Constitutive Models of Complex Fluids

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Abstract This chapter provides an overview of the most common constitutive models used to describe the behaviour of non-Newtonian flows. For practical purposes, models are sorted into generalised Newtonian models, viscoelastic flow models and models for viscoplastic flows.

1 Introduction

Constitutive models, or constitutive equations, express in general a relationship between the force applied to a material and the consequent deformation; in the case of a fluid, which does not have a reference shape, the relationship is between the applied force and the rate of deformation. Since the applied force is always distributed over the fluid, usually constitutive models relate, more conveniently, the applied stress to the rate of deformation, or velocity gradient, which is expressed in tensorial form as

$$\mathbf{\Sigma} = f(\mathbf{\Gamma}) \tag{1}$$

where $\mathbf{\Sigma}$ is the symmetric stress tensor, with six independent components:

$$\mathbf{\Sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \tag{2}$$

with $\sigma_{xy} = \sigma_{yx}$, $\sigma_{xz} = \sigma_{zx}$ and $\sigma_{yz} = \sigma_{zy}$, and $\mathbf{\Gamma}$ is the deformation rate tensor, also symmetric:

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$$\mathbf{\Gamma} = \frac{1}{2}\begin{pmatrix} 2\frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} & \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \\ \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} & 2\frac{\partial v}{\partial y} & \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \\ \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} & \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} & 2\frac{\partial w}{\partial z} \end{pmatrix} = \frac{1}{2}\left(\nabla \boldsymbol{v} + \nabla \boldsymbol{v}^T\right) \tag{3}$$

where u, v and w are the velocity components in the three Cartesian directions x, y, z, and $\nabla \boldsymbol{v}$ is the velocity gradient tensor.

Such constitutive equations can be obtained directly from first principles using a statistical mechanics approach, such as in the case of the steady flow of a hard sphere gas (Zwanzig 1979), from empirical measurements, or, more frequently, from purely mathematical models that are able to reproduce certain behaviours observed either at macroscopic or at molecular level.

In order to formulate mathematical models that are physically significant, it is necessary to introduce at least two assumptions: (i) the system is local and causal, i.e. the stress at a material point depends only on the history of that material point and its neighbours, and cannot depend on future events; (ii) constitutive models should not depend on the translation, rotation or acceleration of the reference frame (e.g. Cartesian), i.e. the stress at a material point does not change if calculated before and after any transformation of the reference frame. Of course, these assumptions are necessary but not sufficient, which explains why mathematical models can only approximate the behaviour of a physical system within a limited range of the system parameters. The assumption of material frame indifference has important consequences on the mathematical formulation of constitutive models of viscoelastic flows, which will be discussed in Sect. 3.

The simplest constitutive equation describes the so-called Newtonian flows, where the stress tensor is a linear function of the deformation rate:

$$\mathbf{\Sigma} = -p\boldsymbol{I} + 2\eta\mathbf{\Gamma} \tag{4}$$

where p is pressure, $\boldsymbol{I}$ is the identity matrix, and η is the Newtonian viscosity. The Newtonian constitutive model given by Eq. (4) is commonly used to describe the flow of simple fluids, such as water and air. Constitutive models that cannot be reduced to Eq. (4) describe non-Newtonian flows. Since Eq. (4) expresses a relationship between flow variables, the attributes "Newtonian" and "non-Newtonian" always refer to a flowing fluid, therefore they are by no means attributes of the fluid itself. For example, fluids that usually exhibit Newtonian behaviour may become shear-thinning at high shear rates (Pipe et al. 2008).

Non-Newtonian constitutive models can be sorted into two main families: time-independent fluids, if the response of the material to an applied stress is instantaneous and fully reversible, and time-dependent, if the material response depends on its previous history. It is important to remark that, depending on the flow parameters, the behaviour of the same fluid can be described either by a time-independent or by a time-dependent model.

A comprehensive analysis of constitutive models can be found in a number of excellent reference books (Larson 1999; Bird et al. 1987; Joseph 1990; Phan-Thien 2002). In the following sections, the most common constitutive models to describe the flow of complex fluids are sorted into generalised Newtonian models, viscoelastic flow models and models for viscoplastic flows.

2 Constitutive Models for Generalised Newtonian Flows

In generalised Newtonian constitutive models, viscosity is a function of the second invariant (or quadratic invariant) of the strain rate tensor, defined as

$$\begin{aligned} I_2 &= \frac{1}{2}\left[(tr\mathbf{\Gamma})^2 - tr\,(\mathbf{\Gamma})^2\right] = \\ &= \frac{1}{4}\left[\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}\right)^2+\left(\frac{\partial v}{\partial z}+\frac{\partial w}{\partial y}\right)^2+\left(\frac{\partial w}{\partial x}+\frac{\partial u}{\partial z}\right)^2\right]+ \\ &\quad -\left(\frac{\partial u}{\partial x}\frac{\partial v}{\partial y}+\frac{\partial u}{\partial x}\frac{\partial w}{\partial z}+\frac{\partial v}{\partial y}\frac{\partial w}{\partial z}\right) \end{aligned} \tag{5}$$

Similar to Newtonian flows, in generalised Newtonian flows the stress depends only on the instantaneous flow and not on the flow history. In simple shear flow, Eq. (5) reduces to

$$I_2 = \frac{1}{4}\left(\frac{\partial u}{\partial y}\right)^2 = \frac{1}{4}\dot{\gamma}^2 \tag{6}$$

where $\dot{\gamma} = \partial u/\partial y$ is the shear rate.

The simplest type of generalised Newtonian flow behaviour occurs when the viscosity coefficient is a monomial function of the shear velocity gradient (power law, or Ostwald–De Waele model):

$$\eta = K\dot{\gamma}^{n-1} \tag{7}$$

where the consistency coefficient, K, and the power-law index, n, are empirical constants. The power-law index is indicative of the shear-thinning ($n < 1$) or shear-thickening ($n > 1$) behaviour of the fluid, whereas for $n = 1$ the Newtonian behaviour is retrieved. The consistency coefficient describes the fluid viscosity at low shear rates, and coincides with the Newtonian viscosity for $n = 1$. The shear-thinning, shear-thickening and Newtonian behaviours of the shear stress and of the viscosity as described by the power-law constitutive model are shown, respectively, in Fig. 1a, b.

In the limit $n \to 0$, the shear stress has a constant value, irrespective of the imposed shear rate. Although this picture may seem unphysical, stress plateaus can be observed experimentally over limited shear rate intervals, for example in the flow

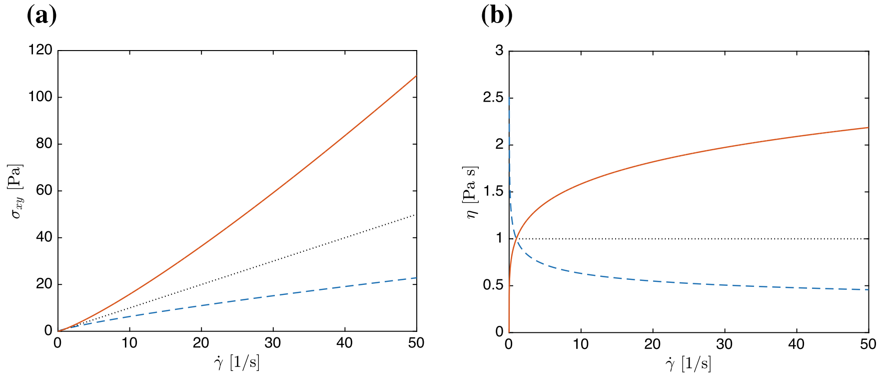

Fig. 1 Shear stress (**a**) and viscosity (**b**) obtained with the power-law model (Eq. 7) with $K = 1$ and: $n > 1$ (shear-thickening, solid line); $n = 1$ (Newtonian, dotted line); $n < 1$ (shear-thinning, dashed line)

of monodispersed polymer melts and solutions (Yang et al. 1998). For $n < 0$, the shear stress decreases monotonically upon increasing the shear rate, which means the flow is unstable.

Power-law fluids are time-independent, i.e. the shear stress does not depend on the previous deformation history. Physically, shear-thinning is usually explained by the breakdown of structure formed by interacting particles within the fluid, while shear-thickening is often due to flow-induced jamming (Frith et al. 1996).

The Ostwald–De Waele equation implies that viscosity will change indefinitely for any values of the shear rate. In other words, in the case of shear-thinning fluid ($n < 1$) viscosity tends to grow unlimited for $\dot{\gamma} \to 0$, and to vanish for $\dot{\gamma} \to \infty$; in these limits, the power-law model fails to describe the behaviour of real fluids accurately. To account for a more realistic behaviour, where viscosity varies between a minimum and a maximum value, respectively, at very low and very high shear rates, a number of constitutive equations have been proposed, such as the Cross model (Cross 1965):

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (C\dot{\gamma})^{1-n}} \tag{8}$$

and the Bird–Carreau–Yasuda model (Bird and Carreau 1968; Carreau 1972; Yasuda and Cohen 1981), which was initially developed to describe shear-thinning observed in many viscoelastic (i.e. time-dependent) flows:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{[1 + (C\dot{\gamma})^a]^{(1-n)/a}} \tag{9}$$

where η_0 and η_∞ are the viscosities at zero shear and infinite shear, respectively, a is a parameter with a default value of 2, and C is the Cross time constant. This parameter is the reciprocal of the strain rate at which the zero-strain rate component and the power-law component of the flow curve intersect.

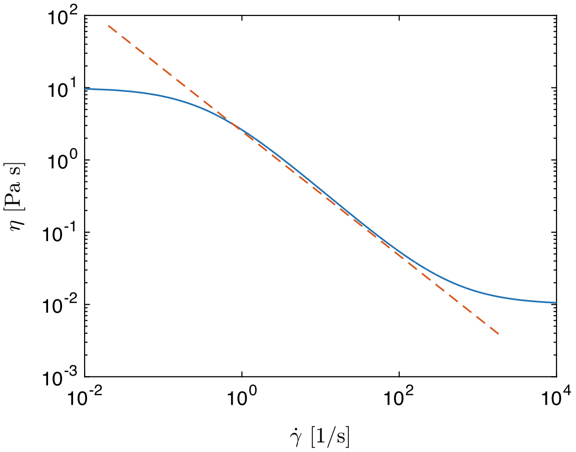

Fig. 2 Comparison between the power-law model (dashed line) with parameters $K = 2.5$, $n = 0.14$ and the Cross model (solid line) with parameters $C = 3$, $n = 0.05$; for $\dot\gamma \to 0$ and $\dot\gamma \to \infty$ the Cross model tends to the asymptotic values $\eta_0 = 10$ Pa s and $\eta_\infty = 0.01$ Pa s, respectively, whereas the power-law model continues to grow or decrease indefinitely

Figure 2 shows a comparison between the viscosities calculated with the power-law model (Eq. 7) and the Cross model (Eq. 8). Although the model parameters can be adjusted so that the two constitutive equations coincide within a certain range of shear rates, there is a significant deviation at low and at large shear rates.

Finally, the Ellis model is obtained by setting $\eta_\infty = 0$ in the Cross model:

$$\frac{\eta}{\eta_0} = \frac{1}{1 + \left(\frac{\sigma_{xy}}{\sigma_{1/2}}\right)^{n-1}} \tag{10}$$

where σ_{xy} is the applied shear stress, and $\sigma_{1/2}$ is the shear stress at which viscosity is exactly half of the zero-shear viscosity value, η_0.

3 Constitutive Models for Viscoelastic Flows

In viscoelastic fluids, such as polymer melts or solutions, a part of the deformation energy is stored as elastic energy, and released with a certain delay depending on the relaxation time of the fluid. The basic feature that essentially all viscoelastic fluids share is the occurrence of elastic stress effects: when the shear rate is sufficiently strong, the forces along the normals of a little cubical fluid element are different in different directions, unlike what happens for a Newtonian fluid where the pressure is isotropic. From the microscopic point of view, this behaviour is usually related to conformational rearrangements of the macromolecules which compose the fluid under the action of hydrodynamic forces. The entropic tendency of polymers that are stretched by the flow to recover their equilibrium chain conformation generates an elastic stress, the macroscopic manifestation of which is a difference in stress between the flow direction and the direction normal to it. Viscoelasticity manifests itself in a variety of phenomena, including creep (the time-dependent strain resulting from a constant applied stress), stress relaxation resulting from a steady deformation, the Weissenberg rod-climbing effect due to nonzero normal stress difference, and many others, as discussed in Chapters Introduction to Transport Phenomena in Complex Fluids and Transport Phenomena in Viscoelastic Fluids.

The non-isotropic principal components of the stress tensor allow one to characterise the elasticity of polymer solutions and melts through normal stress differences: the first normal stress difference, $N_1 = \sigma_{xx} - \sigma_{yy}$, and the secondary normal stress difference, $N_2 = \sigma_{zz} - \sigma_{yy}$. In most cases, the magnitude of N_2 is around 10% of N_1 or less. The ratio N_1/σ is often taken to be a measure of the severity of viscoelastic behaviour, and can be used to classify a fluid as inelastic ($N_1 \ll \sigma$) or as viscoelastic ($N_1 \gg \sigma$).

The dissipation of energy associated to the process of stretching and relaxation of macromolecules is described by introducing the concept of elongational (or extensional) viscosity, the ratio of the first normal stress difference to the rate of elongation of the fluid:

$$\eta_E = \frac{\sigma_{xx} - \sigma_{yy}}{\epsilon_{xx}} \tag{11}$$

where $\epsilon_{xx} = \mathbf{\Gamma}_{1,1}$ is the rate of deformation in the direction of stretching. For a Newtonian incompressible fluid, one can easily verify that the elongational viscosity is three times the shear viscosity (Trouton 1906). For a polymer solution the ratio η_E/η, also known as the Trouton ratio, can be of the order of 10^3–10^4.

If the relaxation time is small compared to the characteristic time of the flow ($\tau = L/v$, where L is a characteristic length scale and v a characteristic velocity), the material structure rearranges almost instantaneously in response to any imposed deformation, and consequently the stress decays abruptly once the material has been deformed; this response is characteristic of simple liquids which exhibit Newtonian

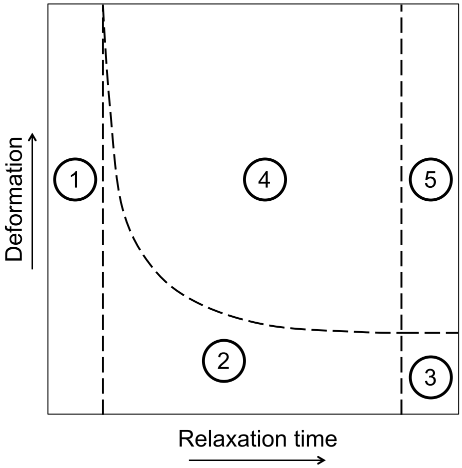

Fig. 3 Schematic of Newtonian, elastic, linear, and non-linear viscoelastic regimes as a function of deformation and relaxation time during deformation of polymeric materials (Phan-Thien 2002). (1) Newtonian regime; (2) linear viscoelasticity; (3) elastic regime; (4) non-linear viscoelasticity; (5) non-linear elasticity/viscoplastic regime

behaviour (Fig. 3). When the relaxation time increases, and becomes of the same order of the characteristic time of the flow, the material structure takes time to re-arrange, therefore it is necessary to apply a stress in order to keep the material deformed; as the material structure rearranges, the stress decays exponentially. This behaviour is typical of viscoelastic materials, and one can distinguish a linear viscoelastic behaviour in case of small deformations, and a non-linear viscoelastic behaviour in case of large deformations. When the relaxation time becomes very large compared to the characteristic time of the flow, the material structure takes such a long time to rearrange that in practice it never rearranges; thus, in order to keep the material deformed one must continuously apply a stress, which does not decay in time. If the stress is removed, the material returns to its initial shape (i.e. the shape of the material before the deformation). This behaviour is characteristic of elastic materials; again, one can distinguish a linear elastic regime in case of small deformations, and a non-linear elastic regime in case of large deformations; sometimes, large deformations cause a permanent change of the material structure, resulting into plasticity.

3.1 Linear Viscoelasticity

In linear viscoelasticity, the elastic component of the material behaves like an ideal Hookean spring, i.e. the elastic force is proportional to the spring extension through the spring constant. Linear viscoelasticity applies only to materials undergoing small deformations; non-linearities arise as soon as the deformation is large enough to alter significantly the conformation of the polymer chains or more in general the material microstructure. In the following sections, linear viscoelastic constitutive models are discussed with reference to single shear stress and shear deformation components, however, their extension to their tensorial equivalent is straightforward.

Lumped parameters models The earliest constitutive model to describe linear viscoelastic fluids, which combined elastic and viscous effects, was introduced by Maxwell (1867), and can be represented graphically by an instantaneous extension of a spring and a time-dependent reaction of a dash-pot in series, as illustrated in Fig. 4a. In this system, mechanical equilibrium is satisfied if the stress, σ_{xy}, is the same in the elastic and in the viscous element, while the total rate of deformation, $\dot{\gamma}_{xy}$, is the sum of the deformation rates in the two elements:

$$\dot{\gamma}_{xy} = \frac{d}{dt}\left(\frac{\sigma_{xy}}{G}\right) + \frac{\sigma_{xy}}{\eta} \tag{12}$$

where G is the elastic modulus, and η the fluid viscosity. This equation can be rearranged as

$$\lambda \frac{d\sigma_{xy}}{dt} + \sigma_{xy} = \eta \dot{\gamma}_{xy} \tag{13}$$

where $\lambda = \eta / G$ is the relaxation time.

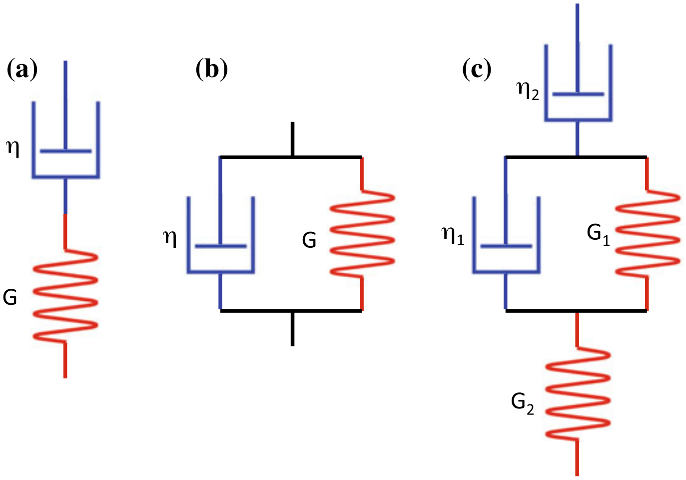

Fig. 4 Lumped parameter schematic of simple linear viscoelastic constitutive models: **a** Maxwell model; **b** Kelvin–Voigt model; **c** Burgers model

In a similar fashion to Maxwell's approach, one can derive a constitutive model where the elastic and the viscous element are connected in parallel (Voigt 1890), which is known as the Kelvin–Voigt model (Fig. 4b). In this case, the two components experience the same deformation, but their reacting forces have different magnitude:

$$\sigma_{xy} = G\gamma_{xy} + \eta\dot{\gamma}_{xy} \tag{14}$$

Linear viscoelastic models of increasing complexity can be built by combining together an arbitrary number of elastic and viscous elements. For example, one can connect in series one Maxwell element and one Kelvin–Voigt element as illustrated in Fig. 4c (Burgers 1935). The resulting constitutive equation is

$$\sigma_{xy} + \left(\frac{\eta_1 + \eta_2}{G_1} + \frac{\eta_2}{G_2}\right)\frac{d\sigma_{xy}}{dt} + \frac{\eta_1\eta_2}{G_1G_2}\frac{d^2\sigma_{xy}}{dt^2} = \eta_2\dot{\gamma}_{xy} + \frac{\eta_1\eta_2}{G_1}\frac{d\dot{\gamma}_{xy}}{dt} \tag{15}$$

Another example is the generalised Maxwell model, where an arbitrary number of Maxwell elements are combined in parallel, i.e. they are all subjected to the same deformation. Since each element has a different viscosity and a different elastic modulus, increasing the number of elements generates models featuring a spectrum of relaxation times, which provide a more accurate description of real materials.

Response to Heaviside forcing The simplest way to analyse the dynamic response of linear viscoelastic models to an external forcing is to apply a Heaviside stress step, $\sigma(t) = \sigma_0 H(t)$, or a Heaviside deformation step, $\gamma(t) = \gamma_0 H(t)$, where the Heaviside step function is defined as

$$H(t) = \begin{cases} 0 & t < 0 \\ 1 & t \geq 0 \end{cases} \tag{16}$$

When a constant stress, σ_0, is applied to the Maxwell model (Eq. 13), the response is

$$\gamma_{xy} = \frac{\sigma_0}{\eta}t + \frac{\sigma_0 \lambda}{\eta} \tag{17}$$

One can observe an instantaneous elastic deformation in the spring, followed by a constant rate of deformation in the viscous element, $\dot{\gamma}_{xy} = \sigma_0/\eta$, as shown schematically in Fig. 5a. If after a certain time the stress is removed, the elastic deformation is entirely recovered, while the viscous deformation is permanent. When the Maxwell model is forced by imposing a fixed deformation, γ_0, solution of Eq. (13) yields

$$\sigma_{xy} = \frac{\eta}{\lambda}\gamma_0 e^{-t/\lambda} \tag{18}$$

As the deformation is applied, there is an instantaneous buildup of stress due to the spring loading; however, when the viscous element starts to move the spring elongation reduces, which means the stress decays exponentially with time, a phenomenon commonly referred to as stress relaxation. This behaviour is illustrated qualitatively in Fig. 5b.

If a constant stress, σ_0, is applied to the Kelvin–Voigt model at $t = 0$, the solution of Eq. (14) is:

$$\gamma_{xy} = \frac{\sigma_0}{G}\left(1 - e^{-t/\lambda}\right) \tag{19}$$

Initially, the spring cannot stretch, because it is held back by the viscous element, which cannot react instantaneously and therefore takes up all the stress, while the spring is unloaded. After some strain starts to take place, the stress starts to decrease in the viscous element and increase in the spring, i.e. the stress is transferred from the viscous element to the elastic element. In the limit $t \to \infty$, the viscous element is unloaded and the spring carries all the stress; thus, the maximum strain is $\gamma_{\max} = \sigma_0/G$. If after a certain time $t = \tau$ the applied stress is removed, the spring will not be able to contract instantaneously due to the resistance of the viscous element, but eventually pulls the viscous element back to its initial position. The Kelving–Voigt response to a constant applied stress is depicted qualitatively in Fig. 5c. Unlike in the case of the Maxwell model, it is not possible to apply a fixed deformation to a Kelvin–Voigt element instantaneously.

Response to harmonic forcing The dynamic response of linear viscoelastic models to a harmonic forcing, either $\sigma(t) = \sigma_0 \sin(\omega t)$ or $\gamma(t) = \gamma_0 \sin(\omega t)$, is another canonical case in the theory of linear dynamical systems (Casti 1987). In particular, for a sinusoidal forcing the response is another sinusoid with the same frequency,

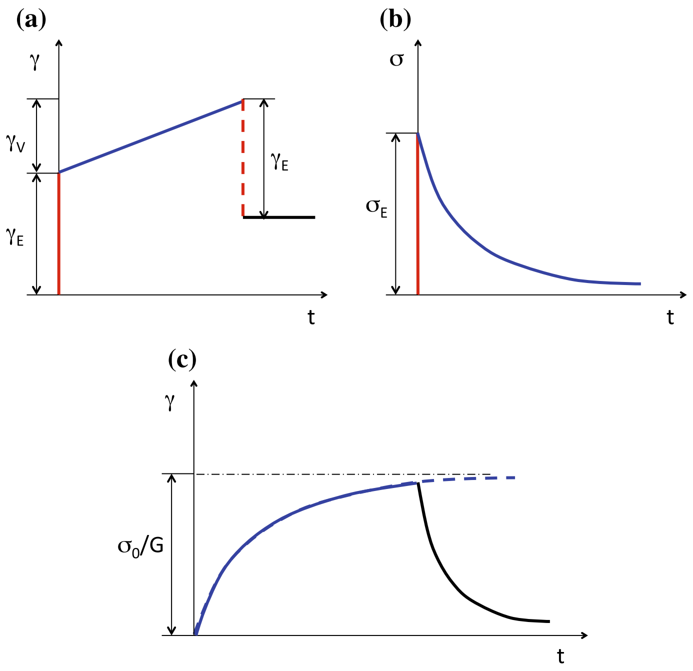

Fig. 5 Qualitative response of the Maxwell model (Eq. 13) to a constant applied stress, where γ_E and γ_V are the elastic and viscous deformations, respectively (**a**), and to a constant deformation, where σ_E is the elastic stress buildup (**b**). Qualitative response of the Kelvin–Voigt model (Eq. 19) to a constant applied stress, σ_0 (**c**)

but with a different amplitude and a phase shift; thus, the response to a sinusoidal stress is

$$\gamma_{xy}(t) = \gamma_0 \sin(\omega t + \phi) \tag{20}$$

and the response to a sinusoidal deformation is

$$\sigma_{xy}(t) = \sigma_0 \sin(\omega t + \phi) \tag{21}$$

In the limit of a Hookean solid (purely elastic limit), the stress is related linearly to strain, and the response to a shear deformation which varies sinusoidally with time, $\gamma(t) = \gamma_0 \sin(\omega t)$, is

$$\sigma_{xy}(t) = G\gamma_0 \sin(\omega t) \tag{22}$$

Thus, in elastic solids there is no phase shift between the shear stress and shear strain. In the Newtonian fluid limit, the response to the same type of forcing is

$$\sigma_{xy}(t) = \eta\dot{\gamma} = \eta\gamma_0 \cos(\omega t) = \eta\gamma_0 \sin(\omega t + \frac{\pi}{2}) \tag{23}$$

In this case, the resulting shear stress is out of phase from the applied strain by $\pi/2$. In a viscoelastic material, the phase angle can vary continuously between zero (purely elastic response) and $\pi/2$ (purely viscous response), therefore, it provides a quantitative indicator of the level of viscoelasticity. In particular, small values of the phase angle represent predominantly elastic behaviour whereas large values of the phase angle correspond to viscous behaviour.

In the general viscoelastic case, the elastic and viscous parts of the response can be made explicit by expanding the harmonic terms in Eqs. (20) and (21):

$$\gamma_{xy}(t) = \gamma_0 \cos\phi \sin(\omega t) + \gamma_0 \sin\phi \cos(\omega t) \tag{24}$$

$$\sigma_{xy}(t) = \sigma_0 \cos\phi \sin(\omega t) + \sigma_0 \sin\phi \cos(\omega t) \tag{25}$$

For a harmonic imposed deformation, the amplitude of the component of the response in phase with the forcing is expressed by introducing the *storage modulus*, $G' = \sigma_0 \cos\phi/\gamma_0$, which reflects the elastic energy stored in the fluid, and the the component out of phase by $\pi/2$ is expressed by the *loss modulus*, $G'' = \sigma_0 \sin\phi/\gamma_0$, which reflects the energy loss by viscous dissipation. For a harmonic imposed stress, the amplitude of the component in phase with the forcing is expressed by the *storage compliance*, $J' = \gamma_0 \cos\phi/\sigma_0$, and the component out of phase is expressed by the *loss compliance*, $J'' = \gamma_0 \sin\phi/\sigma_0$. Using these quantities Eqs. (24) and (25) become, respectively,

$$\gamma_{xy}(t) = \sigma_0 \left[J' \sin(\omega t) + J'' \cos(\omega t)\right] \tag{26}$$

and

$$\sigma_{xy}(t) = \gamma_0 \left[G' \sin(\omega t) + G'' \cos(\omega t)\right] \tag{27}$$

The problem of harmonic forcing is often formulated in terms of complex numbers using Euler's formula:

$$e^{\pm i\theta} = \cos\theta \pm i \sin\theta \tag{28}$$

For a harmonic stress input $\sigma(t) = \sigma_0 e^{i\omega t}$ the response is:

$$\begin{aligned}\gamma_{xy}(t) &= \gamma_0 e^{i\omega t + \phi} = \gamma_0 e^{\phi} e^{i\omega t} = \gamma_0 (\cos\phi + i \sin\phi)\, e^{i\omega t} = \\ &= \sigma_0 \left(J' + i J''\right) e^{i\omega t}\end{aligned} \tag{29}$$

while for a harmonic deformation $\gamma(t) = \gamma_0 e^{i\omega t}$ the response is

$$\begin{aligned}\sigma_{xy}(t) &= \sigma_0 e^{i\omega t + \phi} = \sigma_0 e^{\phi} e^{i\omega t} = \sigma_0 (\cos\phi + i \sin\phi)\, e^{i\omega t} = \\ &= \gamma_0 \left(G' + i G''\right) e^{i\omega t}\end{aligned} \tag{30}$$

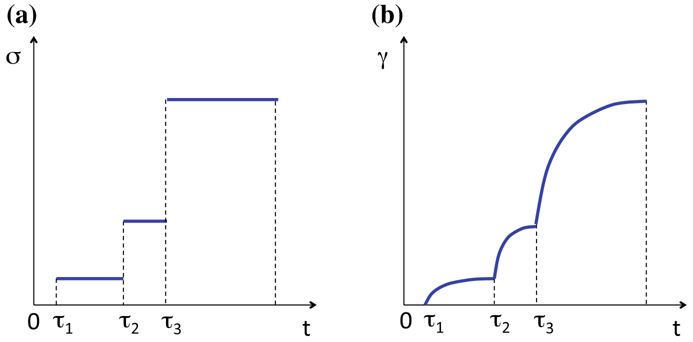

Fig. 6 Example of application of Boltzmann's superposition principle (Eq. 31); for a stepped ramp of the applied stress (**a**), the response of the system is the sum of the responses to individual steps (**b**)

Thus, the phenomenological coefficients related to the elastic and viscous properties of the substance can be expressed through a single complex number, either the *complex modulus*, $G^* = G' + iG''$, or the *complex compliance*, $J^* = J' + iJ''$.

Superposition principle The linearity of Eqs. (12)–(15) implies their solutions can be combined linearly. The Boltzmann superposition principle states that the response of a material to a given load is independent of the response of the material to its previous loading history. For example, in the case of a loading consisting of a sequence of Heaviside steps with different magnitudes of the applied stress, the total strain may be expressed by

$$\gamma_{xy} = \frac{\sigma_1}{G}(t-\tau_1) + \frac{\sigma_2-\sigma_1}{G}(t-\tau_2) + \cdots + \frac{\sigma_n-\sigma_{n-1}}{G}(t-\tau_n) \qquad (31)$$

A qualitative example of the behaviour described by Eq. (31) is displayed in Fig. 6. In the limit of small stress increments, Eq. (31) becomes

$$\gamma_{xy} = \int_{-\infty}^{t} \frac{1}{G}(t-\tau)\, d\sigma(t) = \int_{-\infty}^{t} \frac{1}{G}(t-\tau)\frac{d\sigma(t)}{dt}dt \qquad (32)$$

3.2 *The Problem of Time Derivatives*

The assumption of material frame indifference has important consequences on the mathematical formulation of constitutive models of viscoelastic flows, which descend from simple vector calculus, and which were addressed systematically in this context by Oldroyd and Wilson (1950). In a generic reference frame, a material point is characterised by its position vector, $\boldsymbol{r}$, its velocity, $\boldsymbol{v} = d\boldsymbol{r}/dt$, and its acceleration, $\boldsymbol{a} = d\boldsymbol{v}/dt$. In a second reference frame in relative motion with respect to the initial reference frame, the position vector is given by

$$\boldsymbol{r}' = \boldsymbol{Q}(t)\boldsymbol{r} + \boldsymbol{c}(t) \tag{33}$$

where $\boldsymbol{Q}$ is an orthogonal matrix such that $\boldsymbol{Q}\boldsymbol{Q}^T = \boldsymbol{Q}^T\boldsymbol{Q} = \boldsymbol{I}$ and $|\boldsymbol{Q}| = 1$, and $\boldsymbol{c}$ is a vector representing a linear displacement. Since orthogonal matrices preserve isometries, one can easily verify that the distance between two points in the first reference frame, $|\boldsymbol{r}_2 - \boldsymbol{r}_1|$, does not change in the second reference system:

$$\begin{aligned} |\boldsymbol{r}'_2 - \boldsymbol{r}'_1| &= |\boldsymbol{Q}(t)\boldsymbol{r}_2 + \boldsymbol{c}(t) - \boldsymbol{Q}(t)\boldsymbol{r}_1 - \boldsymbol{c}(t)| = \\ &= |\boldsymbol{Q}(t)\,(\boldsymbol{r}_2 - \boldsymbol{r}_1)\,| = |\boldsymbol{r}_2 - \boldsymbol{r}_1| \end{aligned} \tag{34}$$

This conclusion does not apply to velocities and accelerations, which in the second reference frame are written, respectively, as

$$\begin{aligned} \boldsymbol{v}' = \frac{d\boldsymbol{r}'}{dt} &= \frac{d}{dt}\left[\boldsymbol{Q}(t)\boldsymbol{r} + \boldsymbol{c}(t)\right] = \boldsymbol{Q}\frac{d\boldsymbol{r}}{dt} + \frac{d\boldsymbol{Q}}{dt}\boldsymbol{r} + \frac{d\boldsymbol{c}}{dt} = \\ &= \boldsymbol{Q}\boldsymbol{v} + \frac{d\boldsymbol{Q}}{dt}\boldsymbol{r} + \frac{d\boldsymbol{c}}{dt} \end{aligned} \tag{35}$$

and

$$\begin{aligned} \boldsymbol{a}' = \frac{d\boldsymbol{v}'}{dt} &= \frac{d}{dt}\left[\boldsymbol{Q}\boldsymbol{v} + \frac{d\boldsymbol{Q}}{dt}\boldsymbol{r} + \frac{d\boldsymbol{c}}{dt}\right] = \\ &= \frac{d\boldsymbol{Q}}{dt}\boldsymbol{v} + \boldsymbol{Q}\frac{d\boldsymbol{v}}{dt} + \frac{d\boldsymbol{Q}}{dt}\frac{d\boldsymbol{r}}{dt} + \frac{d^2\boldsymbol{Q}}{dt^2}\boldsymbol{r} + \frac{d^2\boldsymbol{c}}{dt^2} = \\ &= \boldsymbol{Q}\boldsymbol{a} + 2\frac{d\boldsymbol{Q}}{dt}\boldsymbol{v} + \frac{d^2\boldsymbol{Q}}{dt^2}\boldsymbol{r} + \frac{d^2\boldsymbol{c}}{dt^2} \end{aligned} \tag{36}$$

Thus, velocities and accelerations are invariant under a coordinate transformation only if the time derivatives on the r.h.s. of Eqs. (35) and (36) are zero, i.e. the two reference frames are not in relative motion. In other terms, velocity and acceleration are not objective and depend on the motion of the observer.

When one considers a tensor representing a physical quantity (e.g. the stress tensor) in a given coordinate system, it must be objective with respect to a change of the coordinate system:

$$\boldsymbol{\Sigma}' = \boldsymbol{Q}\boldsymbol{\Sigma}\boldsymbol{Q}^T \tag{37}$$

However, one can easily verify its time derivative is not objective:

$$\frac{d\boldsymbol{\Sigma}'}{dt} = \frac{d}{dt}\left(\boldsymbol{Q}\boldsymbol{\Sigma}\boldsymbol{Q}^T\right) = \frac{d\boldsymbol{Q}}{dt}\boldsymbol{\Sigma}\boldsymbol{Q}^T + \boldsymbol{Q}\frac{d\boldsymbol{\Sigma}}{dt}\boldsymbol{Q}^T + \boldsymbol{Q}\boldsymbol{\Sigma}\frac{d\boldsymbol{Q}^T}{dt} \tag{38}$$

To preserve the objectivity of a tensor with respect to time derivation, it is necessary to introduce a new definition of derivative operator (Jaumann 1905):

$$\frac{D_\nabla}{Dt}(\cdot) = \frac{d}{dt}(\cdot) - (\nabla \boldsymbol{v})(\cdot) - (\cdot)(\nabla \boldsymbol{v})^T \tag{39}$$

In fact, the velocity gradient tensor transforms in the new coordinate system as

$$(\nabla \boldsymbol{v}') = \boldsymbol{Q}(\nabla \boldsymbol{v})\boldsymbol{Q}^T + \frac{d\boldsymbol{Q}}{dt}\boldsymbol{Q}^T \tag{40}$$

Thus, the *upper convected*[1] derivative defined by Eq. (39) is objective with respect to a transformation of the coordinate system:

$$\begin{aligned}
\frac{D_\nabla}{Dt}(\boldsymbol{\Sigma}') &= \frac{D_\nabla}{Dt}\left(\boldsymbol{Q}\boldsymbol{\Sigma}\boldsymbol{Q}^T\right) = \\
&= \frac{d}{dt}\left(\boldsymbol{Q}\boldsymbol{\Sigma}\boldsymbol{Q}^T\right) - \boldsymbol{Q}(\nabla \boldsymbol{v})\boldsymbol{Q}^T\left(\boldsymbol{Q}\boldsymbol{\Sigma}\boldsymbol{Q}^T\right) - \frac{d\boldsymbol{Q}}{dt}\boldsymbol{Q}^T\left(\boldsymbol{Q}\boldsymbol{\Sigma}\boldsymbol{Q}^T\right) + \\
&- \left(\boldsymbol{Q}\boldsymbol{\Sigma}\boldsymbol{Q}^T\right)\boldsymbol{Q}(\nabla \boldsymbol{v})^T\boldsymbol{Q}^T - \left(\boldsymbol{Q}\boldsymbol{\Sigma}\boldsymbol{Q}^T\right)\boldsymbol{Q}\frac{d\boldsymbol{Q}^T}{dt} = \\
&= \boldsymbol{Q}\frac{d\boldsymbol{\Sigma}}{dt}\boldsymbol{Q}^T + \frac{d\boldsymbol{Q}}{dt}\boldsymbol{\Sigma}\boldsymbol{Q}^T + \boldsymbol{Q}\boldsymbol{\Sigma}\frac{d\boldsymbol{Q}^T}{dt} - \boldsymbol{Q}(\nabla \boldsymbol{v})\boldsymbol{\Sigma}\boldsymbol{Q}^T + \\
&- \frac{d\boldsymbol{Q}}{dt}\boldsymbol{\Sigma}\boldsymbol{Q}^T - \boldsymbol{Q}\boldsymbol{\Sigma}(\nabla \boldsymbol{v})^T\boldsymbol{Q}^T - \boldsymbol{Q}\boldsymbol{\Sigma}\frac{d\boldsymbol{Q}^T}{dt} = \\
&= \boldsymbol{Q}\frac{d\boldsymbol{\Sigma}}{dt}\boldsymbol{Q}^T - \boldsymbol{Q}(\nabla \boldsymbol{v})\boldsymbol{\Sigma}\boldsymbol{Q}^T - \boldsymbol{Q}\boldsymbol{\Sigma}(\nabla \boldsymbol{v})^T\boldsymbol{Q}^T
\end{aligned} \tag{41}$$

Similarly, one can define a *lower convected* derivative as

$$\frac{D_\Delta}{Dt}(\cdot) = \frac{d}{dt}(\cdot) + (\nabla \boldsymbol{v})(\cdot) + (\cdot)(\nabla \boldsymbol{v})^T \tag{42}$$

Finally, the co-rotational derivative for a second-order tensor is formed from the appropriate linear combination of the upper and lower convected derivatives:

$$\begin{aligned}
\frac{D_\circ}{Dt}(\cdot) &= \frac{d}{dt}(\cdot) + \frac{1}{2}\left[(\nabla \boldsymbol{v})^T - (\nabla \boldsymbol{v})\right](\cdot) + \frac{1}{2}(\cdot)\left[(\nabla \boldsymbol{v}) - (\nabla \boldsymbol{v})^T\right] = \\
&= \frac{d}{dt}(\cdot) - \boldsymbol{W}(\cdot) + (\cdot)\boldsymbol{W}
\end{aligned} \tag{43}$$

where $\boldsymbol{W}$ is the spin tensor.

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[1] The name upper convected arises because the derivative represents the material derivative of the upper (contravariant) components of a vector when convected with the motion.

3.3 Oldroyd-B Model

The most popular constitutive equation for viscoelastic fluids is the Oldroyd-B model, which captures the main features of viscoelastic flows but at the same time is simple enough to allow finding the analytical solution for the flow field in many circumstances. In this model, the total stress tensor, $\mathbf{\Sigma}$, is decomposed into the Newtonian solvent component, $2\eta_S\mathbf{\Gamma}$, where η_S is the solvent viscosity, and $\mathbf{\Gamma}$ is the velocity gradient tensor (Eq. 3), and the viscoelastic polymeric component, $\mathbf{\Sigma}_P = \mathbf{\Sigma} - 2\eta_S\mathbf{\Gamma}$, for which one can write the relation with the velocity gradient as

$$(\mathbf{\Sigma} - 2\eta_S\mathbf{\Gamma}) + \lambda_1 \frac{D_\nabla}{Dt}(\mathbf{\Sigma} - 2\eta_S\mathbf{\Gamma}) = 2\eta_P\mathbf{\Gamma} \tag{44}$$

where λ_1 is the relaxation time, η_P the polymer viscosity, and D_∇/Dt is the co-deformational (or upper convected) derivative (Oldroyd and Wilson 1950). Rearranging Eq. (44) into a more compact form yields

$$\mathbf{\Sigma} + \lambda_1 \frac{D_\nabla\mathbf{\Sigma}}{Dt} = 2\left(\eta_S + \eta_P\right)\left(\mathbf{\Gamma} + \lambda_2\frac{D_\nabla\mathbf{\Gamma}}{Dt}\right) \tag{45}$$

where $\lambda_2 = \lambda_1\eta_S/(\eta_S + \eta_P)$ is the retardation time. When $\lambda_2 = 0$, the Oldroyd-B model reduces to the Upper Convected Maxwell (UCM) model, which has the same structure as Eq. (13) but uses a different derivative operator; when $\lambda_2 = \lambda_1$ the model reduces to viscous Newtonian.

For the Oldroyd-B fluid in steady-state shear flow, the viscosity $\eta = \eta_S + \eta_P$ is constant, the second normal stress difference is zero, and the first normal stress difference is a quadratic function of the shear rate:

$$N_1 = 2\eta\left(\lambda_2 - \lambda_1\right)\dot{\gamma}^2 \tag{46}$$

The main limitation of the Oldroyd-B model is due to the fact that the coefficient of the deformation rate in Eqs. (44) and (45) is constant; this means that its contribution to the stress is the same independently of the deformation magnitude or, in other words, a fluid element can be deformed indefinitely keeping its elasticity unchanged. From the microscopic point of view, this means polymer molecules can be stretched to an infinite length behaving like an ideal spring, which is clearly unphysical.

3.4 FENE Model

The Finitely Extensible Non-linear Elastic (FENE) constitutive model was developed to achieve a more realistic description of the long-chained polymers behaviour (Bird et al. 1980). In particular, it accounts for the fact that, unlike ideal elastic springs, polymer molecules can be stretched only up to a maximum length, and the required stretching force increases more than linearly as the molecule approaches the maximum stretching. In the FENE model, polymers molecules are represented by connecting a sequence of beads with non-linear springs; the elastic force between two consecutive beads is

$$\boldsymbol{F} = \frac{K\boldsymbol{r}}{1 - r^2/r_{\max}^2} \tag{47}$$

where $\boldsymbol{r}$ is the connector vector between the beads, K is the spring constant, r and $r_{\max}$ the instantaneous and maximum lengths of the stretched molecule, respectively. At small extension, the spring is nearly Hookean, when further extended, it becomes strongly non-linear. The connector force grows rapidly so that the spring cannot be stretched beyond some maximal length.

The instantaneous position of a FENE dumbbell as a function of time is described by the following Langevin stochastic differential equation:

$$d\boldsymbol{r} = \left[(\nabla \boldsymbol{v})^T \cdot \boldsymbol{r} - \frac{2}{\zeta}\boldsymbol{F} \right] + \sqrt{\frac{4k_B T}{\zeta}} d\boldsymbol{W}(t) \tag{48}$$

where ζ is the friction coefficient of a bead, k_B is Boltzmann's constant, T is the absolute temperature, and $\boldsymbol{W}(t)$ is a Wiener stochastic process (Soong 1973). In this equation, the first term represents the distortion of the beads due to the velocity gradient, the second term represents the effect of the restoring spring force, and the stochastic term models the Brownian motion of the beads. The time evolution of the connector vector of the dumbbell (i.e. the distance between the beads) must be integrated and then averaged over all connectors to describe the macroscopic flow behaviour.

The polymer contribution to the stress is given by

$$\boldsymbol{\Sigma}_P = -N \langle \boldsymbol{r}\boldsymbol{F} \rangle + N k_B T \boldsymbol{I} \tag{49}$$

where N is the total number of connectors, and $\boldsymbol{I}$ the identity matrix. Introducing the expression of the connector force (Eq. 47) yields:

$$\boldsymbol{\Sigma}_P = -NK \left\langle \frac{\boldsymbol{r}\boldsymbol{r}}{1 - r^2/r_{\max}^2} \right\rangle + N k_B T \boldsymbol{I} \tag{50}$$

The ensemble average quantity in Eq. (50) can be calculated using Peterlin's approximation (Peterlin 1966):

$$\left\langle \frac{\boldsymbol{r}\boldsymbol{r}}{1 - r^2/r_{\max}^2} \right\rangle = \frac{\langle \boldsymbol{r}\boldsymbol{r} \rangle}{1 - \langle r^2/r_{\max}^2 \rangle} + r_{\max}^2 \boldsymbol{I} \tag{51}$$

Evaluating the ensemble averages yields the FENE-P constitutive equation for the polymer contribution to the stress:

$$Z\boldsymbol{\Sigma}_P + \lambda \frac{D_\nabla \boldsymbol{\Sigma}_P}{Dt} - \lambda \left[\boldsymbol{\Sigma}_P + \frac{\eta_P}{\lambda} \boldsymbol{I} \right] \frac{d \ln Z}{dt} = 2\eta_P \dot{\boldsymbol{\Gamma}} \tag{52}$$

where Z is a function of the spring constant and of the maximum stretching:

$$Z = 1 + \frac{3k_B T}{K r_{\max}^2} \left[1 + \frac{\lambda}{3\eta_P} tr(\boldsymbol{\Sigma}) \right] \tag{53}$$

A modified version of the FENE-P model includes the effect of repulsive charges between the beads in an attempt to incorporate the effect of charge repulsion between ionizable groups on the polymer (Dunlap and Leal 1984). This leads to the same constitutive equation but a different form of Z.

3.5 Other Constitutive Models for Viscoelastic Flows

Whilst the Oldroyd-B and the FENE models provide the most popular constitutive equations used in modelling viscoelastic flows, many other constitutive equations were derived to provide a better match with experimental data for particular fluids and/or flow conditions.

White–Metzner model The White–Metzner model (White and Metzner 1963) was developed for viscoelastic fluids that exhibit also shear-thinning. In summary, it is a modified Maxwell model that allows incorporation of experimental data on viscosity as a function of shear rate. The deviatoric stress is given by

$$\boldsymbol{\Sigma} + \frac{\eta(\dot{\gamma})}{G} \frac{D_\nabla \boldsymbol{\Sigma}}{Dt} = 2\eta(\dot{\gamma}) \boldsymbol{\Gamma} \tag{54}$$

The shear-thinning viscosity, $\eta(\dot{\gamma})$, is often described by a power law. This model can predict correctly the behaviour of nonpolar solutions and polymeric melts and it may work well on polar systems in the range of high deformation rates, i.e. the region of primary industrial interest.

Giesekus model The Giesekus model (Giesekus 1982) includes an additional quadratic term. In this model, the deviatoric stress is divided into a solvent contribution, $\eta_S \boldsymbol{\Gamma}$, and a polymer contribution, which is given by

$$\boldsymbol{\Sigma}_P + \lambda_1 \frac{D_\nabla \boldsymbol{\Sigma}_P}{Dt} + \frac{\alpha \lambda_1}{\eta_P} \boldsymbol{\Sigma}_P^2 = 2\eta_P \boldsymbol{\Gamma} \tag{55}$$

Phan-Thien–Tanner model The Phan-Thien–Tanner constitutive equation (Phan-Thien and Tanner 1977) has a similar structure to the Giesekus model, but has a different non-linear term:

$$\boldsymbol{\Sigma}_P + \lambda_1 \frac{D_\nabla \boldsymbol{\Sigma}_P}{Dt} + \left\{ \exp \left[\frac{\lambda_1}{\eta_P} Tr\left(\boldsymbol{\Sigma}_P\right) \right] - 1 \right\} \boldsymbol{\Sigma}_P = 2\eta_P \boldsymbol{\Gamma} \tag{56}$$

4 Constitutive Models for Viscoplastic Flows

An important type of non-Newtonian fluid is the viscoplastic or yield-stress fluid, which responds like elastic solids for applied stresses lower than a certain threshold value, called the yield stress, and flows only when the yield stress is overcome. Practically, such flow behaviour occurs in many situations, including slurries and suspensions, certain polymer solutions, lavas, muds and clays, heavy oils, avalanches, cosmetic creams, hair gel, liquid chocolate, pasty materials, foams and emulsions.

Research into viscoplastic fluids, their measurement and characterization is extensive and has been summarised in numerous reviews (Barnes 1999; Coussot 2007). One matter still subject of debate is the definition of yield-stress fluid itself, that is, whether fluids can actually exhibit such a physical property as the yield stress. The review by Barnes (1999) examines the evidence for and against its existence, and argues that whereas the concept of a definable yield stress has proven and continues to prove useful in a whole range of applications, if viscosity is plotted as a function of the shear stress, one can clearly identify a Newtonian plateau when the velocity gradient tends to zero (typically less than 10^{-5} s^{-1}), which implies that the material continues to creep although this can be observed only on very long timescales. However, in many practical situations the time frame of observation is much shorter than the time necessary for viscoplastic fluids to exhibit measurable flow characteristics.

Whilst several fluids exhibit an apparent yield stress, Carbopol dispersions are probably the most thoroughly studied model viscoplastic fluid system. Carbopol consists of highly cross-linked polymer particles, with dangling free ends of polymer gel strands that strongly interact with adjacent microgel particles, resulting into to a very high viscosity at low shear stress (Nguyen and Boger 1992; Roberts and Barnes 2001). Carbopol dispersions and gels are found in dozens of everyday products, ranging from toothpastes, through hair and shower gels, to artificial tears.

The simplest constitutive model describing viscoplastic fluids was introduced by Bingham to characterise the behaviour of paints (Bingham 1917), and represents the shear stress component as a linear function of the velocity gradient, with the intercept σ_c corresponding to the threshold yield point:

$$\begin{array}{ll} \dot{\gamma} = 0 & \sigma_{xy} \leq \sigma_c \\ \sigma_{xy} = \sigma_c + \eta\dot{\gamma} & \sigma_{xy} > \sigma_c \end{array} \tag{57}$$

A more refined model is the Herschel–Bulkley equation (Herschel and Bulkley 1926), given by:

$$\begin{array}{ll} \sigma_{xy} = G\gamma & \sigma_{xy} \leq \sigma_c \\ \sigma_{xy} = \sigma_c + K\dot{\gamma}^n & \sigma_{xy} > \sigma_c \end{array} \tag{58}$$

where G is the shear modulus, and γ is the shear deformation. This model is well established and probably the most widely used when analysing yield-stress behaviour; another popular model, suitable to characterise the behaviour of particle suspensions used in printing inks, was proposed by Casson (1959):

$$\sqrt{\sigma_{xy}} = \sqrt{\sigma_c} + \sqrt{\eta\dot{\gamma}} \qquad \sigma_{xy} > \sigma_c \tag{59}$$

According to Eqs. (57)–(59), the transition from the elastic regime to the fluid regime is abrupt, which means that the shear stress derivative with respect to the shear rate exhibits a first-order discontinuity. This represents a major technical issue when the yield-stress fluid constitutive equation is implemented to find analytical or (especially) numerical solutions of fluid flows. To remove this discontinuity, Papanastasiou proposed a constitutive equation featuring a smooth transition between the two regimes (Papanastasiou 1987), which provides a better description of real materials:

$$\sigma_{xy} = \sigma_c\left[1 - \exp\left(-m\dot{\gamma}\right)\right] + K\dot{\gamma}^n \tag{60}$$

where m is a material-dependent constant with values of the order of 10^2. Figure 7 shows the qualitative flow curves for Bingham fluids (Eq. 57) and Herschel–Bulkley fluids (Eq. 58), as well as the effect of the Papanastasiou regularisation (Eq. 60). A detailed discussion of advanced and time-dependent constitutive models for viscoplastic flows is presented in Chapter Transport Phenomena in Viscoplastic Materials.

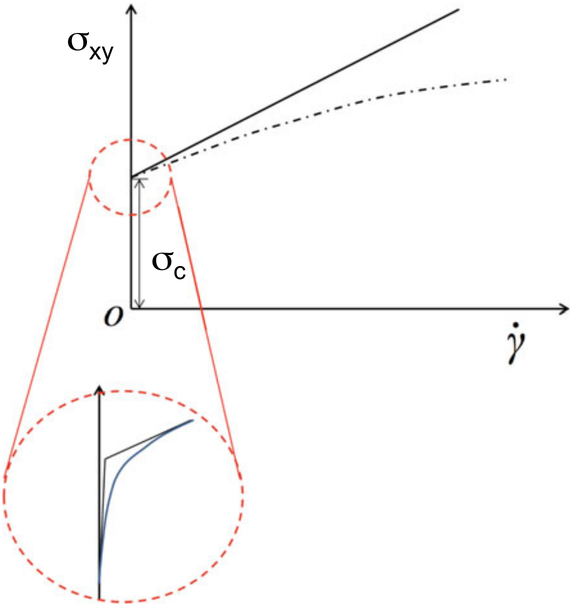

Fig. 7 Comparison between the qualitative flow curves of the Bingham model (solid line) and of the Herschel–Bulkley model (dash-dot line); the inset shows the effect of Papanastasiou regularisation (Eq. 60) on the Herschel–Bulkley flow curve

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