescale is frequently deliberately chosen by formulation adjustments. The reason is that it is in the middle of *our*, the human, timescale. Our nervous system responds over the timescale of ~ 1 ms to ~ 1 ks and so, if a material has relaxation time within that region, we will observe an "interesting" or useful texture. Reiner³ pointed out that our observation time could be quite long with some material, set concrete for example, and so ultimately our definition of solid-like can become one of practical rather than philosophic origin.

1.3.2 The Péclet Number

Although a mechanism for stress relaxation was described in Section 1.3.1, the Deborah number is purely based on experimental measurements, *i.e.* an observation of a bulk material behaviour. The Péclet number, P_e , though is determined by the diffusivity of the microstructural elements, and is the dimensionless group given by the timescale for diffusive motion relative to that for convective or flow. The diffusion coefficient, D , is given by the Stokes–Einstein equation:

$$D = \frac{k_B T}{6\pi\eta_0 a} \quad (1.12)$$

where k_B is the Boltzmann constant, η_0 is the viscosity of the liquid medium, and a is the radius of the diffusing moiety, whether a molecule or a particle. This has dimensions of $\text{m}^2 \text{s}^{-1}$. We can use eqn (1.12) to estimate the time taken for the diffusing moiety to move a characteristic distance. It makes sense to choose the radius as this distance and this gives us the Einstein–Smoluchowski equation:

$$t_a = \frac{a^2}{D} = \frac{6\pi\eta_0 a^3}{k_B T}$$

and so

$$t_a = \frac{6\pi\eta_0 a^3}{k_B T} \quad (1.13)$$

Now the characteristic time for shear flow is the reciprocal of the shear rate. This is the time taken for a cubic element of material to be transformed to a

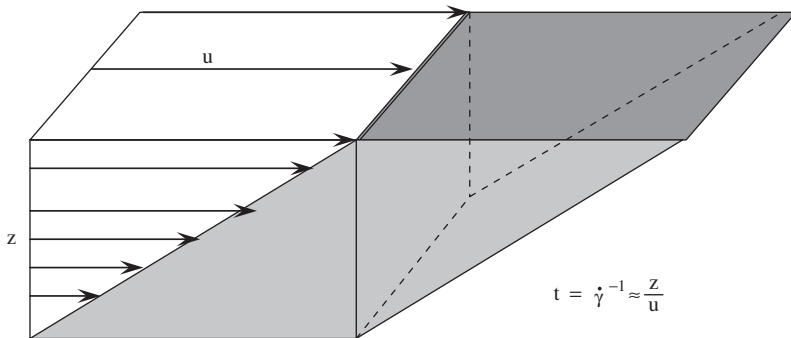


Figure 1.6 The time taken for unit shear strain is $\dot{\gamma}^{-1} = z/u$.

parallelogram with angles of 45° (*i.e.* the time for unit strain to be applied) as shown in Figure 1.6. The Péclet number can now be written:

$$P_e = \frac{6\pi\eta_0 a^3 \dot{\gamma}}{k_B T} \quad (1.14)$$

Now, an interesting problem arises when we consider solutions or colloidal sols where the diffusing component is much larger in size than the solute molecules. In dilute systems eqn (1.14) would give an adequate value of the Péclet number but not so when the system becomes concentrated, *i.e.* the system itself becomes a condensed phase. The interactions between the diffusing components slow the motion and, as we shall see in detail in Chapter 3, increase the viscosity. The appropriate dimensionless group should use the system viscosity and not that of the medium and now becomes:

$$P_e = \frac{6\pi a^3 \sigma}{k_B T} \quad (1.15)$$

where the shear stress, $\sigma = \eta\dot{\gamma}$, has been used to make a clear distinction from eqn (1.14). Of course for a simple system, such as cyclohexane in decane for example, eqns (1.14) and (1.15) would give the same result as the intermolecular interactions between the species are similar, and the viscosity of a mixture of the two is similar to that of the two components.

However, we shall use eqn (1.15) throughout this work as the use of the stress indicates the importance of the interactions and gives a useful approximation to the change in diffusivity of the components of the material.

1.3.3 The Reduced Stress

The *reduced stress*, σ_r was introduced by Krieger⁴ from a dimensional analysis and has the form:

$$\sigma_r = \frac{a^3 \sigma}{k_B T} \quad (1.16)$$

The similarity to the Péclet number is obvious but we should also bear in mind the relationship to the Deborah number. This becomes clear when we consider

the fact that the mechanism of stress relaxation is due to the diffusion of the microstructural components. For slow deformation processes – the low Deborah number, low Péclet number, or low reduced-stress limit – the rate at which the structural elements can rearrange is great enough that the structure has little or no perturbation from that found in the quiescent state. Viscous deformation then occurs. Now, if the straining is rapid, relaxation cannot take place and energy is stored. If the deformation is continuous, the structure must yield and breaking or “melting” is then observed.

1.3.4 The Taylor Number

A common geometry used to make viscosity measurements over a range of shear rates is a Couette, that is a concentric cylinder, or cup and bob system. The gap between the two cylinders is usually small so that a constant shear rate can be assumed at all points in the gap. When the liquid is in laminar flow, any small element of the liquid moves along lines of constant velocity known as streamlines. The translational velocity of the element is the same as that of the streamline at its centre. There is, of course, a velocity difference across the element equal to the shear rate and this shearing action means that there is a rotational or vorticity component to the flow field that is numerically equal to the shear rate/2. The geometry is shown in Figure 1.7.

When the shear rate reaches a critical value secondary flows occur. In the concentric cylinder, a stable secondary flow is set up with a rotational axis perpendicular to both the shear gradient direction and the vorticity axis, *i.e.* a rotation occurs around a streamline. Thus, a series of rolling toroidal flow patterns occur in the annulus of the Couette. This, of course, enhances the energy dissipation and we see an increase in the stress over what we might expect. The critical value of the angular velocity of the moving cylinder, Ω_c , gives the Taylor number:

$$T_a = \Omega_c \left(\frac{R_o + R_i}{2} \right)^{\frac{1}{2}} \frac{\rho(R_o - R_i)^{\frac{3}{2}}}{2\eta} \quad (1.17)$$

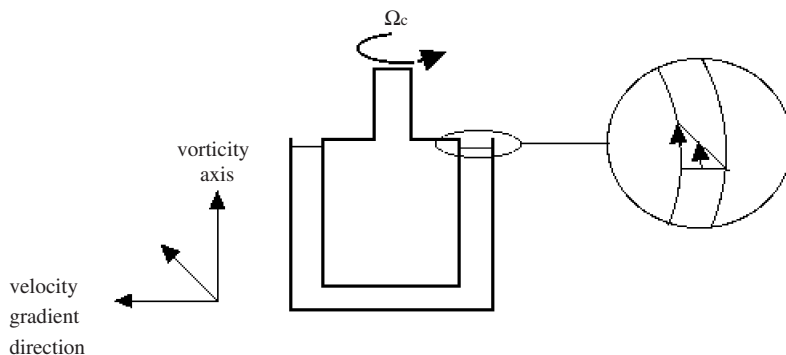


Figure 1.7 Couette geometry.

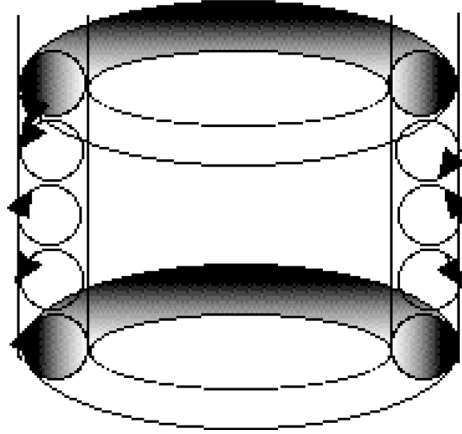


Figure 1.8 Taylor vortices.

R_o and R_i are the outer and inner cylinder radii of the Couette filled with a fluid of density ρ and viscosity η . Figure 1.8 illustrates the flow pattern of Taylor vortices that are formed when the Taylor number is exceeded.

1.3.5 The Reynolds Number

The Taylor vortices described above are an example of *stable* secondary flows. Now, at even high shear rates the secondary flows become chaotic and turbulent flow occurs. This happens when the inertial forces exceed the viscous forces in the liquid. The Reynolds number gives the value of this ratio and in general is written in terms of the linear liquid velocity, u , the dimension of the shear gradient direction (the gap in a Couette or the radius of a pipe), the liquid density and the viscosity. For a Couette we have:

$$R_e = \frac{\Omega_c(R_o + R_i)(R_o - R_i)\rho}{2\eta} \quad (1.19a)$$

where R is the radius of the moving cylinder. When we write this in terms of the shear rate:

$$R_e \approx \frac{\dot{\gamma}(R_o - R_i)^2\rho}{\eta} \quad (1.19b)$$

Another common geometry used for laboratory measurement of viscosity is a cone and plate with a small included angle, α . Values of α are typically in the range $1-5^\circ$. This geometry is used to give a constant shear rate because at any point on the plate the ratio of the tangential velocity ($r\Omega$) to the gap is constant. A suitable expression for the Reynolds number with the cone angle in degrees is:

$$R_e \approx \frac{\dot{\gamma}\rho}{\eta} \left(\frac{\pi R \alpha}{180} \right)^2 \quad (1.20)$$

In a tube of radius R , we use the volumetric flow rate, Q , to calculate a mean velocity along the tube and we have:

$$R_e \approx \frac{Q\rho}{\pi R\eta} \quad (1.21)$$

It is important that we know at what Reynolds number our instrumental configurations give turbulent flow and work below this figure or we will think that shear thickening is occurring! A figure of $R_e < 3000$ to 10 000 is usually satisfactory for cone and plates or capillary viscometers, but values as low as 300 may be the maximum for some cup and bob units.

1.4 MACROMOLECULAR AND COLLOIDAL SYSTEMS

The range of diffusional timescales for dilute systems that are shown in Figure 1.9 and were calculated using eqn (1.13) immediately shows us that macromolecules and colloidal particles have diffusional timescales that are within the range covered by our laboratory instrumentation. Moreover, as soon as we concentrate these systems, the motion of each unit is slowed by the interaction with its neighbours and timescales become much longer. Hence, quite slow motions may be in the region of large Deborah or Péclet numbers. It is for this reason that polymers and clay particles are often added to formulations as “thickeners” or “viscosity modifiers”. We will deal with these systems in considerable detail in subsequent chapters and we shall see that it is their chemical nature, and the chemical environment that we put them in, which gives such a rich pattern of behaviour.

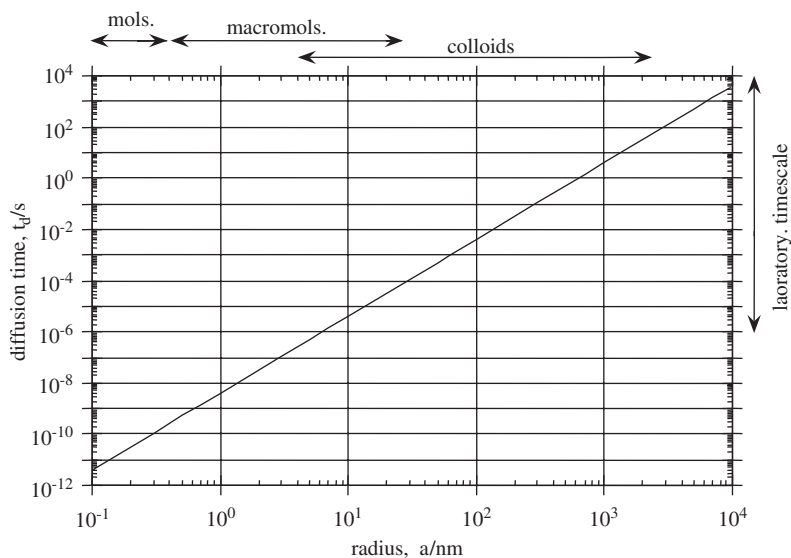


Figure 1.9 Diffusional timescale from eqn (1.13).

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