1

General points on materials and their rheophysical behaviour

The term ‘rheology’ was invented by E. C. Bingham in 1928.[1] In the beginning, it encompassed an extremely wide topic, dealing with the *study of the deformation and flow of matter*. This definition was finally adopted one year later, at the creation of the American Society of Rheology[2] (for a review of the history of rheology, see (Doraiswamy, 2002).

Nevertheless, this term became more ‘specialised’ with time and only applies today to fluids exhibiting behaviour intermediate between that of ordinary liquids and that of perfectly elastic solids. For this reason, we employ the term ‘rheophysics’ to define the science of deformation and flow in the general sense defined by Bingham, reserving the term ‘rheology’ for the study of complex fluids, as in modern use.

Schematically, matter can be found in either of two states, entailing extremely different rheological (or rheophysical) properties:[3]

The solid state This is the case for a block of metal at room temperature, which will conserve its shape indefinitely in the absence of applied forces. This holds, up to a small deformation, invisible to the naked eye, even under the influence of moderate forces, such as gravity. This deformation is *reversible*, since it disappears once the stress is removed. One speaks in this case of *elastic deformation*. *Elasticity* is one of the defining properties of solids. For most of them, it is of *enthalpic* origin, stemming from the variation in energy of bonds between atoms or molecules upon deformation of the sample. To this concept one associates that of *elastic modulus*, quantifying the resistance of the material to a small deformation (generally below 10^{-3}, for ordinary solids). It is worth remembering that the elastic response of a solid is often *anisotropic*, meaning that it depends on the direction of the applied forces with respect to the crystal axes. This anisotropy reflects the *crystal symmetry* of the material.

Experiment also shows that a distinction must be made between *‘hard’ solids* and *‘soft’ solids*.

For the first category, including *metals* and *minerals*, the elastic moduli are of the order of 10^{11} Pa. *Dissipation* is negligible in these materials in the elastic deformation regime up

---

[1] The word is coined from the Greek words ‘ρέω’ and ‘λόγοσ’ (pronounced rheos and logos) meaning ‘to flow’ and ‘study’, respectively.

[2] Counting among its founders M. Reiner, E. C. Bingham and G. S. Blair.

[3] At this point, one should note that we group the liquid, gas and liquid crystalline states under the denomination ‘fluid state’, a simplification justified as far as rheology is concerned, as we will show throughout this work.

to very high frequencies, in the gigahertz range. For this reason, sound experiences very little attenuation and can propagate over very large distances (thousands of kilometres) within them.

The second category have much smaller elastic moduli and dissipative effects are much more important. *Elastomers* (such as natural rubber), and also *polymer gels* and *colloidal crystals*, belong to this category of materials. Thus, colloidal crystals exhibit very low elastic moduli, typically a few tens of pascals, while for elastomers moduli vary between 10^5 and 10^8 Pa; gels (very often swollen by a solvent) have intermediate values. Dissipative effects also appear at very low frequencies, from the hertz to the kilohertz as the case may be: for this reason, waves are strongly attenuated in these solids, termed *viscoelastic*.

Elastomers and polymer gels are also peculiar in that they can sustain huge reversible deformations (sometimes by more than 100% in relative value). The reason is that their elasticity is of an *entropic* nature (instead of enthalpic, as in ordinary or colloidal crystals), originating in the loss of configuration entropy of the constituent polymer chains under elongation or compression.

We end this presentation of solids by noting that they can be in *crystalline* or *amorphous* form. In crystals,[4] the elastic properties are anisotropic, the deformation depending on the direction of the applied forces. Amorphous solids, on the other hand, exhibit isotropic elasticity. Finally, each type of solid has a *yield stress* (or *elastic limit*) above which it breaks or starts to *creep* (that is, to ‘flow’) *irreversibly*. One speaks of *rupture* in the first case, and of *plastic deformation* in the second one. In this latter regime, the material behaves more like a fluid, the other state of matter to be discussed in the following.

The fluid state This is the case for gases and simple or complex liquids, which always end (after a certain time) by taking the shape of their container. The time taken is longer for a more *viscous* material, an intuitive concept that we will return to in more detail. Most fluids are *isotropic*, but there are also some that are *anisotropic*.

This latter type, also termed *liquid crystals*, are intermediate between liquids and crystals. Discovered at the beginning of the twentieth century by G. Friedel, they behave as solids in certain directions (along which they exhibit elasticity), and as liquids in the complementary directions (viscous behaviour). These *anisotropic* materials are thus *viscoelastic*, since their elastic or viscous behaviour depends on the direction of the applied stress.

There are also *isotropic viscoelastic fluids*, whose elastic or viscous behaviour depends on the *time scale* over which the deformation is applied. More precisely, these fluids respond elastically at short times, while they behave as viscous fluids over long times.

We emphasise that the behaviour of the viscoelastic solids mentioned above (elastomers, gels and colloidal crystals) is the exact opposite; their response being viscous over short times and elastic at long times (provided, however, their elastic limit is not exceeded).

---

[4] More precisely, in monocrystals.

In practice, the characteristic time separating these two regimes is called the *viscoelastic relaxation time*.[5] Obviously, this time varies enormously among materials, and can take values from 10^{-12} s (in the case of water, which will hence behave as an ordinary viscous fluid under normal conditions) and several hundred years (in the case of the Earth's mantle, behaving as a solid over the human lifetime and as a very viscous fluid over geological time scales).

These two examples show that the concepts of viscous or viscoelastic fluids, and more generally the distinction between solids and fluids, are only *relative*, crucially depending on the time scale over which one watches the material evolve.

After these comments, let us detail the contents of this chapter. We will begin by recalling the limiting behaviours one can encounter, which will lead us to defining the concepts of Hookean elastic solid and Newtonian viscous fluid (Section 1.1). We will then see that a solid can undergo plastic deformation and that a fluid can exhibit non-Newtonian (Section 1.2) and thixotropic (Section 1.3) behaviour. Finally, we will discuss the concepts of yield stress fluid (Section 1.4), and isotropic viscoelastic fluid and solid (Sections 1.5 and 1.6), ending with liquid crystals (Section 1.7).

1.1 The Hookean elastic solid and the Newtonian viscous fluid

As we have just shown, matter can be found in various forms. The two extreme cases are the elastic solid, described by Hooke's law (1678), and the viscous fluid, whose behaviour follows Newton's law (published in the *Principia* in 1687).

1.1.1 Hooke's law

This constitutive equation describes the behaviour of a perfect elastic solid.[6] It reads:

$$\sigma = G\gamma, \tag{1.1}$$

where σ is the applied stress (force per unit surface), $\gamma = u/d$ the strain (Fig. 1.1) and G the elastic modulus (the shear modulus in the case of Fig. 1.1). A proper definition of the concept of stress, fundamental in continuum mechanics, will be given in the next chapter. Since the stress is measured in Pa (the unit of pressure in the SI system) or in dyn/cm^2 in the CGS system (1 Pa = 10 dyn/cm^2) while the strain is dimensionless, the elastic modulus is also measured in Pa (or in dyn/cm^2).

The order of magnitude of the elastic modulus varies enormously, from 10^{10} or 10^{11} Pa for a metal or a rock, to a few tens of pascals for a colloidal crystal or a very dilute polymer gel in a solvent.

---

[5] This definition applies equally well to fluids and viscoelastic solids.
[6] It also applies to viscoelastic liquids 'at short times' and to viscoelastic solids 'at long times' (see Sections 1.5 and 1.6).

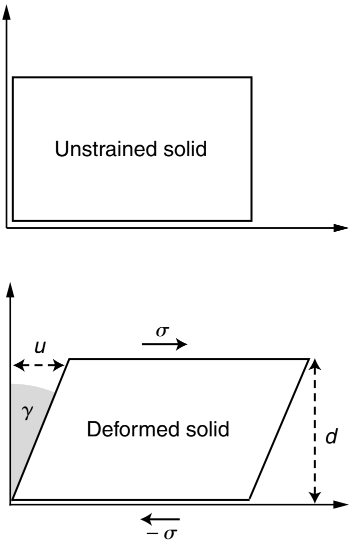

Fig. 1.1 Shear deformation of an elastic solid under an applied stress σ.

The theory of elasticity, dealing with the study of Hookean elastic solids, will be discussed in Chapter 4.[7]

Hooke's law states that the strain γ is proportional to the applied stress σ. Hence, if the stress is removed, the strain vanishes and the body recovers its initial shape, meaning that it keeps the memory of its previous state.

The concept of elasticity is thus intimately related to that of memory, the Hookean elastic solid representing the limiting case of a body endowed with *infinite memory*.[8]

It is noteworthy that Hooke's law makes the implicit assumption that the material *responds instantaneously* to mechanical action (since the law contains no characteristic time).

1.1.2 Newton's law

This constitutive law applies to viscous fluids.[9] It reads:

$$\sigma = \eta\dot{\gamma}, \tag{1.2}$$

where σ is the applied stress, $\dot{\gamma} = v/d$ the velocity gradient (or shear rate defined in Fig. 1.2) and η the *dynamic shear viscosity*. Viscous fluids obeying this law are termed

---

[7] In that chapter we will also study the response of a solid to deformation modes other than shear, namely elongation, flexion and torsion.

[8] The concept of 'memory' will exhibit its full importance when we consider the case of viscoelastic materials (see Sections 1.5 and 1.6).

[9] It also applies to viscoelastic liquids in the 'long time' limit, and to viscoelastic solids 'at short times' (see Sections 1.5 and 1.6).

Cambridge University Press
978-1-107-43952-8 - Rheophysics: The Deformation and Flow of Matter
Patrick O Swald
Excerpt
More information

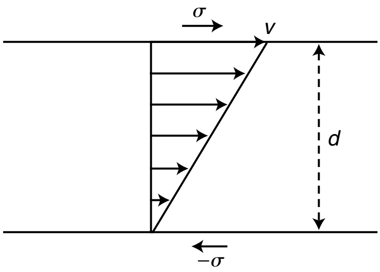

Fig. 1.2 Fluid under constant shear: v is the velocity of the upper plate with respect to the lower one and d is the thickness of the fluid layer.

Newtonian (this definition will be further refined in Section 1.5). Since $\dot{\gamma}$ is in units of s^{-1}, the viscosity is measured in pascal seconds, Pa s (also known as poiseuille in the SI system) or in poise in the CGS system (1 Pa s = 10 P).

At room temperature, water has a viscosity of 10^{-3} Pa s. Silicone oils, on the other hand, can exhibit viscosities up to several million Pa s, showing that this parameter can have hugely different values (without even mentioning the Earth's mantle, where the viscosity approaches 10^{21} Pa s).[10]

Let us also emphasise that *the Newtonian fluid responds instantaneously to shear* (since there is no characteristic time in Newton's law, just as there is none in Hooke's law) and *has no memory*, in contrast with the elastic solid. Indeed, after a stress σ is applied during a time t, the fluid undergoes a *permanent and irreversible deformation*, $\gamma = \sigma t/\eta$ and never again recovers its initial state after the force is removed.

The theory of hydrodynamics, describing the flow of Newtonian viscous fluids, will be treated in Chapter 3.

Let us now see in what way material behaviour differs from these ideal models. To start with, we will consider the case of the plastic solid, followed by that of the non-Newtonian viscous fluid.

1.2 The plastic solid and the non-Newtonian viscous fluid

For a long time (from the seventeenth century until the beginning of the nineteenth century), physicists contented themselves with classifying materials either in the family of Hookean elastic solids, or in that of Newtonian viscous fluids. It was only in the nineteenth century that they started having doubts.

In 1835, W. Weber (Weber, 1835), who was studying silk thread, noted that it is not perfectly elastic, and that it keeps on elongating slowly under the action of a load, even a moderate one. When the load is removed, the thread contracts but never recovers its initial length. Thus, under traction it undergoes a *permanent irreversible deformation*, also

---

[10] Other values will be given in Chapter 3, where we will also discuss the physical parameters that influence viscosity (temperature and pressure).

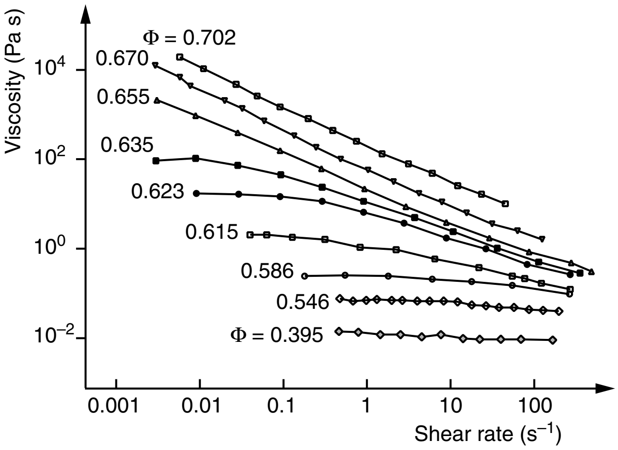

Fig. 1.3 Constant shear viscosity for suspensions of silica hard spheres with a diameter of 0.49 µm, for different values of the volume fraction Φ (Jones *et al.*, 1991).

called *plastic* deformation.[11] *Plasticity* is specific to solids and in particular to crystals, which exhibit long-range positional order in three dimensions. We will see in Chapters 3 and 4 that plastic deformation is intimately connected to the presence of topological defects within the crystal (these defects can be point-like, such as vacancies or interstitials, linear, such as dislocations, or surface-like, such as grain boundaries).

In the nineteenth century it was also realised, owing to the development of devices for measuring the viscosity (called *rheometers*), that many fluids depart from the ideal Newtonian behaviour, in that their viscosity depends on the applied shear rate $\dot{\gamma}$. In most cases, the fluids are *shear-thinning*, i.e. their viscosity decreases as $\dot{\gamma}$ increases. As examples of shear-thinning viscous fluids, one can cite solid particle suspensions as long as they are not too concentrated, and for moderate shear rates. Such an example is given in Fig. 1.3 (see also Section 7.5.1).

In other (much less common) cases, the viscosity increases with the shear rate. The fluid is then termed *shear-thickening*. Concentrated suspensions of solid particles can exhibit this type of behaviour, in a specific range of shear rate. They can even start by being shear-thinning, then shear-thickening, and then again shear-thinning, with increasing shear rate.

Liquid crystals, and in particular nematics (described in Section 1.7), can also exhibit shear-thinning or shear-thickening behaviour, depending on the way the molecules are anchored at the surface of the walls delimiting the sample (see Chapter 7).

Finally, viscoelastic liquids, consisting of a wide range of materials (polymer melts, emulsions, etc.), almost always behave under continuous shear (and in the stationary regime) as viscous non-Newtonian fluids, usually shear-thinning (see for instance Fig. 1.15).

We will now try to give precise definitions for the concepts of plastic solids and non-Newtonian viscous fluids. To this end, let us analyze the action of shear on these materials and trace some typical graphs.

---

[11] Plastic comes from the Greek adjective '*πλαστικόσ*'(pronounced 'plastikos') meaning 'capable of being molded'.

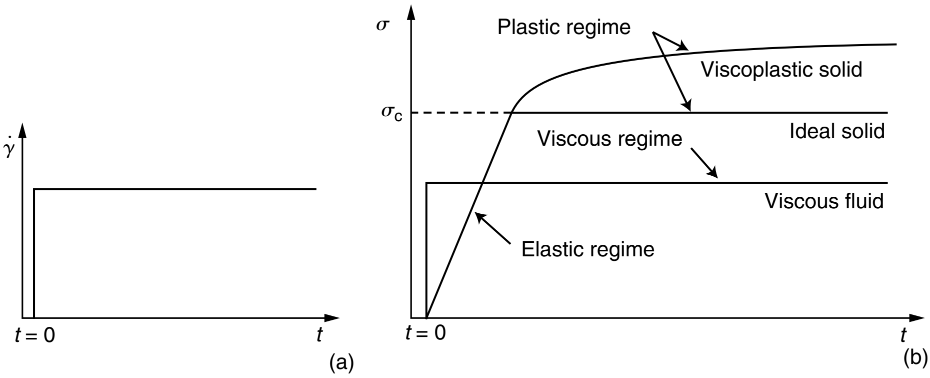

Fig. 1.4 Response of a viscous fluid, or of a solid, to the sudden onset of shear. (a) Shear rate as a function of time; (b) stress as a function of time.

1.2.1 Response to a sudden onset of shear (transient regime)

Consider a material, initially at rest, which is subjected to a constant shear rate $\dot{\gamma}$ starting at the moment $t = 0$, and let us plot the evolution of the stress as a function of time (Fig. 1.4).[12]

In the ideal case of a *Newtonian viscous fluid*, the stress 'immediately' reaches its stationary regime value,[13] here proportional to the shear rate ($\sigma = \eta\dot{\gamma}$).

For a *non-Newtonian viscous fluid*, the response to the sudden onset of shear is once again assumed to be instantaneous; namely, the stress shoots from 0 to a plateau value $\sigma(\dot{\gamma})$; however, this value is no longer proportional to the shear rate.

In the case of *solids*, on the other hand, the stress increases linearly with time (an elastic regime during which $\sigma = G\dot{\gamma}t$ according to Hooke's law), and then saturates upon reaching a *critical stress* σ_c. At this point, the material enters the *plastic regime*.[14] The value σ_c defines the *elastic limit* of the material or, equivalently, its *critical stress*. Two situations can occur, depending on whether the stress immediately reaches saturation at σ_c, defining the *ideal plastic solid* (fairly well represented by foams and concentrated emulsions[15]) or, on the contrary, it keeps on increasing (a feature known as *work hardening*) until it saturates at a new plateau value, which depends on $\dot{\gamma}$: this defines the *viscoplastic solids*, comprising most ordinary solids, such as metals or minerals (Fig. 1.4).

Note that the stress σ_c is independent of $\dot{\gamma}$, but it does depend strongly on the material under consideration, varying from a few Pa for a foam, to several MPa or even GPa for a metal at room temperature. These extreme values show that the parameter is strongly

---

[12] Nowadays, rheometers can impose either the shear rate or the stress, while measuring the conjugate parameter. In the experiment we describe, the shear rate is fixed.

[13] This assumption will be discussed in more detail in Section 1.5.

[14] Assuming the material does not break, which means that its temperature is above the brittle–ductile transition temperature T_{BD} (see Section 5.4.1).

[15] Concentrated emulsions are foams wherein the gas (air, usually) is replaced by a liquid. The physics of foams is described in the excellent book by D. Weaire and M. A. Fortes, *The Physics of Foams*, Oxford: Oxford University Press, 1999.

related to the microstructure of the material (bubble size in a foam or dislocation density and grain size in a polycrystalline metal, as we will see in Chapter 5).

Finally, let us comment on the tacit assumption that below σ_c, the material does not flow or, more precisely, it behaves like a perfect elastic solid. In hard solids, such as metals, this behaviour is only really observed at low enough temperature.[16] In foams, on the other hand, the temperature hardly matters, because of the macroscopic size of the bubbles. But this does not necessarily mean that their elastic behaviour is easy to observe. One reason is that foams tend to exhibit slip at the confining surfaces, which are used to shear them. This artefact can be avoided by rendering the surfaces rough. Another problem stems from the *drainage* of the interstitial liquid under the action of gravity, and most of all from *Ostwald ripening*, a process by which small bubbles empty their content into larger ones (where gas pressure is lower) owing to the finite permeability of the films separating them (Gandolfo *et al.*, 1997). Under these conditions, foam structure evolves constantly with time, a process referred to as *aging*. Thus, its 'ideal' elastic behaviour can only be observed over relatively short time intervals, during which surface slippage and aging can be neglected.[17] The same problems are encountered in the case of concentrated emulsions, except that Ostwald ripening is much less pronounced than in ordinary foams. For this reason, concentrated emulsions are closer to the ideal plastic solid than foams.

Putting aside for now these experimental problems, let us again focus on describing the behaviour of stress in the stationary regime.

1.2.2 Behaviour under continuous shear (permanent regime)

In Fig. 1.5, we plot the stress measured in the stationary regime $\sigma(t \to \infty)$ as a function of $\dot{\gamma}$. Figure 1.6 shows the corresponding viscosity $\eta(t \to \infty)$ (by definition, it is given by $\sigma(t \to \infty)/\dot{\gamma}$). These graphs demonstrate that a clear distinction is to be made between fluids and solids above the 'plastic threshold'.

For a Newtonian viscous fluid, the stress increases linearly with $\dot{\gamma}$, the viscosity being constant by definition.

In a shear-thinning fluid the stress increases more slowly than $\dot{\gamma}$, such that the viscosity decreases with $\dot{\gamma}$. In this case, the viscosity often exhibits two plateau values, at low and high shear rates, denoted by η_0 and η_∞, with a 'power law' crossover behaviour. Several phenomenological equations were put forward to explain this behaviour, among them that of Cross (1965), of the form:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (k\dot{\gamma})^p}. \tag{1.3}$$

---

[16] Typically, below a temperature of the order of $0.5T_m$, where T_m is the melting point of the body. At higher temperature, and in particular on approaching T_m, solids behave as extremely viscous Newtonian liquids. The flow is then due to the diffusion of vacancies across or at the surface of the grains in the polycrystal, as will be shown in Sections 5.3.4.1 and 5.3.4.2.

[17] The same difficulties appear under continuous shear, as soon as one tries to study the ideal plastic behaviour of foams.

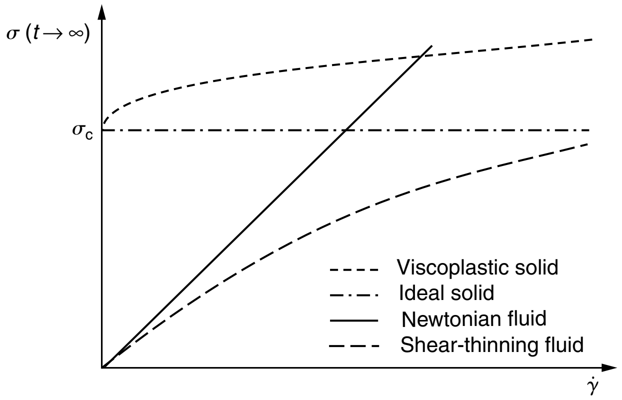

Fig. 1.5 The stress measured in the stationary regime as a function of the shear rate for a plastic solid (ideal or viscoplastic), a Newtonian viscous fluid and a shear-thinning viscous fluid.

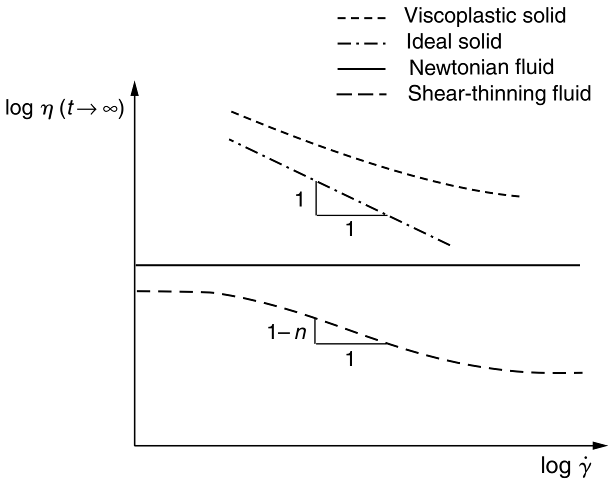

Fig. 1.6 The viscosity measured in the stationary regime as a function of the shear rate (in a log–log plot). Each graph corresponds to a different type of material.

In this expression, the constant k (with time dimensions) and the exponent p are two adjustable coefficients. Note that, over the shear rate range where $\eta_0 \gg \eta \gg \eta_\infty$, this equation reduces to:

$$\eta = \eta_0 (k\dot{\gamma})^{-p} = m\dot{\gamma}^{n-1}, \tag{1.4}$$

with $p = 1 - n$ and $m = \eta_0 k^{n-1}$. This is the *Ostwald–de Waehle law*. The exponent n is smaller than 1 for shear-thinning fluids. The coefficient m, termed ‘consistence’, is measured in peculiar units: Pa s^n.

We emphasise that the concept of shear-thinning is closely related to that of *structural change* affecting the sheared material. Thus, in a hard sphere suspension, this effect can

Cambridge University Press
978-1-107-43952-8 - Rheophysics: The Deformation and Flow of Matter
Patrick O Swald
Excerpt
More information

be related to the particles tending to form layers, thus facilitating the flow. If the solid particles are rod-shaped, they will tend to align with their long axes along the velocity (Section 7.5.1). The same occurs for elongated molecules in nematic phases (defined in Section 1.7), their orientation changing as a function of the applied shear rate (see Section 8.1.7), etc.

Solids, on the other hand, exhibit at 'low' temperature a behaviour completely different from that of fluids.[18] Thus, for the *ideal plastic solid*, $\sigma(t \to \infty) = \sigma_c$, meaning that the viscosity of the medium $\eta(t \to \infty)$ (defined using the same relation (1.2)) decreases as the reciprocal of the shear rate. In a log–log plot, it is represented by a straight line of slope -1. In practice, solids seldom behave this way (with the possible exception of foams and concentrated emulsions). Usually, they follow more complicated laws. Most common among them are power laws:

$$\sigma - \sigma_c \propto \dot{\gamma}^{1/n} \quad \text{with} \quad n > 1, \tag{1.5}$$

or logarithmic dependences:

$$\sigma - \sigma_c \propto \ln(\dot{\gamma}). \tag{1.6}$$

In this case, one speaks of *viscoplastic flow*. For crystals, some examples will be given in Section 5.3. We stress that in these materials plastic deformation is due to defects, and in particular to dislocations.

1.3 Thixotropy and antithixotropy

This new concept (Barnes, 1997) applies to viscous fluids, for which we considered so far that, at a fixed shear rate $\dot{\gamma}$, the viscosity is constant in time (although it can vary with $\dot{\gamma}$, if the fluid is non-Newtonian).

However, there are also some fluids (such as paint or print ink, but also mud, cement, mortar, mastics, etc. [35, 36]) whose viscosity changes 'slowly' with time, under shear (at constant $\dot{\gamma}$), before reaching a constant value. This behaviour indicates that *the structure of the fluid evolves under shear*, before reaching a stationary regime. For this reason, it is not surprising that this behaviour is also manifest in non-Newtonian fluids, whose shear-thinning or shear-thickening properties are also related to a structural change under shear. One then speaks of *thixotropy* or *antithixotropy* when the fluid is shear-thinning or shear-thickening, respectively.

In the following, we consider the more common case of a shear-thinning fluid. In Fig. 1.7, we show its response to two successive jumps in shear rate. The fluid, initially at rest and in thermodynamic equilibrium, is set in motion at the instant t_1, with a shear rate $\dot{\gamma}_1$. The measured stress is zero initially, 'jumps' to the value σ_1^i, then decreases slowly, tending towards a constant value σ_1^∞. The corresponding viscosity shows the

---

[18] We emphasise that at high temperature ($T > 0.5\,T_m$), polycrystalline solids behave more like yield stress fluids (see Figure 1.10, Section 5.3.4.5 and Footnote 14).