Non-Newtonian Fluids: An Introduction

R.P. Chhabra

Abstract The objective of this chapter is to introduce and to illustrate the frequent and wide occurrence of non-Newtonian fluid behaviour in a diverse range of applications, both in nature and in technology. Starting with the definition of a non-Newtonian fluid, different types of non-Newtonian characteristics are briefly described. Representative examples of materials (foams, suspensions, polymer solutions and melts), which, under appropriate circumstances, display shear-thinning, shear-thickening, visco-plastic, time-dependent and visco-elastic behaviour are presented. Each type of non-Newtonian fluid behaviour has been illustrated via experimental data on real materials. This is followed by a short discussion on how to engineer non-Newtonian flow characteristics of a product for its satisfactory end use by manipulating its microstructure by controlling physico-chemical aspects of the system. Finally, we touch upon the ultimate question about the role of non-Newtonian characteristics on the analysis and modeling of the processes of pragmatic engineering significance.

1 Introduction

Most low molecular weight substances such as organic and inorganic liquids, solutions of low molecular weight inorganic salts, molten metals and salts, and gases exhibit Newtonian flow characteristics, i.e., at constant temperature and pressure, in simple shear, the shear stress(σ) is proportional to the rate of shear ($\dot{\gamma}$) and the constant of proportionality is the familiar dynamic viscosity (η). Such fluids are classically known as the Newtonian fluids, albeit the notion of flow and of viscosity predates Newton [40]. For most liquids, the viscosity decreases with temperature and increases with pressure. For gases, it increases with both temperature and pres-

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sure [35]. Broadly, higher is the viscosity of a substance, more resistance it presents to flow (and hence more difficult to pump!). Table 1 provides typical values of viscosity for scores of common fluids [12]. As we go down in the table, the viscosity increases by several orders of magnitude, and thus one can argue that a solid can be treated as a fluid whose viscosity tends towards infinity, $\eta \to \infty$. Thus, the distinction between a fluid and a solid is not as sharp as we would like to think! Ever since the formulation of the equations of continuity (mass) and momentum (Cauchy, Navier-Stokes), the fluid dynamics of Newtonian fluids has come a long way during the past 300 or so years, albeit significant challenges especially in the field of turbulence and multi-phase flows still remain.

Table 1 Values of viscosity for common fluids at room temperature

Substance	η (Pa.s)
Air	10^{-5}
Water	10^{-3}
Ethyl alcohol	1.2×10^{-3}
Mercury	1.5×10^{-3}
Ethylene glycol	20×10^{-3}
Olive oil	0.1
100% Glycerol	1.5
Honey	10
Corn syrup	100
Bitumen	10^8
Molten glass	10^{12}

During the past 50-60 years, there has been a growing recognition of the fact that many substances of industrial significance, especially of multi-phase nature (foams, emulsions, dispersions and suspensions, slurries, for instance) and polymeric melts and solutions (both natural and man made) do not conform to the Newtonian postulate of the linear relationship between (σ) and $(\dot{\gamma})$ in simple shear, for instance. Accordingly, these fluids are variously known as non-Newtonian, non-linear, complex, or rheologically complex fluids. Table 2 gives a representative list of fluids which exhibit different kinds and with varying severity of non-Newtonian flow behavior [12]. Indeed so widespread is the non-Newtonian fluid behavior in nature and in technology that it would be no exaggeration to say that the Newtonian fluid behavior is an exception rather than the rule! This chapter endeavours to provide a brief introduction to the different kinds of non-Newtonian flow characteristics, their characterization and implications in engineering applications. The material presented herein is mainly drawn from our recent books [11, 12]. The assumptions of material isotropy and incompressibility are implicit throughout our discussion.

Table 2 Examples of substances exhibiting non-Newtonian Fluid Behaviour

●Adhesives (wall paper paste, carpet adhesive, for instance)	●Food stuffs (Fruit/vegetable purees and concentrates, sauces, salad dressings, mayonnaise, jams and marmalades, ice-cream, soups, cake mixes and cake toppings, egg white, bread mixes, snacks)
●Ales (beer, liqueurs, etc.)	●Greases and lubricating oils
●Animal waste slurries from cattle farms	●Mine tailings and mineral suspensions
●Biological fluids (blood, synovial fluid, saliva, etc.)	●Molten lava and magmas
●Bitumen	●Paints, polishes and varnishes
●Cement paste and slurries	●Paper pulp suspensions
●Chalk slurries	●Peat and lignite slurries
●Chocolates	●Polymer melts and solutions, reinforced plastics, rubber
●Coal slurries	●Printing colors and inks
●Cosmetics and personal care products (nail polish, lotions and creams, lipsticks, shampoos, shaving foams and creams, toothpaste, etc)	●Pharmaceutical products (creams, foams, suspensions, for instance)
●Dairy products and dairy waste streams (cheese, butter, yogurt, fresh cream, whey, for instance)	●Sewage sludge
●Drilling muds	●Wet beach sand
●Fire fighting foams	●Waxy crude oils

2 Classification of Fluid Behavior

2.1 Definition of a Newtonian Fluid

It is useful to begin with the definition of a Newtonian fluid. In simple shear (Fig. 1), the response of a Newtonian fluid is characterized by a linear relationship between the applied shear stress and the rate of shear, i.e.,

$$\sigma_{yx} = \frac{F}{A} = \eta \dot{\gamma}_{yx} \tag{1}$$

Fig. 2 shows experimental results for a corn syrup and for a cooking oil confirming their Newtonian fluid behavior; the flow curves pass through the origin and the viscosity values are $\eta = 11.6$ Pa.s for corn syrup and $\eta = 64$ mPa.s for the cooking oil. Fig. 1 and equation (1), of course, represent the simplest case wherein there is only one non-zero component of velocity, V_x, which is a function of y. For the general case of three dimensional flow (Fig. 3), clearly there are six shearing and three normal components of the stress tensor, **S**. It is customary to split the total stress into an isotropic part (pressure) and a deviatoric part as

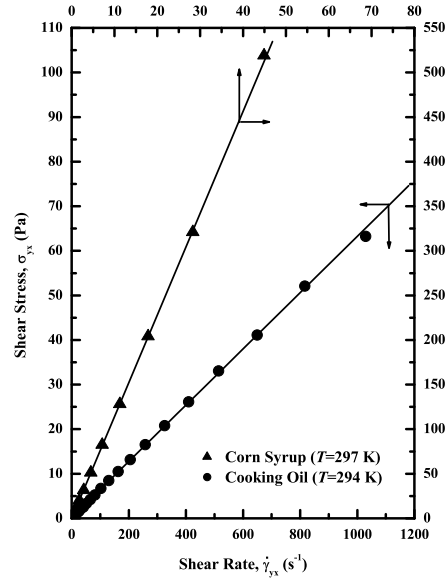$$\mathbf{S} = -p\mathbf{I} + \sigma \tag{2}$$

Fig. 1 Schematic represen-
tation of an unidirectional
shearing flow
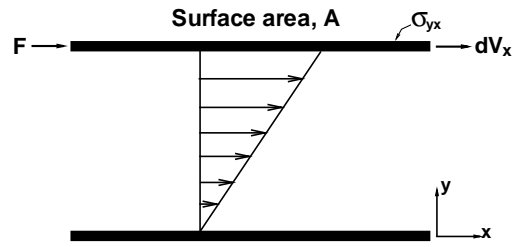
Where σ is traceless, i.e., $tr \cdot \sigma = 0$, and pressure is consistent with the conti-

Fig. 2 Typical shear stress-
shear rate data for two New-
tonian fluids

nuity equation. The tracefree requirement together with the physical requirement
of symmetry $\sigma = \sigma^T$ imply that there are only three independent shear components
(off-diagonal elements) and two normal stress differences (diagonal elements) of the
deviatoric stress. Thus, in Cartesian coordinates, these are $\sigma_{xy}(= \sigma_{yx})$, $\sigma_{xz}(= \sigma_{zx})$,
$\sigma_{yz}(= \sigma_{zy})$and the two normal stress differences defined as

$$\text{Primary normal stress difference, } N_1 = \sigma_{xx} - \sigma_{yy} \tag{3}$$

$$\text{Secondary normal stress difference, } N_2 = \sigma_{zz} - \sigma_{yy} \tag{4}$$

For Newtonian fluids, these components are related linearly to the rate of deforma-
tion tensor components via the scalar viscosity. For instance, the three stress com-

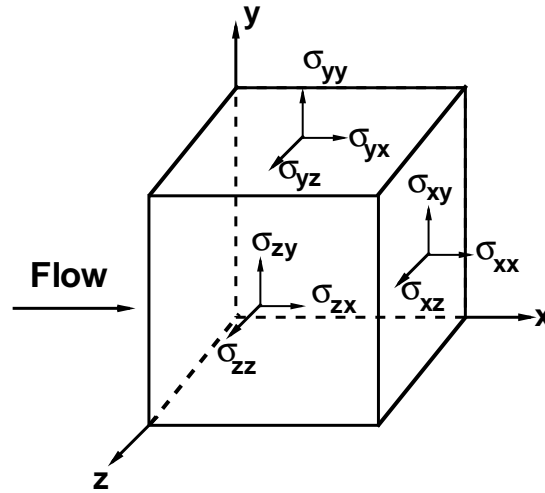ponents acting on the $x-$face (oriented normal to the $x-$axis) in Fig. 3 are written as follows

$$\sigma_{xx} = -2\eta \frac{\partial V_x}{\partial x} \tag{5}$$

$$\sigma_{xy} = -\eta \left(\frac{\partial V_x}{\partial y} + \frac{\partial V_y}{\partial x} \right) \tag{6}$$

$$\sigma_{xz} = -\eta \left(\frac{\partial V_x}{\partial z} + \frac{\partial V_z}{\partial x} \right) \tag{7}$$

Similar sets of equations can be set up for the stress components relevant to the $y-$

Fig. 3 Stress components in three dimensional flow

and $z-$ planes. For a Newtonian fluid, in simple shear, $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0$, because V_x only varies in the $y-$direction. Thus, the complete definition of a Newtonian fluid requires it to satisfy the complete Navier-Stokes equations rather than simply exhibiting a constant value of shear viscosity.

2.2 Non-Newtonian Fluid Behaviour

The simplest possible deviation from the Newtonian fluid behavior occurs when the simple shear data $\sigma - \dot{\gamma}$ does not pass through the origin and/ or does not result into a linear relationship between σ and $\dot{\gamma}$. Conversely, the apparent viscosity, defined as $\sigma/\dot{\gamma}$, is not constant and is a function of σ or $\dot{\gamma}$. Indeed, under appropriate circumstances, the apparent viscosity of certain materials is not only a function of flow conditions (geometry, rate of shear, etc.), but it also depends on the kinematic history of the fluid element under consideration. It is convenient, though arbitrary

(and probably unscientific too), to group such materials into the following three categories:

1. Systems for which the value of $\dot{\gamma}$ at a point within the fluid is determined only by the current value of σ at that point; these substances are variously known as *purely viscous, inelastic, time-independent* or *generalized Newtonian fluids (GNF)*;
2. Systems for which the relation between σ and $\dot{\gamma}$ shows further dependence on the duration of shearing and kinematic history; these are called *time-dependent fluids*, and finally,
3. Systems which exhibit a blend of viscous fluid behavior and of elastic solid-like behaviour. For instance, this class of materials shows partial elastic recovery, recoil, creep, etc. Accordingly, these are called *visco-elastic* or *elastico-viscous fluids*.

As noted earlier, the aforementioned classification scheme is quite arbitrary, though convenient, because most real materials often display a combination of two or even all these types of features under appropriate circumstances. For instance, it is not uncommon for a polymer melt to show time-independent (shear-thinning) and visco-elastic behavior simultaneously and for a china clay suspension to exhibit a combination of time-independent (shear-thinning or shear-thickening) and time-dependent (thixotropic) features at certain concentrations and /or at appropriate shear rates. Generally, it is, however, possible to identify the dominant non-Newtonian aspect and to use it as basis for the subsequent process calculations. Each type of non- Newtonian fluid behavior is now dealt with in more detail.

3 Time-Independent Fluid Behaviour

As noted above, in simple unidirectional shear, this sub-set of fluids is characterized by the fact that the current value of the rate of shear at a point in the fluid is determined only by the corresponding current value of the shear stress and vice versa. Conversely, one can say that such fluids have no memory of their past history. Thus, their steady shear behavior may be described by a relation of the form,

$$\dot{\gamma}_{yx} = f(\sigma_{yx}) \tag{8}$$

Or, its inverse form,

$$\sigma_{yx} = f^{-1}(\dot{\gamma}_{yx}) \tag{9}$$

Depending upon the form of equation (8) or (9), three possibilities exist:

1. Shear- thinning or pseudoplastic behavior
2. Visco-plastic behavior with or without shear-thinning behavior
3. Shear- thickening or dilatant behavior.

Fig. 4 shows qualitatively the flow curves (also called rheograms) on linear coordinates for the above- noted three categories of fluid behavior; the linear relation typical of Newtonian fluids is also included in Fig. 4.

Fig. 4 Qualitative flow curves for different types of non-Newtonian fluids
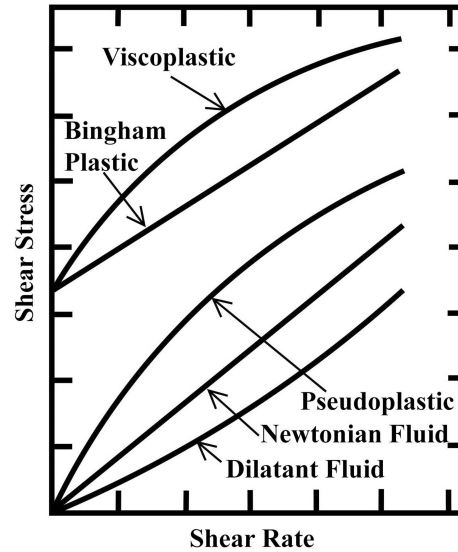

3.1 Shear-Thinning Fluids

This is perhaps the most widely encountered type of time-independent non-Newtonian fluid behavior in engineering practice. It is characterized by an apparent viscosity η (defined as $\sigma_{yx}/\dot{\gamma}_{yx}$) which gradually decreases with increasing shear rate. In polymeric systems (melts and solutions), at low shear rates, the apparent viscosity approaches a Newtonian plateau where the viscosity is independent of shear rate (zero shear viscosity, η_0).

$$\lim_{\dot{\gamma}_{yx} \to 0} \frac{\sigma_{yx}}{\dot{\gamma}_{yx}} = \eta_0 \qquad (10)$$

Furthermore, only polymer solutions also exhibit a similar plateau at very high shear rates (infinite shear viscosity, η_∞), i.e.,

$$\lim_{\dot{\gamma}_{yx} \to \infty} \frac{\sigma_{yx}}{\dot{\gamma}_{yx}} = \eta_\infty \qquad (11)$$

In most cases, the value of η_∞ is only slightly higher than the solvent viscosity η_s. Fig. 5 shows this behavior in a polymer solution embracing the full spectrum of values going from η_0 to η_∞. Obviously, the infinite-shear limit is not seen for polymer melts and blends, or foams or emulsions or suspensions. Thus, the apparent viscosity of a pseudoplastic substance decreases with the increasing shear rate, as shown in Fig. 6 for three polymer solutions where not only the values of η_0 are seen to be different in each case, but the rate of decrease of viscosity with shear rate is also seen to vary from one system to another as well as with the shear rate interval considered. Lastly, the value of shear rate marking the onset of shear-thinning is influenced by several factors such as the nature and concentration of polymer, the nature of solvent, etc for polymer solutions and particle size shape, concentration of solids in suspensions, for instance. Therefore, it is impossible to suggest valid generalizations, but many polymeric systems exhibit the zero-shear viscosity region below $\dot{\gamma} < 10^{-2}$ s^{-1}. Usually, the zero-shear viscosity region expands as the molecular weight of polymer falls, or its molecular weight distribution becomes narrower, or as the concentration of polymer in the solution is reduced.
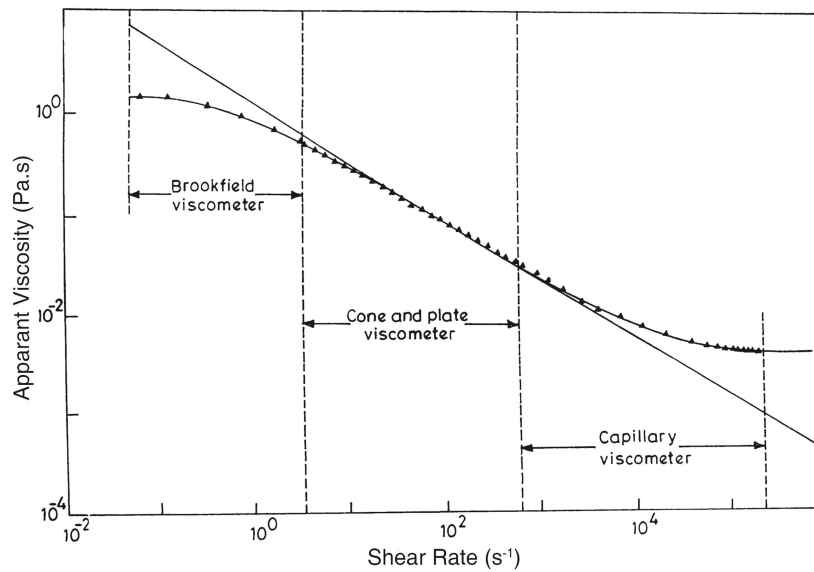

Fig. 5 Demonstration of zero shear and infinite shear viscosities for a polymer solution

The next question which immediately comes to mind is that how do we approximate this type of fluid behavior? Over the past 100 years or so, many mathematical equations of varying complexity and forms have been reported in the literature; some of these are straightforward attempts at curve fitting the experimental data $(\sigma - \dot{\gamma})$ while others have some theoretical basis (blended with empiricism) in statistical mechanics as an extension of the application of kinetic theory to the liquid state, etc. [9]. While extensive listing of viscosity models is available in several

books e.g., see, Ibarz and Barbosa-Canovas [23] and Govier and Aziz [19], a representative selection of widely used expressions is given here.
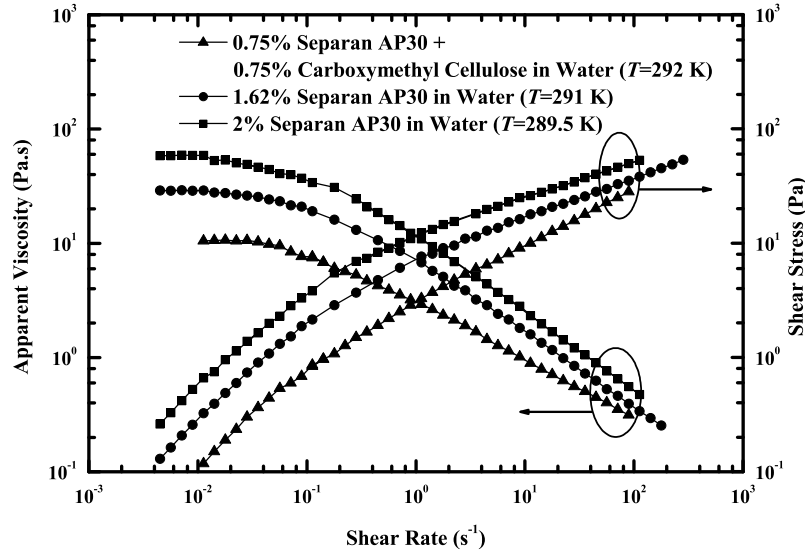
Fig. 6 Representative shear stress and apparent viscosity behaviour for three pseudoplastic polymer solutions

3.1.1 Power Law or Ostwald de Waele Equation

Often the relationship between shear stress (σ) − shear rate$(\dot{\gamma})$ plotted on log-log co-ordinates for a shear-thinning fluid can be approximated by a straight line over an interval of shear rate, i.e.,

$$\sigma = m(\dot{\gamma})^n \qquad (12)$$

or, in terms of the apparent viscosity,

$$\eta = m(\dot{\gamma})^{n-1} \qquad (13)$$

Obviously, $0 < n < 1$ will yield $(d\eta/d\dot{\gamma}) < 0$, i.e., shear-thinning behaviour fluids are characterized by a value of n (power-law index) smaller than unity. Many polymer melts and solutions exhibit the value of n in the range 0.3-0.7 depending upon the concentration and molecular weight of the polymer, etc. Even smaller values of power-law index $(n \sim 0.1 - 0.15)$ are encountered with fine particle suspensions like kaolin-in-water, bentonite-in-water, etc. Naturally, smaller is the value of n,

more shear-thinning is the material. The other constant, m, (consistency index) is a measure of the consistency of the substance.

Although, eq. (12) or (13) offers the simplest approximation of shear-thinning behaviour, it predicts neither the upper nor the lower Newtonian plateaus in the limits of $\dot{\gamma} \to 0$ or $\dot{\gamma} \to \infty$. Besides, the values of m and n are reasonably constant only over a narrow interval of shear rate range whence one needs to know *a priori* the likely range of shear rate to be encountered in an envisaged application.

3.1.2 The Cross Viscosity Equation

In order to rectify some of the weaknesses of the power-law, Cross [14] presented the following empirical form which has gained wide acceptance in the literature. In simple shear, it is written as

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + m(\dot{\gamma})^n} \tag{14}$$

It is readily seen that for $n < 1$, this model also predicts shear-thinning behavior. Furthermore, the Newtonian limit is recovered here when $m \to 0$. Though initially Cross[14] proposed that $n = 2/3$ was satisfactory for numerous substances, it is now thought that treating it as an adjustable parameter offers significant improvement in terms of the degree of fit [4]. Evidently, eq. (14) correctly predicts $\eta = \eta_0$ and $\eta = \eta_\infty$ in the limits of $\dot{\gamma} \to 0$ and $\dot{\gamma} \to \infty$ respectively.

3.1.3 The Ellis Fluid Model

While the two viscosity models presented thus far are examples of the form of eq. (9), the Ellis model is an illustration of the inverse form, eq. (8). In unidirectional simple shear, it is written as

$$\eta = \frac{\eta_0}{1 + (\frac{\sigma}{\sigma_{1/2}})^{\alpha - 1}} \tag{15}$$

In eq. (15), η_0 is the zero shear viscosity and the remaining two parameters $\sigma_{1/2}$ and $\alpha > 1$ are adjusted to obtain the best fit to a given set of data. Clearly, $\alpha > 1$ yields the decreasing values of shear viscosity with increasing shear rate. It is readily seen that the Newtonian limit is recovered by setting $\sigma_{1/2} \to \infty$. Furthermore, when $(\sigma/\sigma_{1/2}) \gg 1$, eq. (15) reduces to the power-law model, eq. (12) or (13).

3.2 Visco-plastic Fluid Behavior

This type of non-Newtonian fluid behavior is characterized by the existence of a threshold stress (called yield stress or apparent yield stress, σ_0) which must be exceeded for the fluid to deform (shear) or flow. Conversely, such a substance will behave like an elastic solid (or flow *en masse* like a rigid body) when the externally applied stress is less than the yield stress, σ_0. Of course, once the magnitude of the external yield stress exceeds the value of σ_0, the fluid may exhibit Newtonian behaviour (constant value of η) or shear-thinning characteristics, i.e., $\eta(\dot{\gamma})$. It therefore stands to reason that, in the absence of surface tension effects, such a material will not level out under gravity to form an absolutely flat free surface. Quantitatively this type of behavior can be hypothesized as follows: such a substance at rest consists of three-dimensional structures of sufficient rigidity to resist any external stress less than $|\sigma_0|$ and therefore offers an enormous resistance to flow, albeit it still might deform elastically. For stress levels above $|\sigma_0|$, however, the structure breaks down and the substance behaves like a viscous material. In some cases, the build-up and breakdown of structure has been found to be reversible, i.e., the substance may regain its (initial or somewhat lower) value of the yield stress.

A fluid with a linear flow curve for $|\sigma| > |\sigma_0|$ is called a Bingham plastic fluid, and is characterized by a constant value of viscosity η_B. Thus, in one-dimensional shear, the Bingham model is written as:

$$\sigma_{yx} = \sigma_0^B + \eta_B \dot{\gamma}_{yx} \qquad\qquad \left|\sigma_{yx}\right| > \left|\sigma_0^B\right| \qquad\qquad (16a)$$

$$\dot{\gamma}_{yx} = 0 \qquad\qquad \left|\sigma_{yx}\right| < \left|\sigma_0^B\right| \qquad\qquad (16b)$$

On the other hand, a visco-plastic material showing shear-thinning behavior at stress levels exceeding $|\sigma_0|$ is known as a yield-pseudoplastic fluid, and their behavior is frequently approximated by the so-called Herschel-Bulkley fluid model written for 1-D shear flow as follows:

$$\sigma_{yx} = \sigma_0^H + m(\dot{\gamma}_{yx})^n \qquad\qquad \left|\sigma_{yx}\right| > \left|\sigma_0^H\right| \qquad\qquad (17a)$$

$$\dot{\gamma}_{yx} = 0 \qquad\qquad \left|\sigma_{yx}\right| < \left|\sigma_0^H\right| \qquad\qquad (17b)$$

Another commonly used viscosity model for visco-plastic fluids is the so-called Casson model, which has its origins in modeling the flow of blood, but it has been found a good approximation for many other substances also [4, 7]. It is written as:

$$\sqrt{\left|\sigma_{yx}\right|} = \sqrt{\left|\sigma_0^C\right|} + \sqrt{\eta_C \left|\dot{\gamma}_{yx}\right|} \qquad\qquad \left|\sigma_{yx}\right| > \left|\sigma_0^C\right| \qquad\qquad (18a)$$

$$\dot{\gamma}_{yx} = 0 \qquad\qquad \left|\sigma_{yx}\right| < \left|\sigma_0^C\right| \qquad\qquad (18b)$$

While quantitative flow curves for a Bingham fluid and for a yield-pseudoplastic fluid are included in Fig. 4, experimental data for a synthetic polymer solution and a

meat extract are shown in Fig 7. The meat extract ($\sigma_0 = 17$ Pa) conforms to eq. (16) whereas the carbopol solution ($\sigma_0 = 68$ Pa) shows yield-pseudoplastic behavior.
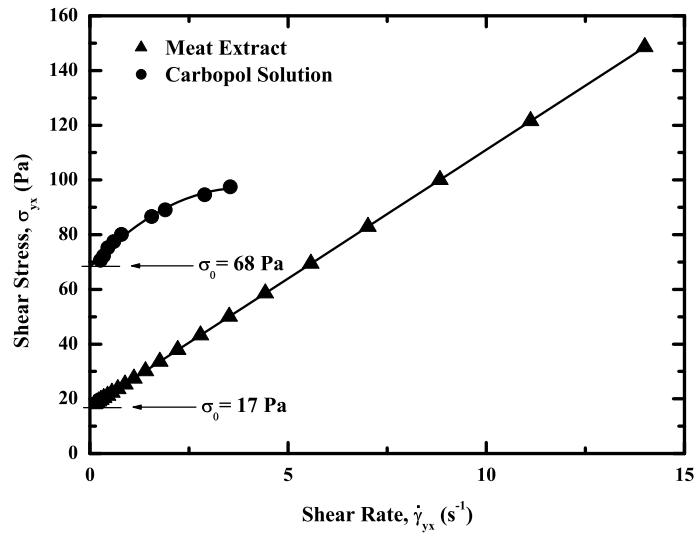
Fig. 7 Shear stress-shear rate data for a meat extract and for a carbopol solution displaying Bingham plastic and visco-plastic behaviours respectively

Typical examples of yield-stress fluids include blood, yoghurt, tomato puree, molten chocolate, tomato sauce, cosmetics, nail polishes, foams, suspensions, etc. Thorough reviews on the rheology and fluid mechanics of visco-plastic fluids are available in the literature [3, 7].

Finally, before leaving this sub-section, it is appropriate to mention here that it has long been a matter of debate and discussion in the literature whether a true yield stress exists or not, e.g., see the trail blazing paper of Barnes and Walters [5] and the review of Barnes [3] for different viewpoints on this matter. Many workers view the yield stress in terms of a transition from solid-like behavior to fluid-like behavior which manifests itself in terms of an abrupt decrease in viscosity (by several orders of magnitude in many substances) over an extremely narrow range of shear rate [43]. Evidently, the answer to the question whether a substance has a yield stress or not seems to be closely related to the choice of a time scale of observation. In spite of this fundamental difficulty, the notion of an apparent yield stress is of considerable value in the context of engineering applications, especially for product development and design in food, pharmaceutical and healthcare sectors [3, 36].
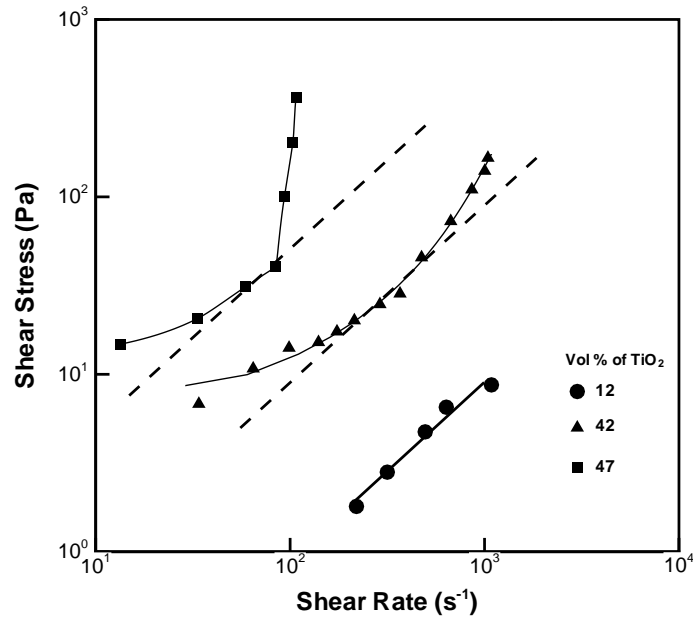
3.3 Shear-Thickening or Dilatant Behaviour

This class of fluids is similar to pseudoplastic systems in that they show no yield stress, but their apparent viscosity increases with the increasing shear rate and hence the name *shear-thickening*. Originally this type of behavior was observed in concentrated suspensions, and one can qualitatively explain it as follows: At rest, the voidage of the suspension is minimum and the liquid present in the sample is sufficient to fill the voids completely. At low shearing levels, the liquid lubricates the motion of each particle past another thereby minimizing solid-solid friction. Consequently, the resulting stresses are small. At high shear rates, however, the mixture expands (dilates) slightly (similar to that seen in sand dunes) so that the available liquid is no longer sufficient to fill the increased void space and to prevent direct solid-solid contacts (and friction). This leads to the development of much larger shear stresses than that seen in a pre-dilated sample at low shear rates. This mechanism causes the apparent viscosity $\eta (= \sigma/\dot{\gamma})$ to rise rapidly with the increasing rate of shear. Fig. 8 shows the representative data for TiO_2 suspensions of various concentrations[30]. For reference, the lines of slope unity (Newtonian behaviour) are included in this figure. Evidently, these suspensions exhibit both shear-thinning and shear-thickening behavior over different ranges of shear rate and/or at different concentrations.

Of the time-independent fluids, this sub-class has generated very little interest and hence very few reliable data are available. Indeed, until up to about early 1980s, this type of flow behavior was considered to be rare, but, however, with the recent growing interest in the handling and processing of systems with high solids loadings, it is no longer so, e.g., see the works of Barnes [1], Boersma et al.[8], Goddard and Bashir [17], for instance. Typical examples of fluids showing shear-thickening behavior include thick suspensions and pastes of kaolin, TiO_2, corn flour in water, etc.

The currently available limited information (mostly restricted to simple shear) suggests that it is possible to approximate $\sigma - \dot{\gamma}$ data for these systems also by the power law model, eq. (12), with the power-law index (n) taking on values greater than unity. Notwithstanding the paucity of rheological data on such systems, it is not yet possible to say with confidence whether these materials also display limiting viscosities in the limits of $\dot{\gamma} \rightarrow 0$ and $\dot{\gamma} \rightarrow \infty$.

4 Time Dependent Behaviour

Many substances, notably in food, pharmaceutical and personal care product manufacturing sectors display flow characteristics which cannot be described by a simple mathematical expression of the form of eq. (8) or (9). This is so because their apparent viscosities are not only functions of the applied shear stress (σ) or the shear rate ($\dot{\gamma}$), but also of the duration for which the fluid has been subjected to shearing as well as their previous kinematic history. For instance, the way the sample is loaded into

Fig. 8 Typical shear stress-shear rate data for TiO_2 suspensions displaying shear-thickening behaviour

a viscometer, by pouring or by injecting using a syringe, etc. influences the resulting values of shear stress σ or shear rate $\dot{\gamma}$. Similarly, for instance, when materials such as bentonite-in-water, coal-in-water suspensions, red mud suspensions (a waste from alumina industry), cement paste, waxy crude oil, hand lotions and creams, etc. are sheared at a constant value of $\dot{\gamma}$ following a long period of rest, their viscosities gradually decrease as the internal structures present are progressively broken down. As the number of such structural linkages capable of being broken down reduces, the rate of change of viscosity with time approaches zero. Conversely, as the structure breaks down, the rate at which linkages can re-build increases, so that eventually a state of dynamic equilibrium is reached when the rates of build-up and of break down are balanced. Similarly, there are a few systems reported in the literature in which the imposition of external shear promotes building up of internal structures and consequently their apparent viscosities increase with the duration of shearing.

Depending upon the response of a material to shear over a period of time, it is customary to sub-divide time-dependent fluid behavior into two types, namely, thixotropy and rheopexy (or negative thixotropy). These are discussed in some detail in the next section.
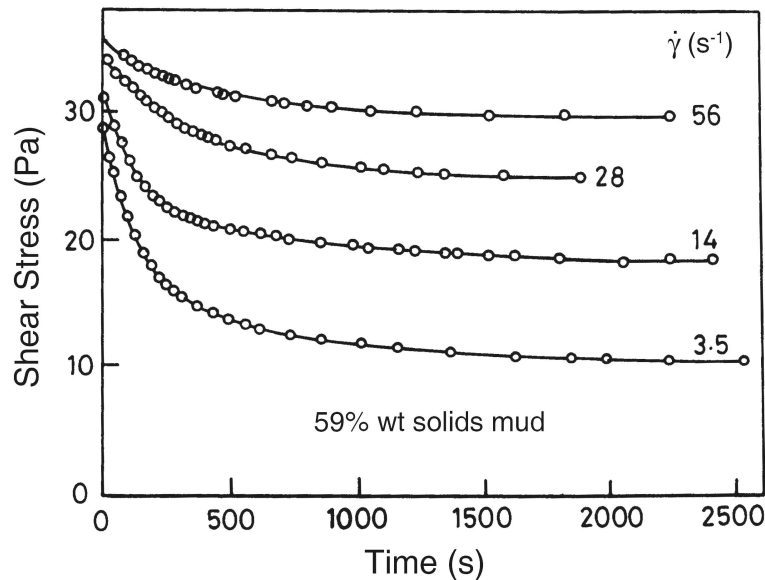
Fig. 9 Typical experimental data showing thixotropic behaviour in a red mud suspension [33]
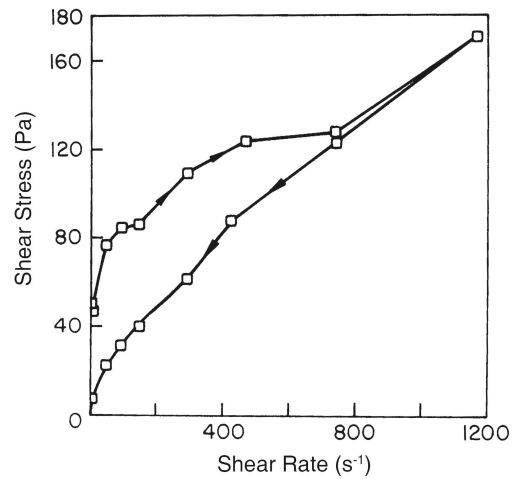
4.1 Thixotropic Behaviour

A material is classified as being thixotropic if, when it is sheared at a constant rate, its apparent viscosity $\eta = \sigma/\dot{\gamma}$ (or the value of σ because $\dot{\gamma}$ is constant) decreases with the duration of shearing, as shown in Fig. 9 for a red mud suspension containing 59% (by wt) solids [33]. As the value of $\dot{\gamma}$ is gradually increased, the time needed to reach the equilibrium value of σ is seen to drop dramatically. For instance, at $\dot{\gamma} = 3.5$ s^{-1}, it is of the order of ~ 1500 s which drops to the value of ~ 500 s at $\dot{\gamma} = 56$ s^{-1}. Conversely, if the flow curve of such a fluid is measured in a single experiment in which the value of $\dot{\gamma}$ is steadily increased at a constant rate from zero to some maximum value and then decreased at the same rate, a hysteresis loop of the form shown schematically in Fig. 10 is obtained. Naturally, the height, shape and the area enclosed by the loop depend on the experimental conditions like the rate of increase/decrease of shear rate, the maximum value of shear rate, and the past kinematic history of the sample. It stands to reason that, the larger the enclosed area, more severe is the time-dependent behavior of the material under discussion. Evidently, the enclosed area would be zero for a purely viscous fluid, i.e., no hysteresis effect is expected for time-independent fluids. Data for a cement paste [38] shown in Fig. 11 confirms its thixotropic behavior. Furthermore, in some cases, the breakdown of structure may be reversible, i.e., upon removal of the external shear and following a long period of rest, the fluid may regain (rebuilding of structure) the initial value of viscosity. The data for a lotion shown in Fig. 12 illustrates this aspect of thixotropy. Here, the apparent viscosity is seen to drop from ~ 80 Pa.s

to $\sim$ 10 Pa.s in about $5 - 10$ s when sheared at $\dot{\gamma} = 100$ s^{-1} and upon removal of the shear, it builds up to almost its initial value in about $50 - 60$ s. Barnes [2] has written a thorough review of thixotropic behavior encountered in scores of systems of industrial significance.

Fig. 10 Qualitative shear stress-shear rate behaviour for thixotropic and rheopectic materials
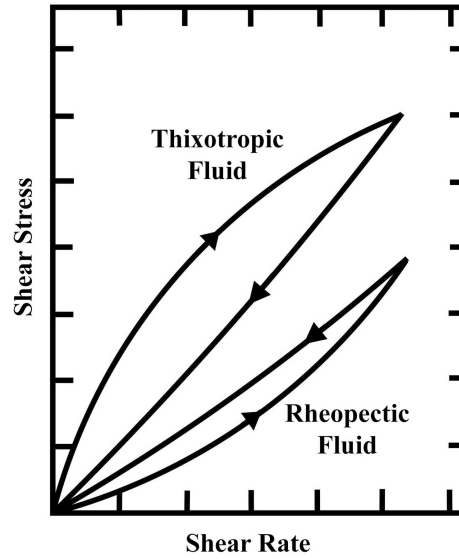
Fig. 11 Thixotropy in a cement paste

4.2 Rheopectic Behaviour

The relatively few fluids which show the negative thixotropy, i.e., their apparent viscosity (or the corresponding shear stress) increases with time of shearing are also known as rheopectic fluids. In this case, the hysteresis loop is obviously inverted (Fig. 10). As opposed to thixotropic fluids, external shear fosters the build up of structure in this case. It is not uncommon for the same fluid to display both thixotropy as well as rheopexy under appropriate combinations of concentration and shear rate. Fig. 13 shows the gradual onset of rheopexy for a saturated polyester at 60^0C [37]. Note that it exhibits time-independent behaviour up to about $\dot{\gamma} \approx 1377$ s^{-1} and the first signature of rheopexy appears only at about $\dot{\gamma} \sim 2755$ s^{-1} which intensifies further with the increasing value of the externally applied shear. Other examples where rheopexy has been observed include suspensions of Ammonium oleate, of Vanadium pentoxide at moderate shear rates, coal-water slurries and protein solutions.
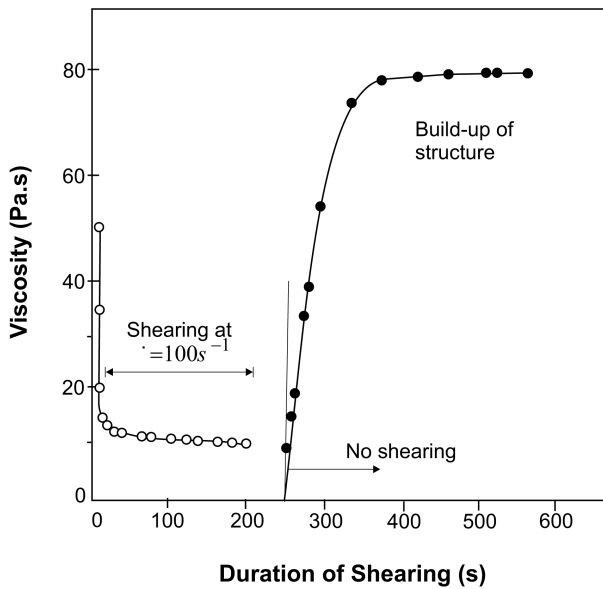

Fig. 12 Breakdown and buildup of structure in a proprietary body lotion

Owing to the frequent occurrence of thixotropic behavior in a range of industrial settings, much research effort has been devoted to the development of mathematical frameworks to model this type of rheological behaviour [15, 16, 32]. Broadly speaking, three distinct approaches can be discerned, namely, continuum, microstructural and structural kinetics. Within the framework of the continuum approach, existing viscosity models (such as Bingham plastic, eq. (16), Herschel-Bulkley, eq. (17), or the Reiner-Rivlin, etc.) are amended by postulating the viscosity, yield stress
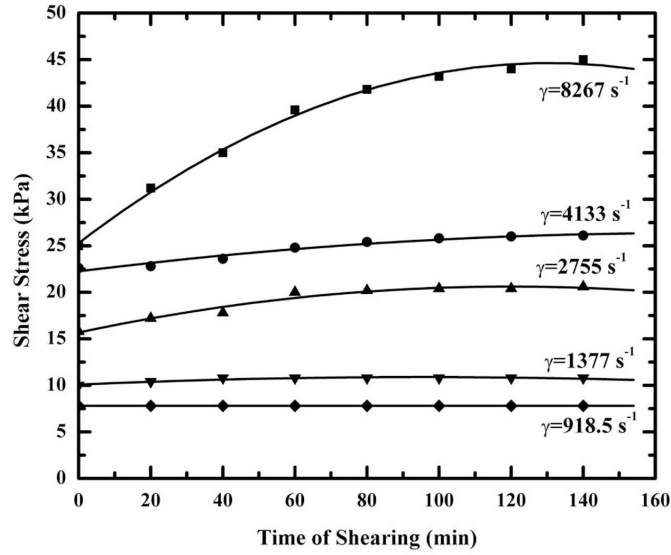
Fig. 13 Rheopectic behaviour in a saturated polyester [37]

to be functions of time. This, in turn, leads to the power-law consistency and flow behavior indices to be functions of time. Obviously, the details of micro-structure and changes thereof are completely disregarded in this approach; consequently it is not at all possible to connect the model parameters to the underlying physical processes responsible for the structural changes in the material under shear and for the subsequent buildup of structure upon the removal of shear. On the other hand, the modeling approach based on the consideration of micro-structure requires a detailed knowledge of inter-particle forces which unfortunately are seldom available for systems of practical significance thereby severely hampering the advancements in this direction. Finally, the thixotropy models based on the structural kinetic arguments hinge on the validity of a single scalar parameter, ξ, which is some how a measure of the state of the structure in a system. Obviously, it ranges from being zero (completely broken down structure or structure-less!) to being unity (complete buildup of structure). This approach thus comprises two equations: $\sigma - \dot{\gamma}$ relationship for a fixed value of ξ and $\xi - t$ variation, akin to the rate equation for a reversible chemical reaction. This approach is exemplified by the following form of equation due to Houska [22] which has been fairly successful in approximating thixotropic behavior of scores of systems:

$$\sigma_{yx} = (\sigma_0 + \sigma_{01}) + (m_0 + \xi m_1)\dot{\gamma}^n \tag{19a}$$

$$\dot{\xi} = a(1-\xi) - b\xi\dot{\gamma}^{\varepsilon} \tag{19b}$$

where σ_0 and m_0 are the so-called permanent values of the yield stress and consistency coefficient respectively; σ_{01} and m_1 are the corresponding time-dependent contributions which are assumed to be linearly dependent on the current value of ξ. Thus eq. (19a) is valid for a fixed value of the structure parameter ξ. Eq. (19b) is the kinetic relation which governs the $\xi - t$ relationship. The first term, namely $a(1 - \xi)$, gives the rate of structure buildup (assumed to occur under rest state, i.e., $\dot{\gamma} = 0$) whereas the second term on the right hand side of eq. (19b) gives the rate of breakdown which is a function of both ξ and $\dot{\gamma}$. Altogether, this model contains 8 parameters, three (a, b, ε) are kinetic constants and the remaining 5 are material parameters. Clearly, their evaluation warrants experimental protocols which are far more complex than that needed to characterize the behavior of time-independent fluids even in one-dimensional shear. Some guidelines in this regard are available in the literature [10, 15, 16].

5 Visco-elastic behavior

For an ideal elastic solid, stress in a sheared state is directly proportional to strain. For tension, the familiar Hookes law is applicable, and the constant of proportionality is the usual Young's modulus, G, i.e.,

$$\sigma_{yx} = -G\frac{dx}{dy} = G(\gamma_{yx}) \tag{20}$$

When an ideal elastic solid is deformed elastically, it regains its original form on removal of the stress. However, if the applied stress exceeds the characteristic yield stress of the material, complete recovery will not occur and *creep* will take place-i.e., the solid will have flowed! Table 3 presents typical values of the Young's modulus G for a range of materials including metals, plastics, polymer and colloidal solutions, foodstuffs, etc. and these values provide a basis to label some of the substances as *soft solids*.

At the other extreme is the Newtonian fluid for which the shearing stress is proportional to the rate of shear, eq. (1). Many materials of engineering importance show both elastic and viscous effects under appropriate circumstances. In the absence of thixotropy and rheopexy effects, the material is said to be visco-elastic. Obviously, perfectly viscous flow and perfectly elastic deformation denote the two limiting cases of visco-elastic behavior. In some materials, only these limiting conditions are observed in practice. Thus, for example, the viscosity of ice and the elasticity of water may generally go unnoticed!! Furthermore, the response of a material is not only governed by its structure, but also by the kinematic conditions it experiences. Therefore, the distinction between a *solid* and a *fluid*, and between an *elastic* and a *viscous* response is to some extent arbitrary and subjective whence is far from being clearcut. Conversely, it is not uncommon for the same material to

exhibit viscous fluid-like behavior in one situation and elastic solid-like behaviour in another situation.

Table 3 Representative (approximate) values of Young's modulus [29, 36]

Material	Value of G
Glass	70 GPa
Aluminium, Copper and alloys	100 GPa
Steel	200 GPa
High modulus oriented fibers	>300 GPa
Concrete	$10 - 20$ GPa
Stones	$40 - 60$ GPa
Wood	$1 - 10$ GPa
Ice	10 GPa
Engineering Plastics	$5 - 20$ GPa
Leather	$1 - 100$ MPa
Rubber	$0.1 - 5$ MPa
Polymer and colloidal solutions	$1 - 100$ Pa
Dry spaghetti	3 GPa
Carrots	$20 - 40$ MPa
Pears	$10 - 30$ MPa
Potatoes	$6 - 14$ MPa
Peach	$2 - 20$ MPa
Raw apples	$6 - 14$ MPa
Gelatin Gel	0.2 MPa
Banana	$0.8 - 3$ MPa

Many materials of pragmatic significance (particularly polymeric melts and so-lutions, soap solutions, gels, synovial fluid, emulsions, foams, etc.,) exhibit visco-elastic behavior. Thus, for instance, such materials have some ability to store and recover shear energy. One consequence of this type of fluid behavior is that shearing motion gives rise to stresses (the so-called normal stresses) in the direction normal to that of shear. The resulting normal stresses or normal stress differences N_1 and N_2, defined by eq. (3) and (4), are also proportional to shear rate in simple shear. Fig. 14 and Fig. 15 show representative data on the first and second normal stress differences for polystyrene-in-toluene solutions at 298K. Sometimes, it is custom-ary to introduce the first (primary) and second (secondary) normal stress difference coefficients ψ_1 and ψ_2 defined as follows:

$$\psi_1 = \frac{N_1}{(\dot{\gamma})^2} \tag{21a}$$

$$\psi_2 = \frac{N_2}{(\dot{\gamma})^2} \tag{21b}$$

Though the actual rates of variation of N_1 and N_2 with shear rate vary from one system to another, some general observations can be made here. Generally, the rate of decrease of ψ_1 with $\dot{\gamma}$ is greater than that of the apparent viscosity. At very low
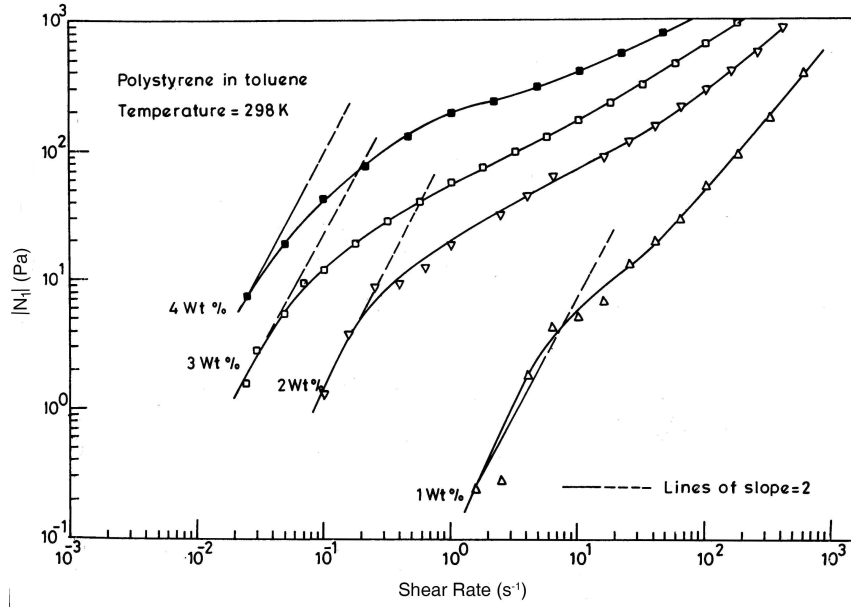
Fig. 14 Typical first normal stress difference data for Polystyrene in toluene solutions [26]
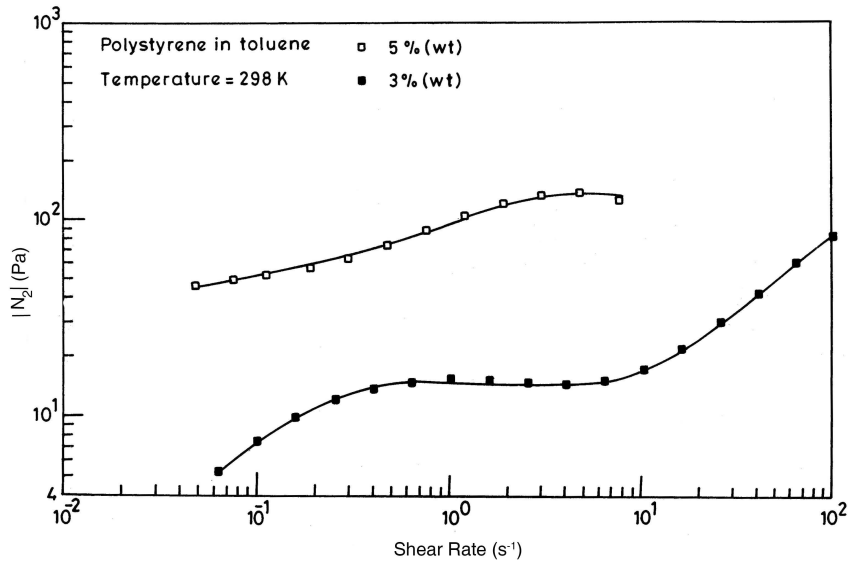

Fig. 15 Typical second normal stress difference data for polystyrene in toluene solutions [26]

shear rates, N_1 is expected to vary as $\dot{\gamma}^2$, i.e., ψ_1 will approach a constant value in this limit, as is borne out by some of the data shown in Fig. 14. The ratio (N_1/σ) is often taken to be a measure of the severity of visco-elastic behavior, specifically $(N_1/2\sigma)$ is called the recoverable shear (its values > 0.5 are not uncommon for polymeric systems which are highly visco-elastic). Generally, experimental determination of N_1 is more difficult than that of shear stress, σ. On the other hand, the measurements of the second normal stress difference are even more difficult than that of the first normal stress difference. In most cases, N_2 is typically 10% of N_1 in its magnitude and it is negative. Untill mid 1970's, N_2 was assumed to be zero, but it is no longer known to be correct.

Thus, in simple shear, a visco-elastic material is characterized in terms of $N_1(\dot{\gamma})$, $N_2(\dot{\gamma})$ and $\sigma(\dot{\gamma})$; furthermore, the normal stress differences are as such used to classify a fluid as inelastic $(N_1 \ll \sigma)$ or as visco-elastic $(N_1 \gg \sigma)$.

So far the discussion has been restricted to the simple unidirectional shearing flow, now we turn our attention to the two other model flow cofigurations, namely, oscillatory shear flow and elongational flow. While the first one offers a convenient method to characterize linear visco-elastic behaviour, the latter denotes idealization of several industrially important flows.

6 Oscillatory shear motion

Another common form of motion used to characterize visco-elastic fluids is the so-called oscillatory shearing motion. It is useful to consider here the response of a Newtonian fluid and of a Hookean solid to a shear strain which varies sinusoidally with time as:

$$\gamma = \gamma_m \sin\omega t \tag{22}$$

where γ_m is the amplitude and ω is the frequency of applied strain. For an elastic Hookean solid, the stress is related linearly to strain, i.e.,

$$\sigma = G\gamma = G\gamma_m \sin\omega t \tag{23}$$

Thus, there is no phase shift between the shear stress and shear strain in this case. On the other hand, for a Newtonian fluid, the shear stress is related to the rate of shear, i.e.,

$$\dot{\gamma} = \frac{d\gamma}{dt} = \gamma_m \omega \cos\omega t = \gamma_m \omega \sin(\frac{\pi}{2} + \omega t) \tag{24}$$

and here

$$\sigma = \eta\dot{\gamma} = \eta\gamma_m \omega \sin(\frac{\pi}{2} + \omega t) = \sigma_m \sin(\frac{\pi}{2} + \omega t) \tag{25}$$

Obviously in this case, the resulting shear stress is out of phase by $(\pi/2)$ from the applied strain. Thus, the measurement of the phase angle δ which can vary between zero (purely elastic response) and $(\pi/2)$ (purely viscous response) provides a convenient means of quantifying the level of viscoelasticity of a substance. Needless

to add here that small values of δ represent predominantly elastic behavior whereas large values of δ correspond to viscous behaviour. For the linear visco-elastic region, one can define the complex viscosity η^* as follows:

$$\eta^* = \eta' + i\eta'' \tag{26}$$

where the real and imaginary parts, η' and η'', in turn, are related to the storage (G') and loss (G'') modulii as:

$$\eta'' = \frac{G'}{\omega} \text{ and } \eta' = \frac{G''}{\omega} \tag{27}$$

The storage and loss modulii G' and G'' are defined as:

$$G' = \frac{\sigma_m}{\gamma_m}\cos\delta \tag{28}$$

$$G'' = \frac{\sigma_m}{\gamma_m}\sin\delta \tag{29}$$

Many of the commercially available instruments are equipped for oscillating shear tests [28].

7 Elongational flow

This model flow is also known as extensional or stretching flow. In this type of flow, a fluid element is stretched in one or more directions, similar to that encountered in fiber spinning and film blowing. Other examples where this type of flow occurs include coalescence of bubbles, enhanced oil recovery using polymer flooding. There are three forms of elongational flows: uniaxial, biaxial and planar, as shown schematically in Fig. 16.
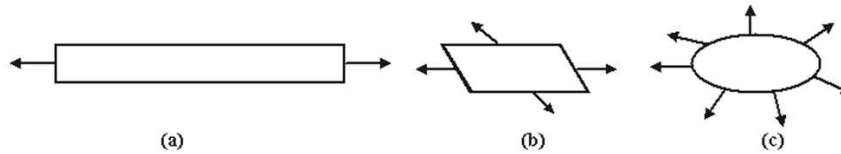
Fig. 16 Schematic representation of uniaxial (a), biaxial (b) and planar (c) extension

Fiber spinning is an example of uniaxial extension (but the rate of stretching varies along the length of the fiber). Tubular film blowing which entails extrusion of molten polymers through slit die and pulling the sheet forward and sideways is an illustration of biaxial stretching. Another example is the manufacture of plastic bottles which are made via extrusion or injection molding, followed by heating and

blowing it to the desired size using a high pressure air stream. Due to symmetry, the blowing step is an example of biaxial extension with equal stretching rates in the two directions.
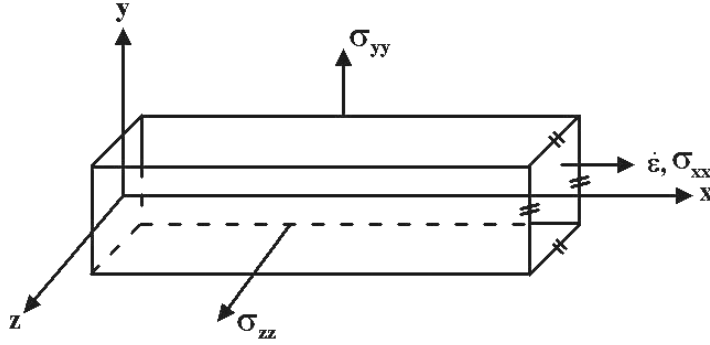

Fig. 17 Uniaxial extensional flow

Naturally, the mode of extension influences the way in which the fluid resists deformation and this resistance can be referred to loosely as being quantified in terms of an elongational viscosity which depends not only upon the rate of stretching but also on the type of extensional flow. For the sake of simplicity, we consider the uniaxial extension of a fluid element at a constant rate $\dot{\varepsilon}$ in the x-direction as shown in Fig. 17. For an incompressible fluid, the volume of the fluid element is conserved, i.e., if it is being stretched in the $x-$directions at the rate of $\dot{\varepsilon}$, it must shrink in the other directions at the rate of $\dot{\varepsilon}/2$ if the element is symmetrical in $y-$ and $z-$ directions. Under these conditions, the velocity vector $\mathbf{V}$ is given by:

$$\mathbf{V} = \dot{\varepsilon}\, x\hat{i} - (\dot{\varepsilon}/2)\, y\hat{j} - (\dot{\varepsilon}/2)\, z\hat{k} \tag{30}$$

And the rate of elongation $\dot{\varepsilon}$ in the $x-$ direction is given by:

$$\dot{\varepsilon} = \frac{\partial V_x}{\partial x} \tag{31}$$

The extensional viscosity η_E is, in turn, defined as:

$$\eta_E = \frac{\sigma_{xx} - \sigma_{yy}}{\dot{\varepsilon}} = \frac{\sigma_{xx} - \sigma_{zz}}{\dot{\varepsilon}} \tag{32}$$

Early experiments of Trouton [42] on uniaxial elongation by stretching a fiber or a filament of liquid and subsequent studies confirmed that at low elongation rates, the elongational viscosity η_E was three times the corresponding shear viscosity η, and the ratio of the two values is called the Trouton ratio, T_r, i.e.,

$$T_r = \frac{\eta_E}{\eta} \tag{33}$$

The value of three for the Trouton ratio for an incompressible Newtonian fluid is valid for all values of $\dot{\varepsilon}$ and $\dot{\gamma}$. By analogy, when this definition of the Trouton ratio, T_r, is extended to include non-Newtonian fluids, one runs into a conceptual difficulty. This is simply due to the fact that for a non-Newtonian fluid the shear viscosity is a function of the shear rate, $\eta(\dot{\gamma})$ and the elongational viscosity is a function of the rate of stretching, $\eta_E(\dot{\varepsilon})$. Therefore, one needs to adopt a convention for establishing the equivalence between $\dot{\gamma}$ and $\dot{\varepsilon}$. Jones et al. [24] proposed the equivalence as $\dot{\gamma} = \sqrt{3}\dot{\varepsilon}$ and hence the Trouton ratio for a non-Newtonian (incompressible) fluid can now be defined as:

$$T_r = \frac{\eta_E(\dot{\varepsilon})}{\eta(\dot{\varepsilon}\sqrt{3})} \tag{34}$$

Furthermore, Jones et al. [24] proposed that for inelastic isotropic fluids, $T_r = 3$ is applicable for all values of $\dot{\varepsilon}$ and $\dot{\gamma}$, and any departure from the value of 3 can unambiguously be ascribed to visco-elastic nature of the substance. For an inelastic shear-thinning fluid, this argument predicts tension-thinning in elongation also. On the other hand, the values of T_r as large as 1000 have been documented in the literature for visco-elastic shear-thinning fluids. In other words, such a fluid thins in shear but thickens in tension (strain hardening). Therefore, except in the limits of $\dot{\gamma} \to 0$ and $\dot{\varepsilon} \to 0$, there does not appear to be any simple way enabling the prediction of η_E from a knowledge of η (or vice versa), and the determination of η_E rests entirely on experiments. Fig. 18 shows representative results on extensional viscosity of a polymer solution at a range of values of $\dot{\varepsilon}$.

Fig. 18 Extensional behaviour of a PIB solution [41]
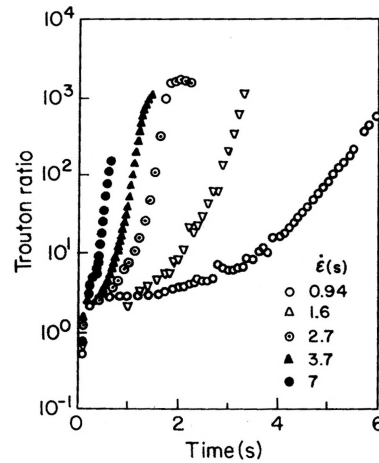
While the foregoing discussion shows how a visco-elastic substance displays a blend of fluid-like and solid-like response under appropriate conditions, the mathematical equations need to be quite complex in order to adequately describe the behavior of a real fluid. However, the early attempts are based on the use of mechanical analogues involving different combinations of springs (elastic) and dashpots

(viscous) in series, or in parallel, or a combination thereof, three common possibilities are shown in Fig. 19. One distinct feature of visco-elastic fluids is the so-called memory effects. For instance, viscous fluids have no memory whereas an ideal elastic solid has a perfect memory as long as the stress is within the linear limit. Thus, visco-elastic fluids are characterized by using a relaxation time, or a spectrum of relaxation times which is roughly a measure of the span of their memory. The relevant dimensionless parameter is the well known Deborah number, *De*:

$$De = \frac{\text{Relaxation time of fluid}(\lambda)}{\text{time scale of process}} \qquad (35)$$

For the purpose of illustration here, let us consider the flow of a polymer solution

Fig. 19 Schematic representation of the Maxwell model (a) the Kelvin-Voigt model (b) the Burgers model (c)
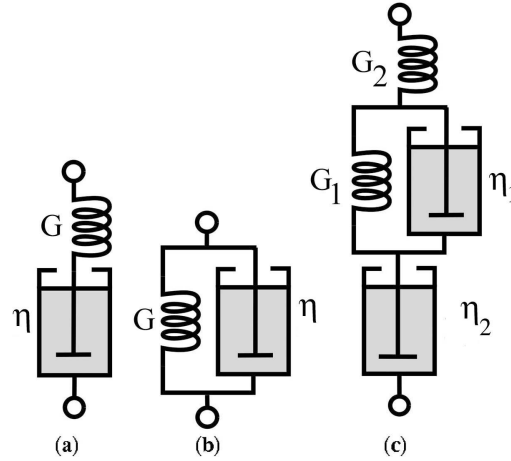
(with a relaxation time of 10ms) in a packed bed of spheres where a fluid element experiences acceleration and deceleration as it flows through the interstices of the bed. For a particle size of 25 mm in an industrial scale packed column and fluid velocity of 250 mm/s, the time scale of process is of the order of $25/250 \sim 0.1$ s which is much larger than the fluid relaxation time of 10 ms. Therefore, the fluid elements are able to adjust to the changing flow area and one would not expect to see the visco-elastic effects in this case. The corresponding value of the Deborah number is $De = 0.1$. On the other hand, in a laboratory size smaller column comprising 250 μm diameter spheres at the same fluid velocity, the time scale of the process is $250 \times 10^{-6}/250 \times 10^{-3} = 10^{-3}$ s which is much shorter than the fluid relaxation time of 10 ms whence under these conditions, a fluid element is not able to adjust to the changing flow area and hence, visco-elastic effects will manifest. The value of Deborah number in this case is $10 \times 10^{-3}/10^{-3} = 10$. This reinforces the point made earlier that the response of a substance is not governed solely by its structure, but also in conjunction with the type of flow. This section is concluded by noting

that $De \rightarrow 0$ represents purely viscous response and $De \rightarrow \infty$ denotes purely elastic response, and most interesting applications occur in between these two limits.

8 Origins of Non-Newtonian Behaviour

The foregoing discussion clearly establishes that not only in most cases non-Newtonian characteristics are observed in the so-called structured fluids, but there is a direct link between the type and extent of non-Newtonian fluid behavior and the influence of the externally applied stress on the state of the structure. Therefore, the measurement of non-Newtonian characteristics is frequently used to ascertain the state of structure in a fluid. Conversely, one can engineer the structure of a substance to impart the desired rheological properties to a product. However, before examining the role of structure, it is useful to review two key assumptions implicit in the concept of shear or elongational or complex viscosity, and the other material functions like η, σ_0, N_1, N_2, G, etc. Firstly, the validity of continuum hypothesis is implicitly assumed, i.e., micro structural details are deemed unimportant in evaluating the gross flow characteristics, albeit no real fluids are truly structureless continua. Hence, the use of viscosity as a space-and time-averaged physical property poses no problems for low molecular weight substances (molecular dimensions $\sim 1 - 10$ nm). Similarly, concentrated polymer solution or melts, colloidal systems, foams, worm-like micellar systems, etc. all possess "micro-structures" of a size approaching 1-2 μm which can be approximated as a continuum, except during their flow in very fine and/or twisted flow channels. This, in turn, allows the average properties to be defined and assigned values which are not influenced by the dimensions of flow passages. Therefore, as long as the size of micro-structures in much smaller than the characteristic linear scales of the apparatus, one can safely invoke the continuum hypothesis. The second issue concerns the assumption of spatial homogeneity (isotropy?) of a substance so that the space-averaging is meaningful. Finally, as noted here, if all fluids are "structured" to varying extents, what is so special about substances exhibiting non-Newtonian characteristics? The main distinguishing feature is that the structures present in the rheologically complex systems are not only transient in nature, but can easily be perturbed by the application of relatively low stresses. For instance, the structure of cyclohexane remains unperturbed by the application of stresses up to about 1 MPa. In contrast, the corresponding value is of the order of 100 Pa for a polymer of moderate molecular weight and about 200 mPa for a colloidal dispersion containing flow units of the order of 100 nm. It is this degree of ease with which the structure can be perturbed that gives rise to non-Newtonian flow characteristics in a system.

Fig. 20 and Fig. 21 show schematically the various types of micro-structures encountered in rheologically complex systems in a rest state (relevant to storage conditions) and how these get perturbed under the action of shear (in a flowing condition). Most systems contain irregularly shaped particles with size distribution (drops and bubbles in emulsions and foams respectively), or branched and/or

Fig. 20 Schematics of struc-
tures in non-Newtonian dis-
persions at rest and under
shear

Dispersion at rest   Dispersion in flow

Orientation

Stretching

Deformation

Disintegration
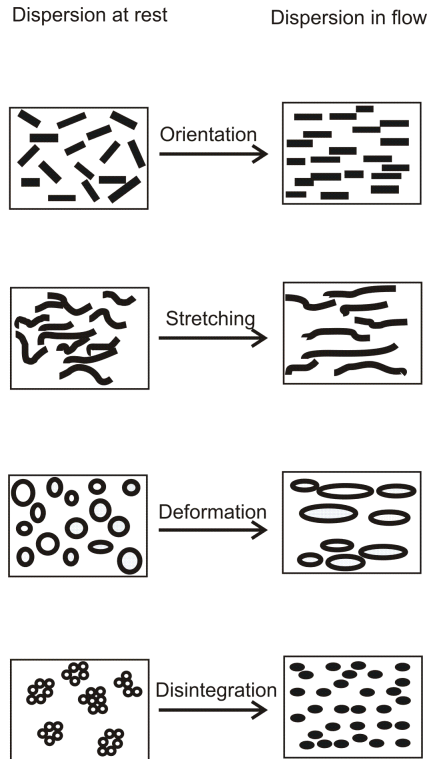
entangled molecules in case of polymeric systems, or loosely formed clusters of
particles in suspensions, etc. At rest, micro-structured units are oriented randomly
corresponding to their minimum energy state. At low levels of shearing, the system
resists any deformation by offering a very high resistance either by exhibiting a very
high value of viscosity or a yield stress. As the magnitude of external shear stress
is gradually increased, the structural units (also known as "flow units") respond by
aligning themselves with the direction of flow, or by deforming to orient along the
streamlines, or by way of disintegration of aggregates into small flow units or into
primary particles. Polymer molecules which are coiled and entangled at low shear
rates gradually become disentangled, and finally fully straighten out (Fig. 21). All
these changes in micro-structures facilitate flow, i.e., these lead to the the lowering
of their apparent viscosity with shear which leads to shear-thinning behavior.

Many other possibilities exist which contribute to micro-structural changes de-
pending upon the relative magnitudes of various forces at play. For instance, in
sub-micron (large surface area) particle suspensions, the van der Waals attraction
forces between particles can cause them to stick to each other. This is responsible
for coagulation in colloidal systems (particle size $\sim 1\mu$m). Similarly, repulsion be-
tween like charges on the surface of a particle produces a repulsive force which
prevents coagulation. The rheological behavior of aqueous kaolin suspensions thus

At rest

Under shear
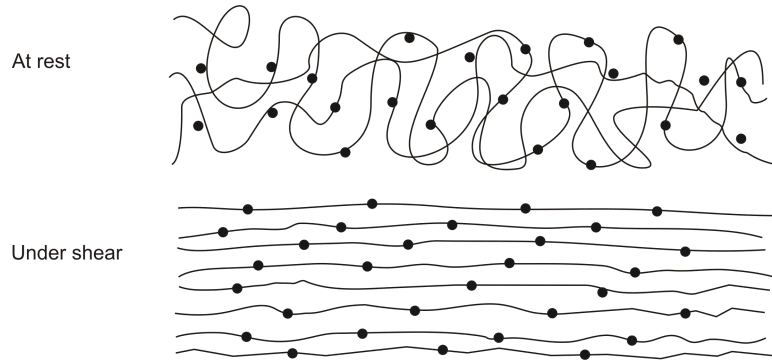
Fig. 21 Schematic representation of uncoiling of a macromolecule under the influence of shear

can be modified by adjusting the pH of a system or by adding a surfactant solution. The kaolin consists of plate-like particles and depending upon the type of surface charges, it can form different types of aggregates like edge-face or face-face type in nonflowing conditions (e.g., see Fig. 22). As expected, these two possibilities result in completely different rheological behavior, e.g., see Fig. 23.

The preceding short discussion is included here to give the reader a feel that it is possible to impart desirable non-Newtonian characteristics by tuning the physico-chemical factors. More detailed treatments of property-structure links for suspensions, surfactant and polymeric systems are available in the literature [12, 20, 21, 27]. Suffice it to say here that the ultimate goal is to be able to predict *a priori* the type of micro-structure needed for a product to have the desirable rheological characteristics for its satisfactory end use.
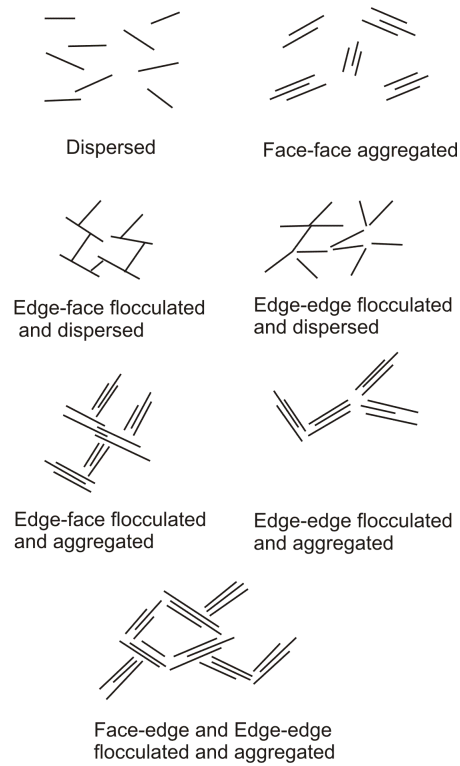
9 Implications in Engineering Applications

It is natural to ask the question that how does it all impact on the engineering applications involving flow, heat and mass transfer with non-Newtonian fluids? In order to answer this question, for the sake of simplicity, let us restrict our discussion to the flow part only. In principle, one can always set up the equation of continuity and Cauchy's momentum equations (written in their compact form for an incompressible fluid) as follows:

$$\nabla \cdot \mathbf{V} = 0 \tag{36}$$
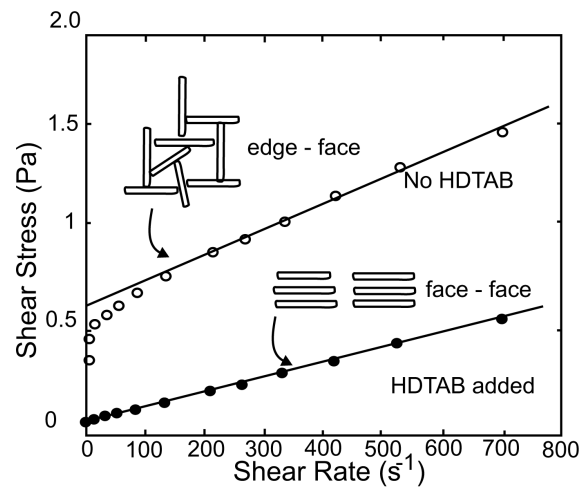
$$\rho \frac{D\mathbf{V}}{Dt} = -\nabla p + \rho g + \nabla \cdot \sigma \tag{37}$$

For Newtonian fluids, the deviatoric stress tensor σ is related to the rate of deformation tensor by equations similar to that given by equations 5 to 7. Significant research effort has been expended in seeking a similar expression for σ for non-

Fig. 22 Possible forms of
agglomerates in kaolin sus-
pensions

Dispersed   Face-face aggregated

Edge-face flocculated   Edge-edge flocculated
and dispersed   and dispersed

Edge-face flocculated   Edge-edge flocculated
and aggregated   and aggregated

Face-edge and Edge-edge
flocculated and aggregated

Fig. 23 Effect of the shape
of agglomerates on the steady
shear behaviour of Kaolin
suspensions [18]

Newtonian fluids which should be able not only to predict shear-dependent viscosity, yield stress, visco-elastic effects in shear and extensional flows, rheopexy and thixotropy but should also satisfy the requirements of frame indifference, material objectivity, etc. [6]. Given the diversity of the materials ranging from homogeneous polymer solutions to liquid crystalline polymers, worm-like micellar solution, suspensions, foams, for instance, this is indeed a tall order to expect that a single constitutive equation will perform satisfactorily under all circumstances for all types of materials. Notwithstanding the significant advances made in this field, the choice of an appropriate constitutive relation is (and will continue to be) guided by intuition and by experience is so far to identify the dominant characteristic of the material at hand in conjunction with the type of flow (shear dominated, strongly extensional, mixed, etc.). Critical appraisals of the current state of the art and useful guidelines for the selection of an appropriate expression for σ (constitutive equation) are available in the literature, e.g., see Graessley [20], Kroger [25], Morrison [31], Tanner [39] amongst others. Therefore, if one were able to develop an appropriate constitutive equation and/or to choose one from the existing selection, it is possible to set up the governing differential equations together with suitable boundary conditions, albeit there are situations in which the prescription of boundary conditions is also far from obvious, particularly in flows with a free surface, slip etc.

Furthermore, even when the non-linear inertial terms (corresponding to zero Reynolds number flow) are neglected altogether in the momentum equation, the resulting equations are still highly non-linear due to the constitutive equation (shear-dependent viscosity, other non-linear effects due to visco-elasticity, etc.) Therefore, except for the simple flows like the fully developed 1-dimensional flow in circular and planar ducts, one frequently resorts to numerical solutions which themselves pose enormous challenges in terms of being highly resource intensive and in terms of acute convergence difficulties thereby breaking down for large values of Deborah and Weissenberg numbers [34]. Finally, experimentalists also confront similar challenges both in terms of material characterization (rheometry) as well as in terms of the interpretation and representation of data using dimensionless groups, e.g. see Coussot [13] and Macosko [28] for rheometry.

In summary, the analysis of transport phenomena problems of engineering significance involving non-Newtonian fluid behavior is far more challenging than that entailing the simple Newtonian fluids. Indeed, it is such an easy task to produce an experimental effect using a non-Newtonian fluid in laboratory, which cannot be explained even qualitatively with the help of Newtonian fluid model. It is also appropriate to mention here that it is not always possible to justify the assumptions of incompressibility (think of foams, gas-liquid dispersions) and isotropy (think of fiber-reinforced plastics, liquid crystalline polymers, nano composites, etc.) implicit in the discussion presented in this introductory chapter.

10 Concluding Remarks

In this chapter, consideration has been given to the different types of non-Newtonian characteristics displayed by pseudo-homogeneous mixtures including foams, emulsions, suspensions and pastes, macro-molecular systems (polymer melts and solutions, protein solutions), surfactants (soap solutions), reinforced plastics and polymers in their molten state. The discussion here is restricted primarily to the response of such structured fluids in unidirectional steady shearing motion (with limited reference to oscillatory shear and elongational flows) which leads to the manifestation of shear-thinning, shear-thickening, visco-plastic, thixotropic, rheopectic, visco-elastic characteristics. Each of these is described in some detail supported by representative experimental data on real materials. Qualitative explanation for each type of behaviour is advanced to provide some insights into the nature of underlying physical processes. This, in turn, provides some ideas on how to manipulate the microstructure of a system to realize desirable non-Newtonian features. Conversely, the measurement and monitoring of viscosity, yield stress etc. is frequently used to control product quality in food and personal care product sectors, for instance. The chapter is concluded by emphasizing the influence of non-Newtonian flow properties in modeling engineering processes.

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